Enhancing the Ethylene and Propylene Selectivities in the Methanol-to-Olefins Reaction by Exploiting the Intricate Relationship between Framework Topology and Acidity

> Thesis by Faisal H. Alshafei

In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy



CALIFORNIA INSTITUTE OF TECHNOLOGY Pasadena, California

> 2023 (Defended 7 April 2023)

© 2023

Faisal H. Alshafei ORCID: 0000-0003-1808-1374

All rights reserved except where otherwise noted.

ACKNOWLEDGEMENTS

The incredible opportunity to pursue a doctorate degree from Caltech and complete the work presented herein would not have been possible without the support and contributions of many individuals. First and foremost, I would like to thank my advisor, Prof. Mark E. Davis, for the opportunity to work in his research group. I am grateful for his support and encouragement.

In the Mark E. Davis (MED) group, I would like to thank all current and former members, with whom I interacted and/or collaborated during my time at Caltech, including Dr. Jong Hun Kang, Dr. Marcella Lusardi, Dr. Donglong Fu, and Youngkyu Park. A special thanks goes to Jong Hun for all the time he spent in my first year at Caltech training me and helping me get started with my experiments. I only wish we had more time together as I think we could have collaborated more and published several more papers.

I am also grateful to Chevron for generously funding the projects that make up my thesis. I would like to especially thank several individuals at Chevron, including Drs. Stacey Zones, Chris Lew, Dan Xie, and C.Y. Chen for their time, helpful suggestions, feedback, and encouragement.

I also would like to thank Aramco R&D for sponsoring my graduate studies at Caltech. I am particularly thankful to Drs. Omer Koseoglu and Sohel Shaikh for their mentorship and support.

Additionally, I would like to thank Drs. Richard Flagan, Stacey Zones, Jay Labinger, and Karthish Manthiram for serving on my candidacy and thesis committees. I thank them for their insights and input. In the broader Caltech community, I would like to thank Dr. Sonjong Hwang at the solid-state NMR facility for his help with the NMR experiments, Dr. Chi Ma at the Analytical Facilities for his help with the SEM/EDS, and Dr. Nathan Dalleska at the Resnick Water and Environment Laboratory for his help with the GC-MS. I also would like to thank the support staff within the Division of Chemistry and Chemical Engineering, including, Martha Hepworth, Allison Kinard, and Suresh Guptha.

I also would like to thank numerous previous mentors, advisors, and/or professors who encouraged me to pursue a PhD. Specifically, I would like thank Dr. Abraham Clearfield (TAMU) for taking a chance on me as a freshman at Texas A&M University and allowing me to work in his lab. Prof. Simonetti, my advisor at UCLA, has been very supportive of me. I am lucky to have worked with him during my MS degree.

Finally, I would like to thank all my friends at Caltech and beyond as well as my family for supporting me and being there for me. This would not have been possible with you all. So, thank you, again. Now on to the "sciencey" stuff...

ABSTRACT

This thesis describes and presents results from several related projects within the theme of molecular sieve synthesis and catalysis. The early part of the thesis focuses on understanding the link between cage size/dimension and acidity (i.e., acid site density and strength) in the methanol-to-olefins (MTO) reaction. This relationship between cage size and acidity, once identified and investigated, is exploited in the latter parts of the thesis to rationally design materials that are able to steer the light olefins product distribution toward either more ethylene or propylene in a significant improvement over SAPO-34 (CHA), the commercial catalyst.

In Chapters 2, 44 zeolites and silicoaluminophosphates (SAPOs) belonging to five frameworks (AEI, CHE, LEV, SWY, and ERI) with a wide range of Si/Al=4-31 and Si/(Al+P)=0.04-0.3, are synthesized and characterized using a myriad of techniques. Their MTO behavior is then systematically investigated to rationalize the effect of cage dimensions on the olefins product distribution as a function of acid site density and strength. The results from this study show that changes in acid site density and strength play a secondary role to the dominating influence of cage architecture on product distribution in AEI- and CHA-type molecular sieves. Decreasing the cage size, in going from AEI and CHA to LEV, SWY, and ERI, however, results in substantial changes in the ethylene-to-propylene ratio (E/P) as a function of acidity. These changes are attributed to differences in the identity and concentration of the hydrocarbon-pool (HP) species that form, particularly in early stages of the reaction.

In Chapters 3 and 4, ERI-type molecular sieves (e.g., SSZ-98, UZM-12, ERI-type zeolites, and SAPO-17) are thoroughly investigated as promising methanol-to-ethylene

materials due to their narrow cage size. Specifically, numerous ERI-type molecular sieves are synthesized using several organic structure-directing agents (OSDAs) with varied Si/Al or Si/T-atoms ratios. The list of ERI-related materials synthesized and tested in MTO included a new disordered SAPO, denoted as CIT-16P, which upon thermal treatment in air transforms to SAPO-17 (ERI). The reaction results show that decreasing the Si/Al (or increasing the Si/T) ratio, irrespective of other material properties, improves the E/P of ERI-type molecular sieves (E/P=1.1-1.9) over CHA-type molecular sieves (E/P=0.82-0.85) in MTO. Dissolution-extraction experiments reveal that the rapid formation of cyclic intermediates and the shift in their composition toward less-methylated methylbenzenes and methylnaphthalenes are found to be key to enhancing the ethylene selectivity in ERI-type molecular sieves.

In Chapter 5, several SAT-type molecular sieves are investigated as promising methanol-to-propylene catalysts. This effort entails the synthesis of CIT-17, an SAT SAPO-type molecular sieve, which is isostructural to STA-2 (MgAPO-SAT). Following the successful synthesis of CIT-17, the MTO behavior of several SAT-type molecular sieves (MgAPO, CoAPO, and SAPO) are investigated in MTO. The combination of low acidity of CIT-17 and unique structural features of the narrow SAT-cage lead to a catalytic pathway and mechanism that predominantly favors propylene (propylene-to-ethylene ratios (P/E) of 2-4.2; propylene selectivity of 40-50%). Indeed, CIT-17 achieves one of the highest P/E ratio values reported for this class of materials.

PUBLISHED CONTENT AND CONTRIBUTIONS

Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. *ACS Catal.* **2019**, *9* (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.

F.H.A. performed reaction experiments and analyzed reaction data. All authors wrote the paper.

Alshafei, F. H.; Park, Y.; Zones, S. I.; Davis, M. E. Methanol-to-Olefins Catalysis on ERI-Type Molecular Sieves: Towards Enhancing Ethylene Selectivity. *Journal of Catalysis* **2021**, *404*, 620–633. https://doi.org/10.1016/j.jcat.2021.10.025.

F.H.A. designed the research and performed the experimental work. All authors wrote the paper.

Alshafei, F. H.; Kang, J. H.; Cho, S. J.; Davis, M. E. Synthesis and Characterization of Silicoaluminophosphate CIT-16P and its Transformation to SAPO-17, *accepted*.

F.H.A. and J.H.K. designed the research and F.H.S. performed the experimental work. All authors wrote the paper.

Alshafei, F. H.; Zones, S. I.; Davis, M. E. Enhancing the Propylene Selectivity in the Methanol-to-Olefins Reaction over SAT-Type Molecular Sieves, *in preparation*.

F.H.A. designed the research and performed the experimental work. All authors wrote the paper.

Alshafei, F. H.; Zones, S. I.; Davis, M. E. Unraveling the Intricate Relationship between Framework Topology and Acidity on the Light Olefins Selectivities in the Methanol-to-Olefins Reaction, *in preparation*.

F.H.A. designed the research and performed the experimental work. All authors wrote the paper.

Table of Contents

Acknowledgementsiii
Abstract v
Published Content and Contributionsvii
List of Figures xii
List of Tables xxiv
Chapter 1 Introduction to the Methanol-to-Olefins Reaction 1
1.1 Motivation1
1.2 Background and Literature Review 4
1.2.1 Small-pore, Cage-type Molecular Sieves 5
1.2.2 Methanol-to-Olefins Reaction Mechanism: Dual Catalytic Cycles
1.2.3 Effect of Cage Size/Dimension on the MTO Product Distribution12
1.2.4 Effect of Catalyst Acidity (Concentration, Distribution and Strength) on the MTO Behavior
1.2.5 Effect of Reaction Conditions on the MTO Behavior
1.3 Prior Work on the Methanol-to-Light Olefins Reaction in the Mark E. Davis Group 20
1.3.1 Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction
1.3.2 Treatment of Zeolites with Steam to Improve Framework Si/Al: A Case Study on SSZ-39
1.3.3 Organic-free Synthesis of Zeolite Catalysts and Their Post-Synthetic Treatments
1.3.4 Effect of Cage Dimension on the Product Distribution in MTO
1.4 Overview of Thesis
1.5 References



68
69
70
74
75
76
77
77
81
88
91
93
93
wards 101
101
102
107
107
113
115
116

Chapter 4 Synthesis and Characterization of Silicoaluminophosphate Transformation to SAPO-17	CIT-16P	and its 152
Abstract		152
4.1 Introduction		153

3.3.1 Characterization1163.3.2 MTO Catalytic Activity1263.3.3. Relationships between Effluent Product and Retained Hydrocarbons Selectivity1313.4 Conclusion1373.5 Acknowledgements1383.6 References139

4.2 Experimental	
4.2.1 Chemicals and Materials	
4.2.2 Synthesis of the OSDAs	
4.2.3 Synthesis of SAPO CIT-16P	
4.2.4 Characterization	
4.2.5 Catalytic Testing	
4.3 Results and Discussion	
4.3.1 Synthesis	
4.3.2 Characterization of CIT-16P	
4.3.3 Transformation of CIT-16P to SAPO-17 (ERI)	
4.3.4 Structure Solution of CIT-16P	170
4.3.5 MTO Reaction	
4.4 Conclusion	
4.5 Acknowledgements	177
4.6 References	

Chapter CIT-17,	5 Improving the Propylene Selectivity in the Methanol-to-Olefins Reaction an SAT-Type Molecular Sieve	over 182
Abstra	act	182
5.1	Introduction	183
5.2	Experimental Section	187
5.2.	1 Materials	187
5.2.	2 OSDA Syntheses	188
5.2.	3 Ion Exchange and Titration	190
5.2.	4 Molecular Sieve Syntheses	190
5.2.	5 Product Recovery and Thermal Treatment	193
5.2.	6 Characterization	194
5.2.	7 Catalytic Testing	196
5.3	Results and Discussion	197
5.3.	1 Synthesis and Characterization of CHA- and AEI-type Materials	197
5.3.	2 Synthesis and Characterization of SAT-type Molecular Sieves	199
5.3.	3 MTO Reaction Testing	205
5.3.	4 Changing the Reaction Conditions to Further Enhance the P/E	212
5.3.	5 Relationships between Effluent Product and Retained Hydrocarbons	213

5.3.	6 Cyclic Testing	
5.4	Conclusion	
5.5	Acknowledgements	
5.6	References	
Chapter	6 Conclusions and Outlook	
6.1 Co	onclusions	
6.2 Oi	ıtlook	
Appendi	x A Supplemental Information – Chapter 2	
Appendi	x B Supplemental Information – Chapter 3	
Appendi	x C Supplemental Information – Chapter 4	
Appendi	x D Supplemental Information – Chapter 5	

List of Figures

Figure 1.4. Relationships between experimental propylene-to-ethylene ratios (P/E) (blue) and (B+P)/E (B=butenes). (Reproduced with permission from ⁴⁷). Copyright 2021 Wiley-VCH.

Figure 1.8. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for SSZ-39 samples as well as solid-state NMR spectra of various SSZ-39 samples steamed at different temperatures (550, 650, and 850 °C). (a) MTO reaction results of parent/control SSZ-39. (b) MTO reaction results of H-SSZ-39-st-750. (c) ²⁹Si and ²⁷Al MAS NMR spectra of the

Figure 2.3. GC-MS distribution of the extracted hydrocarbon species for 17 molecular sieves after 5 minutes of reaction with methanol at 400 $^{\circ}$ C and WHSV of 1.3 h⁻¹. The relative concentration of the aromatic species retained were relative to SAPO-34-0.4Si.91

Figure 3.1. Organic structure-directing agents (OSDAs) used in this work. OSDA 1 was used for the synthesis of SSZ-13. OSDA 2 was used for the synthesis of SAPO-34. OSDAs

Figure 4.5. Structure refinement of CIT-16P. (a) Dual-phase refinement for the main-phase CIT-16P and the AFX impurity. (b) Electron density map of the OSDA occluded within the CIT-16P cavities. (c) Idealized structure of CIT-16P occluded with DiQ-C₄ OSDA dications. 169

Figure 4.7. Visualized structural characteristics of CIT-16P reproduced from the binary structure refinement result of CIT-16P and impurity AFX. (a) Wireframe side-views of visualizations of CIT-16P (left) compared to SAPO-17 (ERI) (right). (b) Side-views of a pre-can and a can CBU. The top A, middle B, and bottom A layers are denoted in purple, blue, and green colors, respectively. The oxygen site (O16) that directly connects the top and bottom layers is highlighted. (c) A top view of a pre-can CBU of CIT-16P revealing the position of the oxygen site (O26) that forms pentacoordinated Al-sites. (d) A perspective view that shows the highly-strained T-sites (Al5 and P6) of CIT-16P....... 173

Figure 5.3. Propylene-to-ethylene (P/E) ratio of the various materials investigated..... 209

Figure 5.4. Representative MTO reaction data obtained at 350 °C and WHSV 0.65 h ⁻¹ for CIT-17-4
Figure 5.5. GC-MS distribution of the extracted hydrocarbon species after five minutes of reaction with methanol at 400 °C and WHSV of 1.3 h ⁻¹ and their relative concentration (relative to SAPO-34-1)
Figure 5.6. Time-on-stream (TOS) plot of six consecutive reactions with CIT-17-4 at the optimized reaction conditions (350 °C and WHSV of 1.3 h ⁻¹)
Figure A2.1. Powder XRD patterns of AEI-type molecular sieves. (a) SAPO samples and (b) zeolites
Figure A2.2. Powder XRD patterns of CHA-type molecular sieves. (a) SAPO samples and (b) zeolites
Figure A2.3. Powder XRD patterns of LEV-type molecular sieves. (a) SAPO samples and (b) zeolites
Figure A2.4. Powder XRD patterns of ERI-type molecular sieves. (a) SAPO samples and (b) zeolites
Figure A2.5. Powder XRD patterns of SWY-type molecular sieves. (a) SAPO samples (STA-20) and (b) zeolite (STA-30)

Figure A2.6. ²⁹ Si MAS NMR for selected SAPOs and zeolites (proton-form)	240
Figure A2.7. ¹ H MAS NMR spectra for dehydrated SAPOs and zeolites (proto	on-form). 241
Figure A2.8. MTO reaction on SAPO-18 obtained at T=400 °C	242
Figure A2.9. MTO on AEI zeolites obtained at T=400 °C	243
Figure A2.10. MTO reaction on SAPO-34 obtained at T=400 °C	244
Figure A2.11. MTO on CHA zeolites obtained at T=400 °C.	245
Figure A2.12. MTO on SAPO-LEV materials obtained at T=400 °C	246
Figure A2.13. MTO on LEV-type zeolites obtained at T=400 °C	247
Figure A2.14. MTO on SAPO-ERI materials obtained at T=400 °C	248
Figure A2.15. MTO on ERI zeolites obtained at T=400 °C.	249
Figure A2.16. MTO on SAPO-SWY obtained at T=400 °C	250
Figure A2.17. MTO on STA-30-(8) (SWY Zeolite) obtained at T=400 °C	250

Figure A3.2. ¹³C-NMR of the OSDAs used in this work. 10% D₂O (with the remaining being water) was used as an NMR solvent for OSDAs 1-3, 5, 7-8, and 10. The other OSDAs Figure A3.3. TGA profiles of the fresh (as-synthesized) CHA-type materials: (a) SSZ-13 **Figure A3.4.** TGA profiles of the fresh (as-synthesized) ERI-type zeolite catalysts: (a) SSZ-98-1, (b) SSZ-98-2, (c) UZM-12, (d) ERI zeolite-1, and (e) ERI zeolite-2. ERI zeolite-Figure A3.5. TGA profiles of the fresh (as-synthesized) SAPO-17 catalysts: (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-4, (d) SAPO-17-5, and (e) SAPO-17-6. SAPO-17-3 is not **Figure A3.8.** N₂-adsorption-desorption isotherms of thermally treated CHA-type materials. (a) SAPO-34 and (b) SSZ-13. Circles (darker) correspond to adsorption and Figure A3.9. N₂-adsorption-desorption isotherms of thermally treated ERI-type zeolites. (a) SSZ-98-1, (b) SSZ-98-2, (c) UZM-12, (d) ERI zeolite-1, (e) ERI zeolite-2, and (f) ERI zeolite-3. Circles (darker) correspond to adsorption and triangles (lighter) to desorption. **Figure A3.10.** N₂-adsorption-desorption isotherms of thermally treated SAPO-17s. (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-3, (d) SAPO-17-4, (e) SAPO-17-5, and (f) SAPO-17-6. Circles (darker) correspond to adsorption and triangles (lighter) to desorption. Figure A3.11. SEM images at 5k magnification of the CHA samples, SSZ-13 (left) and **Figure A3.12**. SEM images at 20k magnification as of the ERI-type zeolites (scale bar = 1

Figure A3.14.	(a-c) ²⁹ Si, ²⁷ Al, ar	nd ¹ H MAS NM	R spectra for S	SZ-13 (CHA-ty	ype) and (d-
e) ²⁹ Si and ¹ H I	MAS NMR spectr	a for SAPO-34	(CHA-type)		

Figure A3.17. (a) ¹ H MAS NMR	spectra of selected ERI-type zeolites. (b) ¹ H MAS NM	ЛR
spectra of selected SAPO-17s		67

Figure A3.18. TGA profiles of the spent (deactivated) CHA-type cat	alysts: (a) SSZ-13 and
(b) SAPO-34. (10 °C/min in air).	

Figure A3.20. TGA profiles of the spent (deactivated) SAPO-17 catalysts: (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-3, (d) SAPO-17-4, (e) SAPO-17-5, and (f) SAPO-17-6. (10 °C/min in air).

Figure A3.24. MTO reaction data obtained at 400 °C and WHSV of 1.3 h ⁻¹	for ERI Zeolite-
2-IE2 (left) and ERI Zeolite-3-IE2 (right).	

Figure A4.3. XRD	patterns of	the SAPO	materials	that wer	e synthesized	using DiQ-C ₄ -
(OH) ₂ as an OSDA.	•••••					

Figure A4.4. 8k MAS solid-state ¹³C NMR spectrum of as-made CIT-16P compared to the solution ¹³C NMR spectrum of DiQ-C₄ OSDA. For the solution NMR spectrum, CD₃OD was used as the solvent. 280

Figure A4.10. TGA profile of the CIT-16P sample after 4 weeks of ozone treatment. The amount of OSDA remaining in the sample following 4 weeks of ozone treatment is about 4.8%.

Figure	A5.1.	Molecular	sieve	topologies	(obtained	from	IZA)	for	SAT	(left),	CHA
(middle), and A	AEI (right).			•••••	•••••		•••••			303

Figure A5.4. PXRD patterns of the CHA/AEI-type molecular sieve (SAPO-34/18). The sample is mostly CHA, with a small amount of AEI. CHA/AEI intergrowth materials typically display this shoulder (shown with an arrow) due to the presence of AEI. 307

Figure A5.8. Characterization on SAPO-34/18. (a) 29 Si MAS NMR spectrum. (b) 27 Al MAS NMR spectrum. (c) 31 P MAS NMR spectrum. (d) 1 H MAS NMR spectrum. 312

Figure A5.12. PXRD patterns of several CIT-17 samples with different Si/T-atom ratios synthesized using DiQ-C₅. CIT-17-1 (bottom; Entry 33), CIT-17-4 (middle; Entry 32; different batch than the one reported in the main-text), and CIT-17-5 (top; Entry 31).. 315

Figure A5.16. MTO reaction data on AEI-type molecular sieves obtained at 400 °C and WHSV of 1.3 h⁻¹. (a) SAPO-18-1, (b) SAPO-18-2, (c) SAPO-18-3, (d) MgAPO-18, and (e) CoAPO-18. 319

Figure A5.18. MTO Reaction data on CIT-17-type molecular sieves obtained at 400 °C and WHSV of 1.3 h⁻¹. MgAPO-SAT is on the left whereas CoAPO-SAT is on the right.

List of Tables

 Table 1.2. Summary of MTO reaction data for the steamed zeolites before and after trimethylphosphite treatment. (Reproduced with permission from ⁸⁶). Copyright 2016 Elsevier.

 38

Table 1.3. Characterization results and reaction data on the three zeolites tested in MTO(T=400 °C, WHSV=1.3 h⁻¹). (Reproduced with permission from ⁹⁰). Copyright 2012American Chemical Society.39

Table 2.5. Averaged product selectivities for the zeolites tested in this work when
conversion >97%. Reactions were performed at 400 °C and a WHSV(MeOH) of 1.3 h^{-1} .[a] Reported from our previous work.85

Table 3.1. Cages/materials studied in this work and their dimensions.
 105

Table 3.2. Characterization data of the CHA-type and ERI-type zeolites.
 118

Table 3.3. Characterization data of the SAPO-34 and SAPO-17 materials
Table 3.4. Reaction results of the molecular sieves investigated
Table 5.1. Reaction results of the SAPO materials investigated
Table A2.1. Sample IDs of the ERI-type molecular sieves tested in this work and their corresponding IDs in our previous work, where they were also characterized (refer to the Materials Section). 234
Table A3.1. Products and chemical compositions of selected syntheses for ERI-typezeolites. These gels were slightly modified from the references $^{2-5}$
Table A3.2. Products and chemical compositions for SAPO-17. 258
Table A4.1. Products and gel chemical compositions for the synthesis of CIT-16P/ERI using DiQ-C ₃ -(OH) ₂ as an OSDA
Table A4.2. Products and gel chemical compositions for the synthesis of CIT-16 using DiQ-C ₄ -(OH) ₂ as an OSDA. 278
Table A4.3. Framework energy of ERI and CIT-16P obtained from GULP or DFT calculations. 286
Table A4.4. Lattice parameters and reliability factors obtained from the Rietveld refinement. 290
Table A4.5. Crystallographic Information File (atomic positions and anisotropic tensors of atoms) of CIT-16P acquired by the Rietveld refinement
Table A4.6. Bond valences and bond distances for specific positions. 295
Table A4.7. Topological analysis results for CIT-16P
Table A4.8. Stabalization energy of CIT-16P obtained from GULP or DFT calculations. 297

Table A5.1. Products and gel chemical compositions of SAT-type molecular sieves using DiQ-C₄ as an OSDA. [a] "N" indicates no, whereas "Y" indicates yes. Entries highlighted in orange are samples that were tested in MTO. Entry 5 refers to CIT-17-2. Entry 25 refers to MgAPO-SAT.

Table A5.4. Elemental composition data for the various samples tested in this work. [a]Refers to the Entry numbers in Tables A5.1 to A5.3. [b] Determined by EDS.T=Si(M)+Al+P and M is either Co or Mg.309

Chapter 1 | Introduction to the Methanol-to-Olefins Reaction

1.1 Motivation

Ethylene (ethene; E) and propylene (propene; P) are by far the two largest-volume chemicals produced by the petrochemicals industry. Indeed, light olefins are the feedstock employed in the production of a vast array of chemicals, including but not limited to, polymers (e.g., polyethylene and polypropylene), oxygenates (e.g., ethylene glycol, acetaldehyde, and propylene oxide), and various important chemical intermediates (e.g., ethylbenzene and propylene oxide).^{1,2} According to several reports, global demand for ethylene and propylene is expected to grow at an annual rate of 5% for propylene and 4% for ethylene.^{2,3} Today, the majority of light olefins are produced from pyrolysis (steam cracking) or from the fluid catalytic cracking (FCC) of naphtha.² The recent fluctuations in oil prices and changing feedstocks (e.g., away from oil and toward natural gas) are reviving a strong interest in the production of ethylene and propylene from other non-petroleum sources. The methanol-to-olefins (MTO) reaction, touted as one of the most important reactions in C₁ chemistry,⁴ offers an opportunity to produce these essential molecules from non-oil resources such as natural gas, coal, and biomass.

At the nexus of this reaction is methanol, a molecule which is known to be highly reactive, as it can be catalyzed by acidic zeolites to form various hydrocarbons.^{5,6} Although methanol is a small and simple molecule, the reactions it can undergo have been demonstrated to be very complicated, leading to a variety of products (e.g., olefins, paraffins, aromatics, etc.) over different molecular sieves .^{6–19} Indeed, establishing a product selectivity control for this complex reaction system while also achieving better carbon efficiency remains a scientific challenge as it requires

profound understanding of reaction and deactivation mechanisms. It also requires understanding of how material synthesis affects catalyst properties and reaction performance.

It's been demonstrated previously that zeolite topology/framework plays an instrumental role in product selectivity and distribution: because of that, it can be used as a powerful tool to propagate one product over another in MTO (discussed in more depth in subsequent sections).^{20,21} Small-pore 8-member ring (8-MR) molecular sieves (also discussed in more depth in subsequent sections), which are the catalysts of choice in the MTO reaction, are made up of large cavities that are interconnected by narrow window openings.²² Due to their dimensions, they are ideal for the MTO reaction because they guarantee high selectivity to short-chain olefins (~80%, for SAPO-34, a silicoaluminophosphate (SAPO) with a CHA pore topology; the catalyst used commercially).⁴ Figure 1.1 shows a few examples of small-pore, cage-type molecular sieves. These molecular sieves have been utilized quite extensively in the MTO literature,²³⁻²⁷ as they contain openings that are large enough to allow olefins such as ethylene, propylene, and butenes to pass through, but small enough to retain larger molecules inside their cages.²⁸ Indeed, these small cavity dimensions often create an ideal environment for the incubation of deactivation-causing hydrocarbon pool species.⁴



Figure 1.1. Examples of small-pore, cage-type molecular sieves that have been previously tested in MTO.

Chabazite (CHA), one of the most studied topologies in MTO (due to its commercial success), is composed of cylinder-like cavities with big dimensions that can accommodate and hold aromatic molecules up to pyrene.²⁹ The catalyst used commercially is denoted as SAPO-34 and is a CHA-type molecular sieve. Because of its cavity structure and size, SAPO-34 ensures a long lifetime when compared to other 8-MR molecular sieves.³⁰ Despite its high selectivity toward light olefins (ethylene and propylene) and appreciable lifetime, its ethylene-to-propylene selectivity ratio is often fixed at approximately 1. Changes in catalyst acidity (strength as well concentration of acid sites) allow for slight changes in the product distribution of CHA as well as several other small-pore, cage-type molecular sieves (e.g., AEI and AFX).^{31,32} However, from our group's findings over the years (discussed in more depth in a subsequent section), these changes due to Brønsted acidity in small-pore molecular sieves are *typically* inconsequential when compared to the effect of cage topology on product distribution.

In spite of the commercial success of SAPO-34 (CHA), there is a growing interest in the field in developing strategies that would augment the olefins product distribution to favor the formation of either more ethylene or propylene, depending on market demand and/or profitability. This would certainly improve the versatility of the MTO process, particularly with the deployment and commercialization of other competing olefins on-purpose production technologies such as, propane/ethane dehydrogenation, butenes metathesis, and enhanced FCC processes. To that end, the work in this thesis aims to thoroughly investigate the combined effects of cage size/dimension and acidity (both acid site density and strength) on the olefins product distribution (discussed in Chapter 2) and then utilize these findings and mechanistic insights to rationally design materials that would significantly improve the ethylene-to-propylene ratio (or propylene-to-ethylene ratio) over CHA-type molecular sieves (Chapters 3-5).

1.2 Background and Literature Review

The possibility of converting methanol-to-hydrocarbons (MTH) was first discovered by Mobil Oil Company in 1976 using ZSM-5 and later commercialized.³³ Even though this reaction was initially considered a new route for the procurement of gasoline, further research on this topic revealed that it is possible to obtain a wide array of hydrocarbons from methanol. The key to changing the product distribution lies in the selection of an appropriate catalyst (e.g., small-pore, medium-pore, or large-pore) and optimization of the reaction conditions.^{34,35} For instance, in the case of methanol-to-hydrocarbons (MTH) or methanol-to-gasoline (MTG), which typically proceeds in medium- and large-pore molecular sieves (e.g., MFI), a wide range of products can be obtained, including olefins, aromatics, and paraffins. However, this is fundamentally different than what occurs in MTO, which typically proceeds in small-pore, cage-type molecular sieves (e.g., CHA), where the aromatic species are trapped as intermediates (as opposed to contributing to the product), thus, leading to improved light olefins selectivities.

As mentioned in the previous section, short-chain olefins are particularly important in the petrochemical industry. Indeed, the importance of ethylene and propylene coupled with the ability to obtain these two molecules with exceptionally high selectivities using small-pore molecular sieves paved the road for the commercialization of the methanol-to-olefins technology, a spin-off of MTH. The first production plant for MTO was set–up in China in 2010 using SAPO-34 (CHA) as the commercial catalyst, with many more plants expected to come on stream in the next decade. There are numerous attempts, too, to make the MTO process more selective toward either more ethylene to propylene, leading to methanol-to-ethylene (MTE) or methanol-to-propylene (MTP) processes.^{36,37}

1.2.1 Small-pore, Cage-type Molecular Sieves

Molecular sieves refer to a group of crystalline, microporous solid materials that are constructed with any elemental composition or framework charge. Zeolites are one type of molecular sieves. Strictly speaking, a zeolite is an aluminosilicate (therefore, not all molecular sieves are zeolites). Substitution of ions other than Al³⁺ into a pure SiO₂ yield molecular sieves that are called metallosilicates.³⁸ To date, thousands of synthetic zeolites and related metallosilicates have been synthesized and many have been used in catalytic applications. There are also many zeolites that occur naturally such as, clinoptilolite, mordenite, phillipsite, and stilbite.

Aluminosilicates (zeolites) are synthesized by substituting Al for Si within the neutral SiO₂ framework. In doing so, for every Al that is substituted, one negative charge is formed due the difference in oxidation state between Al and Si. This negative charge is balanced by a proton (in the thermally treated form of the zeolite; H⁺), thus enabling zeolites to play a role as solid acid catalysts such as in the MTO reaction. Two neighboring aluminum atoms cannot exist next to each other (O-Al-O-Al-O) in a zeolite due to Loewenstein's rule.³⁹ Therefore, this rule bounds the lower limit of Si/Al in any zeolite to unity even though there isn't a theoretical upper limit to the Si/Al ratio (you could have a pure silica zeolite).

Crystalline microporous aluminophosphates (designated as AlPO₄-n or AlPO-n for short), which are composed of tetrahedral AlO₄ and PO₄ units, are a new family of molecular sieves. Similar to aluminosilicates (i.e., zeolites), the incorporation of heteroatoms into an otherwise neutral aluminophosphate generates a solid acid catalyst with variable strength, depending on the element selected. Generally, this element is Si, which yields silicoaluminosphosphates (SAPOs) (**Figure 1.2**).



Figure 1.2. Idealized 2D connectivity of tetrahedral AlPOs and SAPOs. (a) Idealized 2D connectivity of tetrahedral AlPO4 framework showing a neutral framework. (b) An isolated Si, which formed following the substitution of Si for P to give a SAPO. Si substitution for P in AlPO4 yields a charge, which creates a Brønsted acid site (SM2). No Si-O-P or P-O-P can be formed. (c) A Si island with 5 Si substituting for 4 Ps and 1 Al, generating 3 H⁺ (SM2 and SM3).

SAPO materials are essentially isostructural to their zeolite counterparts. They are synthesized by incorporating Si into the framework of the aluminophosphate molecular sieve. Because of the neutral frameworks of AlPO₄-based materials, their applications as acidic catalysts are limited. However, partial substitution of P with Si generates negatively charged frameworks resulting in SAPOs, which can be used as acidic catalysts (**Figure 1.2**). The use of SAPOs for the conversion of methanol to ethylene and propylene in MTO, much like in the case of zeolites, relies on the properties of the material used particularly structure, and to a certain extent, acidity. SAPOs generally have lower acid site densities (due to their low Si content) than traditional zeolites, though, this concentration increases as a function of Si content. This increase in concentration of Brønsted acid sites as a function of Si content occurs due of the assumption that SAPO materials are obtained from AlPO₄ frameworks by an ideal silicon substitution.

The primary mechanism is believed to be silicon substitution for phosphorous (referred to as SM2), which results in a negative charge that is balanced by a protonated template (in the assynthesized material) or a proton (in the thermally treated form). In this mechanism, a Si(4Al) environment is formed following the substitution, and this leads to the formation of a bridging Si-OH-Al hydroxyl group that exhibits Brønsted acidity. The other plausible mechanism for the silicon substitution in SAPOs involves the replacement of two silicon atoms for one aluminumphosphorous pair (referred to as SM3). This kind of substitution does not alter the framework charge neutrality, so it does not result in the generation of a Brønsted acid site. Therefore, the concentration of Brønsted acid sites in SAPO materials can be equal to the total Si content or less, depending on the type of incorporation. In most cases, the incorporation of Si into an AlPO4 framework takes places either by SM2 alone or a combination of SM2 and SM3 in a way that prevents the formation of unstable bonds (e.g., Si-O-P). As such, Si atoms in SAPO-type molecular sieves can have up to five different environments Si(nAl) (where n=0-4). It has been postulated that the acid strength of the Si-OH-Al group associated with a given Si(nAl) site increases as n decreases.⁴⁰⁻⁴³

While zeolites and SAPOs are two of the most common types/classes of molecular sieves used in MTO, there are a few other compositions that could also react with and convert methanol, including metalloaluminophosphates (MAPOs). Magnesium, cobalt, zinc, and nickel are a few examples of metals (M) that can be introduced into an AlPO₄ structure to form a MAPO. And, just like in the case of SAPOs, substituting M (II) into the framework leads to the generation of an acid site, which can then catalyze methanol. The key difference between MAPOs and SAPOs generally lies in the strength of the acid site that is generated (due to differences in the elemental composition).⁴⁴

Even though molecular sieves can have different compositions, leading to different materials, several materials could share a framework or "topology." Topology, in essence, is a geometric concept that describes how the tetrahedral atoms that make up a given molecular sieve

are connected together. The International Zeolite Association (IZA) structure database provides crystallographic data of 240+ frameworks/topologies which have been discovered to date. Some frameworks can be synthesized only as one class of materials (e.g., as a zeolite or an AIPO/SAPO) with a narrow Si/Al (or Si/T-atoms) whereas others can be synthesized both as SAPOs and also as zeolites over a wide range of synthetic conditions.

Frameworks are typically denoted using three-letter codes. An example of this would be the zeolite 'chabazite,' a common MTO topology/framework, which is abbreviated as CHA. Albeit 'CHA' refers to the framework, there are many materials that share this topology. These include, for instance, SSZ-13 (a zeolite), AIPO-34 (an AIPO), and SAPO-34 (a SAPO). Indeed, zeotype nomenclature can be particularly complex, as each new zeotype composition synthesized may be given trade-names based on the research group (e.g., CIT-17 (SAT)). To simplify things, throughout this thesis, three-letter codes will be used frequently and will appear often in parentheses following the name of a given material (e.g., SSZ-13 (CHA) or SAPO-34 (CHA)).

1.2.2 Methanol-to-Olefins Reaction Mechanism: Dual Catalytic Cycles

Since the discovery of the MTH process by Mobil, there has been considerable discussion regarding the origin of the first C-C bond and the mechanism by which the MTH reaction network proceeds. There is now consensus over the methanol's inability to couple directly for steady-state MTH catalysis. For instance, Lesthaeghe et al.²⁹ used ONIOM to calculate the activation energies required to form C-C, starting from two methanol molecules. The authors found that the activation energy barrier for direct C-C coupling to be "prohibitively high," ~200 kJ/mol.

Dahl and Kolboe⁴⁵ proposed in their seminal work a hydrocarbon pool mechanism in which methanol forms a pool of $(CH_2)_n$ (**Figure 1.3**). These species then produce various hydrocarbons, including light olefins, alkanes, and aromatics. It is now widely agreed upon that MTH (and by

extension MTO) proceeds via this indirect hydrocarbon pool mechanism, which comprises of an olefin cycle and an aromatic cycle (the combination of these two cycles is often referred to as "dual cycle" for short).⁴⁶ In the case of MTO, which as mentioned previously, typically employs molecular sieves with cages interconnected through small-pore 8-ring windows (e.g., SSZ-13 or SAPO-34), the hydrocarbon pool intermediates consist predominantly of aromatic species.⁴⁷



Figure 1.3. MTO hydrocarbon-pool mechanism. (a) The hydrocarbon pool mechanism proposed by Dahl and Kolboe. (Reproduced with permission from ⁴⁸). Copyright 1994 Elsevier. (b) The aromatic cycle showing the paring and side-chain routes. (Reproduced with permission from ⁴⁹). Copyright 2009 Wiley-VCH. (c) Dual cycle concept, which incorporates the olefins cycle as well as the aromatics cycle (Reproduced with permission from ³⁴). Copyright 2012 Wiley-VCH.

Indeed, the emergence of the dual cycle mechanism has contributed to the general understanding of the hydrocarbon pool mechanism taking place in acidic molecular sieves. Recently, Bhan et al.⁴⁶ pointed out to six major chemistries that occur within the dual cycle mechanism in MTH: olefin methylation, olefin cracking, hydrogen transfer, cyclization, aromatic methylation, and aromatic dealkylation. The extent to which these chemistries occur varies vastly from one framework to another (and reaction conditions), thus, further adding to the complexity of this reaction. Fundamentally, the goal of ongoing research in this area is to understand how

these chemistries and the forming intermediates that comprise the MTH/MTO hydrocarbon pool mechanism contribute to the observed product distribution.

Several authors have shown that polymethylbenzenes (aromatic cycle species) are active hydrocarbon pool species for the production of light olefins for various frameworks (e.g., *BEA, MOR, MFI, CHA, and AEI).^{47,50–53} The current data suggests that methylbenzenes and their protonated counterparts are vital reaction intermediates. It's been postulated that alkenes are formed from the aromatics cycle via either a paring mechanism (paring refers to an initial ring contraction that forms a bicycle-hexenyl-type cation that splits off either propene or iso-butene followed by a ring expansion and methylation) or a side-chain scheme (side-chain refers to the exo-methylation of a polymethylbenzenium cation to form an alkyl chain that after some methyl-shifts is eliminated yielding preferentially ethene).⁴⁹ The two aforementioned aromatic routes are shown in **Figure 1.3**, and they work in tandem, particularly in small-pore, cage-type molecular sieves, to dictate the product distribution.

Numerous groups have demonstrated that the contribution of each cycle (olefins or aromatics) as well as each pathway within the aromatics cycle (paring or side-chain) influences the final light olefin product distribution.^{47,49,54,55} Again, as mentioned earlier, in the case of smallpore, cage-type molecular sieves, the hydrocarbon pool species are typically aromatic in nature and remain entrapped within the cages of these catalysts. Thus, the differences observed in the olefins product distribution are due to differences in the species that form/propagate as a result of differences in the contribution of each route (paring or side-chain). Indeed, the contribution of the olefins cycle is often small or negligible in small-pore, cage-type molecular sieves.

Svelle and coworkers⁵⁶ suggested based on their carbon isotope $({}^{12}C/{}^{13}C)$ switching experiments that ethylene is formed exclusively from the aromatics cycle, whereas the alkenes
(olefins) cycle generated propylene. Sun et al.⁵⁷ demonstrated that both ethylene and propylene can be formed from the aromatics cycle in ZSM-5 (MFI). Additionally, previous research on the type of hydrocarbon pool (HP) intermediates formed in the MTO reaction has pointed to cage geometry as a key parameter that affects the type of carbenium intermediates formed.⁵⁸ Zhang et al.⁵⁸ tested SSZ-13 (6.7 x 10 Å), DNL-6 (11.4 x 11.4 Å), and RUB-50 (6.3 x 7.3 Å) and found different carbenium ions residing within each of these materials, which correlated with the cavity structure of the zeolite catalysts.

Additionally, Corma et al.^{47,52} performed a comprehensive study that demonstrated that the light olefins product distribution catalyzed by acidic zeolites and zeotypes (e.g., SAPOs) depends on the nature of the entrapped hydrocarbon pool species that act as co-catalysts. Indeed, the authors showed computationally and experimentally that the product distribution in MTO depends on the ability of the catalyst cage (e.g., ERI, LEV, AEI, CHA, DDR, AFX, ITE, RTH, UFI, KFI, and LTA) to preferentially stabilize the penta-methylbenzene cation (5MB⁺), which is involved in the side-chain pathway and produces primarily ethylene or the fully methylated (7MB⁺) cation, which is involved in the paring pathway and produces primarily propylene and butenes. In this work, there were a few materials that deviated from the predicted behavior, which included ERI and LEV. The authors postulated that the deviation in the MTO behavior for ERI and LEV is likely due to a non-negligible contribution from the alkene (or olefins) cycle, which their predictor parameter (E_{int(7/5}) did not account for (Figure 1.4). The authors also indicated that SAV, UFI, RHO, KFI, and LTA-type materials (all have larger cages than CHA) formed significant amounts of alkanes and other products (similar to what we observed in our group's studies) due to the loss of confinement effects in those relatively large cages.



Figure 1.4. Relationships between experimental propylene-to-ethylene ratios (P/E) (blue) and (B+P)/E (B=butenes). (Reproduced with permission from ⁴⁷). Copyright 2021 Wiley-VCH.

1.2.3 Effect of Cage Size/Dimension on the MTO Product Distribution

Previous research efforts on the MTH/MTO mechanism have pointed out to a plausible structure-intermediate relationship. Haw et al.²⁹ suggested that the formation of higher olefins occurs from hydrocarbon pool intermediates that have more methyl groups. Specifically, less methylated benzenes (e.g., trimethylbeneze) were found to be more selective for ethylene (associated with more ethylene; and higher ethylene-to-propylene ratios) whereas hexamethylbenzene is more selective for propylene. Several other groups reached similar conclusions. Bhan et al.,⁵⁹ for instance, performed site-specific isotope tracing experiments that distinguished between isotope labels in aromatic methyl and aromatic ring positions for each methylbenzene that demonstrated that tetramethylbenzene gives ethylene via the side-chain mechanism and penta- and hexamethylbenzenes give propylene via the paring mechanism. Additionally, Ferri et al.⁶⁰ rationalized that the differences observed in the olefins product distribution between CHA (SSZ-13 and SAPO-34) and AEI (SSZ-39 and SAPO-18) are primarily

due to differences in the preferential stabilization of fully-methylated hydrocarbon intermediates. Specifically, the authors concluded that AEI leads to the formation of a higher P/E ratio than CHA because of the ability of the AEI cage to better stabilize fully and near fully methylated benzenes, which favor the paring pathway.

Pinilla-Herrero and coworkers⁴⁰ investigated the MTO behavior of four SAPO materials: SAPO-35 (LEV), SAPO-56 (AFX), STA-7 (SAV), and SAPO-42 (LTA). The authors synthesized these materials with similar silicon contents. However, despite having similar Si contents, the ²⁹Si NMR results revealed some differences in the Si distribution among the four. The authors attributed these differences in Si distribution to differences in the molecular sieve structures and synthesis conditions, which affected the Si incorporation mechanism. The MTO behavior of these four frameworks was tested at 400 °C. The time-on-stream (TOS) data showed that both cage-type and pore window size influenced the olefins product distribution as well as catalyst lifetime. Indeed, their results show that framework topology has a greater influence on the catalytic behavior of SAPO materials than acidity. Generally, larger cages formed longer olefins. Specifically, the formation of C₄ olefins was enhanced in materials with larger pores and larger cage sizes (e.g., SAPO-42 and STA-7) whereas ethylene selectivity was higher in materials with smaller cages and smaller pores (e.g., SAPO-35).

Castro et al.⁶¹ investigated the MTO behavior of STA-7 (SAV), STA-14 (KFI), and SAPO-34 (CHA), and found that catalytic performance was dictated by crystallite size, cage connectivity, and topology. Moreover, ex-situ GC-MS analyses on the aforementioned SAPO catalysts after the MTO reaction revealed that the uniformity of the cage shape and its size were critical factors governing the type of accumulated aromatic hydrocarbons, hence, influencing the MTO behavior and deactivation profile of each material. For example, in the case of SAPO-34 (CHA), the major aromatic hydrocarbon species detected early in the reaction were tetramethylbenzene (4MB), followed by penta- (5MB) and hexamethylbenzenes (6MB). As pointed out earlier, tetramethylbenzenes are known to preferentially produce ethylene. In the case of STA-7, the hydrocarbon-pool species included higher amounts of 5MB and 6MB than CHA. As indicated earlier, both of these compounds are associated with propylene. The authors also showed that after prolonged time-on-streams, all the catalysts formed larger aromatic molecules (i.e., deactivating species). These mostly comprised of di- and tricyclic compounds (e.g., polymethylated naphthalenes). STA-7 (SAV) formed larger cyclic compounds than SAPO-34 (CHA), including pyrenes.

Indeed, there has been tremendous interest in trying to correlate the olefins product distribution in MTO with a structural parameter while also identifying a structure-property relationship that would aid in the prediction of the olefins product distribution. Our group has made significant contributions in this area (not discussed yet). I discuss our group's findings in a separate section.

1.2.4 Effect of Catalyst Acidity (Concentration, Distribution and Strength) on the MTO Behavior

The MTO literature is rife with reports investigating the effect of catalyst acidity on the MTO activity and behavior. Indeed, this parameter is often investigated in combination with the effect of structure (i.e., framework). Acidity, of course, can refer to concentration, distribution, and/or strength. In this thesis, I focus on the effects of acid site density and strength on the olefins product distribution.

Sastre and coworkers⁶² evaluated the MTO performance of several SAPO-34 (CHA) materials at 400 and 450 °C that were prepared hydrothermally using tetraethylammonium

hydroxide (TEAOH). The authors noted that increasing the Si content in the gel resulted in the formation of SAPO-34 molecular sieves with smaller crystallites. Moreover, their ²⁹Si CP/MAS NMR spectra revealed that all their SAPO-34 samples had a broad envelope in the -80 to -120 ppm range, corresponding to several resonances due to different Si(nAl) environments (n=0-4). Therefore, in these samples, the Si incorporation occurred not only by SM2 but also by simultaneous substitution of a pair adjacent Al-P atoms (SM3). The authors also observed that a higher number of acid sites were generated through the SM2 mechanism, while substitution via SM2+SM3 yielded less but stronger acid sites. Despite these differences in terms of acid strength and density, the olefins product distribution of the various SAPO-34 tested did not show considerable changes. In fact, the authors pointed out to crystallite size as the main parameter affecting their reaction performance (lifetime).

Corma et al.⁶³ compared the performance of two SAPO-34 (CHA) materials: one nano-SAPO-34 synthesized in a microwave environment which had crystal sizes of approximately 20 nm and the other being a conventional hydrothermally prepared SAPO-34. The authors then exposed both samples to moisture for an extended amount of time, to change the Si distribution and study that effect on the hydrocarbon product distribution. The authors reported that Si distribution affected the lifetime and selectivity of the catalyst (~15% change in the C₂/C₃ ratio). A higher C₂/C₃ ratio was due to higher population of Si in the border of the Si islands. Despite Corma and coworkers' observations regarding the effect of acidity on the C₂/C₃ ratio, that change in C₂/C₃ is still relatively smaller when compared to the effects of cage size.

Pinilla-Herrero et al.⁴⁰ investigated the catalytic performance of three small-pore SAPOs with LEV, LTA, and SAV topologies that were synthesized using various silicon concentrations. The authors observed differences in the Si incorporation, showing that topological features and the

structure directing agent employed played an important role in controlling not only the Si location in the framework, but also the amount of Si incorporated. They also observed Si islands for all the frameworks when the Si content was high in the gel. Their catalytic experiments revealed that framework topology had a far greater influence than acidity on the catalytic behavior of SAPO materials in MTO. The authors observed that the ethylene-to-propylene ratio decreased (or did not change) with increasing Si content for both LTA and SAV, but increased, and rather significantly, for LEV. The reason why the LEV-type materials improved the E/P by increasing the Si content, whereas LTA- and SAV-type materials did not was not thoroughly explained, however.

Chen et al.⁶⁴ investigated the incorporation of silicon via direct synthesis into AIPO-18 (AEI), a material/structure that is related, but is crystallographically distinct from SAPO-34 (CHA). A wide range of Si/T=0-0.1 (T=Si+Al+P) ratios were investigated and compared to SAPO-34 (CHA). The authors found that the neutral AIPO-18 material catalyzed methanol conversion only to dimethyl ether (DME) due to the absence of bridging Si-OH-Al groups or Brønsted acid sites. The other SAPO-18 materials (even ones with low Si content) converted methanol to light olefins with high activity and selectivity over a wide range of temperatures (T=300-400 °C). Generally, the change in the E/P ratio was fairly small across the various SAPO-18 samples tested at identical reaction conditions. The key difference between the performances of the various SAPO-18 catalysts was lifetime, where increasing the Si content, in the low Si content range, resulted in longer lifetimes. The catalytic results also demonstrated that samples with very low Si content (i.e., lower acid sites) require higher temperatures to achieve high methanol conversion. These results suggest that the ideal Si/T ratio for AEI-type materials in MTO is likely in the region of 0.04-0.09, in order to achieve both high methanol conversion and long lifetime. Indeed,

operating below this limit appears to lead to lower methanol conversions and/or the formation of DME as the main product (particularly when the catalyst is an AlPO₄).

Another approach to changing the acidity of a catalyst involves incorporating a metal (e.g., Ni) into the structure. The concept of incorporating nickel into SAPO-34 for use in MTO was first performed by Inui and Kang⁶⁵ and later expanded by Kevan et al.⁶⁶ Kevan et al.⁶⁶ examined the selectivity of four small-pore SAPO molecular sieves, including SAPO-34 (CHA), SAPO-35 (LEV), SAPO-17 (ERI), and SAPO-18 (AEI), toward light olefins. The authors work focused on understanding the effects of framework type (structure type), presence of a transition metal ion (Ni), and amount of incorporated metal on the MTO performance (olefin selectivities). Kevan and coworkers' results show that these three factors indeed play an important role on the MTO catalytic behavior, particularly in the cases in which Ni(II) was incorporated into the SAPO materials (except, oddly, in the case of AEI). Incorporation of Ni(II) into the framework of SAPO-34, for example, increased the lifetime and catalyst selectivity toward ethylene (70+% compared to $\sim 35\%$) (by reducing the catalyst acidity), whereas the incorporation of Ni(II) by means of solid-state ion exchange increased only the ethylene selectivity. The authors also reported that the increase in ethylene selectivity was more prominent in the synthesized samples (~80%) than the ionexchanged samples (~70%).

The various studies outlined in this section, which broadly examined the effect of acidity on the olefins product distribution in MTO, suggest that this parameter's influence on selectivity is not straightforward. If anything, the various studies discussed in this section hint to a possible missing link between cage size and acidity. Together, these two parameters appear to affect the olefins product distribution. I uncover this missing relationship and elaborate on it in Chapter 2 of this thesis.

1.2.5 Effect of Reaction Conditions on the MTO Behavior

As indicated earlier, there are many physiochemical catalyst properties that influence the MTO reaction behavior, including but not limited to, cage/pore size, acid site density and strength, elemental composition (metal incorporation), and crystallite/particle sizes. The influence of cage size and acidity on MTO were discussed in the last two sections. In addition to these material properties, there are many reaction parameters that could also influence the observed product distribution, including, temperature, feed composition, and methanol partial pressure/weight hourly space velocity (WHSV). These reaction parameters are not thoroughly investigated as a part of this thesis, but we employ some of these strategies in Chapter 5, to further push the olefins product distribution toward forming more propylene in CIT-17 (SAT-type molecular sieve). As such, they are briefly discussed in this section.

The MTO reaction is typically performed at temperatures of 350-450 °C. This temperature range typically allows for the formation of olefins with high selectivities at complete methanol conversion while also abating the formation of undesired products (e.g., alkanes and methane).⁶⁷ Borodina et al.⁶⁸ investigated the selectivity toward lower olefins over SAPO-34 at reaction temperatures between 300-500 °C with a combination of operando UV-vis diffuse reflectance spectroscopy and online gas chromatography. The authors found that the selectivity toward propylene increases in the temperature range of 300-350 °C while it decreases in the temperature range of 350 to 500 °C. The authors show that the high degree of incorporation of olefins, particularly propylene, into the hydrocarbon pool species affects the product selectivity at the lower reaction temperatures (thus, leading to more propylene). The nature of the active hydrocarbon pool species also varied considerably as a function of temperature. At temperatures between 300-325°C the active hydrocarbon pool species were found to be mainly methylated

benzenes. At temperatures around 350°C, the hydrocarbon pool species included both methylated benzenes as well as methylated naphthalenes. At temperatures higher than 400°C, the main hydrocarbon pool species included methylated naphthalenes. The authors suggested that monoenylic and highly methylated benzenes were more selective to the formation of propylene at low temperatures whereas low methylated benzenes and methylated naphthalenes at higher temperatures favored the formation of ethylene. The authors also observed that increasing the reaction temperature above 350 °C led to catalyst deactivation with molecules that were neutral poly-aromatics, including phenanthrene/anthracene, with their respective contribution increasing with increasing reaction temperature (i.e., higher temperatures lead to larger and bulkier coke molecules). These results demonstrate the important role that temperature plays on the nature of the hydrocarbon pool species that form in small pore, cage-type molecular sieves (e.g., CHA) as part of the dual cycle, which then influences the olefins product distribution.

In addition to temperature, WHSV (or methanol partial pressure) was also found to influence the olefins product distribution. Recently, Shi et al.⁶⁹ demonstrated that decreasing the inlet methanol partial pressure and methanol space velocity in SAPO-34 (CHA), SSZ-13 (CHA), and SSZ-39 (AEI) increases the cumulative ethylene-to-propylene ratio. The authors performed dissolution-extraction experiments that revealed that the composition of hydrocarbons occluded in the catalysts suggest that decreasing the methanol concentration decreases the extent of methylbenzenes homologation within the entrained aromatics, resulting in increments in the concentration of aromatic precursors (e.g., tetramethylbenzenes) to ethylene relative to those for propylene (e.g., penta- and hexamethylbenzenes) (**Figure 1.5**).



Figure 1.5. Cumulative ethylene-to-propylene carbon ratio on SAPO-34 (CHA) with varying inlet methanol partial pressures (black circles), varying space velocities at 30kPa (diamonds), and 1kPa (triangles) with respect to the molar ratio of tetramethylbenzenes to the sum of penta- and hexa-methylbenzenes. (Reproduced with permission from ⁶⁹). Copyright 2021 Elsevier.

The results in this section show that changing the reaction parameters has an impact of the observed product distribution because changing these reaction parameters indirectly changes the type and concentration of the hydrocarbon pool species that form as a part of the dual cycle. Changing these species then leads to changes in the olefins product distribution.

1.3 Prior Work on the Methanol-to-Light Olefins Reaction in the Mark E. Davis Group

Our group has been studying the methanol-to-olefins reaction for over a decade. Our research efforts covered four broad areas: (1) understanding the effect of paired/adjacent Brønsted acid sites on reactivity and performance, (2) introducing steaming as a technique to post-synthetically modify small-pore, cage-type zeolites (that are normally synthesized over a narrow Si/Al range; e.g., SSZ-39 (AEI)) and increase their Si/Al_T, to make them more suitable for MTO, (3) developing OSDA-free synthesis routes for MTO-relevant zeolites and then post-synthetically treating them to obtain zeolites that are not only suitable for MTO, but are 'environmentally

friendly' (i.e., don't require the removal of a toxic OSDA) and are more affordable to produce, and lastly (4) developing structure-property relationships that relate cage size/dimensions to the observed olefins product distribution (i.e., Cage-Defining Ring (CDR)). Each of these areas is discussed in more depth in this section.

1.3.1 Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction

SAPO-34 and SSZ-13 are two molecular sieves commonly encountered and frequently investigated in the MTO literature. Both of these materials have a CHA topology. SAPO-34 was discovered in 1984 by Union Carbide (now UOP) and has now been commercialized for more than a decade.^{70,71} SSZ-13, which was discovered by Zones at Chevron in 1985, is the zeolite analogue of SAPO-34.⁷² Despite having similar crystal structures, the observed reactivities (during induction, reaction and deactivation periods) of SAPO-34 and SSZ-13 are quite different in MTO.⁷³ SSZ-13, for instance, typically exhibits differences in the light olefin selectivities and a higher alkane formation (particularly early in the reaction) than SAPO-34. These differences in reaction behavior are typically attributed to disparities in acid site strength between the two classes of materials. The stronger Brønsted acid sites of SSZ-13, for instance, are implicated for increasing the reaction rates and therefore leading to faster coking and deactivation. However, the effect of heteroatom concentration and thus acid site density and proximity in these two materials is typically overlooked. As such, the goal of this research effort was to investigate whether paired/adjacent Brønsted acid sites within the cages of SSZ-13 contribute to the observed reactivity differences between SSZ-13 and SAPO-34. This was a particularly interesting topic to study, as Dahl et al.⁷⁴ speculated at the possibility of two acid sites interacting within the same cage.

Mark Deimund, a former member of the MED Group, and coworkers³¹ investigated the effect of heteroatom concentration in SSZ-13 on the methanol-to-olefins reaction. To answer some

of these lingering questions regarding the role of paired/adjacent sites on MTO performance, several SSZ-13 materials were synthesized by varying the amount of Al in the gel to produce samples with different Brønsted acid site concentrations, and consequently, materials that contained different numbers of paired Al heteroatoms (**Table 1.1**). To determine paired/adjacent site content, the SSZ-13 samples were titrated using a Cu²⁺ ion exchange procedure while holding the solution pH to 5 to prevent the formation of copper hydroxide (**Table 1.1**). The copper exchange experiments confirm that Al paired sites decrease with increasing Si/Al, thus, allowing for the investigation of a wide range of compositions (Si/Al) and Al site proximities in MTO for the first time. For comparison, a SAPO-34 sample was synthesized, which was made up of isolated Si sites, as confirmed by ²⁹Si MAS NMR which showed a single resonance corresponding to isolated Si(4Al) sites.

Mate II	erial)	Si/Al (EDS)	Primary Crystallite Size (µm)	Micropore Volume (cc/g)	Acid Site Density by NH3 (mmol/g)	Cu/Al Molar Ratio
SSZ-	13A	4.70	0.025	-	0.65	0.19
SSZ-	13B	17.0	0.034	-	0.49	0.08
SSZ-	13C	21.2	0.049	0.23	0.47	0.06
SSZ-	13D	45.9	0.055	-	0.26	0.03
SSZ-	13E	54.5	0.058	0.21	0.18	-

Table 1.1. SSZ-13 Characterization Data. (Adapted from ³¹). Copyright 2015 American Chemical Society.

Figure 1.6 illustrates the time-on-stream (TOS) reaction data obtained at 400 °C and methanol WHSV of 1.3 h⁻¹ for the ammonium-exchanged and thermally treated SSZ-13 samples and SAPO-34. Each of the SSZ-13 catalysts was active for MTO, producing primarily C_2 - C_4 olefins at or near 100% methanol conversion, consistent with prior reports. We observed that the

SSZ-13 materials exhibit significant differences in MTO reactivity as the Si/Al ratio was varied. Reducing the Al content led to more stable light olefin selectivities, with a reduced initial transient period, lower initial propane selectivities, and longer catalyst lifetime. SAPO-34 also behaved rather differently than the SSZ-13 samples (i.e., SAPO-34 had a longer lifetime and produced less propane). Interestingly, as the Si/Al ratio increased, the SSZ-13 samples began to resemble SAPO-34 in their reactivities. This similarity in behavior across two different types of materials (zeolites and SAPOs) is likely due to the increase in isolation of Al sites in the samples with higher Si/Al, in an analogous way to the more isolated acid sites in SAPO-34.

Corma et al.⁶⁰ recently investigated the MTO reaction of several CHA-type materials, including both SSZ-13 and SAPO-34, using a combination of static DFT calculations, AIMD (ab initio molecular dynamics) simulations, and catalytic testing. The authors concluded that not only does the strength, amount, and location of the Brønsted acid sites in the catalyst structure influence the olefins production distribution in CHA-type molecular sieves, but also the larger volume and framework flexibility afforded by SAPO-34 relative to SSZ-13. This difference in framework flexibility (between zeolites and SAPOs in CHA) leads to differences in the stabilization of 7MB⁺, which could also affect the ethylene-to-propylene ratio.



Figure 1.6. MTO reaction data obtained at 400 °C for (A) SSZ-13A, (B) SSZ-13B, (C) SSZ-13C, (D) SSZ-13D, (E) SSZ-13E, and (F) SAPO-34. (Adapted from ³¹). Copyright 2015 American Chemical Society.



Figure 1.7. Paired Al site content and initial propane selectivity as a function of Si/Al. The theoretical line is from Bates et al.⁷⁵ (Adapted from ³¹). Copyright 2015 American Chemical Society.

Figure 1.7 shows the paired Al site content and initial propane selectivity as a function of Si/Al ratio. The data suggests that when the initial propane selectivities are overlaid with the theoretical paired Al site content as a function of Si/Al, a decreasing trend with increasing framework Si/Al is observed. To further demonstrate the importance of paired Al sites on the formation of propane during the initial transient period for SSZ-13, another series of experiments were conducted, where an SSZ-13 sample (Si/Al=13) in the proton-form was ion exchanged with Cu²⁺, then steamed, and then back ion exchanged to the proton-form. The goal behind these experiments was to understand the role that Al paired sites play in propane formation. We speculated that if paired Al sites indeed do contribute to the observed propane formation in SSZ-13, then the initial SSZ-13 sample would exhibit high initial propane selectivity, whereas the copper exchanged sample would not, as the copper ions will partially block the paired Al sites. Moreover, one would expect that the steamed SSZ-13 samples as well as the Cu-exchanged SSZ-

13 sample will not exhibit significant initial propane selectivity (since steaming removes paired Al sites). Additionally, the steamed Cu-exchanged SSZ-13 sample can be back ion exchanged to its proton-form. During steaming, the copper ions may help protect the paired Al sites from hydrolysis, and as such, if these paired Al sites are responsible for the high propane formation (and transient behavior) then we would expect to see a return of this relatively high initial propane following this back-ion-exchange procedure. The results from these sets of experiments were as expected. The alkanes selectivities measured from these experiments were as follows for each of these SSZ-13 samples: H-form, unsteamed (45%), H-form steamed (5%), Cu-form, unsteamed (30%), Cu-form, steamed (7%), and Cu-form, back ion-exchanged to H form (13%).

To investigate the post-reaction coke, dissolution-extraction experiments were performed on the ammonium-exchanged samples following deactivation. The distribution of the occluded organic species obtained from the GC-MS analysis following deactivation were different for the SAPO-34 and the SSZ-13 samples. SAPO-34 showed a very clear trend of increasing aromatic rings with the highest concentration of pyrenes (46%) of all the samples tested. The SSZ-13 samples showed a different pattern, with the majority of the occluded species concentrated in the naphthalenes-range and trailing off with 3- to 4-ring aromatics. Although the amount of naphthalenes was relatively similar in all SSZ-13 samples, the highest Si/Al SSZ-13 samples showed a tendency for higher alkylated species, in agreement with the notion that higher alkylated (or methylated) species tend to correlate with higher propylene-to-ethylene (P/E) ratios.

The results in this study not only demonstrate the role that the Si/Al ratio plays in influencing the olefins product distribution in SSZ-13 (CHA), but it also reveals, for the first time, the role that Al paired sites play in influencing the MTO behavior in CHA-type molecular sieves

27

(i.e., initial propane formation and transient behavior). Indeed, the effect of Si/Al on the olefins product distribution in MTO is rarely decoupled from the effect of Al paired sites.

While zeolites are more attractive as catalysts in general compared to SAPOs, particularly in refining processes and petrochemicals (due to their higher hydrothermal stability), they have generally taken a backseat to SAPO-type molecular sieves in MTO because their stronger acid sites generally tend to form products that have relatively high alkane content. Separating light alkanes (e.g., ethane and propane) from alkenes (e.g., ethene and propene) industrially can be challenging and costly. Therefore, this finding gives us a handle over reducing the alkane contribution in zeolite-type molecular sieves in MTO (by simply reducing the paired Al sites in a catalyst).

We took advantage of this finding when investigating the MTO behavior of SSZ-39 (AEI), another important zeolite material. SSZ-39, also co-invented by Zones, with a bulk Si/Al of 6-13, typically, is often synthesized in the presence of sodium using dimethylpiperdinium-type OSDAs.⁷⁶ Gounder et al.⁷⁷ recently provided a strategy to prepare SSZ-13 (CHA) at fixed elemental compositions but with different arrangements of framework Al atoms (paired or isolated) by varying the relative ratio of the organic and inorganic (Na⁺) cations in the gel. We extended the finding by Gounder and coauthors to AEI-type zeolites. Specifically, we were able to synthesize SSZ-39 (inspired by the original recipe) but without sodium. This effectively allowed us to compare the MTO behavior of SSZ-39 synthesized with sodium (thus, containing paired Al sites) and SSZ-39 synthesized without sodium (thus containing *less* paired Al sites). The reaction results proved that by simply changing the sodium content in the gel, we were able to reduce the initial propane from (54%) to (41%) in SSZ-39 (both catalysts had bulk Si/Al of approximately 10).^{9,65} As such, the results demonstrated for SSZ-13 in this section regarding the role of paired Al

sites on influencing propane formation could be extended to other zeolites belonging to different frameworks as well.

1.3.2 Treatment of Zeolites with Steam to Improve Framework Si/Al: A Case Study on SSZ-39

SSZ-39 is a zeolite with an AEI framework. The intrazeolitic pore space of AEI consists of a three-dimensional (3D) interconnected channel system, bounded by eight-member (8MR) rings (3.8 x 3.8 Å) and basket-like shaped cages. Our group investigated the synthesis of this zeolite in hydroxide-media with various ratios of isomeric mixtures of OSDA instead of the purified single compound.⁷⁶ The hydroxide-based recipes typically yield materials with Si/Al molar ratios ranging from 6 to 13.^{76,78,79} Higher Si/Al ratios (>200) have so far been achieved only with the aid of hydrofluoric acid (HF) using diethyl-quaternized OSDAs. Scaling up HF-based zeolite recipes is challenging due to the toxicity and difficulty in handling HF. Moreover, MTO ideally operates on AEI-type zeolites with Si/Al ratios of approximately 20-100, owing to the increased deactivation and poor selectivities of AEI-type zeolites that have Si/Al ratios that fall outside of this range.^{80,81} The difficulty in synthesizing SSZ-39 with high Si/Al likely resulted in SSZ-39 receiving less attention in the MTO literature (aside from the brief mentions in the patent literature) despite the excellent catalytic performance exhibited by SAPO-18 (AEI).⁶⁴

To investigate the performance of SSZ-39 in MTO, we performed a systematic study with several SSZ-39 catalysts that were synthesized in hydroxide media. We then introduced a simple steaming treatment method to modify the framework Al content (i.e., increase framework Si/Al) since the hydroxide route for synthesizing SSZ-39 produces materials with a very limited range of Si/Al. Steaming is known to remove Al_T (tetrahedral Al; framework Al) from the zeolite framework by hydrolysis and creates penta-coordinated and octahedral species. Typically, in 8MR

zeolites, the extra-framework (hydrated) Al cannot be removed due to their size. As such, even though the bulk Si/Al ratio is not changed, steaming effectively enhances the Si/Al_T ratio. Al_T is what ultimately gives the catalyst its Brønsted acidity for MTO catalysis.

Initially, three SSZ-39 samples were synthesized in the hydroxide media with different isomeric OSDAs (cis-2,6-, cis-3,5-, and cis-trans-3,5-dimethylpiperdinium hydroxide) and tested in MTO. These three samples had a bulk Si/Al between 8 to 9 and behaved comparably, consistent with their similar physiochemical properties. A typical reaction profile of SSZ-39 synthesized via this hydroxide route (without any post-synthetic modification) is given in **Figure 1.8**. The time-on-stream reaction profile shows that SSZ-39 has an initially high alkane production (mainly propane), a time-dependent olefin selectivities, and rapid deactivation. The high initial alkane renders this catalyst effectively undesirable. The deactivation of this catalyst, which is shown in **Figure 1.8**, is likely due to the high alkane production (because the presence of saturated hydrocarbon species requires hydrogen that evolves from the formation of dehydrogenated and unsaturated aromatic species). Indeed, these MTO trends demonstrated by SSZ-39 likely find their origin in the high acid-site density of this material.

To change the Si/Al_T ratio, we explored steaming as a method to post-synthetically alter SSZ-39. We conducted an experiment where an SSZ-39 sample was steamed at 750 °C. The removal of Al_T atoms was confirmed by ²⁷Al and ²⁹Si NMR data, the former showing that approximately 13% of all the Al remained in the framework after steaming (**Figure 1.8**). ²⁹Si NMR also hardly detected any (Si)₃-Si-(Al) signals when compared to the parent SSZ-39 sample (prior to steaming). Based on these two characterization techniques, an effective framework Si/Al (or Si/Al_T) of about 62 was calculated. Additionally, other characterization techniques (e.g., N₂-

physisorption) showed that steaming does not affect the pore volume of the catalyst when compared to the parent material (~ 0.23 cc/g).



Figure 1.8. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for SSZ-39 samples as well as solid-state NMR spectra of various SSZ-39 samples steamed at different temperatures (550, 650, and 850 °C). (a) MTO reaction results of parent/control SSZ-39. (b) MTO reaction results of H-SSZ-39-st-750. (c) ²⁹Si and ²⁷Al MAS NMR spectra of the samples steamed at different temperatures. (Adapted from ⁹). Copyright 2015 American Chemical Society.

The steamed zeolite sample at 750 °C, denoted as H-SSZ-39-st-750, gave an excellent MTO behavior. The deactivation of this catalyst was significantly slower than the parent sample (unsteamed SSZ-39). Additionally, 10% of alkanes were formed with the steamed catalyst (again, much lower than control) as shown in **Figure 1.8**. Moreover, a stable, high olefins selectivity was measured. The measured propylene/ethylene/butenes ratios at maximum olefin yields were 2.8/1/1.1, which are higher than the ratios obtained for SSZ-13 (CHA) with similar framework Si/Al (~55, non-steamed; 0.8/1/0.3). Comparing SSZ-39 (both before and after steaming) to

SAPO-18 shows that all three catalysts have similar selectivity trends: they give more propylene than ethylene and a significant amount of butenes, and their propylene-to-ethylene ratio is higher than CHA-type materials.

These differences in selectivity between CHA- and AEI-type molecular sieves are due to differences in the shape and size of the of AEI and CHA cages (discussed in more depth in a subsequent section). Nevertheless, it is interesting that the steamed SSZ-39 selectivities are very similar to those of the unsteamed SSZ-39 sample but without the high initial alkane formation and fast deactivation. Indeed, the high density of framework acid sites in the unsteamed SSZ-39 sample appears to be causing the production of alkanes and concomitant carbon deposition that leads to the rapid deactivation of this catalyst. We also performed Cu ion exchange experiments similar to those performed in our SSZ-13 work (discussed in the prior section). The MTO results from the use of copper-exchanged, steamed, and back-exchanged samples strongly suggest that the high initial alkane production (and related rapid deactivation) in the parent/control SSZ-39 is caused by the presence of closely associated (bridged) Al_T sites.

Because the steaming treatment at 750 °C (in the absence of copper) transformed SSZ-39 into an interested MTO catalyst, the effect of steaming temperature (T=550, 650, 850, 900 °C) was further explored. Solid state ²⁹Si and ²⁷Al NMR were run on each of these materials, showing that higher steaming temperatures were associated with a higher degree of Al_T removal. Up to a steaming temperature of about 850 °C, virtually all of the steamed SSZ-39 samples had similar powder X-ray diffraction (PXRD) patterns, roughly similar micropore volumes (no mesopores), and similar morphologies, indicating no sign of structural collapse. The reaction data on these samples were consistent with the trends observed in the characterization data. For instance, H-SSZ-39-st-550 showed some improvements over the parent/control SSZ-39 material (in line with

its intermediate framework Si/Al=37) but did not perform as well as the H-SSZ-39-st-750 sample (discussed previously), which had a higher framework Si/Al of 62.

On the other hand, steaming at temperatures higher than 850 °C led to the formation of materials with reduced crystallinities (i.e., presence of amorphous phases) and when tested in MTO, these materials deactivated rather rapidly. The faster deactivation in MTO is likely due, in part, to the lack of sufficient active sites remaining after steaming (framework Si/Al of 124 for the SSZ-39 sample steamed at 850 °C). These results suggest that the optimal steaming temperatures appear to be in the range of 550 to 850 °C depending on the desired framework Si/Al ratio. Additionally, although not attempted in this work, the steaming conditions (i.e., duration, etc.) could be tweaked further to influence the degree of Al_T removal. While we investigated the performance of these steamed SSZ-39 samples in MTO, steamed SSZ-39 could be useful in other applications, including in gas separation and adsorption.

1.3.3 Organic-free Synthesis of Zeolite Catalysts and Their Post-Synthetic Treatments

The previous two sections described the utilization of CHA- and AEI-type molecular sieves in MTO. SSZ-13, the zeolite analogue of the commercial catalyst, SAPO-34, is typically synthesized using a quarternized adamantammonium (AD) cation as an OSDA. The preparation of this OSDA has numerous shortcomings and, indeed, AD-free routes to synthesize SSZ-13 (CHA) catalysts are currently being explored.^{82,83} SAPO-34 (CHA), in spite of its success, also requires the use of an OSDA to crystallize. Albeit zeolites can catalyze the MTO reaction, as demonstrated in the previous sections, synthesizing them with high Si/Al ratios, in order to improve the olefins selectivities and reduce deactivation, require the use of OSDAs. However, the high cost and environmental concerns associated with the use and removal of the OSDAs from the materials prior to reaction has generated considerable interest in developing OSDA-free synthesis methods. Ironically, the earliest synthetic zeolites were prepared in the absence of OSDAs, using only inorganic cations as structure-directing species. However, these zeolites typically have high aluminum contents (Si/Al<5) and thus limited uses in applications requiring solid acid catalysis, including in MTO.

Therefore, in this section, we present an approach for the synthesis of small-pore, cagetype zeolites in the absence of an OSDA, which are then subjected to one or more post-synthetic treatments to modify their physiochemical properties (including acidity) and thus catalytic behavior. This strategy enabled the preparation of a low-cost CHA-type MTO catalyst (presented first), but we also extended this strategy to two other frameworks, e.g., RHO and KFI, to demonstrate that the approach could be extended to other frameworks and materials that have previously not received much attention in the MTO literature.

CHA was first synthesized from the conversion of USY in the presence of potassium hydroxide.⁸⁴ The product was found to have a bulk Si/Al of 2.4. This CHA sample was then steamed at different tempertures, 500-700 °C, under an identical steam partial pressure (though, we also performed separate experiments to determine the effect of steam partial pressure on product quality; not discussed here). Unlike the SSZ-39 catalysts described in the previous section, the baseline signal of the PXRD patterns of the steamed CHA-type zeolites were elevated relative to the peaks of the unsteamed CHA sample, indicating the presence of amorphous material and a loss in crystallinity upon steaming. The higher the steaming temperature, the higher the structural degradation. The PXRD peak positions also shifted to lower d-spacings with increasing steam temperature. We also performed acid treatment (acid washing) following steaming on one of the samples. Characterization on this sample demonstrates that acid washing results in additional degradation and increases the bulk Si/Al (from 2.4 to 7.8 for the sample steamed at 600 °C and

treated with acid afterwards). ²⁷Al MAS NMR was used to indicate the degree of Al removal. The solid-state NMR results show that increasing the steaming temperature increases the relative intensity of the peaks at approximately 30 and 0 ppm, which are attributed to penta-coordinated and octahedral aluminum species, respectively. Following acid washing, we observe that the peaks associated with penta- and octa-coordinated Al are significantly reduced. Furthermore, unlike SSZ-39, Ar-physisorption performed on the CHA steamed samples show a reduction in the micropore adsorption volume, although the acid-washed sample produced a significant increase in the adsorption volume that is likely due to the removal of the extra-framework Al (in agreement with the ²⁷Al MAS NMR results). We also performed *i*-propylamine temperature-programmed desorption (TPD) experiments because this molecule is too large to fit within the 8MR pores and as such it can access acid sites external to the 8MR pore system (and in areas of meso-porosity introduced from steaming). The sites accessible by this molecule were highest for the CHA sample that was steamed at 600 °C. Indeed, based on these characterization results, one can infer that the steaming process on CHA-type zeolites has an optimal temperature at approximately 600 °C before framework degradation becomes too severe and access to acid sites decreases dramatically.

Figure 1.9 illustrates the representative time-on-stream reaction data obtained at 400 °C for the various CHA-type zeolites synthesized and post-synthetically modified via steaming alone or steaming and acid washing. These results were compared to SAPO-34. Each of these catalysts is initially active in producing short-chain (C_2 - C_4) olefins at complete and near complete methanol conversion. The non-modified CHA sample (denoted as "unsteamed H-CHA") had the shortest lifetime of all the catalysts tested. The fast deactivation was attributed to the high framework Al content in the sample (Si/Al=2.4). Whereas deactivation occurred abruptly for the unsteamed CHA sample, the steamed materials showed more gradual deactivation profiles that varied depending

on the severity of steaming. Of the catalysts tested, CHA that was steamed at 600 °C ("600 °Csteamed CHA") showed promise in terms of stability and lifetime. The lifetime and stability of the 600 °C steamed catalyst was further enhanced by acid washing the catalyst ("600 °C-steamed and acid-wash CHA"). The improvements exhibited by the 600 °C-series catalysts were attributed to the modifications applied to the acidity of the catalysts, which resulted in the extraction of framework Al, and also the presence of mesopores, which played a role in extending the lifetime of the catalysts (because mesopores facilitate mass transport to the micropores).⁸⁵ These results on CHA-type zeolites that were prepared from the hydrothermal conversion of faujasite (FAU)-type zeolites, dealuminated by high-temperature steam treatments, and washed with acid provide a costeffective and useful strategy for preparing small-pore, cage-type zeolites with proper framework Si/Al for applications such as, in MTO or deNO_x.

To further build on these results, we synthesized RHO- and KFI-type zeolites also in the absence of OSDAs. These samples were then post-synthetically dealuminated via steam treatment, in an identical fashion to the CHA-type zeolites. The proton-forms of the unmodified (parent) zeolites had high Al contents (RHO Si/Al=2.8 and KFI Si/Al=3.1); however, steaming extracted the framework Al, leading to reductions in the total number of acid sites and creating mesopores that facilitated the transport of reactants. The steamed samples also had lower accessible micropore volume than the control samples (again, in agreement with the results observed for CHA-type zeolites).

When tested in MTO, the proton-form of the unmodified zeolites deactivated rather rapidly due to their high Al content. Steam treatments led to improvements in the olefin selectivities and catalyst lifetime, with the samples steamed at 600 °C showing the most promise. The estimated Si/Al_T of these steamed samples at 600 °C were 25 and 17 for RHO and KFI, respectively. A comparison of the reaction behaviors of the three frameworks (CHA, RHO and KFI) shows stark differences in their product distribution. In particular, the steamed RHO and KFI samples had higher selectivities toward butenes (mainly 2-butenes and isobutene) compared to CHA-type zeolites.



Figure 1.9. Representative time-on-stream MTO reaction data obtained at 400 °C and WHSV 1.3 h^{-1} . (A) unsteamed H-CHA, (B) 500 °C-steamed CHA, (C) 600 °C-steamed CHA, (D) 700 °C-steamed CHA, (E) 600 °C-steamed and acid-washed CHA, and (F) SAPO-34. (Adapted from ⁸⁴). Copyright 2015 American Chemical Society.

To assess whether the differences in selectivities among the three zeolites can be attributed to secondary reactions occurring at acid sites in the mesopores of the steamed zeolites (e.g., dimerization of ethylene to butenes), trimethylphosphite treatments were performed to selectively poison the mesopores and external surface of the acid sites. Due to its size, trimethylphosphite is expected to be too large to fit through 8MR pores (leaving those acid sites un-poisoned), and thus it can only access acid sites in the mesopores and on the crystallite surface. TPD experiments with *i*-propylamine indicate that this treatment method was, indeed, able to poison a significant portion of the accessible mesopores and external surface sites.

These three steamed samples (now treated with phosphite) did not show any differences in their light olefins selectivity when compared to the steamed samples (prior to the phosphite treatment). The main difference observed was the increase in lifetime. Whereas the steamed samples showed a deactivation that is marked by a sudden decrease in conversion and olefins selectivities, conversion decreased more gradually for the phosphite-treated samples (**Table 1.2**). As such, introducing mesopores in these samples via steaming and then poisoning these sites via treatment with trimethylphosphite appears to limit coking reactions that occur at acid sites external to the 8MR pores which then maintains the accessibility of the pore structure for a longer period of time. Furthermore, the lack of changes in the observed olefin selectivities after poisoning the mesopores and surface acid sites suggests that the olefins produced inside the 8MR cages do not undergo further dimerization or methylation reactions. Therefore, the increased butenes-to-ethylene (B/E) ratio in RHO and KFI compared to CHA are likely due differences in the cage size (discussed in more detail in the next section).

Sample	Averaged Sele	ectivities Ratio (hig	Catalyst	Coke	
ID	Ethylene	Propylene	Butenes	Lifetime (mins) ^[a]	Content (%)
CHA-S	1.00	1.20	0.49	119	16.9
CHA-P	1.00	1.10	0.46	160	16.7
RHO-S	1.00	1.80	1.00	101	16.9
RHO-P	1.00	1.80	0.99	134	16.8
KFI-S	1.00	1.60	1.00	72	18.7
KFI-P	1.00	1.50	1.00	102	9.80

Table 1.2. Summary of MTO reaction data for the steamed zeolites before and after trimethylphosphite treatment. (Reproduced with permission from ⁸⁶). Copyright 2016 Elsevier.

[a] First time point where conversion drops below 80%.

1.3.4 Effect of Cage Dimension on the Product Distribution in MTO

The conversion of methanol-to-olefins on acidic molecular sieves (e.g., zeolites and SAPOs) takes place through a complex network of chemical reactions, where numerous catalyst properties and reaction parameters can influence the product distribution.^{34,64,80,87} It's now widely accepted that of these various parameters, cage topology plays an instrumental role in affecting the olefins product distribution.^{40,47,60,80} From the point of view of the dual cycle, which governs this reaction, cage structure can either limit the formation of certain polyalkyl or polymethyl aromatic intermediate species (due to size restrictions) or preferentially stabilize certain aromatic species over others, thus, influencing the product distribution.^{52,53,88,89} One area that our group has fundamentally focused on understanding is how small-pore, cage-type molecular sieve structures influence the light olefins product distributions. In this section, we outline our efforts over the years in understanding and developing structure-property relationships for the MTO reaction, which ultimately led us to introduce the concept of a Cage-Defining Ring (CDR), a structural parameter that, for the first time, reliably correlates the MTO light olefins product distribution to a structural parameter.⁶⁵

Our first investigation into the effect of cage size on the selective conversion of methanolto-light olefins did not start with the CDR work, but almost a decade prior. Our first work entailed comparing the MTO behavior of several zeolites that contained 8MR pores with different cage geometries (e.g., LEV, CHA, and AFX). Each of these zeolites, belonging to the aforementioned frameworks, was synthesized at similar Si/Al (14-16) ratios and crystal sizes (364-395 Å) (aggregate crystal sizes were 1-5 microns). Since Al content in zeolites and crystallite size are both parameters that slightly affect product distribution, we kept these parameters constant across the catalysts, as shown in **Table 1.3**. We then studied the behavior of these catalysts in MTO.

Table 1.3. Characterization results and reaction data on the three zeolites tested in MTO (T=400 °C, WHSV=1.3 h⁻¹). (Reproduced with permission from ⁹⁰). Copyright 2012 American Chemical Society.

Framework	Si/Al	Aggregate Crystal Size (µm)	Primary Crystallite Size (Å)	Maximum Propylene Selectivity	Maximum Ethylene Selectivity
LEV (SSZ-17)	16.8	1-3	389	32	43
CHA (SSZ-13)	14.4	1-3	364	44	46
AFX (SSZ-16)	16.7	3-5	395	31	23

The most apparent trend from the MTO reactivity data of these catalysts was that the maximum ethylene-to-propylene selectivity ratio was generally higher for materials with smaller cages. The overall ethylene selectivities for LEV, CHA, and AFX (when methanol conversion was at or near 100%) were 33.8%, 28.4%, and 16.6%, respectively. These data suggest that smaller cages favor the formation of ethylene whereas larger cages favor the formation of larger olefins. Indeed, SSZ-17 (LEV) was the only catalyst that produced more ethylene than propylene after 90 mins on-stream. SSZ-16 (AFX), on the other hand, produced more propylene and also had the shortest lifetime and worst carbon balance of the three materials studied. Separate studies on the

occluded organics during reaction and following deactivation revealed that the partially deactivated catalysts showed that the size of the organics at maximum propylene selectivity correlated with cage size (C_2 -benzenes for LEV), (C_3 - C_4 -benzenes for CHA), and (C_5 -anthracenes for AFX). The presence of polycyclic species in the cages of AFX explains the rapid deactivation of this sample relative to LEV and CHA.



Figure 1.10. Product selectivities of the various zeolite materials investigated. The selectivity values were obtained by averaging hydrocarbon selectivities for conversions of methanol in the range of 98–100%. Selectivity data for SSZ-17 (LEV),⁹⁰ SSZ-39 (AEI),⁹ SSZ-50 (RTH),⁹¹ LTA,⁹² and RHO⁸⁶ are from previous literature reports at identical reaction conditions. (Reproduced with permission from ¹⁰). Copyright 2018 John Wiley and Sons.

While the results of this study clearly showed that cage size influences the olefins product distribution, it did not lead to a clear correlation between these two parameters. In 2017, Jong Hun Kang and coauthors synthesized a series of small-pore zeolites, including, SSZ-13 (CHA), SSZ-16 (AFX), SSZ-27, SSZ-28 (DDR), SSZ-52 (SFW), SSZ-98 (ERI), SSZ-99 (CHA/GME), SSZ-104 (CHA-related), SSZ-105 (ERI/LEV), and ITQ-3-type material (ITE) and investigated these materials in the MTO reaction.¹⁰ The behavior of these zeolites was compared to SAPO-34 (CHA). Our goal again was to develop a structure-property/performance relationship between cage structure/size and the resultant product distributions. Despite investigating a plethora of materials this second time around (**Figure 1.10**), no clear relationship between zeolite cage-architecture and the olefin selectivities emerged from this study, although several trends were presented.

These included the following: (i) the production of propane correlated with lifetime (higher initial propane yielded shorter lifetimes), (ii) larger cages had higher propane yields at fixed Si/Al ratios, and (iii) four different reaction patterns were observed. These reaction patterns allowed us to divide our materials to different categories depending on their product distribution. From the reaction data, we observed materials that gave (a) ethylene greater than propylene with low butenes (SSZ-17, SSZ-98, and SSZ-105); (b) equal amounts of ethylene and propylene with low butenes (SAPO-34, SSZ-13, SSZ-16, SSZ27, SSZ-52, SSZ-99, and SSZ-104); (c) propylene greater than ethylene with butenes roughly similar to ethylene (SSZ-28, and SSZ-39); and (d) generally high butenes (RHO).



Figure 1.11. Product selectivities for the various materials/frameworks tested by our group in 65 . Orange bars indicate propylene; red bars indicate butenes; black bars indicate ethylene. The results were obtained by averaging the selectivities when the methanol conversion was over 98%. All reactions were performed at 400 °C with a WHSV(MeOH) of 1.3 h⁻¹.

All of our previous studies effectively reached similar conclusions (i.e., larger cages form longer olefins); however, a structure-property relationship was still missing. To take one more aim at developing this property-structure relationship, we investigated the MTO behavior of 30 different zeolitic and AlPO₄-based (SAPOs, CoAPOs and MgAPOs) molecular sieves belonging to 14 different topologies (e.g., CHA, AFX, SFW, LEV, ERI, DDR, AEI, RTH, ITE, SAV, LTA, RHO, KFI, and UFI) at identical reaction conditions (400 °C and WHSV of 1.3 h⁻¹). We essentially expanded the list of materials that we previously investigated in our second study to incorporate more frameworks as well as non-zeolitic materials (e.g., SAPOs). This study due to its size did not feature a careful control over the Si/Al (or Si/T-atom ratio), as did the first study performed by Bhawe et al.,⁹⁰ although the majority of the zeolites tested had a Si/Al of 4-30. We employed a similar classification system (4 types of light olefin behaviors; 4 categories) as the one utilized in our second study. **Figure 1.11** shows the product selectivities of the various materials tested.

Category I materials comprised of 3 topologies (CHA, AFX, and SFW). Materials belonging to this category gave similar ethylene and propylene selectivities (an ethylene to propylene selectivity ratio of approximately 1) and had low butenes despite inherent differences in their cage topology as well as elemental composition (thus, acidity). Category II materials, on the other hand, behaved rather differently from Category I, as they produced more ethylene than propylene. Specifically, we identified two topologies, LEV (SSZ-17, Nu-3, and SAPO-35) and ERI (SSZ-98), as belonging to this category. An ethylene-to-propylene selectivity of more than 1.2 was observed for SSZ-17/Nu-3 (LEV) and SSZ-98 (ERI); however, the SAPO analogs of these zeolites, specifically, SAPO-35 (LEV) and SAPO-17 (ERI), did not form as much ethylene as their zeolitic counterparts. In the case of SAPO-35 (LEV), as justified in the prior art and observed in our experiments, this was likely attributed to the catalyst's rapid deactivation at our experimental

conditions and low acidity.⁴⁰ Category III materials included AEI, DDR, RTH, ITE, and SAV topologies. Materials in this category formed more propylene than ethylene due to their geometry. The AEI materials tested, much like CHA in Category I, showed no changes in product distribution even when the acidity (strength) of the molecular sieve was changed by altering the elemental composition of the AlPO₄-based materials (i.e., SAPO-18, CoAPO-18, and MgAPO-18, all gave similar propylene-to-ethylene ratios when methanol conversion was 98+%). Lastly, Category IV materials (LTA, RHO, KFI, UFI) yielded high amounts of butenes that were much higher than the other categories. However, their ethylene and propylene selectivities were less predictable (likely due to the loss in confinement effects).



Figure 1. 12. Concept of cage-defining ring (CDR) size. (a) Ellipsoidal model of the CDR and the cage-defining ring size. (b) Demonstration of the CDR size for CHA. (c) Correlation chart of the CDR size by framework. (Reproduced with permission from ⁶⁵). Copyright 2019 American Chemical Society.

To establish a structure-activity relationship, the concept of a cage-defining ring (CDR) size, which corresponds to the minimum number of tetrahedral atoms of the ring encircling the center of the framework cages in the molecular sieve topology, was introduced by our group and applied to the 14 frameworks that were studied. **Figure 1.12** shows a correlation chart relating this newly pitched concept to the various frameworks/topologies tested. The data shows that that the smaller the CDR (e.g., Category II materials), the higher the ethylene-to-propylene ratio (i.e., more ethylene) whereas the larger the CDR (e.g., Category IV materials), the higher the butenes-to-ethylene (i.e., more butenes). These results also demonstrate that for the *majority* of small-pore, cage-type frameworks, cage size (rather than acidity) is what influences the olefins product distribution. Chapter 2 will explain why acidity (both strength and density) influences the olefins product distribution of a few frameworks (e.g., LEV and ERI).

1.4 Overview of Thesis

As outlined in the abstract, this thesis is comprised of two parts that are divided into 6 chapters and a number of appendices. Chapter 1 provided a brief introduction to the MTO reaction. It also highlighted the MTO work done in our group over the last decade. Thus, it set the stage for the remainder of this thesis.

Chapter 2 examines the important relationship between cage size and acidity on the olefins product distribution. It uncovers a missing link between these two parameters. This discovery explains from a mechanistic standpoint why a few frameworks respond favorably to changes in the Si/Al (or Si/T-atom) ratio whereas the majority of others don't. Chapter 2 also highlights the importance of accounting for the olefins cycle in a number of small-pore, cage-type molecular sieves. Chapter 3 investigates the MTO behavior of several ERI-type molecular sieves. These materials include, SSZ-98, UZM-12, ERI-type zeolites, and SAPO-17. ERI-type zeolites with low Si/Al are found to considerably enhance the ethylene-to-propylene ratio in MTO. The rapid formation of cyclic intermediates and the shift in their composition toward less methylated methylbenzenes or methylnaphthalenes are found to be key in enhancing the ethylene selectivity in ERI-type molecular sieves.

Chapter 4 introduces the synthesis of CIT-16P, a new disordered silicoaluminophosphate (SAPO), which upon thermal treatment in air transforms to SAPO-17. The MTO behavior of SAPO-17 derived from CIT-16P shows that this catalyst behaves similarly to other SAPO-17 materials with similar physiochemical properties.

Chapter 5 describes the synthesis of CIT-17. The MTO behavior of CIT-17, a SAPO-SATtype molecular sieve, that is synthesized for the first time without an AFX impurity (as determined by powder X-ray diffraction (PXR)), is compared to other SAT-, CHA-, and AEI-type molecular sieves, including SAPOs, CoAPOs, and MgAPOs. The experimental results show that the combination of low acidity and unique structural features of the narrow SAT-cage lead to a catalytic pathway and a mechanism that predominantly favors propylene. Indeed, CIT-17 achieves one of the highest propylene-to-ethylene ratios (P/E=2-4.2) for this class of materials.

Chapter 6 presents a summary of key findings and offers recommendations for future work.

1.5 References

 PRODUCTION: GROWTH IS THE NORM. Chemical & Engineering News Archive 2006, 84 (28), 59–68. https://doi.org/10.1021/cen-v084n028.p059.
(2) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. *Chemical Reviews* 2014, *114*(20), 10613–10653. https://doi.org/10.1021/cr5002436.

(3) Amghizar, I.; Vandewalle, L. A.; Geem, K. M. V.; Marin, G. B. New Trends in Olefin Production. *Engineering* **2017**, *3* (2), 171–178. https://doi.org/10.1016/J.ENG.2017.02.006.

(4) Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catal.* 2015, 5 (3), 1922–1938. https://doi.org/10.1021/acscatal.5b00007.

(5) Svelle, S.; Olsbye, U.; Joensen, F.; Bjørgen, M. Conversion of Methanol to Alkenes over Medium- and Large-Pore Acidic Zeolites: Steric Manipulation of the Reaction Intermediates Governs the Ethene/Propene Product Selectivity. *The Journal of Physical Chemistry C* 2007, *111*(49), 17981–17984. https://doi.org/10.1021/jp077331j.

(6) Olsbye, U.; Svelle, S.; Bjørgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity. *Angewandte Chemie International Edition* **2012**, *51* (24), 5810–5831. https://doi.org/10.1002/anie.201103657.

(7) Chen, D.; Moljord, K.; Holmen, A. A Methanol to Olefins Review: Diffusion, Coke Formation and Deactivation on SAPO Type Catalysts. *Microporous and Mesoporous Materials* 2012, *164*, 239–250. https://doi.org/10.1016/j.micromeso.2012.06.046.

(8) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E. Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction. *ACS Catalysis* 2016, *6* (2), 542–550. https://doi.org/10.1021/acscatal.5b01450.

(9) Dusselier, M.; Deimund, M. A.; Schmidt, J. E.; Davis, M. E. Methanol-to-Olefins Catalysis with Hydrothermally Treated Zeolite SSZ-39. *ACS Catal.* **2015**, *5* (10), 6078–6085. https://doi.org/10.1021/acscatal.5b01577.

(10) Kang, J. H.; Walter, R.; Xie, D.; Davis, T.; Chen, C.-Y.; Davis, M. E.; Zones, S. I. Further Studies on How the Nature of Zeolite Cavities That Are Bounded by Small Pores Influences the Conversion of Methanol to Light Olefins. *ChemPhysChem* **2018**, *19* (4), 412–419. https://doi.org/10.1002/cphc.201701197.

(11) Nawaz, S.; Kolboe, S.; Stöcker, M. Conversion of Methanol to Light Olefins over Sapo17 Molecular Sieve. In *Natural Gas Conversion II*; Curry-Hyde, H. E., Howe, R. F., Eds.; Studies
in Surface Science and Catalysis; Elsevier, 1994; Vol. 81, pp 393–398.
https://doi.org/10.1016/S0167-2991(08)63901-4.

Wang, Y.; Chen, S.-L.; Gao, Y.-L.; Cao, Y.-Q.; Zhang, Q.; Chang, W.-K.; Benziger, J. B.
Enhanced Methanol to Olefin Catalysis by Physical Mixtures of SAPO-34 Molecular Sieve and
MgO. ACS Catalysis 2017, 7 (9), 5572–5584. https://doi.org/10.1021/acscatal.7b01285.

(13) Chen, J.; Li, J.; Yuan, C.; Xu, S.; Wei, Y.; Wang, Q.; Zhou, Y.; Wang, J.; Zhang, M.; He,
Y.; Xu, S.; Liu, Z. Elucidating the Olefin Formation Mechanism in the Methanol to Olefin Reaction over AlPO-18 and SAPO-18. *Catal. Sci. Technol.* 2014, *4* (9), 3268–3277. https://doi.org/10.1039/C4CY00551A.

(14) Dubois, D. R.; Obrzut, D. L.; Liu, J.; Thundimadathil, J.; Adekkanattu, P. M.; Guin, J. A.;
Punnoose, A.; Seehra, M. S. Conversion of Methanol to Olefins over Cobalt-, Manganese- and
Nickel-Incorporated SAPO-34 Molecular Sieves. *Fuel Processing Technology* 2003, *83* (1), 203–218. https://doi.org/10.1016/S0378-3820(03)00069-9.

(15) Ahn, N. H.; Seo, S.; Hong, S. B. Small-Pore Molecular Sieves SAPO-57 and SAPO-59:
 Synthesis, Characterization, and Catalytic Properties in Methanol-to-Olefins Conversion. *Catal. Sci. Technol.* 2016, 6 (8), 2725–2734. https://doi.org/10.1039/C5CY02103K.

(16) Liang, T.; Chen, J.; Qin, Z.; Li, J.; Wang, P.; Wang, S.; Wang, G.; Dong, M.; Fan, W.;
Wang, J. Conversion of Methanol to Olefins over H-ZSM-5 Zeolite: Reaction Pathway Is Related to the Framework Aluminum Siting. *ACS Catal.* 2016, *6* (11), 7311–7325.
https://doi.org/10.1021/acscatal.6b01771.

(17) ZENG, P.; ZHANG, L.; GUO, X.; LI, M.; GUO, Q.; NIU, C.; SHEN, B. Catalytic Performances of Al-ITQ-13 Zeolites with Different SiO2/A12O3 Ratios in the Conversion of Methanol to Propene. *Journal of Fuel Chemistry and Technology* **2017**, *45* (11), 1349–1355. https://doi.org/10.1016/S1872-5813(17)30059-2.

(18) Min, H.-K.; Park, M. B.; Hong, S. B. Methanol-to-Olefin Conversion over H-MCM-22 and
H-ITQ-2 Zeolites. *Journal of Catalysis* 2010, 271 (2), 186–194.
https://doi.org/10.1016/j.jcat.2010.01.012.

(19) Lee, J. H.; Park, M. B.; Lee, J. K.; Min, H.-K.; Song, M. K.; Hong, S. B. Synthesis and Characterization of ERI-Type UZM-12 Zeolites and Their Methanol-to-Olefin Performance. *Journal of the American Chemical Society* **2010**, *132* (37), 12971–12982. https://doi.org/10.1021/ja105185r.

(20) Dai, W.; Wang, X.; Wu, G.; Guan, N.; Hunger, M.; Li, L. Methanol-to-Olefin Conversion on Silicoaluminophosphate Catalysts: Effect of Brønsted Acid Sites and Framework Structures. *ACS Catalysis* **2011**, *1* (4), 292–299. https://doi.org/10.1021/cs200016u.

(21) Pinilla-Herrero, I.; Olsbye, U.; Márquez-Álvarez, C.; Sastre, E. Effect of Framework Topology of SAPO Catalysts on Selectivity and Deactivation Profile in the Methanol-to-Olefins Reaction. *Journal of Catalysis* **2017**, *352*, 191–207. https://doi.org/10.1016/j.jcat.2017.05.008.

Moliner, M.; Martínez, C.; Corma, A. Synthesis Strategies for Preparing Useful Small Pore
 Zeolites and Zeotypes for Gas Separations and Catalysis. *Chemistry of Materials* 2014, *26* (1), 246–258. https://doi.org/10.1021/cm4015095.

(23) Smith, R. L.; Svelle, S.; Campo, P. del; Fuglerud, T.; Arstad, B.; Lind, A.; Chavan, S.; Attfield, M. P.; Akporiaye, D.; Anderson, M. W. CHA/AEI Intergrowth Materials as Catalysts for the Methanol-to-Olefins Process. *Applied Catalysis A: General* **2015**, *505*, 1–7. https://doi.org/10.1016/j.apcata.2015.06.027.

(24) Ono, K.; Miyake, K.; Nakai, M.; Al Jabri, H.; Hirota, Y.; Uchida, Y.; Tanaka, S.;
Miyamoto, M.; Nishiyama, N. Development of AEI Type Germanoaluminophosphate (GeAPO-18) with Ultra-Weak Acid Sites and Its Catalytic Properties for the Methanol to Olefin (MTO)
Reaction. *Catal. Sci. Technol.* 2017, 7 (20), 4622–4628. https://doi.org/10.1039/C7CY01153A.

(25) Zhu, Q.; Kondo, J. N.; Ohnuma, R.; Kubota, Y.; Yamaguchi, M.; Tatsumi, T. The Study of Methanol-to-Olefin over Proton Type Aluminosilicate CHA Zeolites. *Microporous and Mesoporous Materials* **2008**, *112* (1), 153–161. https://doi.org/10.1016/j.micromeso.2007.09.026.

(26) Yarulina, I.; Goetze, J.; Gücüyener, C.; van Thiel, L.; Dikhtiarenko, A.; Ruiz-Martinez, J.;
Weckhuysen, B. M.; Gascon, J.; Kapteijn, F. Methanol-to-Olefins Process over Zeolite Catalysts
with DDR Topology: Effect of Composition and Structural Defects on Catalytic Performance. *Catal. Sci. Technol.* 2016, 6 (8), 2663–2678. https://doi.org/10.1039/C5CY02140E.

(27) ghavipour, M.; Behbahani, R. M.; Rostami, R. B.; Lemraski, A. S. Methanol/Dimethyl Ether to Light Olefins over SAPO-34: Comprehensive Comparison of the Products Distribution and Catalyst Performance. *Journal of Natural Gas Science and Engineering* **2014**, *21*, 532–539. https://doi.org/10.1016/j.jngse.2014.09.015.

(28) Li, J.; Wei, Y.; Chen, J.; Xu, S.; Tian, P.; Yang, X.; Li, B.; Wang, J.; Liu, Z. Cavity Controls the Selectivity: Insights of Confinement Effects on MTO Reaction. *ACS Catalysis* 2015, *5* (2), 661–665. https://doi.org/10.1021/cs501669k.

(29) Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B. The Mechanism of Methanol to Hydrocarbon Catalysis. *Accounts of Chemical Research* **2003**, *36* (5), 317–326. https://doi.org/10.1021/ar0200060.

(30) Yarulina, I.; Chowdhury, A. D.; Meirer, F.; Weckhuysen, B. M.; Gascon, J. Recent Trends and Fundamental Insights in the Methanol-to-Hydrocarbons Process. *Nature Catalysis* 2018, *1* (6), 398–411. https://doi.org/10.1038/s41929-018-0078-5.

(31) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E.
Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction. *ACS Catal.* **2016**, *6* (2), 542–550. https://doi.org/10.1021/acscatal.5b01450.

(32) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. *ACS Catal.* **2019**, *9* (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.

(33) Chang, C. D.; Silvestri, A. J. The Conversion of Methanol and Other O-Compounds to Hydrocarbons over Zeolite Catalysts. *Journal of Catalysis* **1977**, *47* (2), 249–259. https://doi.org/10.1016/0021-9517(77)90172-5. (34) Olsbye, U.; Svelle, S.; Bjørgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga,
S.; Lillerud, K. P. Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size
Controls Product Selectivity. *Angewandte Chemie International Edition* 2012, *51* (24), 5810–
5831. https://doi.org/10.1002/anie.201103657.

(35) Stöcker, M. Methanol-to-Hydrocarbons: Catalytic Materials and Their Behavior1Dedicated to My Wife Wencke Ophaug.1. *Microporous and Mesoporous Materials* **1999**, 29 (1), 3–48. https://doi.org/10.1016/S1387-1811(98)00319-9.

(36) Zhang, C.; Ng, K. L. A.; Yan, L.; Feng, X.; Jiang, B.; Liao, Z.; Wang, J.; Yang, Y. Kinetic Perspective on Methanol to Propylene Process via HZSM-5 Catalyst: Balancing between Reaction and Diffusion. *Ind. Eng. Chem. Res.* 2022, 61 (5), 2055–2067. https://doi.org/10.1021/acs.iecr.1c04589.

(37) Jasper, S.; El-Halwagi, M. M. A Techno-Economic Comparison between Two Methanolto-Propylene Processes. *Processes* **2015**, *3* (3), 684–698. https://doi.org/10.3390/pr3030684.

(38) Davis, M. E. Zeolites and Molecular Sieves: Not Just Ordinary Catalysts. *Ind. Eng. Chem. Res.* 1991, *30* (8), 1675–1683. https://doi.org/10.1021/ie00056a001.

(39) Loewenstein, W. The Distribution of Aluminum in the Tetrahedra of Silicates and Aluminates. *American Mineralogist* **1954**, *39* (1–2), 92–96.

(40) Pinilla-Herrero, I.; Márquez-Álvarez, C.; Sastre, E. Complex Relationship between SAPO Framework Topology, Content and Distribution of Si and Catalytic Behaviour in the MTO Reaction. *Catal. Sci. Technol.* **2017**, *7* (17), 3892–3901. https://doi.org/10.1039/C7CY01250K.

(41) del Val, S.; Blasco, T.; Sastre, E.; Pérez-Pariente, J. Synthesis of SiVPI-5 with Enhanced Activity in Acid Catalysed Reactions. *J. Chem. Soc., Chem. Commun.* **1995**, No. 7, 731–732. https://doi.org/10.1039/C39950000731.

(42) Prakash, A. M.; Unnikrishnan, S.; Rao, K. V. Synthesis and Characterization of Silicon-Rich SAPO-44 Molecular Sieves. *Applied Catalysis A: General* **1994**, *110* (1), 1–10. https://doi.org/10.1016/0926-860X(94)80100-2.

(43) Bordiga, S.; Regli, L.; Lamberti, C.; Zecchina, A.; Bjørgen, M.; Lillerud, K. P. FTIR
Adsorption Studies of H2O and CH3OH in the Isostructural H-SSZ-13 and H-SAPO-34:
Formation of H-Bonded Adducts and Protonated Clusters. *J. Phys. Chem. B* 2005, *109* (16), 7724–
7732. https://doi.org/10.1021/jp044324b.

(44) Xie, J.; Firth, D. S.; Cordero-Lanzac, T.; Airi, A.; Negri, C.; Øien-Ødegaard, S.; Lillerud,
K. P.; Bordiga, S.; Olsbye, U. MAPO-18 Catalysts for the Methanol to Olefins Process: Influence of Catalyst Acidity in a High-Pressure Syngas (CO and H2) Environment. *ACS Catal.* 2022, *12*(2), 1520–1531. https://doi.org/10.1021/acscatal.1c04694.

(45) Dahl, I. M.; Kolboe, S. On the Reaction Mechanism for Propene Formation in the MTO Reaction over SAPO-34. *Catalysis Letters* 1993, 20 (3), 329–336. https://doi.org/10.1007/BF00769305.

(46) Ilias, S.; Bhan, A. Mechanism of the Catalytic Conversion of Methanol to Hydrocarbons.
 ACS Catal. 2013, 3 (1), 18–31. https://doi.org/10.1021/cs3006583.

(47) Ferri, P.; Li, C.; Paris, C.; Rodríguez-Fernández, A.; Moliner, M.; Boronat, M.; Corma, A.
The Limits of the Confinement Effect Associated to Cage Topology on the Control of the MTO
Selectivity. *ChemCatChem* 2021, *13* (6), 1578–1586. https://doi.org/10.1002/cctc.202001760.

(48) Dahl, I. M.; Kolboe, S. On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: I. Isotopic Labeling Studies of the Co-Reaction of Ethene and Methanol. *Journal of Catalysis* **1994**, *149* (2), 458–464. https://doi.org/10.1006/jcat.1994.1312.

(49) Lesthaeghe, D.; Horré, A.; Waroquier, M.; Marin, G. B.; Van Speybroeck, V. Theoretical Insights on Methylbenzene Side-Chain Growth in ZSM-5 Zeolites for Methanol-to-Olefin Conversion. *Chemistry – A European Journal* 2009, *15* (41), 10803–10808. https://doi.org/10.1002/chem.200901723.

(50) Mikkelsen, Ø.; Rønning, P. O.; Kolboe, S. Use of Isotopic Labeling for Mechanistic Studies of the Methanol-to-Hydrocarbons Reaction. Methylation of Toluene with Methanol over H-ZSM-5, H-Mordenite and H-Beta. *Microporous and Mesoporous Materials* **2000**, *40* (1), 95–113. https://doi.org/10.1016/S1387-1811(00)00245-6.

(51) Mole, T.; Bett, G.; Seddon, D. Conversion of Methanol to Hydrocarbons over ZSM-5 Zeolite: An Examination of the Role of Aromatic Hydrocarbons Using 13carbon- and Deuterium-Labeled Feeds. *Journal of Catalysis* **1983**, *84* (2), 435–445. https://doi.org/10.1016/0021-9517(83)90014-3.

(52) Ferri, P.; Li, C.; Paris, C.; Vidal-Moya, A.; Moliner, M.; Boronat, M.; Corma, A. Chemical and Structural Parameter Connecting Cavity Architecture, Confined Hydrocarbon Pool Species, and MTO Product Selectivity in Small-Pore Cage-Based Zeolites. *ACS Catal.* **2019**, *9* (12), 11542–11551. https://doi.org/10.1021/acscatal.9b04588.

(53) Hwang, A.; Prieto-Centurion, D.; Bhan, A. Isotopic Tracer Studies of Methanol-to-Olefins
Conversion over HSAPO-34: The Role of the Olefins-Based Catalytic Cycle. *Journal of Catalysis*2016, *337*, 52–56. https://doi.org/10.1016/j.jcat.2016.01.021.

(54) Fečík, M.; Plessow, P. N.; Studt, F. Theoretical Investigation of the Side-Chain Mechanism of the MTO Process over H-SSZ-13 Using DFT and Ab Initio Calculations. *Catal. Sci. Technol.* **2021**, *11* (11), 3826–3833. https://doi.org/10.1039/D1CY00433F.

(55) Hemelsoet, K.; Van der Mynsbrugge, J.; De Wispelaere, K.; Waroquier, M.; Van Speybroeck, V. Unraveling the Reaction Mechanisms Governing Methanol-to-Olefins Catalysis by Theory and Experiment. *ChemPhysChem* **2013**, *14* (8), 1526–1545. https://doi.org/10.1002/cphc.201201023.

(56) Svelle, S.; Joensen, F.; Nerlov, J.; Olsbye, U.; Lillerud, K.-P.; Kolboe, S.; Bjørgen, M.
Conversion of Methanol into Hydrocarbons over Zeolite H-ZSM-5: Ethene Formation Is
Mechanistically Separated from the Formation of Higher Alkenes. *J. Am. Chem. Soc.* 2006, *128*(46), 14770–14771. https://doi.org/10.1021/ja065810a.

(57) Sun, X.; Mueller, S.; Shi, H.; Haller, G. L.; Sanchez-Sanchez, M.; van Veen, A. C.; Lercher, J. A. On the Impact of Co-Feeding Aromatics and Olefins for the Methanol-to-Olefins Reaction on HZSM-5. *Journal of Catalysis* **2014**, *314*, 21–31. https://doi.org/10.1016/j.jcat.2014.03.013.

(58) Zhang, W.; Chen, J.; Xu, S.; Chu, Y.; Wei, Y.; Zhi, Y.; Huang, J.; Zheng, A.; Wu, X.;
Meng, X.; Xiao, F.; Deng, F.; Liu, Z. Methanol to Olefins Reaction over Cavity-Type Zeolite:
Cavity Controls the Critical Intermediates and Product Selectivity. *ACS Catal.* 2018, 8 (12), 10950–10963. https://doi.org/10.1021/acscatal.8b02164.

(59) Hwang, A.; Johnson, B. A.; Bhan, A. Mechanistic Study of Methylbenzene Dealkylation in Methanol-to-Olefins Catalysis on HSAPO-34. *Journal of Catalysis* **2019**, *369*, 86–94. https://doi.org/10.1016/j.jcat.2018.10.022. (60) Ferri, P.; Li, C.; Millán, R.; Martínez-Triguero, J.; Moliner, M.; Boronat, M.; Corma, A.
Impact of Zeolite Framework Composition and Flexibility on Methanol-To-Olefins Selectivity:
Confinement or Diffusion? *Angewandte Chemie International Edition* 2020, *59* (44), 19708–19715. https://doi.org/10.1002/anie.202007609.

(61) Castro, M.; Warrender, S. J.; Wright, P. A.; Apperley, D. C.; Belmabkhout, Y.; Pirngruber, G.; Min, H.-K.; Park, M. B.; Hong, S. B. Silicoaluminophosphate Molecular Sieves STA-7 and STA-14 and Their Structure-Dependent Catalytic Performance in the Conversion of Methanol to Olefins. *J. Phys. Chem. C* 2009, *113* (35), 15731–15741. https://doi.org/10.1021/jp904623a.

(62) Álvaro-Muñoz, T.; Márquez-Álvarez, C.; Sastre, E. Effect of Silicon Content on the Catalytic Behavior of Chabazite Type Silicoaluminophosphate in the Transformation of Methanol to Short Chain Olefins. *Catalysis Today* 2013, 213, 219–225. https://doi.org/10.1016/j.cattod.2013.04.031.

(63) Li, Z.; Martínez-Triguero, J.; Concepción, P.; Yu, J.; Corma, A. Methanol to Olefins: Activity and Stability of Nanosized SAPO-34 Molecular Sieves and Control of Selectivity by Silicon Distribution. *Phys. Chem. Chem. Phys.* **2013**, *15* (35), 14670–14680. https://doi.org/10.1039/C3CP52247D.

(64) Chen, J.; Wright, P. A.; Thomas, J. M.; Natarajan, S.; Marchese, L.; Bradley, S. M.; Sankar,
G.; Catlow, C. R. A.; Gai-Boyes, P. L. SAPO-18 Catalysts and Their Broensted Acid Sites. *J. Phys. Chem.* 1994, 98 (40), 10216–10224. https://doi.org/10.1021/j100091a042.

(65) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. *ACS Catal.* **2019**, *9* (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.

(66) Djieugoue, M.-A.; Prakash, A. M.; Kevan, L. Catalytic Study of Methanol-to-Olefins Conversion in Four Small-Pore Silicoaluminophosphate Molecular Sieves: Influence of the Structural Type, Nickel Incorporation, Nickel Location, and Nickel Concentration. *The Journal of Physical Chemistry B* **2000**, *104* (27), 6452–6461. https://doi.org/10.1021/jp000504j.

(67) Castellanos-Beltran, I. J.; Assima, G. P.; Lavoie, J.-M. Effect of Temperature in the Conversion of Methanol to Olefins (MTO) Using an Extruded SAPO-34 Catalyst. *Frontiers of Chemical Science and Engineering* **2018**, *12* (2), 226–238. https://doi.org/10.1007/s11705-018-1709-8.

(68) Borodina, E.; Sharbini Harun Kamaluddin, H.; Meirer, F.; Mokhtar, M.; Asiri, A. M.; Al-Thabaiti, S. A.; Basahel, S. N.; Ruiz-Martinez, J.; Weckhuysen, B. M. Influence of the Reaction Temperature on the Nature of the Active and Deactivating Species During Methanol-to-Olefins Conversion over H-SAPO-34. *ACS Catal.* 2017, 7 (8), 5268–5281. https://doi.org/10.1021/acscatal.7b01497.

(69) Shi, Z.; Bhan, A. Tuning the Ethylene-to-Propylene Ratio in Methanol-to-Olefins Catalysis
on Window-Cage Type Zeolites. *Journal of Catalysis* 2021, 395, 266–272.
https://doi.org/10.1016/j.jcat.2021.01.015.

(70) Chen, H.; Shang, W.; Yang, C.; Liu, B.; Dai, C.; Zhang, J.; Hao, Q.; Sun, M.; Ma, X. Epitaxial Growth of Layered-Bulky ZSM-5 Hybrid Catalysts for the Methanol-to-Propylene Process. *Ind. Eng. Chem. Res.* **2019**, *58* (4), 1580–1589. https://doi.org/10.1021/acs.iecr.8b05472.

(71) Li, J.; Liu, M.; Li, S.; Guo, X.; Song, C. Influence of Diffusion and Acid Properties on Methane and Propane Selectivity in Methanol-to-Olefins Reaction. *Ind. Eng. Chem. Res.* 2019, *58*(5), 1896–1905. https://doi.org/10.1021/acs.iecr.8b03969. (72) Zones, S. Zeolite SSZ-13 and Its Method of Preparation. 4,544,538, 1985.

(73) Bleken, F.; Bjørgen, M.; Palumbo, L.; Bordiga, S.; Svelle, S.; Lillerud, K.-P.; Olsbye, U. The Effect of Acid Strength on the Conversion of Methanol to Olefins Over Acidic Microporous Catalysts with the CHA Topology. *Topics in Catalysis* **2009**, *52* (3), 218–228. https://doi.org/10.1007/s11244-008-9158-0.

(74) Dahl, I. M.; Mostad, H.; Akporiaye, D.; Wendelbo, R. Structural and Chemical Influences on the MTO Reaction: A Comparison of Chabazite and SAPO-34 as MTO Catalysts. *Microporous and Mesoporous Materials* 1999, 29 (1), 185–190. https://doi.org/10.1016/S1387-1811(98)00330-8.

(75) Bates, S. A.; Verma, A. A.; Paolucci, C.; Parekh, A. A.; Anggara, T.; Yezerets, A.;
Schneider, W. F.; Miller, J. T.; Delgass, W. N.; Ribeiro, F. H. Identification of the Active Cu Site in Standard Selective Catalytic Reduction with Ammonia on Cu-SSZ-13. *Journal of Catalysis* 2014, *312*, 87–97. https://doi.org/10.1016/j.jcat.2014.01.004.

(76) Dusselier, M.; Schmidt, J. E.; Moulton, R.; Haymore, B.; Hellums, M.; Davis, M. E.
Influence of Organic Structure Directing Agent Isomer Distribution on the Synthesis of SSZ-39. *Chem. Mater.* 2015, 27 (7), 2695–2702. https://doi.org/10.1021/acs.chemmater.5b00651.

(77) Di Iorio, J. R.; Gounder, R. Controlling the Isolation and Pairing of Aluminum in Chabazite
Zeolites Using Mixtures of Organic and Inorganic Structure-Directing Agents. *Chem. Mater.* 2016, 28 (7), 2236–2247. https://doi.org/10.1021/acs.chemmater.6b00181.

(78) Maruo, T.; Yamanaka, N.; Tsunoji, N.; Sadakane, M.; Sano, T. Facile Synthesis of AEI Zeolites by Hydrothermal Conversion of FAU Zeolites in the Presence of Tetraethylphosphonium Cations. *Chem. Lett.* **2014**, *43* (3), 302–304. https://doi.org/10.1246/cl.130996.

Martín, N.; Boruntea, C. R.; Moliner, M.; Corma, A. Efficient Synthesis of the Cu-SSZ-39
Catalyst for DeNOx Applications. *Chem. Commun.* 2015, *51* (55), 11030–11033.
https://doi.org/10.1039/C5CC03200H.

(80) Bhawe, Y.; Moliner-Marin, M.; Lunn, J. D.; Liu, Y.; Malek, A.; Davis, M. Effect of Cage
Size on the Selective Conversion of Methanol to Light Olefins. *ACS Catal.* 2012, 2 (12), 2490–
2495. https://doi.org/10.1021/cs300558x.

(81) Kumita, Y.; Gascon, J.; Stavitski, E.; Moulijn, J. A.; Kapteijn, F. Shape Selective Methanol to Olefins over Highly Thermostable DDR Catalysts. *Applied Catalysis A: General* 2011, *391* (1), 234–243. https://doi.org/10.1016/j.apcata.2010.07.023.

(82) Nasser, G. A.; Muraza, O.; Nishitoba, T.; Malaibari, Z.; Al-Shammari, T. K.; Yokoi, T. OSDA-Free Chabazite (CHA) Zeolite Synthesized in the Presence of Fluoride for Selective Methanol-to-Olefins. *Microporous and Mesoporous Materials* **2019**, *274*, 277–285. https://doi.org/10.1016/j.micromeso.2018.07.020.

(83) Martín, N.; Moliner, M.; Corma, A. High Yield Synthesis of High-Silica Chabazite by Combining the Role of Zeolite Precursors and Tetraethylammonium: SCR of NOx. *Chem. Commun.* 2015, *51* (49), 9965–9968. https://doi.org/10.1039/C5CC02670A.

(84) Ji, Y.; Deimund, M. A.; Bhawe, Y.; Davis, M. E. Organic-Free Synthesis of CHA-Type Zeolite Catalysts for the Methanol-to-Olefins Reaction. *ACS Catal.* **2015**, *5* (7), 4456–4465. https://doi.org/10.1021/acscatal.5b00404.

(85) Hartmann, M. Hierarchical Zeolites: A Proven Strategy to Combine Shape Selectivity with Efficient Mass Transport. *Angewandte Chemie International Edition* **2004**, *43* (44), 5880–5882. https://doi.org/10.1002/anie.200460644. Ji, Y.; Birmingham, J.; Deimund, M. A.; Brand, S. K.; Davis, M. E. Steam-Dealuminated,
OSDA-Free RHO and KFI-Type Zeolites as Catalysts for the Methanol-to-Olefins Reaction. *Microporous and Mesoporous Materials* 2016, 232, 126–137.
https://doi.org/10.1016/j.micromeso.2016.06.012.

(87) Deimund, M. A.; Schmidt, J. E.; Davis, M. E. Effect of Pore and Cage Size on the Formation of Aromatic Intermediates During the Methanol-to-Olefins Reaction. *Topics in Catalysis* **2015**, *58* (7), 416–423. https://doi.org/10.1007/s11244-015-0384-y.

(88) Xu, S.; Zheng, A.; Wei, Y.; Chen, J.; Li, J.; Chu, Y.; Zhang, M.; Wang, Q.; Zhou, Y.; Wang, J.; Deng, F.; Liu, Z. Direct Observation of Cyclic Carbenium Ions and Their Role in the Catalytic Cycle of the Methanol-to-Olefin Reaction over Chabazite Zeolites. *Angewandte Chemie International Edition* **2013**, *52* (44), 11564–11568. https://doi.org/10.1002/anie.201303586.

(89) Chen, J.; Li, J.; Wei, Y.; Yuan, C.; Li, B.; Xu, S.; Zhou, Y.; Wang, J.; Zhang, M.; Liu, Z. Spatial Confinement Effects of Cage-Type SAPO Molecular Sieves on Product Distribution and Coke Formation in Methanol-to-Olefin Reaction. *Catalysis Communications* **2014**, *46*, 36–40. https://doi.org/10.1016/j.catcom.2013.11.016.

(90) Bhawe, Y.; Moliner-Marin, M.; Lunn, J. D.; Liu, Y.; Malek, A.; Davis, M. Effect of Cage
Size on the Selective Conversion of Methanol to Light Olefins. *ACS Catal.* 2012, 2 (12), 2490–
2495. https://doi.org/10.1021/cs300558x.

(91) Schmidt, J. E.; Deimund, M. A.; Xie, D.; Davis, M. E. Synthesis of RTH-Type Zeolites Using a Diverse Library of Imidazolium Cations. *Chem. Mater.* **2015**, *27* (10), 3756–3762. https://doi.org/10.1021/acs.chemmater.5b01003. Zones, S. I.; Davis, M. E. Facile Synthesis and Catalysis of Pure-Silica and Heteroatom LTA. *Chem. Mater.* **2015**, *27* (22), 7774–7779. https://doi.org/10.1021/acs.chemmater.5b03579.

Chapter 2 | Unraveling the Intricate Relationship between Framework Topology and Acidity on the Light Olefins Selectivities in the Methanol-to-Olefins Reaction

Abstract

The methanol-to-olefins (MTO) reaction, touted as one of the most important reactions in C₁ chemistry, is catalyzed by small-pore, cage type molecular sieves to produce a mixture of light olefins, whose selectivities vary with cage size and framework composition (acidity). Herein, we systematically investigate the MTO behavior of 44 molecular sieves belonging to the following framework types (AEI, CHA, LEV, ERI, and SWY) that are synthesized over a wide range of Si/Al=4-31 and Si/T-atom=0.034-0.278, to rationalize the effect of cage dimensions on the olefins product distribution as a function of acid site density and strength. Changes in acid site density and strength are found to play a secondary role to the dominating influence of cage architecture on product distribution in AEI- and CHA-type molecular sieves. Decreasing the cage size, in going from AEI and CHA to LEV, ERI, and SWY, however, results in substantial changes in the E/P ratio as a function of acidity. These results are rationalized based on differences in the nature (both identity and concentration) of the hydrocarbon-pool (HP) species that form as a part of the dual cycle, particularly in early stages of the reaction. This work identifies a missing link between cage size and acidity, which not only illustrates why acidity influences product selectivity differently as a function of cage size (i.e., framework/topology), but provides a roadmap for exploiting this intricate relationship to achieve more selective product distributions in methanol conversion processes.

2.1 Introduction

Ethylene (E) and propylene (P) are key components of the petrochemical industry that are primarily obtained from steam cracking and fluid catalytic cracking (FCC). The methanol-to-olefins (MTO) reaction provides an alternative and attractive route for producing these important platform chemicals from non-petroleum feedstocks such as, natural gas, coal, and biomass.¹ The MTO reaction can be carried out over microporous molecular sieves with Brønsted acid sites such as zeolites and silicoaluminophosphates (SAPOs).²

SAPO-34, a SAPO-type material with a chabazite (CHA) topology, is one of the most studied catalysts for this reaction due its promising catalytic behavior and commercialization.^{3–7} SAPO-34 achieves 70+% selectivity to ethylene and propylene with nearly equal amounts of the two components at complete methanol conversion because of its cage structure/size, mild acidity, and pore size (8-member ring (8-MR) pore size= 3.8 x 3.8 Å).^{8–10} The CHA cage allows for the accommodation of active hydrocarbon-pool (HP) species whereas the small 8-MR pores of SAPO-34 restrict the effusion of aromatic species (e.g., polymethylbenzenes) as well as large or branched aliphatic hydrocarbons, thus, leading to high ethylene and propylene selectivities.^{8,9} This is, indeed, a key difference between channel-type pore structures (e.g., MFI), which form a wide spectrum of hydrocarbons (methanol-to-hydrocarbons (MTH)), and small-pore, cage-based frameworks (e.g., CHA), which limit the product selectivity to lighter, non-aromatic products only.^{11–19}

As in most heterogeneously catalyzed processes, selectivity control is a major challenge, which affects process profitability. The MTO product distribution can be altered by varying numerous parameters including both reaction conditions (e.g., temperature, partial pressure, and flowrate) and molecular sieve properties (e.g., topology, acidity, and crystallite size).^{8,12,19–30} Each

of these parameters can modify the nature of the hydrocarbon pool species that form as a part of the dual cycle (aromatics and olefins) and thus influence the relative contribution of each of these cycles toward the product distribution. It's been shown previously that in small-pore, cage-type molecular sieves, the MTO reaction proceeds primarily via the aromatics cycle, with contributions from both the paring route and the side-chain pathway, depending on cage size as well as other material properties.^{12,22,29,31,32} However, reports on the role of the olefins cycle in small-pore, cage-type molecular sieves are fairly rare, with only a few exceptions.³³ Bhan et al.³², for instance, reported on the role of the olefins cycle in MTO over SAPO-34 using isotopic tracing studies, in which this cycle co-existed with the aromatics cycle at early stages of the reaction.

Of the many parameters that can influence product selectivity in the MTO reaction, cage topology has been recognized as a promising factor that could sway product selectivity toward targeted molecules and enhance the ethylene (or propylene) selectivity over the commercial catalyst.^{24,34} Bhawe et al.,²⁵ for instance, investigated three zeolitic materials belonging to the following frameworks (LEV, CHA, and AFX) while holding other material properties (e.g., crystallite size and Si/Al ratio) constant to isolate the effect of cage geometry. The authors showed that ethylene selectivity decreases as the cage size increases. Additionally, in that work, the Si/Al ratios of the three aforementioned zeolites were altered, to probe the effect of Si/Al ratio on product selectivity. However, changing this parameter (composition; acidity) did not lead to significant changes in the product distribution. Pinilla-Herrero and co-authors also investigated the MTO behavior of several materials, including LEV, AFX, SAV, and LTA-type SAPOs. Each of these frameworks were synthesized with varying amounts of Si/T-atom (T=Si+Al+P) ratios (acid-site densities). The authors concluded that the influence of topology on the product distribution was more significant than acidity.^{35,36} Furthermore, our group recently correlated the light olefins

product distribution with a geometric parameter of the molecular sieve cage architecture, denoted as Cage-Defining Ring (CDR), for a multitude of small-pore, cage-type zeolites and SAPOs, including, LEV, ERI, CHA, AFX, SFW, AEI, DDR, RTH, ITE, SAV, LTA, RHO, KFI, and UFI. We showed that the CDR, defined as the minimum number of tetrahedral atoms of the ring encircling the center of the framework cages in a given molecular sieve topology, correlates with MTO light olefins product distribution, in spite of the presence of some differences in the Si/Al or Si/T-atom ratios between the various materials.

Although these reports suggest that the effect of acidity (acid-site density and strength) on product selectivity is fairly small when compared to the effect of cage size, there appears to be a few exceptions in the literature, which show that acidity can play a larger role. For instance, increasing the Si/T ratio in SAPO-35 (LEV) has been shown to lead to the formation of higher ethylene-to-propylene (E/P) ratios.³⁶ The propylene-to-ethylene (P/E) ratio of DDR-type molecular sieves has also been shown to improve from 1.0 to 1.9 by increasing the Si/Al ratio from 22 to 168.³³ Additionally, we recently showed that acid-site density and strength has an instrumental role in changing the E/P ratio of ERI-type materials: E/P ratios as high as 1.9 were obtained for SSZ-98 zeolites and as low as 0.70 were obtained for SAPO-17 (ERI).²⁷

Table 2.1. Cages studied in this work and their structural properties. [a] Area calculated using the following formula: $A = (\pi ab)/4$, where A is the pore area, and a and b are the shortest and longest pore diameters.

Framework	AEI	CHA	LEV	ERI	SWY
Channel Dimensionality	3	3	2	3	3
8-MR Pore Size (Å)	3.8 x 3.8	3.8 x 3.8	3.6 x 4.8	3.6 x 5.1	3.9 x 4.0
8-MR Pore Area (Ų)	11.34	11.34	13.57	14.42	12.25
Maximum Diameter of Sphere (Å) ^[a]	7.33	7.37	7.10	7.04	7.06
Cage-defining Ring (CDR) (Å)	8.5	7.5	7.2	6.8	6.8
Materials Tested	SAPO-18 SSZ-39 AEI Zeolite	SAPO-34 SSZ-13	SAPO-67 SAPO-35 SSZ-17 LEV Zeolite	SAPO-17 SSZ-98 ERI Zeolite	STA-20 STA-30

Therefore, in order to rationalize the effect of cage size on the olefin product distribution as a function of acid-site density and strength and, more generally, develop strategies that would augment the olefins product distribution to favor the formation of either more ethylene or propylene, in this work, we systematically investigate the MTO behavior of 44 molecular sieves. These molecular sieves belong to five framework types (namely, AEI, CHA, LEV, ERI, and SWY) and have a wide range of Si/Al=4-31 and Si/T=0.034-0.28 (**Table 2.1**). In investigating the catalytic behaviors of these materials, we aim to address the key question as to why acidity significantly influences the E/P ratio of some frameworks but not others. All catalysts tested in this work were investigated with a battery of characterization techniques outlined in the next section. Partially reacted samples (after 5 minutes of reaction) were dissolved in hydrofluoric (HF) acid to extract and analyze the occluded organic components in an effort to identify differences between the composition and concentration of the entrapped hydrocarbon pool species formed during reaction. These species assist in understanding the observed differences in the catalytic behaviors (i.e., product distribution) between the various materials.

2.2 Experimental Section

The various small-pore, cage-type molecular sieves investigated in this work were synthesized based on previously reported (albeit with slight modifications) procedures as outlined below. Detailed synthesis procedures of the organic structure-directing agents (OSDAs) used in this work are also provided. The moisture contents of the solid sources were determined by temperature-gravimetric analysis (TGA).

2.2.1 Materials

All materials, unless otherwise noted, were used as-received without further purification from the stated vendors: aluminum hydroxide (Barcroft 205, SPI Pharma), pseudoboehmite alumina (Catapal B, VISTA), hydrated alumina (Reheis F2000), aluminum isopropoxide (Sigma-Aldrich, 98%), phosphoric acid (H₃PO₄; Macron, 85%), colloidal silica Ludox AS-40 (Sigma-Aldrich, 40%), fumed silica (Cab-O-Sil, ACROS), sodium silicate (PQ corporation, 8.9 wt.% Na₂O, 28.7 wt.% SiO₂ in H₂O), Zeolyst CBV500 (Si/Al=2.6), sodium aluminate (Strem, 99.9% Al and 8% H₂O), sodium hydroxide (Sigma-Aldrich, 50%), potassium hydroxide (Sigma Aldrich, 45%), 1,4-diazabicylco[2.2.2]octane (DABCO) (Sigma-Aldrich, 99%), quinuclidine (Alfa Aesar, 97%), 1,8-dibromooctane (Sigma-Aldrich, 98%), 1,6-dibromohexane (Thermo Scientific Chemicals, 98%), iodomethane (Sigma-Aldrich, 99.5%), N-methylpiperidine (Aldrich, 99%), 1,4dibromobutane (Sigma-Aldrich, 99%), sodium bicarbonate (Mallinckrodt Chemicals, 99.7%), trans-1,4-diaminocyclohexane (Aldrich, 98%), formaldehyde (Sigma, 36.5-38%), 1,3dibromopropane (Sigma-Aldrich, 99%), trimethylamine solution (25% in water, Sigma-Aldrich), hydrochloric acid (J.T. Baker, 2 N), formic acid (Sigma-Aldrich, 95%), diethyl either (VWR, 98%), ethanol (Sigma, 200 proof), chloroform (Alfa Aesar, 99.8+%), methanol (Sigma-Aldrich, 99.9%), and acetone (Fisher Chemical).

2.2.2 OSDA Syntheses

AEI-type molecular sieves (SAPO-18 and SSZ-39) were synthesized using diisopropylethylamine (DIPEA) (Sigma Aldrich) and 1,1,3,5-tetramethylpiperdinium hydroxide (TMPOH, Sachem). CHA-type molecular sieves (SAPO-34 and SSZ-13) were synthesized using morpholine and N,N,N-trimethyladamantylammonium hydroxide. LEV-type molecular sieves (SAPO-67, SAPO-35, SSZ-17, and LEV zeolite) were synthesized using

diethyldimethylammonium hydroxide (DEDMAOH; Sachem, 20%), hexamethyleneimine (Sigma Aldrich, 99%), ethanol, and N-methylquinuclidinium hydroxide. We previously reported on the synthesis of N-methylquinuclidinium hydroxide.²⁴ ERI-type molecular sieves were synthesized using numerous OSDAs outlined in detail in our previous work:²⁷ tetraethylammonium hydroxide 40%), N,N'-dimethyl-DABCO, 18-crown-6 (Sigma-Aldrich, (Aldrich, 99%). N.Ndimethylpiperidinium hydroxide, hexamethonium bromide, butane-1,4-bis(trimethylammonium) dihydroxide, cyclohexane-1,4-bis(trimethylammonium) dihydroxide, cyclohexylamine, and bisquinuclidinium-propane (DiQ- C_3) dihydroxide. SWY-type molecular sieves (STA-20 and STA-30) were synthesized using trimethylamine (25%) in water, Sigma-Aldrich), tetrabutylammonium hydroxide (Sigma-Aldrich, 40% in H₂O), tetrapropylammonium hydroxide (TPAOH; Thermo Scientific Chemicals, 25%), 1,6-(DABCO)hexyl (DiDABCO-C₆) dibromide, and 1,8-(DABCO)octyl (DiDABCO-C₈) dibromide. DiDABCO-C₆ and DiDABCO-C₈ were synthesized based on a generic procedure outlined previously for a similar molecule with different linkers.³⁷

2.2.3 Ion Exchange and Titration

If required by the molecular sieve synthesis procedure, the OSDAs described above were ion exchanged from their halide forms into their hydroxide forms by first dissolving the organic salts in DI water and then adding DOWEXTM MonosphereTM 550A hydroxide ion-exchange resin (Dow chemical). Specifically, for every 100 mmol of OSDA in the halide form, approximately 300 cm³ (by volume) of resin and 500 cm³ of DI water were added. The mixture was then stirred for 24 h at room temperature. After 24 h, the resin was separated by filtration and the process repeated a second time. The quantification of the concentration of the OSDA, now in the hydroxide form, was performed using a Mettler Toledo DL22 Potentiometric pH meter. Five readings were taken for each OSDA concentration and these values were then averaged and used for gel calculations. To differentiate between the OSDAs in the hydroxide form and those in the halide (e.g., bromide form), the OSDAs in the hydroxide form are labeled with "(OH)" (e.g., DiDABCO- C_{6} -(OH)₂).

2.2.4 Molecular Sieve Syntheses

2.2.4.1 AEI-type Molecular Sieves

Several AEI-type molecular sieves were synthesized or provided to us. Several SAPO-18 samples were synthesized with a gel molar composition of 1 Al₂O₃ : 0.9 P₂O₅ : x SiO₂ : 1.6 diisopropylethylamine : 50 H₂O, where x=0.2, 0.4, 0.6, 0.8, and 1.0.³⁸ In a typical synthesis, a solution of phosphoric acid and deionized (DI) water was added to aluminum hydroxide hydrate (Barcroft) and the mixture was stirred overnight. Then, fumed silica was added to this mixture followed by the OSDA. The gel was stirred for an additional 2 h before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 160 °C for 10 days. These samples are denoted as SAPO-18-xSi, where again, x is the Si content in the gel (e.g., SAPO-18-0.2Si).

Two SSZ-39 samples were synthesized. SSZ-39-(7), where 7 indicates the bulk Si/Al ratio obtained from EDS (a similar naming system is used for the other zeolites in this work), was synthesized with a gel molar composition of 0.033 Al : $1.0 \text{ SiO}_2 : 0.57 \text{ Na}^+ : 0.14 \text{ R}^+ (1,1,3,5-$ tetramethylpiperidinium hydroxide) : $0.71 \text{ OH}^- : 28 \text{ H}_2\text{O}^{.39}$ In a typical procedure, the OSDA was mixed with sodium hydroxide and deionized water in a 23-mL Teflon Parr reactor. Then, the silicon and aluminum sources (sodium silicate and CBV500) were added and the solution stirred for approximately 1 h. The Parr reactor was then sealed and placed in a rotating oven at 140 °C for 4 days. SSZ-39-(10) was synthesized without sodium using a modified procedure from the original recipe, which we previously reported on.²⁴ The gel molar composition for this SSZ-39 sample was:

 $0.067 \text{ Al} : 1.0 \text{ SiO}_2 : 0.71 \text{ R}^+$ (1,1,3,5-tetramethylpiperidinium hydroxide) : 0.71 OH⁻ : 20 H₂O. The crystallization was performed in a 140 °C rotating oven for 28 days. An AEI zeolite sample was kindly provided to us by Joseph Fedeyko at Johnson-Matthey USA. This sample is denoted as AEI-zeolite-(11).

2.2.4.2 CHA-type Molecular Sieves

Several CHA-type molecular sieves were synthesized or purchased. SAPO-34-C was kindly provided by Mitsubishi. Several other SAPO-34 samples with higher Si contents were synthesized with a gel molar composition of 0.985 Al₂O₃ : $1 P_2O_5$: x SiO₂ : 2 morpholine : 60 H₂O, where x=0.4, 0.6, 0.8, and 1.0.⁴⁰ In a typical synthesis, a desired amount of pseudoboehmite was slurred in 50% of the required deionized (DI) water for approximately 3 h. Then, phosphoric acid was added dropwise to the alumina slurry and the solution was stirred for another 2 h. After stirring, fumed silica was added along with the remaining water. The mixture was left to stir for 1 hour before adding the OSDA (morpholine). This mixture was stirred overnight before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 200 °C for 48 hours. These SAPO-34 samples are denoted as SAPO-34-xSi, where again, x is the Si content in the gel.

SSZ-13-(8) was purchased from ACS Materials. Three other SSZ-13 samples (SSZ-13-(15), SSZ-13-(24), and SSZ-13-(31)) were synthesized with a gel molar composition of: $x Al_2O_3$: 100 SiO₂ : 10 Na₂O : 20 R⁺ (N,N,N-trimethyl-1-adamantanimonium hydroxide) : 4400 H₂O, where x was varied to generate different gel Si/Al ratios. ⁴¹ Three gel Si/Al ratios were attempted: 20, 30 and 40. In a typical synthesis, sodium hydroxide was mixed with the OSDA in water and stirred for 10 minutes. Then, aluminum isopropoxide was added to this solution and the mixture was stirred for an additional hour. Then, Ludox AS-40 was added and the gel was aged for 24 hours before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 160 °C for 6 days.

2.2.4.3 LEV-type Molecular Sieves

Several LEV-type molecular sieves were synthesized, including SAPO-67, SAPO-35, SSZ-17, and LEV zeolite. Three SAPO-67 samples were synthesized with a gel molar composition of 0.8 Al₂O₃ : 1.0 P₂O₅ : x SiO₂ : 2.5 DEDMAOH : 80 H₂O, where x=0.2, 0.3, and 0.4.⁴² In a typical synthesis, Ludox AS-40 was mixed with DEDMAOH in water. After stirring the solution for 1 h, the mixture was transferred to a 100 °C rotating oven for 1 h. Following that, a desired amount of Barcroft aluminum hydroxide was added to this solution and stirred for 3 additional hours. Lastly, phosphoric acid was added to this mixture and the final gel was stirred overnight before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a tumbling oven to 175 °C for 7 days. These SAPO-67 samples are denoted as SAPO-67-xSi, where again, x is the Si content in the gel.

Two additional SAPO-LEV samples were synthesized. SAPO-35-0.3Si-1 was synthesized with a gel molar composition of $1.0 \text{ Al}_2\text{O}_3 : 1.0 \text{ P}_2\text{O}_5 : 0.3 \text{ SiO}_2 : 1.5$ hexamethyleneimine : 55 H₂O.⁴³ In a typical synthesis, a desired amount of Catapal-B was slurred in DI water (50%) overnight. Then, phosphoric acid was added to this mixture and the solution was stirred for 2 days. To this, Ludox AS-40 was added followed by water. The final mixture was left to stir at room temperature overnight. Crystallization was done at 200 °C for 24 h in a static oven. SAPO-35-0.3Si-2 was synthesized following a similar procedure as SAPO-35-0.3Si-1, but with Barcroft aluminum hydroxide as the Al source.

Three SSZ-17 samples (SSZ-17-(11), SSZ-17-(14), and SSZ-17-(15)) were synthesized following a method previously reported by our group.²⁵ A synthesis gel of the composition $x Al_2O_3$

: 1.0 SiO₂ : 0.2 NaOH : 0.2 ROH (N-methylquinuclidinium hydroxide) : 40 H₂O was prepared with Cab-O-Sil silica, Reheis F2000, and sodium hydroxide solution. The aluminum content (x) in the gel was varied to obtain a gel Si/Al ratio of 12, 16, and 20. The gel was loaded into a Teflon-lined autoclave and heated to 170 $^{\circ}$ C with tumbling for 8 days.

LEV zeolite (denoted as LEV-zeolite-(5)) was synthesized with a gel molar composition of $0.022 \text{ Al}_2\text{O}_3 : 1.0 \text{ SiO}_2 : 0.36 \text{ Na}_2\text{O} : 1.5 \text{ ethanol} : 35 \text{ H}_2\text{O}.^{44}$ In a typical synthesis, sodium aluminate, sodium hydroxide, and water were mixed together and stirred for 10 minutes. Then, fumed silica was added along with SSZ-17 seeds and ethanol. This gel was stirred for 10 additional minutes before being loaded into a Teflon-lined autoclave and heated to 125 °C for 3 days.

2.2.4.4 ERI-type Molecular Sieves

Several ERI-type molecular sieves were synthesized, including SAPO-17, SSZ-98, UZM-12, and ERI zeolites. We reported on the synthesis and characterization of these materials in our previous work.²⁷ **Table A2.1** shows a summary list of the ERI samples tested in this work and their corresponding names in our previous publication. Three additional samples were added in this work. SAPO-17-0.4Si-1 and SAPO-17-0.6Si were synthesized using a similar procedure as SAPO-17-0.2Si, but with higher Si contents (0.4 and 0.6 instead of 0.2). UZM-12-2-(6) was synthesized in a similar fashion as UZM-12-1-(2); however, the crystallization temperature was increased to 160 °C. Increasing the reaction temperature allowed for the synthesis of a UZM-12 sample with better crystallinity.

2.2.4.5 SWY-type Molecular Sieves

A few SWY-type molecular sieves were synthesized (STA-20 and STA-30). Two STA-20 samples (SAPO-SWY-0.1Si and SAPO-SWY-0.2Si) were synthesized with a gel molar composition of 1.0 Al(OH)₃ : 0.9 H₃PO₄ : 0.05 and 0.1 SiO₂ : 0.1 DiDABCO-C₆-Br₂ : 0.42

trimethylamine: 0.08 tetrabutylammonium hydroxide: 40 H_2O .⁴⁵ In a typical synthesis, Barcroft aluminum hydroxide was mixed with water and stirred for 30 minutes. Then, phosphoric acid was added and the mixture stirred for an additional 30 minutes. Following that, Cab-O-Sil silica was added along with the OSDAs and the solution was left to stir for 2 h at room temperature and then transferred to a Teflon-lined Parr reactor. Crystallization was performed in a rotating oven at 160 °C for 1 day.

STA-30 was synthesized with a gel molar composition of $0.04 \text{ Al}_2\text{O}_3$: 1.0 SiO_2 : 0.08 KOH: 0.12 RBr_2 (DiDABCO-C₈-Br₂): 0.4 tetrapropylammonium hydroxide : $20 \text{ H}_2\text{O}.^{37}$ In a typical synthesis, aluminum hydroxide (Barcroft) was first dissolved in a solution of tetrapropylammonium hydroxide and water for 3 h. Ludox AS-40 was then added and the mixture was allowed to stir for an additional 2 h. The gel was then aged at 100 °C for 20 h. Next, potassium hydroxide and DiDABCO-C8 were added to the gel. The resulting mixture was stirred at room temperature for 3 h, after which the autoclaves were placed in a rotating oven and crystallized at 125 °C for 6 days.

2.2.5 Product Recovery, Thermal Treatment, and Ammonium Exchange

Once the above syntheses were completed, each material was washed three times (minimum) with DI water (50 cm³ each time) and once with acetone. After each wash, materials were recovered by centrifugation at 3500+ rpm (Eppendorf model 5810 R). After washing, all samples were dried in air overnight at 80-100 °C. Following drying, all materials were thermally treated (in ceramic calcination boats) under flowing breathing-grade air in a Nabertherm DKN400 muffle furnace. Materials were initially heated to 150 °C at a heating rate of 1 °C/min and held for 3 h before being heated to 580 °C (again at a heating rate of 1 °C/min) and held for 12 h to ensure complete combustion of any remaining organic structure-directing agents (OSDAs).

The zeolites were then converted to their ammonium-form by ion exchange three to seven times with 1 M aqueous NH₄NO₃ solution at 70 °C for 6-8 h. Samples containing potassium generally required multiple ion exchanges to remove the majority of potassium, as measured by energy-dispersive X-ray spectroscopy (EDS). The solid products after the last ion exchange were recovered by centrifugation, washed three times with water and once with acetone, and dried overnight at 100 °C. The dried samples were then thermally treated again using the method described above to convert them to the proton-form.

2.2.6 Characterization

Powder X-ray diffraction (PXRD/XRD) patterns were obtained on a Rigaku MiniFlex II instrument using Cu K α radiation ($\lambda = 1.54184$ Å) at a scan rate of 0.6-1.0 °/min to determine structure type and purity. Morphology and elemental composition were determined via scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) on a ZEISS 1550VP instrument equipped with an Oxford X-Max SDD energy dispersive X-ray spectrometer. Atomic ratios (atomic %) were reported as Si/T-atom ratios, where T=Si+Al+P. To determine micropore volume using the t-plot method, N₂-adsorption/desorption experiments were performed on each sample at 77 K in a Quantachrome Autosorb iQ adsorption instrument using a constant-dose method. Prior to adsorption measurements, all samples were outgassed at 60 °C for 0.5 h, followed by holds of 0.5 h at 120 °C and 6 h at 350 °C (all ramping rates were 1 °C/min). Thermogravimetric analysis (TGA) measurements were performed on Perkin Elmer STA 6000. Fully-coked samples (0.02-0.06 g) were placed in an alumina crucible and heated at 7-10 °C/min in a flowing stream (0.33 cm³/s) of air to 800 °C. Liquid ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer. All

liquid NMR analyses, involving OSDAs, were performed in deuterium oxide (D₂O) (99.9%, Cambridge Isotope Laboratories, Inc.).

All solid-state, magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy experiments were conducted on a Bruker Avance 500 MHz spectrometer using a 4mm ZrO₂ rotor. The number of Brønsted acid sites was measured using quantitative ¹H MAS NMR spectroscopy. In a typical experiment, the thermally treated samples were dehydrated under vacuum (10⁻² Torr) at 400 °C for 10 hours at a ramp rate of 2 °C/min in a dehydration manifold after being pre-packed in an uncapped ZrO₂ rotor that is placed inside of a 5-mm glass NMR tube. The rotor was then capped while under vacuum and inside the dehydration manifold (to minimize sample exposure to moisture) and then loaded into the spectrometer. Spectra were collected at 500.20 MHz and a spinning rate of 12 kHz using a 90° pulse length of 4 µs. Recycle delay time was varied depending on the T₁ relaxation time of the samples. Signal intensities were referenced to hexamethylbenzene and normalized by the mass packed into the rotor for quantification. The spectra were deconvoluted using DMFit, as shown in our previous work.²⁷ For ²⁹Si MAS NMR spectroscopy, oxygen was introduced to the dehydrated sample to reduce the relaxation time. The ¹H-decoupled ²⁹Si MAS NMR spectra were then acquired at 99.38 MHz and a spinning rate of 8 kHz using a 90° pulse length of 4 µs and a cycle delay time of 10 s. The acquired spectra were used to identify different Si environments in the tested samples and to calculate framework Si/Al.

2.2.7 Catalytic Testing

Catalyst evaluation was carried out in a fixed-bed reactor at ambient pressure. In a typical experiment, approximately 200 mg of dried catalyst (35–60 mesh size) was loaded between two layers of quartz wool in a 0.25" × 6" stainless steel (or quartz) tube reactor as a part of a BTRS Jr. continuous flow reactor (Parker Autoclave Engineers). The dry weight of the catalyst was

estimated on the basis of thermogravimetric analysis (TGA; PerkinElmer STA 6000). All catalysts were first pretreated by heating to 150 °C at 1 °C/min, held for 3 hours, and then heated further to 580 °C at 1 °C/min and held for 12 h under flowing air (breathing-grade D, AirGas). Methanol was introduced via a liquid syringe pump (Harvard Apparatus Pump 11 Elite) at 4.0-5.0 μ L/min into a gas stream of an inert blend (95% He and 5% Ar; GC internal standard) at a volumetric flow rate of 30 cm³/min. The methanol flow rate was adjusted, depending on the actual weight of the dried catalyst loaded in the reactor, to achieve a weight hourly space velocity (WHSV) of 1.3 h⁻¹. Reactions were performed at 400 °C. Effluent gases were evaluated using an on-stream Agilent GC-MS (GC 6890N/MSD5793N) equipped with a Plot-Q capillary column. Aliquots of product flow were analyzed every 16 minutes. All selectivity values were calculated on carbon-number basis.

In experiments where the content of the entrained hydrocarbons was of interest, the reaction was quenched rapidly (-7-10 °C/s) after 5 minutes of reaction and a portion of the catalyst bed (20 mg) was transferred to a Teflon tube and suspended in 1.0 cm³ of 48% aqueous hydrofluoric acid (Sigma Aldrich). The solution was stirred for 2 h to allow the framework to dissolve. Following dissolution, the organic material was extracted into 1 cm³ of dichloromethane ($2 \times 0.5 \text{ cm}^3$). Hexachloroethane (Aldrich, 99%) was used as an internal standard. The speciation of aromatics in the organic layer was then identified using a mass spectrometer (Agilent 6890N) and a ZB-5MS column (30 m x 0.25 mm) and quantified using a gas chromatograph (Agilent 7890B) connected to a Polyarc. The organic compounds extracted were identified in comparison with the NIST database as well as standards.

2.3 Results and Discussion

2.3.1 Characterization

A total of 44 small-pore, cage-containing molecular sieves were synthesized and characterized. Below, the characterizations of these materials are discussed and the results are summarized in **Table 2.2** for the SAPO materials and **Table 2.3** for the zeolites.

Figures A2.1-A2.5 show the powder XRD patterns for the various samples investigated in this work. These patterns are in good agreement with simulated patterns (IZA database) as well as diffraction patterns reported previously for these frameworks.^{9,16,26,37,38,45–47} Minor shifts in the diffraction peaks are observed, which are attributed to small differences in the unit cell size caused by differences in composition in the final product and choice of OSDA. For some of the materials, specifically those that were not synthesized in-house, the XRD patterns reflect thermally treated samples.

Particle/crystal size is one parameter that has been shown to affect catalyst lifetime.^{48,49} Therefore, SEM was used to determine particle sizes and morphology. **Figure 2.1** shows the SEM images of selected catalysts. The SEM images show that each framework has a unique morphology, with some frameworks (e.g., ERI and SWY) having multiple morphologies depending on the gel composition and the Si or Al content. Particle sizes, in general, were relatively close, ca. 0.2-10 microns, for all of the samples. SAPO-34 was the only material tested in this work that had particle sizes that fell outside of this range (5-35 microns). **Tables 2.2** and **2.3** show the measured particle sizes for all of the samples investigated in this work.

Elemental composition was obtained using EDS, and these results are shown in **Tables 2.2** and **2.3**, for the SAPOs and zeolites, respectively. The elemental composition data confirm that each framework contains several samples with different Si/Al=4-31 and Si/T=0.034-0.278 ratios. Some frameworks/materials can be synthesized over a wide range of conditions (e.g., SAPO-34, SSZ-13, and SAPO-18), whereas other frameworks/materials can only be synthesized over a

narrow range (e.g., STA-20 and STA-30). We attempted to synthesize materials with a wide range of Si/Al or Si/T ratios, but that was not always possible.

N₂-adsorption-desorption experiments were performed to obtain micropore volumes (denoted as V_{micro}) in **Tables 2.2** and **2.3**. All samples had micropore volumes that were between 0.18 and 0.27 cm³/g, except for UZM-12-1-(2), which had a micropore volume of 0.15 cm³/g (because this sample contained extraframework Al as shown in our previous work).²⁷



Figure 2.1. SEM images of selected catalysts. Each framework (AEI, CHA, LEV, ERI, and SWY) is represented by two SAPO samples and two zeolites, except for STA-30 (SWY).

²⁹Si MAS NMR spectroscopy was used to identify different silicon environments present in the thermally treated samples prior to undergoing reaction, and in the case of the zeolites, to calculate framework Si/Al ratio. **Figure A2.6** shows the ²⁹Si MAS NMR spectra for selected samples. In general, the spectra for the zeolites showed several resonances at approximately -112, -106, -101- and -100 ppm. The peaks observed corresponded to Si(0Al), Si(1Al), Si-OH defects, and Si(2Al), depending on the framework and the number of T-sites it has. For the majority of the samples tested, the bulk Si/Al ratio from EDS was close to the framework Si/Al ratio obtained from solid state NMR, with two exceptions (SSZ-13-(8) and UZM-12-1-(2)). Both of these samples contained considerable amounts of extra framework Al in agreement with the ²⁷Al MAS NMR (not shown).

On the other hand, for the SAPO samples, typically, five bands were present centered at -92 (isolated Si atoms), -97, -101, -106, and -112 (Si islands), corresponding to different silicon environments. In some cases, a small broad peak was present near -116, which is likely associated with amorphous silica.

¹H MAS NMR experiments were performed on the dehydrated samples and the obtained spectra are shown in **Figure A2.7**. For all of the zeolite samples, multiple resonances were observed. A resonance near 1.8 ppm that corresponds to protons in silanols (Si-OH) was present in many of the samples. Additionally, due to the high Al content of many of the samples tested in this work, resonances for protons in aluminum-rich (e.g., extraframework Al) environments were also present between 2 and 3.5 ppm. A main resonance near 4 ppm (for zeolites) was detected that originates from bridging hydroxyl groups that form from tetrahedrally coordinated Al. Deconvolution of the peaks at 4+ ppm gave rise to the total Brønsted acid site density values shown in **Table 2.3**. For the SAPO samples, two main peaks consistent with two differently formed acid sites were present in ¹H MAS NMR spectra: a weaker acid site showing a resonance at ca. 3.6-3.7

ppm, and a stronger acid site (zeolite-like) showing a resonance at 3.9-4 ppm. Deconvolution of the peaks at 3.6+ ppm gave rise to the acid site density values shown in **Table 2.2**.

Following reaction, the deactivated catalysts were tested in TGA. **Tables 2.2** and **2.3** show the organic mass losses of the deactivated catalysts. The organic mass losses were calculated based on the mass losses between 300 and 800 °C in air. The TGA results show that mass losses for AEI and CHA-type molecular sieves were generally higher than LEV, ERI, and SWY-type molecular sieves. This is likely due to differences in cage sizes, which affects how fast each material deactivates.²⁵

2.3.2 MTO Reaction

Tables 2.4 and **2.5** show a summary of the reaction results for the 44 molecular sieves that were investigated in this work. **Figure 2.2** shows the averaged ethylene-to-propylene ratios before deactivation (when methanol conversion is greater than 97%). The time-on-stream (TOS) profiles are shown in **Figures S2.8-S2.17**.

AEI has the largest cage of all the materials tested. All SAPO-18 samples formed primarily propylene (selectivity of 43-47%) followed by ethylene (20-22%) and butenes (16-17%), irrespective of Si/T ratios. These selectivities translated to E/P ratios of 0.45-0.47. The key difference in the catalytic behavior between these various samples was lifetime, with the samples containing higher Si content (higher Si/T ratio) having shorter lifetimes. Indeed, this was the case not just for AEI, but generally for all other frameworks tested in this work. Albeit SAPO-18 gave long lifetimes, AEI zeolites (e.g., SSZ-39) had much shorter lifetimes and formed larger amounts of alkanes (likely due to their low Si/Al ratios and the presence of paired Al sites, as we demonstrated previously).²⁶ However, in spite of these transient differences, AEI zeolites give E/P ratios (0.38-0.41) that are roughly similar to those obtained by SAPO-18.

Table 2.2. Characterization data on the SAPO samples. [a] Measured by EDS. [b] Measured by SEM. [c] Measured from N_2 -physisorption experiments. [d] Measured by ¹H MAS NMR (Brønsted acid site density). [e] Two morphologies are observed. [f] Reported from our previous work.²⁷ [g] Obtained from TGA.

Sample ID –	Gel Product (EDS) ^[a]					Particle Size	V _{micro}	BAS Density	Occluded
	Si/T	Si/T	Si	Al	Р	(μm) ^[b]	(cc/g) ^[c]	(mmol/g) ^[d]	Organics (wt%) ^[g]
SAPO-18-0.2Si	0.050	0.061	6.12	49.30	44.58	0.3-3	0.20	0.86	13.3
SAPO-18-0.4Si	0.095	0.084	8.38	48.13	43.49	0.3-3	-	-	13.4
SAPO-18-0.6Si	0.136	0.109	10.96	47.92	41.91	0.3-3	-	-	13.9
SAPO-18-0.8Si	0.174	0.131	13.06	46.94	40.00	0.7-3	-	-	14.3
SAPO-18-1.0Si	0.208	0.162	16.21	46.43	37.35	0.7-3	0.17	0.92	14.7
SAPO-34-C	N/A	0.019	9.31	48.61	42.07	1-6	-	-	13.5
SAPO-34-0.4Si	0.092	0.127	12.72	50.72	36.55	5-25	0.20	0.2	12.7
SAPO-34-0.6Si	0.131	0.189	18.88	49.27	31.85	8-30	-	-	12.9
SAPO-34-0.8Si	0.168	0.254	25.40	47.28	27.32	8-35	-	-	12.2
SAPO-34-1.0Si	0.201	0.278	27.83	44.46	27.71	8-35	0.19	0.19	12.0
SAPO-67-0.2Si	0.053	0.111	11.09	51.21	37.70	0.4-1.5	0.21	0.41	7.06
SAPO-35-0.3Si-1	0.070	0.083	8.28	49.69	42.02	8-14	0.22	-	4.41
SAPO-35-0.3Si-2	0.070	0.093	9.25	50.17	40.57	20-25	0.23	-	4.01
SAPO-67-0.3Si	0.077	0.121	12.11	49.43	38.45	0.4-2	-	-	6.93
SAPO-67-0.4Si	0.100	0.136	13.55	49.14	37.31	1.5-4	0.24	0.56	7.38
SAPO-17-0.1Si ^[f]	0.024	0.034	3.39	49.83	46.77	2x(2-10)	0.21	-	11.1
SAPO-17-0.2Si ^[f]	0.048	0.042	4.19	49.38	46.43	1-3	0.26	0.19	10.1
SAPO-17-0.3Si-1 ^[f]	0.070	0.071	7.12	48.83	44.05	3-8	0.25	0.42	12.9
SAPO-17-0.3Si-2 ^[f]	0.070	0.073	7.32	48.48	44.21	1-10	0.26	0.45	10.5
SAPO-17-0.4Si-1	0.091	0.091	9.14	48.17	42.68	0.2x1-3 ^[e]	-	-	-
SAPO-17-0.4Si-2 ^[f]	0.095	0.103	10.32	49.51	39.90	2-4	0.18	0.93	11.2
SAPO-17-0.6Si	0.130	0.112	11.02	47.31	41.67	0.2x1-3 ^[e]	-	-	-
SAPO-17-0.8Si ^[f]	0.167	0.120	11.95	46.18	41.86	(0.1-0.3)x3 ^[e]	0.19	0.83	10.4
SAPO-SWY-0.1Si	0.025	0.040	3.97	51.84	44.17	1.5-4	0.18	0.15	7.83
SAPO-SWY-0.2Si	0.050	0.085	8.52	46.68	44.80	3.5-5	0.18	-	8.12
Framework V_{micro} Bulk Particle Size **Brønsted Acid Site** Occluded Sample ID Si/Al^[a] Si /Al^[e] (µm)^[b] <u>(cc/</u>g)^[c] Organics (wt%)^[h] Density (mmol/g)^[d] SSZ-39-(7) 6.51 9.13 0.2-1.5 19.8 0.26 1.160 SSZ-39-(10)^[f] 0.2-1.5 18.3 10.0 ---AEI Zeolite-(11) 10.8 12.2 0.2-1.2 0.27 1.060 18.3 SSZ-13-(8) 7.71 14.9 0.3-1.5 0.24 0.971 18.0 SSZ-13-(15) 15.3 16.36 5-15 0.22 0.924 16.6 SSZ-13-(24) 24.1 -5-20 16.9 --SSZ-13-(31) 30.7 26.7 10-25 0.28 17.0 0.569 LEV Zeolite-(5) 4.67 7.17 0.2-0.4 1.210 12.9 0.18 SSZ-17-(11) 10.9 0.2-1 0.23 0.766 16.3 11.0 SSZ-17-(14) 14.7 0.3-1.1 16.6 ---SSZ-17-(15) 15.3 13.6 0.3-1.4 17.3 0.24 0.367 SSZ-98-(4)^[g] 5.06 3.96 (0.4-1)x10 0.400 14.4 0.18 SSZ-98-(6)^[g] 6.04 7.06 1-6 13.0 -0.19 UZM-12-1-(2)^[g] 1.86 0.1-0.2 5.96 14.9 0.15 0.240 UZM-12-2-(6) 6.03 7.48 0.2-1 0.23 -ERI Zeolite-1-(5) [g] 5.22 0.270 (0.3-0.6)x(2-3)6.20 12.7 0.23 ERI Zeolite-2-(5) [g] 5.32 6.17 0.1-0.2 15.2 -0.20 ERI Zeolite-3-(8)^[g] 8.01 9.25 0.06-0.2 0.070 10.2 0.20 STA-30-(8) 7.72 9.65 (0.03 - 0.06)x(0.5)0.27 0.354 11.6

Table 2.3. Characterization data of the zeolites tested in this work. [a] Measured by EDS. [b] Measured by SEM. [c] Measured from N₂-physisorption experiments. [d] Measured by ¹H MAS NMR (Brønsted acid site density). [e] Measured by ²⁹Si MAS NMR spectroscopy. [f] Reported from our previous work.²⁴ [g] Reported from our previous work.²⁷ [h] Obtained from TGA.

Table 2.4. Averaged product selectivities for the SAPOs tested in this work when conversion >97%. Reactions were performed at 400 °C and a WHSV(MeOH) of 1.3 h^{-1} . [a] Reported from our previous work.

Sample ID	C ₂₌	C ₃₌	C ₂ +C ₃ Alkanes	C ₄	C ₅₊	C _{2=/} C ₃₌
SAPO-18-0.2Si	0.22	0.47	0.007	0.16	0.096	0.46
SAPO-18-0.4Si	0.20	0.45	0.012	0.16	0.116	0.46
SAPO-18-0.6Si	0.20	0.45	0.012	0.16	0.122	0.45
SAPO-18-0.8Si	0.21	0.44	0.021	0.16	0.113	0.47
SAPO-18-1.0Si	0.20	0.43	0.025	0.17	0.113	0.46
SAPO-34-C	0.32	0.42	0.040	0.11	0.050	0.76
SAPO-34-0.4Si	APO-34-0.4Si 0.28		0.098	0.098 0.12		0.74
SAPO-34-0.6Si	0.29	0.40	0.102	0.13	0.049	0.74
SAPO-34-0.8Si	0.28	0.39	0.115	0.115 0.13		0.73
SAPO-34-1.0Si	0-34-1.0Si 0.27 0.3		0.128	0.14	0.054	0.71
SAPO-67-0.2Si	0.20	0.40	0.005	0.06	0.273	0.51
SAPO-35-0.3Si-1	0.20	0.39	0.006	0.07	0.260	0.53
SAPO-35-0.3Si-2	0.21	0.39	0.007	0.07	0.280	0.54
SAPO-67-0.3Si	0.22	0.37	0.007	0.06	0.270	0.58
SAPO-67-0.4Si	0.23	0.36	0.009	0.05	0.259	0.66
SAPO-17-0.1Si ^[a]	0.23	0.33	0.006	0.14	0.283	0.70
SAPO-17-0.2Si ^[a]	0.25	0.35	0.014	0.15	0.214	0.73
SAPO-17-0.3Si-1 ^[a]	0.29	0.34	0.031	0.14	0.190	0.86
SAPO-17-0.3Si-2 ^[a]	0.28	0.33	0.025	0.13	0.186	0.85
SAPO-17-0.4Si-1	0.27	0.29	0.031	0.12	0.188	0.93
SAPO-17-0.4Si-2 ^[a]	0.30	0.31	0.033	0.11	0.174	0.98
SAPO-17-0.6Si	0.28	0.28	0.035	0.11	0.233	1.01
SAPO-17-0.8S i ^[a]	0.30	0.27	0.038	0.13	0.230	1.12
SAPO-SWY-0.1Si	0.14	0.28	0.006	0.13	0.290	0.48
SAPO-SWY-0.2Si	0.16	0.27	0.007	0.13	0.279	0.60

CHA has a smaller cage than AEI (**Figure 2.1**). Because of that, SAPO-34 enhances the ethylene selectivity over AEI-type molecular sieves. However, just like in the case of AEI, changing the acid site density and strength of CHA-type molecular sieves does not significantly alter the MTO E/P ratio. **Table 2.4** shows that all the SAPO-34 samples had an E/P ratio of approximately 0.7 whereas the SSZ-13 samples (**Table 2.5**) had E/P ratios between 0.7 and 0.9,

consistent with our prior report on SSZ-13 materials with different Si/Al ratios and paired sites.⁹ By increasing the Si/Al ratio (i.e., reducing the acid site density), SSZ-13 starts to resemble the behavior of SAPO-34 (i.e., lower alkanes and longer lifetimes). The slight improvement in the E/P ratio exhibited by SSZ-13 over SAPO-34 is likely due to differences in acid strength as well as framework flexibility between these two materials.^{9,50}

Table 2.5. Averaged product selectivities for the zeolites tested in this work when conversion >97%. Reactions were performed at 400 °C and a WHSV(MeOH) of 1.3 h^{-1} . [a] Reported from our previous work.

Sample ID	C ₂₌	C ₃₌	C₂+C₃ Alkanes	C ₄	C5+	C _{2=/} C ₃₌
SSZ-39-(7)	0.12	0.32	0.241	0.14	0.102	0.38
SSZ-39-(10)	0.14	0.38	0.131	0.18	0.120	0.39
AEI Zeolite-(11)	0.15	0.38	0.164	0.14	0.095	0.39
SSZ-13-(8)	0.29	0.41	0.094	0.12	0.117	0.72
SSZ-13-(15)	0.29	0.41	0.090	0.11	0.069	0.70
SSZ-13-(24)	0.31	0.39	0.079	0.12	0.074	0.78
SSZ-13-(31)	0.35	0.39	0.055	0.12	0.061	0.89
LEV Zeolite-(5)	0.25	0.22	0.066	0.07	0.182	1.17
SSZ-17-(11)	0.28	0.23	0.050	0.08	0.229	1.22
SSZ-17-(14)	0.26	0.22	0.041	0.07	0.241	1.18
SSZ-17-(15)	0.25	0.21	0.043	0.07	0.251	1.19
SSZ-98-(4) ^[a]	0.41	0.22	0.167	0.10	0.100	1.86
UZM-12-1-(2) ^[a]	0.39	0.23	0.064	0.12	0.190	1.71
ERI Zeolite-1-(5) ^[a]	0.39	0.25	0.060	0.12	0.169	1.55
ERI Zeolite-2-(5) ^[a]	0.39	0.25	0.075	0.11	0.164	1.52
SSZ-98-(6) ^[a]	0.34	0.24	0.147	0.12	0.153	1.45
UZM-12-1-(6)	0.39	0.23	0.080	0.14	0.179	1.71
ERI Zeolite-3-(8) ^[a]	0.29	0.26	0.049	0.14	0.245	1.12
STA-30-(8)	0.25	0.24	0.057	0.18	0.221	1.02

LEV is one of the smallest cages tested in this work, with the LEV cage being relatively narrower than both AEI and CHA. All of the SAPO-LEV (SAPO-67 and SAPO-35) samples tested in this work deactivated rather rapidly (**Figure A2.12**). However, unlike AEI and CHA-type molecular sieves, SAPO-LEV materials enhanced the E/P ratio when the Si content was increased (i.e., higher Si/T). For instance, SAPO-67-0.2Si registered an E/P ratio of 0.51 whereas SAPO-67-0.4Si registered an E/P ratio of 0.66. Changing the catalysts from SAPO-based materials to zeolites (LEV Zeolite and SSZ-17) allowed for the E/P ratio to almost double. Virtually all LEV zeolites achieved an E/P ratio of approximately 1.2. Even though the LEV zeolites gave higher ethylene and lower propylene selectivities than SAPO-LEV materials, all LEV catalysts gave high C_{5+} . These values were considerably higher than those attained by AEI and CHA (**Tables 2.4** and **2.5**).

We previously investigated the MTO behavior of several ERI-type molecular sieves.²⁷ The data show that much like in the case of LEV, ERI-type zeolites and SAPO-17 catalysts behave very differently, with the zeolite samples (stronger acid sites) registering significantly higher E/P ratios. In fact, E/P increases monotonically, irrespective of other material properties, from 1.12 for ERI Zeolite-3-(8) to 1.86 for SSZ-98-(4). While the E/P also increases as a function of Si/T in the SAPO-17 materials, the ERI zeolites are able to better suppress the C_{3+} fraction (typically early in the reaction) and thus, increase the ethylene selectivity.

The promising behavior of ERI-type molecular sieves prompted us to investigate the MTO activity of STA-20 (SWY) and STA-30 (SWY), two new molecular sieves. Unlike ERI, SWY materials can only be synthesized over a narrow range. However, within the range tested, the SWY samples exhibited a similar behavior as ERI, where the E/P ratio improved by either changing the acid site density or strength. However, both classes of SWY materials (zeolites and SAPOs)



resulted in low E/P ratios and high C_{5+} fractions. This could be due to the length of the SWY cage and the low acidity of the SWY materials.

Figure 2.2. Averaged ethylene-to-propylene ratio when methanol conversion is high (greater than 97%) for the various small-pore, cage-type molecular sieves investigated in this work.

2.3.3 Characterization of the Retained Species

To rationalize the reaction differences observed in the olefin product distributions and overall MTO behavior with respect to changes in acid site density and strength, dissolutionextraction experiments were performed on 17 samples. Each of these catalysts was reacted with methanol and the reaction was stopped after 5 minutes. The reactor was then rapidly cooled to ambient conditions.

Figure 2.3 shows the extracted hydrocarbon distribution for several materials belonging to the various frameworks investigated (AEI, CHA, LEV, ERI, and SWY). The extracted hydrocarbons for all the frameworks studied consisted primarily of poly-methylbenzenes (MB) with up to six methyl groups. Small amounts of 2-ring (naphthalenes) and other 1-ring compounds (alkylated benzenes) were also detected and measured. The amount of naphthalenes was generally higher when the acid site density and strength of a given material was high (i.e., in zeolites with low Si/Al ratios).

The results in **Figure 2.3** demonstrate that the extracted hydrocarbons from AEI-type molecular sieves consisted mainly of penta- (5MB) and hexamethylbenzenes (6MB). These molecules have been associated with the formation of propylene.^{22,32} Increasing the acid site density in SAPO-18 by increasing the Si/T led to the accumulation of more aromatics, but did not significantly alter the composition of the species. Furthermore, AEI-zeolite-(11) formed aromatic species at a much faster rate than the SAPO-18 materials (almost twice as fast as SAPO-34-0.4Si).

Whereas AEI entrapped mostly fully-methylated benzenes, CHA-type molecular sieves entrapped a more diverse set of species, including tetra-methylbenzenes (4MB) as well as 5MB and 6MB. Differences in the catalytic behavior of AEI and CHA-type molecular sieves have been rationalized previously by investigating the nature of the hydrocarbon pool species that form during reaction. AEI, with its larger cage, has been shown to retain higher amounts of 5MB and 6MB. CHA, on the other hand, has been shown to retain tetramethylbenzenes (4MB) as well as 5MB and 6MB. From our experiments, we observe slight changes in the composition of the aromatic species for both CHA and AEI-type materials as a function of acidity.

Further reducing the cage size from CHA to LEV (one of the smallest cages active for MTO), leads to the accumulation of less aromatics. Not only that, but the identity of the formed HP species shifts rather considerably toward partially methylated benzenes (tetramethylbenzenes and below). Ferri et al.²⁹ recently investigated the aromatics cycle in the methanol-to-olefins reaction and observed that LEV type molecular sieves deviate from the predicted behavior, yielding high amounts of C_{3+} and low ethylene. The authors postulated that since the LEV cage cannot accommodate heptamethylbenzenium cations (supported by our work since we don't measure 6MB for the various LEV samples tested), a part of the propylene yield that is formed is likely produced from the olefins cycle. Indeed, the combination of low concentrations of aromatics and high $C_{4+}/C_{2=}$ ratios (discussed in the Reaction Section) suggests that LEV materials proceed not only via the aromatics cycle, but the alkene cycle as well. Increasing the acid strength, in going from SAPOs to zeolites, allows the LEV cage to accumulate aromatic intermediates faster, which results in an enhancement in the ethylene selectivity.

We previously investigated the entrapped hydrocarbon pool species that form inside ERI materials at different times-on-stream (15, 30, and 60 minutes) and showed that ERI-type samples, much like LEV materials, accumulate aromatics at a slower rate than CHA-type materials. Not only that, but ERI materials form significant amounts of other 1-ring molecules, naphthalenes, and 3-ring hydrocarbons when reacted for extended amount of time. **Figure 2.3** shows that SAPO-17-

0.2Si has one of the lowest concentrations of aromatics of the 17 catalysts studied. The other catalyst that also had low concentrations of aromatics was SAPO-SWY-0.1Si. ERI and SWY have similar structures and similar CDR sizes. As such, the fact that these two materials behave similarly in reaction and accumulate a similar type of aromatics is not surprising. The key difference between these two cages is that the SWY cage is bit longer than ERI (thus, likely explaining why SWY-type materials deactivate rather rapidly).

Of the various materials tested that contained LEV, ERI, or SWY cages, only three zeolites with low Si/Al ratio formed more aromatics than SAPO-34-0.4Si. This explains why acidity affects various frameworks differently. When a specific cage structure has the ability to proceed via the olefins cycle (due to a narrow cage size, for instance) then enhancing the acidity becomes imperative to accelerate the formation of aromatic species. Once the aromatic cycle species form, they are able to shift the olefins product distribution toward ethylene. It's interesting that virtually all LEV, ERI, and SWY materials tested in this work contained higher fractions of partially methylated benzenes, which are associated with the formation of ethylene, yet because of the low aromatics concentration exhibited by the majority of the samples tested, this did not translate to enhanced ethylene selectivity.



Figure 2.3. GC-MS distribution of the extracted hydrocarbon species for 17 molecular sieves after 5 minutes of reaction with methanol at 400 °C and WHSV of 1.3 h⁻¹. The relative concentration of the aromatic species retained were relative to SAPO-34-0.4Si.

2.4 Conclusion

AEI, CHA, LEV, ERI and SWY-type molecular sieves were synthesized to form 44 samples with different acid site densities and strengths. The synthesized materials, both zeolites and SAPOs, were characterized and found to have different physiochemical properties. These catalysts were then tested in MTO reaction and their product distributions were analyzed. AEI and CHA-type molecular sieves, the two largest cages tested, showed little changes in the olefins product distribution as a function of Brønsted acidity. Specifically, the AEI samples gave an E/P ratio of approximately 0.5 whereas the CHA samples gave an E/P ratio of approximately 1, irrespective of other material properties. On the other hand, LEV, ERI, and SWY samples, which have cages that are narrower than AEI and CHA, responded more favorably to changes in their acidity. Virtually all LEV, ERI, and SWY samples with low acid site densities (high Si/Al ratios or low Si/T ratios) exhibited high $C_{4+}/C_{2=}$ ratios, particularly in early stages of the reaction.

However, decreasing the Si/Al ratio or increasing the Si/T ratio (to improve the Brønsted acid site density) led to the formation of more ethylene at the expense of the C_{3+} fraction.

To rationalize the differences observed in the MTO behavior, organic species retained in the cavities of the partially reacted catalysts were analyzed via dissolution of the framework and extraction of the organic components (entrapped hydrocarbon pool species). The results from these experiments demonstrated that materials with low acid site densities and strengths (high Si/Al ratios or low Si/T ratios) accumulate aromatic intermediates at a slower rate than CHA and AEItype molecular sieves. As the concentration of these aromatics increases, the ethylene selectivity improves, leading to higher E/P ratios than those obtained on CHA-type molecular sieves (because these narrow frameworks inherently stabilize partially methylated benzenes).

These results suggest that small-pore, cage-type molecular sieves with narrow cages such as ERI, LEV, and SWY proceed via contributions from both the olefins (alkenes) cycle as well as the aromatics cycle. Increasing the acidity in these materials leads to higher contributions from the aromatics cycle, as evidenced by the entrapment of higher concentrations of polymethylbenzenes, which then affects their E/P ratios. On the other hand, AEI, which exhibits high propylene selectivity (irrespective of acidity), improves the P/E ratio of the MTO reaction over CHA by shifting the identity of the hydrocarbon pool species toward fully methylated benzenes (e.g., pentaand hexa-methylbenzenes). This study rationalizes the complex relationship between cage size/geometry and acidity on the light olefins selectivities, and provides insights to the design of materials that enhance the ethylene-to-propylene or propylene-to-ethylene ratio in the MTO reaction.

2.5 Acknowledgements

The Chevron Energy and Technology Company provided financial support for this research. The authors gratefully acknowledge Dr. Nathan Dalleska (Resnick Water and Environment Laboratory at the California Institute of Technology) for assistance with the GC-MS experiments, Dr. Sonjong Hwang for assistance with solid-state NMR, and Youngkyu Park for assistance with the solid-state NMR experiments and analyses. F.H.A. would like to thank Aramco R&D for financially supporting his graduate studies.

2.6 References

(1) Vora, B.; Chen, J. Q.; Bozzano, A.; Glover, B.; Barger, P. Various Routes to Methane Utilization—SAPO-34 Catalysis Offers the Best Option. *Catalysis Today* **2009**, *141* (1), 77–83. https://doi.org/10.1016/j.cattod.2008.05.038.

(2) Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catal.* 2015, 5 (3), 1922–1938. https://doi.org/10.1021/acscatal.5b00007.

(3) Chen, J. Q.; Bozzano, A.; Glover, B.; Fuglerud, T.; Kvisle, S. Recent Advancements in Ethylene and Propylene Production Using the UOP/Hydro MTO Process. *Catalysis Today* **2005**, *106* (1), 103–107. https://doi.org/10.1016/j.cattod.2005.07.178.

(4) Zapater, D.; Lasobras, J.; Soler, J.; Herguido, J.; Menéndez, M. MTO with SAPO-34 in a Fixed-Bed Reactor: Deactivation Profiles. *Ind. Eng. Chem. Res.* **2021**, *60* (45), 16162–16170. https://doi.org/10.1021/acs.iecr.1c02718.

(5) Yang, L.; Wang, C.; Zhang, L.; Dai, W.; Chu, Y.; Xu, J.; Wu, G.; Gao, M.; Liu, W.; Xu, Z.; Wang, P.; Guan, N.; Dyballa, M.; Ye, M.; Deng, F.; Fan, W.; Li, L. Stabilizing the Framework of

SAPO-34 Zeolite toward Long-Term Methanol-to-Olefins Conversion. *Nature Communications* **2021**, *12* (1), 4661. https://doi.org/10.1038/s41467-021-24403-2.

(6) Yu, W.; Wu, X.; Cheng, B.; Tao, T.; Min, X.; Mi, R.; Huang, Z.; Fang, M.; Liu, Y. Synthesis and Applications of SAPO-34 Molecular Sieves. *Chemistry – A European Journal* **2022**, *28* (11), e202102787. https://doi.org/10.1002/chem.202102787.

(7) Ahmad, M. S.; Cheng, C. K.; Bhuyar, P.; Atabani, A. E.; Pugazhendhi, A.; Chi, N. T. L.;
Witoon, T.; Lim, J. W.; Juan, J. C. Effect of Reaction Conditions on the Lifetime of SAPO-34
Catalysts in Methanol to Olefins Process – A Review. *Fuel* 2021, 283, 118851.
https://doi.org/10.1016/j.fuel.2020.118851.

(8) Peng, Q.; Wang, G.; Wang, Z.; Jiang, R.; Wang, D.; Chen, J.; Huang, J. Tuning Hydrocarbon
Pool Intermediates by the Acidity of SAPO-34 Catalysts for Improving Methanol-to-Olefins
Reaction. ACS Sustainable Chem. Eng. 2018, 6 (12), 16867–16875.
https://doi.org/10.1021/acssuschemeng.8b04210.

(9) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E.
Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction. *ACS Catal.*2016, 6 (2), 542–550. https://doi.org/10.1021/acscatal.5b01450.

(10) Stöcker, M. Methanol-to-Hydrocarbons: Catalytic Materials and Their Behavior1Dedicated to My Wife Wencke Ophaug.1. *Microporous and Mesoporous Materials* **1999**, *29* (1), 3–48. https://doi.org/10.1016/S1387-1811(98)00319-9.

(11) Liang, T.; Chen, J.; Qin, Z.; Li, J.; Wang, P.; Wang, S.; Wang, G.; Dong, M.; Fan, W.; Wang, J. Conversion of Methanol to Olefins over H-ZSM-5 Zeolite: Reaction Pathway Is Related to the Framework Aluminum Siting. *ACS Catal.* 2016, *6* (11), 7311–7325. https://doi.org/10.1021/acscatal.6b01771.

(12) Ferri, P.; Li, C.; Paris, C.; Vidal-Moya, A.; Moliner, M.; Boronat, M.; Corma, A. Chemical and Structural Parameter Connecting Cavity Architecture, Confined Hydrocarbon Pool Species, and MTO Product Selectivity in Small-Pore Cage-Based Zeolites. *ACS Catal.* **2019**, *9* (12), 11542–11551. https://doi.org/10.1021/acscatal.9b04588.

(13) Dai, W.; Wang, X.; Wu, G.; Guan, N.; Hunger, M.; Li, L. Methanol-to-Olefin Conversion on Silicoaluminophosphate Catalysts: Effect of Brønsted Acid Sites and Framework Structures. *ACS Catal.* **2011**, *1* (4), 292–299. https://doi.org/10.1021/cs200016u.

(14) Mikkelsen, Ø.; Kolboe, S. The Conversion of Methanol to Hydrocarbons over Zeolite H-Beta. *Microporous and Mesoporous Materials* 1999, 29 (1), 173–184. https://doi.org/10.1016/S1387-1811(98)00329-1.

(15) Bjørgen, M.; Olsbye, U.; Petersen, D.; Kolboe, S. The Methanol-to-Hydrocarbons Reaction: Insight into the Reaction Mechanism from [12C]Benzene and [13C]Methanol Coreactions over Zeolite H-Beta. *Journal of Catalysis* **2004**, *221* (1), 1–10. https://doi.org/10.1016/S0021-9517(03)00284-7.

(16) LI, B.; TIAN, P.; LI, J.; CHEN, J.; YUAN, Y.; SU, X.; FAN, D.; WEI, Y.; QI, Y.; LIU, Z. Synthesis of SAPO-35 Molecular Sieve and Its Catalytic Properties in the Methanol-to-Olefins Reaction. *Chinese Journal of Catalysis* **2013**, *34* (4), 798–807. https://doi.org/10.1016/S1872-2067(12)60557-9.

(17) Martínez-Franco, R.; Li, Z.; Martínez-Triguero, J.; Moliner, M.; Corma, A. Improving the Catalytic Performance of SAPO-18 for the Methanol-to-Olefins (MTO) Reaction by Controlling the Si Distribution and Crystal Size. *Catal. Sci. Technol.* **2016**, *6* (8), 2796–2806. https://doi.org/10.1039/C5CY02298C.

(18) Yarulina, I.; Goetze, J.; Gücüyener, C.; van Thiel, L.; Dikhtiarenko, A.; Ruiz-Martinez, J.; Weckhuysen, B. M.; Gascon, J.; Kapteijn, F. Methanol-to-Olefins Process over Zeolite Catalysts with DDR Topology: Effect of Composition and Structural Defects on Catalytic Performance. *Catal. Sci. Technol.* **2016**, *6* (8), 2663–2678. https://doi.org/10.1039/C5CY02140E.

(19) Kang, J. H.; Walter, R.; Xie, D.; Davis, T.; Chen, C.-Y.; Davis, M. E.; Zones, S. I. Further Studies on How the Nature of Zeolite Cavities That Are Bounded by Small Pores Influences the Conversion of Methanol to Light Olefins. *ChemPhysChem* **2018**, *19* (4), 412–419. https://doi.org/10.1002/cphc.201701197.

(20) Castellanos-Beltran, I. J.; Assima, G. P.; Lavoie, J.-M. Effect of Temperature in the Conversion of Methanol to Olefins (MTO) Using an Extruded SAPO-34 Catalyst. *Frontiers of Chemical Science and Engineering* **2018**, *12* (2), 226–238. https://doi.org/10.1007/s11705-018-1709-8.

(21) Borodina, E.; Sharbini Harun Kamaluddin, H.; Meirer, F.; Mokhtar, M.; Asiri, A. M.; Al-Thabaiti, S. A.; Basahel, S. N.; Ruiz-Martinez, J.; Weckhuysen, B. M. Influence of the Reaction Temperature on the Nature of the Active and Deactivating Species During Methanol-to-Olefins Conversion over H-SAPO-34. *ACS Catal.* 2017, 7 (8), 5268–5281. https://doi.org/10.1021/acscatal.7b01497.

(22) Shi, Z.; Bhan, A. Tuning the Ethylene-to-Propylene Ratio in Methanol-to-Olefins Catalysis on Window-Cage Type Zeolites. *Journal of Catalysis* **2021**, *395*, 266–272. https://doi.org/10.1016/j.jcat.2021.01.015.

(23) Xie, J.; Firth, D. S.; Cordero-Lanzac, T.; Airi, A.; Negri, C.; Øien-Ødegaard, S.; Lillerud, K.P.; Bordiga, S.; Olsbye, U. MAPO-18 Catalysts for the Methanol to Olefins Process: Influence of

Catalyst Acidity in a High-Pressure Syngas (CO and H2) Environment. *ACS Catal.* **2022**, *12* (2), 1520–1531. https://doi.org/10.1021/acscatal.1c04694.

(24) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. *ACS Catal.* **2019**, *9* (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.

(25) Bhawe, Y.; Moliner-Marin, M.; Lunn, J. D.; Liu, Y.; Malek, A.; Davis, M. Effect of Cage Size on the Selective Conversion of Methanol to Light Olefins. *ACS Catal.* **2012**, *2* (12), 2490–2495. https://doi.org/10.1021/cs300558x.

(26) Dusselier, M.; Deimund, M. A.; Schmidt, J. E.; Davis, M. E. Methanol-to-Olefins Catalysis with Hydrothermally Treated Zeolite SSZ-39. *ACS Catal.* **2015**, *5* (10), 6078–6085. https://doi.org/10.1021/acscatal.5b01577.

(27) Alshafei, F. H.; Park, Y.; Zones, S. I.; Davis, M. E. Methanol-to-Olefins Catalysis on ERI-Type Molecular Sieves: Towards Enhancing Ethylene Selectivity. *Journal of Catalysis* 2021, 404, 620–633. https://doi.org/10.1016/j.jcat.2021.10.025.

(28) Zapater, D.; Lasobras, J.; Soler, J.; Herguido, J.; Menéndez, M. Temperature and Dilution Effects on MTO Process with a SAPO-34-Based Catalyst in Fluidized Bed Reactor. *Catalysis Today* **2022**, *394–396*, 219–224. https://doi.org/10.1016/j.cattod.2021.09.010.

(29) Ferri, P.; Li, C.; Paris, C.; Rodríguez-Fernández, A.; Moliner, M.; Boronat, M.; Corma, A. The Limits of the Confinement Effect Associated to Cage Topology on the Control of the MTO Selectivity. *ChemCatChem* **2021**, *13* (6), 1578–1586. https://doi.org/10.1002/cctc.202001760.

(30) Lee, K. Y.; Chae, H.-J.; Jeong, S.-Y.; Seo, G. Effect of Crystallite Size of SAPO-34 Catalysts on Their Induction Period and Deactivation in Methanol-to-Olefin Reactions. *Applied Catalysis A: General* 2009, *369* (1), 60–66. https://doi.org/10.1016/j.apcata.2009.08.033.

(31) Westgård Erichsen, M.; De Wispelaere, K.; Hemelsoet, K.; Moors, S. L. C.; Deconinck, T.; Waroquier, M.; Svelle, S.; Van Speybroeck, V.; Olsbye, U. How Zeolitic Acid Strength and Composition Alter the Reactivity of Alkenes and Aromatics towards Methanol. *Journal of Catalysis* **2015**, *328*, 186–196. https://doi.org/10.1016/j.jcat.2015.01.013.

(32) Hwang, A.; Prieto-Centurion, D.; Bhan, A. Isotopic Tracer Studies of Methanol-to-Olefins Conversion over HSAPO-34: The Role of the Olefins-Based Catalytic Cycle. *Journal of Catalysis* **2016**, *337*, 52–56. https://doi.org/10.1016/j.jcat.2016.01.021.

(33) Hua, J.; Dong, X.; Wang, J.; Chen, C.; Shi, Z.; Liu, Z.; Han, Y. Methanol-to-Olefin Conversion over Small-Pore DDR Zeolites: Tuning the Propylene Selectivity via the Olefin-Based Catalytic Cycle. *ACS Catal.* **2020**, *10* (5), 3009–3017. https://doi.org/10.1021/acscatal.9b05521.

(34) Yang, M.; Li, B.; Gao, M.; Lin, S.; Wang, Y.; Xu, S.; Zhao, X.; Guo, P.; Wei, Y.; Ye, M.; Tian, P.; Liu, Z. High Propylene Selectivity in Methanol Conversion over a Small-Pore SAPO Molecular Sieve with Ultra-Small Cage. *ACS Catal.* **2020**, *10* (6), 3741–3749. https://doi.org/10.1021/acscatal.9b04703.

(35) Pinilla-Herrero, I.; Olsbye, U.; Márquez-Álvarez, C.; Sastre, E. Effect of Framework Topology of SAPO Catalysts on Selectivity and Deactivation Profile in the Methanol-to-Olefins Reaction. *Journal of Catalysis* **2017**, *352*, 191–207. https://doi.org/10.1016/j.jcat.2017.05.008.

(36) Pinilla-Herrero, I.; Márquez-Álvarez, C.; Sastre, E. Complex Relationship between SAPO Framework Topology, Content and Distribution of Si and Catalytic Behaviour in the MTO Reaction. *Catal. Sci. Technol.* **2017**, *7* (17), 3892–3901. https://doi.org/10.1039/C7CY01250K.

(37) Chitac, R. G.; Bradley, J.; McNamara, N. D.; Mayoral, A.; Turrina, A.; Wright, P. A. Designed Synthesis of STA-30: A Small-Pore Zeolite Catalyst with Topology Type SWY. *Chem. Mater.* **2021**. https://doi.org/10.1021/acs.chemmater.1c01329.

(38) Chen, J.; Wright, P. A.; Thomas, J. M.; Natarajan, S.; Marchese, L.; Bradley, S. M.; Sankar, G.; Catlow, C. R. A.; Gai-Boyes, P. L. SAPO-18 Catalysts and Their Broensted Acid Sites. J. *Phys. Chem.* 1994, 98 (40), 10216–10224. https://doi.org/10.1021/j100091a042.

(39) Dusselier, M.; Schmidt, J. E.; Moulton, R.; Haymore, B.; Hellums, M.; Davis, M. E. Influence of Organic Structure Directing Agent Isomer Distribution on the Synthesis of SSZ-39. *Chem. Mater.* 2015, 27 (7), 2695–2702. https://doi.org/10.1021/acs.chemmater.5b00651.

(40) Djieugoue, M.-A.; Prakash, A. M.; Kevan, L. Electron Spin Resonance and Electron Spin–Echo Modulation Studies of Synthesized NiAPSO-34 Molecular Sieve and Comparison with Ion-Exchanged NiH–SAPO-34 Molecular Sieve. *J. Phys. Chem. B* **1999**, *103* (5), 804–811. https://doi.org/10.1021/jp9823897.

(41) Chapter 35 - CHA SSZ-13 Si(93), Al(7). In Verified Syntheses of Zeolitic Materials; Robson,

H., Lillerud, K. P., Eds.; Elsevier Science: Amsterdam, 2001; pp 126–128. https://doi.org/10.1016/B978-044450703-7/50133-2.

(42) Ahn, N. H.; Seo, S.; Hong, S. B. Small-Pore Molecular Sieves SAPO-57 and SAPO-59: Synthesis, Characterization, and Catalytic Properties in Methanol-to-Olefins Conversion. *Catal. Sci. Technol.* **2016**, *6* (8), 2725–2734. https://doi.org/10.1039/C5CY02103K.

(43) Prakash, A. M.; Hartmann, M.; Kevan, L. SAPO-35 Molecular Sieve: Synthesis, Characterization, and Adsorbate Interactions of Cu(II) in CuH–SAPO-35. *Chem. Mater.* 1998, *10*(3), 932–941. https://doi.org/10.1021/cm9707521.

(44) Zhang, H.; Yang, C.; Zhu, L.; Meng, X.; Yilmaz, B.; Müller, U.; Feyen, M.; Xiao, F.-S. Organotemplate-Free and Seed-Directed Synthesis of Levyne Zeolite. *Microporous and Mesoporous Materials* **2012**, *155*, 1–7. https://doi.org/10.1016/j.micromeso.2011.12.051.

(45) Turrina, A.; Garcia, R.; Watts, A. E.; Greer, H. F.; Bradley, J.; Zhou, W.; Cox, P. A.; Shannon, M. D.; Mayoral, A.; Casci, J. L.; Wright, P. A. STA-20: An ABC-6 Zeotype Structure Prepared by Co-Templating and Solved via a Hypothetical Structure Database and STEM-ADF Imaging. *Chem. Mater.* 2017, 29 (5), 2180–2190. https://doi.org/10.1021/acs.chemmater.6b04892.

(46) Lee, J. H.; Park, M. B.; Lee, J. K.; Min, H.-K.; Song, M. K.; Hong, S. B. Synthesis and Characterization of ERI-Type UZM-12 Zeolites and Their Methanol-to-Olefin Performance. *J. Am. Chem. Soc.* **2010**, *132* (37), 12971–12982. https://doi.org/10.1021/ja105185r.

(47) Valyocsik, E.; Ballmoos, R. Synthesis of Crystalline SAPO-17. US4778780A, 1987.

(48) Li, Z.; Martínez-Triguero, J.; Concepción, P.; Yu, J.; Corma, A. Methanol to Olefins: Activity and Stability of Nanosized SAPO-34 Molecular Sieves and Control of Selectivity by Silicon Distribution. *Phys. Chem. Chem. Phys.* **2013**, *15* (35), 14670–14680. https://doi.org/10.1039/C3CP52247D.

(49) Martínez-Franco, R.; Li, Z.; Martínez-Triguero, J.; Moliner, M.; Corma, A. Improving the Catalytic Performance of SAPO-18 for the Methanol-to-Olefins (MTO) Reaction by Controlling the Si Distribution and Crystal Size. *Catal. Sci. Technol.* **2016**, *6* (8), 2796–2806. https://doi.org/10.1039/C5CY02298C.

(50) Ferri, P.; Li, C.; Millán, R.; Martínez-Triguero, J.; Moliner, M.; Boronat, M.; Corma, A. Impact of Zeolite Framework Composition and Flexibility on Methanol-To-Olefins Selectivity: Confinement or Diffusion? *Angewandte Chemie International Edition* 2020, *59* (44), 19708–19715. https://doi.org/10.1002/anie.202007609.

Chapter 3 | Methanol-to-Olefins Catalysis on ERI-type Molecular Sieves: Towards Enhancing Ethylene Selectivity

Information contained in Chapter 3 was originally published in:

Alshafei, F. H.; Park, Y.; Zones, S. I.; Davis, M. E. Methanol-to-Olefins Catalysis on ERI-Type Molecular Sieves: Towards Enhancing Ethylene Selectivity. *Journal of Catalysis* **2021**, *404*, 620–633. https://doi.org/10.1016/j.jcat.2021.10.025.

Abstract

ERI-type molecular sieves (SSZ-98, UZM-12, ERI-type zeolite, SAPO-17) are synthesized with varying Si/Al=5-9 and Si/T-atoms=0.034-0.12 using several organic structure-directing agents (OSDAs), and evaluated as catalysts for the methanol-to-olefins (MTO) reaction. SAPO-34 (Si/T-atoms=0.089) and SSZ-13 (Si/Al=15) are also prepared and tested for comparison. The ERI-type zeolites gave improved ethylene-to-propylene ratios (E/P=1.1-1.9) over SSZ-13 (E/P=0.82) and SAPO-34 (E/P=0.85). The SAPO-17 samples produced an E/P of 0.7-1.1 and a generally high C₄+ fraction. The differences observed in the olefins product distributions between the zeolites with low framework Si/Al (E/P>1.5) and SAPO-17 with low Si/T-atom<0.1 (E/P \leq 1 and high C₄+) are the result of slower maturation of aromatic hydrocarbon-pool (HP) species and the presence of aromatics with bulky alkyl-groups (C₃-C₄) in the SAPO-17 samples. The rapid formation of cyclic intermediates and the shift in their composition toward less-methylated ((CH₃)_{n≤4}) methylbenzene and methylnaphthalenes are found to be key to enhancing the ethylene selectivity in ERI-type molecular sieves.

3.1 Introduction

The methanol-to-olefins (MTO) reaction over small-pore, cage-containing molecular sieves is not only a commercial success for the production of lower olefins (C_2 - C_4), but also a reaction system that has stimulated large efforts on mechanistic understandings $^{1-16}$. The latter issue is due to the fact that the reaction is now known to not proceed through shape selectivity pathways previously exploited for other molecular sieve catalyzed reactions (discussed further below). The invention of silicoaluminophosphate (SAPO) molecular sieves ultimately led to the commercialization of SAPO-34 with a chabazite (CHA) topology for the MTO reaction in China. One of us (M.E.D.) had the pleasure of viewing the original MTO data for SAPO-34 in Dr. S. Kaiser's office in the early 1980s ¹⁷. At the time, the Davis group was working on understanding the atomic arrangements in SAPOs ^{18,19}, and during discussions with Dr. Kaiser, reviewed the initial MTO data on SAPO-34. Since then, the MTO reaction has been investigated on many types of molecular sieves including zeolites, and the mechanistic understanding of the reaction has evolved quite considerably ^{20–30}. Our groups' work with the MTO reaction has fundamentally focused on understanding how small-pore, cage-containing molecular sieve structures influence the light olefin product distributions ^{31–34}. Here, we continue our efforts in understanding structureproperty relationships, something that Professor Boudart would have enjoyed, with a system aimed at increasing the ethylene yield.

It is now widely accepted that the complex reaction network taking place within the smallpore, cages/cavities of MTO catalysts, following an initial induction period, proceeds through a dual-cycle mechanism that comprises of olefins-based chemistries of successive methylation and cracking steps and aromatic-based chemistries of methylation and dealkylation ^{4,5,8–10,35–44}. The two cycles are connected through hydrogen transfer and cyclization events. In small-pore, cagecontaining molecular sieves with CHA, AEI, LEV, DDR, and RHO-type structures, it has been demonstrated that the hydrocarbon-pool (HP) species that remain entrapped inside the cavities of these microporous materials are primarily comprised of cyclic organic species, with aromatic polymethylbenzenes and polymethylbenzenium ions recognized as key active HP compounds ^{1,5,6,12–15,22,25,29,45,46}. This is fundamentally different than what occurs in medium- and large-pore zeolites (e.g., MFI) (i.e., methanol-to-hydrocarbons (MTH)), for instance, where aromatic species can diffuse out of the molecular sieve and contribute to the product distribution as opposed to being trapped. The lack of larger molecule escape in small-pore, cage-type molecular sieves thus leads to improved light olefins selectivities and yields.

Amongst the numerous physiochemical catalyst properties (e.g., acid site density and strength, elemental composition and metal incorporation, crystallite/particle size, etc.) and reaction conditions (temperature, feed composition, methanol partial pressure/weight hourly space velocity (WHSV), etc.) that influence the MTO reaction behavior, cage topology (or simply put, choice of framework) has been recognized as an important parameter that regulates olefins product distribution ^{3,22,25,26,30,32,34,40,46–57}. This is the case because a cage structure impacts/restricts the type of HP species that can be formed. The cage topology thus influences the relative propagation of each of the aforementioned cycles (olefinic and/or aromatic) and contribution of each of the aromatic-cycle routes (paring and/or side-chain) ^{29,40,58,59}.

Our group recently proposed a new molecular sieve structural indicator, the cage-defining ring (CDR), that correlates light olefin product distributions in MTO with a geometric parameter of the molecular sieve cage architecture for a multitude of small-pore, cage-containing zeolites, SAPOs, and metalloaluminophosphates (MAPOs) belonging to the following topology types: LEV, ERI, CHA, AFX, SFW, AEI, DDR, RTH, ITE, SAV, LTA, RHO, KFI, and UFI ³¹. We

showed that the CDR, defined as the minimum number of tetrahedral atoms of the ring encircling the center of the framework cages in a given molecular sieve topology, correlates with the MTO light olefins product distribution. Based on the product effluent, we classified the 14 topologies to four overarching categories that are provided in **Figure A3.1**.

SAPO-34, the commercial catalyst, displays high selectivities to both ethylene and propylene (>70% carbon selectivity, with nearly equal amounts of the two components) due to its cage dimensions/structure, mild acidity, and pore size (8-member ring pore size = $3.8 \times 3.8 \text{ A}$). If enhanced ethylene is desired, forming it (i.e., increasing E/P) from the MTO reaction without deleteriously impacting the overall light olefins selectivity and lifetime remains a challenge. We note that from previous investigations that the ERI-type cage is a promising candidate for shifting the light olefins distribution in favor of ethylene due to its geometry and narrow size (CDR size = 6.75 Å for ERI compared to CDR size = 7.45 Å for CHA) (**Table 3.1**) ³¹. Indeed, UZM-12, an ERI-type material, has been previously reported to crystallize in the presence of K⁺ or Rb⁺ to yield products with a Si/Al = ca. 5.5-6.5, using several linear, diquaternary, alkylammonium ions as organic structure-directing agents (OSDAs), and these materials when tested in MTO had an apparent E/P of approximately 1.3 (when conversion was 90%+ at 350 °C and 0.67 h⁻¹ WHSV) ⁶⁰. Interestingly, this E/P is not too far from the one obtained in our previous work for SSZ-98, another ERI-type material, with a similar Si/Al=6 (E/P=1.5; when conversion was >98%; 400 °C and 1.3 h⁻¹ WHSV) ³¹. Nawaz et al. also tested the MTO behavior of ERI zeolite (Si/Al=3.5) and SAPO-17 ((Al+P)/Si=70; this sample contained an impurity) at various temperatures, confirming the formation of more ethylene than propylene in ERI-type topologies ⁶¹.

Framework	СНА	ERI
Channel Dimensionality	3	3
8-MR Pore Size (Å)	3.8 x 3.8	3.6 x 5.1
8-MR Pore Area (Å) ^[a]	11.34	14.42
Maximum Diameter of Sphere (Å)	7.37	7.04
Cage-defining Ring (CDR) (Å) ^[b]	7.45	6.75
		SAPO-17
Madania In Transferd	SAPO-34	SSZ-98
wrateriais rested	SSZ-13	UZM-12
		ERI Zeolite

Table 3.1. Cages/materials studied in this work and their dimensions.

[a] Area calculated using the following formula: $A = (\pi ab)/4$, where A is the pore area, and a and b are the shortest and longest pore diameters. [b] obtained from ³¹.

Despite their promising MTO behavior and remarkable ability to steer the light olefins selectivities toward ethylene, ERI-type zeolite materials have scarcely been investigated for the MTO reaction, and until very recently, could only be synthesized over a narrow and low Si/Al < ca. 6.5. SAPO-17, the isostructural form of ERI-type zeolite, has also been primarily synthesized with low Si contents (Si/T<0.05) based on Lok et al. gel composition (does not provide for synthesis of pure SAPO-17 with high Si/T without the aid of hydrofluoric acid (HF)) ^{62–65}. However, recent experimental and computational findings have identified newer OSDAs, gel compositions, and crystallization conditions that are more suitable for stabilizing the ERI-type framework than those utilized in the prior art. Thus, the synthesis of phase-pure ERI-type zeolites over a wider range of Si/Al (up to ca. 13) and with different morphologies and particle sizes have now been reported ^{66–68}. We employ some of these OSDAs used to make ERI-type zeolites to synthesize SAPO-17 samples with higher Si/T without the presence of HF. Many of these zeolite

and SAPO materials have not been previously tested in MTO, and now allow for the influence of Brønsted acid site density/strength on MTO behavior for ERI-type materials to be investigated.

Here, we examine the catalytic behavior of several ERI-type materials (SSZ-98, UZM-12, ERI-type zeolite, and SAPO-17) synthesized using various OSDAs (**Figure 3.1**) that cover a wide range of Si/Al=5-9 and Si/T=0.034-0.12 (T=Si+Al+P), with the goal of identifying key material properties that enhance ethylene selectivity. We compare the performance of ERI-type materials to SSZ-13 (Si/Al=15) and SAPO-34 (Si/T=0.089), to discern any differences in reactivity and selectivity between these two framework types. All samples in this work were investigated with a battery of characterization techniques outlined in the next section. Partially reacted/deactivated samples from various reaction time-on-stream (TOS) were dissolved in acid to extract and analyze the occluded organic components in an effort to identify differences between the composition and concentration of the entrained aromatics formed during reaction. These species assist in understanding the observed differences in MTO behavior (i.e., olefins product distribution) between CHA-type and ERI-type materials.



Figure 3.1. Organic structure-directing agents (OSDAs) used in this work. OSDA 1 was used for the synthesis of SSZ-13. OSDA 2 was used for the synthesis of SAPO-34. OSDAs 2-10 were used for the synthesis of ERI-type materials, both zeolites and SAPOs, either individually or incombination, as described in the Experimental Section.

3.2 Experimental Section

3.2.1 Materials Syntheses

The small-pore, cage-containing molecular sieves shown in this work were synthesized based on previously reported (albeit with slight modifications) or newly developed procedures as outlined below. Detailed synthesis procedures of the organic structure-directing agents (OSDAs) used in this work are provided in the Supplemental Information (SI) (**Appendix B**) Section. All materials, unless otherwise noted, were used as-received without further purification from the stated vendors. The moisture contents of the solid sources were determined by temperature-gravimetric analysis (TGA). In addition to the syntheses listed below, summaries of the zeolite and SAPO preparations are provided in **Tables A3.1** and **A3.2**, respectively.

3.2.1.1 SSZ-13 (CHA)

The synthesis gel molar composition for the SSZ-13 sample was 100 SiO₂ : 3.33 Al_{2O_3} : 20 ROH : 10 Na₂O : 4400 H₂O, where ROH is N,N,N-trimethyl-1-adamantammonium hydroxide (OSDA 1) ⁶⁹. In a typical synthesis, desired amounts of sodium hydroxide solution (NaOH, 50%, Sigma-Aldrich), OSDA 1, and deionized (DI) water were added and stirred for approximately 0.5 hr. Aluminum isopropoxide (98%, Sigma-Aldrich) was then added as an aluminum source to this solution, and the mixture was stirred for at least 3 h. Finally, a colloidal silica solution (Ludox AS-40, Sigma-Aldrich) was added, and the gel was stirred until it was homogenous. The gel was placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 160 °C at autogenous pressure for 6 days.

3.2.1.2 SAPO-34 (CHA)

The synthesis gel molar composition for the SAPO-34 sample was $0.06 \text{ SiO}_2 : 0.2 \text{ Al}_2\text{O}_3 :$ $0.2 \text{ P}_2\text{O}_5 : 0.2 \text{ TEA}_20 : 10 \text{ H}_2\text{O}^{51}$. In a typical synthesis, desired amounts of OSDA 2 (tetraethylammonium hydroxide; TEAOH) (40%, Aldrich), DI water, and aluminum isopropoxide were stirred for at least 3 h. Colloidal silica (Ludox AS-40) was then added to this solution followed by phosphoric acid (85%, MACRON). The gel was allowed to age for 24 h before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 200 °C at autogenous pressure for 2 days.

3.2.1.3 SSZ-98-1 (ERI)

The synthesis gel molar composition for SSZ-98-1 was $1 \text{ SiO}_2 : 0.1 \text{ Al}_2\text{O}_3 : 0.3 \text{ R(OH)}_2$ (OSDA 3) : 0.1 OSDA 4 : 0.46 KOH : 22 H₂O ⁶⁸. In a typical synthesis, desired amounts of potassium hydroxide (KOH) solution (45%, Sigma-Aldrich), OSDA 3 (N,N'-dimethyl-1,4-diazabicyclo[2.2.2]octanium dihydroxide; synthesis protocol in SI), OSDA 4 (18-crown-6, 99%, Sigma-Aldrich), and DI water were stirred for approximately 0.5 h. Fumed silica (Cab-O-Sil M5, ACROS) and Barcroft aluminum hydroxide (Barcroft 250, SPI Pharma) were then added to this solution and stirred until the gel became homogenous. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 150 °C at autogenous pressure for 6 days.

3.2.1.4 SSZ-98-2 (ERI)

SSZ-98-2 was prepared by converting commercial Y zeolite using N,Ndimethylpiperdinium hydroxide (OSDA 5; synthesis protocol in SI) ⁷⁰. The synthesis gel molar composition for SSZ-98-2 was $3.75 \text{ SiO}_2 : 0.125 \text{ Al}_2\text{O}_3 : 1.0 \text{ ROH}$ (OSDA 5) : 1.9 KOH : 145 H₂O. In a typical synthesis, desired amounts of CBV720 (Si/Al=15, Zeolyst), KOH solution, OSDA 5, and DI water were added together and stirred for 24 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 150 °C at autogenous pressure for 7 days.

3.2.1.5 UZM-12 (ERI)

The synthesis gel molar composition for UZM-12 was 16 SiO₂ : 0.5 Al₂O₃ : 2.0 R(Br)₂ (OSDA 6) : 13 TEAOH (OSDA 2) : 1.5 KCl : 400 H₂O ⁶⁰. In a typical synthesis, desired amounts of OSDA 2 (TEAOH), OSDA 6 (hexamethonium bromide, Sigma), potassium chloride (Macron), Catapal B alumina (VISTA), and DI water were added and stirred for 0.5 h. Following this, colloidal silica (Ludox AS-40) was added and this solution was allowed to age for 24 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a rotating oven to 100 °C at autogenous pressure for 12 days. As will be shown later, this sample contained notable amount of extra-framework Al. However, the large amount of extra-framework Al in this sample is not representative of all UZM-12 materials. Using this method, we were unable to obtain a well crystallized sample.

3.2.1.6 ERI-type Zeolites-1, 2, and 3

The synthesis gel molar composition for what is denoted as ERI Zeolite-1 was 1 SiO₂ : $0.167 \text{ Al} : 0.1 \text{ R}(\text{OH})_2 (\text{OSDA 7}) : 0.3 \text{ KOH} : 20 \text{ H}_2\text{O}^{66}$. In a typical synthesis, using a FAU-type zeolite as a T-atom source, a mixture of OSDA 7 (butane-1,4-bis(trimethylammonium) dihydroxide; synthesis procedure outlined in the SI), NaOH, and DI water were stirred for 0.5 h. Then, Y zeolite (CBV712, Si/Al=6, Zeolyst) was added, and this solution was stirred at room temperature for an additional 6 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 135 °C at autogenous pressure for 7 days. This sample is denoted as

ERI Zeolite-1. ERI Zeolite-2 was synthesized using a similar procedure as ERI Zeolite-1; however, OSDA 7 was replaced with OSDA 8 (cyclohexane-1,4-bis(trimethylammonium) dihydroxide; synthesis procedure outlined in the SI). ERI Zeolite-3 was synthesized with a similar gel composition and procedure as ERI Zeolite-2 but with a lower aluminum content in the gel (0.067 rather than 0.167) (CBV720, Si/Al=15, Zeolyst).

3.2.1.7 SAPO-17-1

The synthesis gel molar composition was $0.1 \operatorname{SiO}_2$: $1.0 \operatorname{Al}_2\operatorname{O}_3$: $1.0 \operatorname{P}_2\operatorname{O}_5$: $1.0 \operatorname{CHA}$ (OSDA 9) : $50 \operatorname{H}_2\operatorname{O}^{62}$. In a typical synthesis, a desired amount of aluminum isopropoxide was mixed with DI water and stirred overnight. The following day, phosphoric acid (H₃PO₄; 85%, MACRON) was added to this mixture and the solution was stirred for 2 h. Next, colloidal silica (Ludox AS-30, Sigma-Aldrich) was added along with a small amount of AlPO₄-17 seed (2 wt%). (AlPO₄-17 was synthesized using the same gel composition and crystallization conditions as SAPO-17-1 just without any silicon). Lastly, cyclohexylamine (Aldrich; CHA; OSDA 9) was added to this mixture and the gel was stirred overnight. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 200 °C at autogenous pressure for 2 days. (Note: vigorous stirring and seed addition were necessary to make SAPO-17 without impurity phases. These impurity phases do not form when lowering the Si content in the above gel composition.)

3.2.1.8 SAPO-17-2 and SAPO-17-3

The synthesis gel molar composition was 0.2 (or 0.8) SiO_2 : 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.35 $R(OH)_2$: 70 H_2O ⁷¹. In a typical synthesis, H_3PO_4 was diluted with DI water and mixed with pseudobohoehmite alumina (Catapal B, VISTA). This solution was stirred overnight and then digested for 1 h at 90 °C. Next, hexane-1,6-bis(trimethylammonium) dihydroxide (OSDA 6-

(OH)₂) was added to this solution and stirred for 24 h. Lastly, tetraethyl orthosilicate (TEOS) (99.9%, Alfa Aesar) was added to this gel and stirred for 1 h. The gel was then placed in a Teflonlined Parr reactor (23 cm³) and heated in a rotating oven to 180 °C at autogenous pressure for 4 days. The sample with the lower Si content was denoted as SAPO-17-2 (0.2Si) whereas the sample with the higher Si content (0.8 Si) was denoted as SAPO-17-3. SAPO-17 samples with lower Si content (i.e., lower than 0.2 in the gel) led to the formation of an impurity phase. This gel composition allows for the synthesis of SAPO-17 with up to 1.0 Si.

3.2.1.9 SAPO-17-4

The synthesis gel molar composition was 0.4 SiO_2 : 1.0 Al(OH)₃: 0.9 H₃PO₄: 0.37 R(OH)₂ (OSDA 10): 40 H₂O. In a typical synthesis, a desired amount of Barcroft aluminum hydroxide (containing 31% H₂O; 69% aluminum hydroxide) was mixed with DI water for 1 h, which was followed by the addition of H₃PO₄. This solution was stirred for 24 h and then fumed silica was added. Lastly, OSDA 10 was added to this mixture and stirred for another 24 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a rotating oven to 190 °C at autogenous pressure for 3 days.

3.2.1.10 SAPO-17-5 and SAPO-17-6

A similar procedure as the one used for the synthesis of SAPO-17-2 was used for the synthesis of SAPO-17-5 and SAPO-17-6. The only difference between these two latter samples was the choice of OSDA. For SAPO-17-5, the following gel composition was used: $0.3 \text{ SiO}_2 : 1.0 \text{ Al}_2\text{O}_3 : 1.0 \text{ P}_2\text{O}_5 : 0.35 \text{ R}(\text{OH})_2 \text{ (OSDA 7): } 70 \text{ H}_2\text{O}$. For SAPO-17-6, the following gel composition was used: $0.3 \text{ SiO}_2 : 1.0 \text{ Al}_2\text{O}_3 : 1.0 \text{ P}_2\text{O}_5 : 0.35 \text{ R}(\text{OH})_2 \text{ (OSDA 7): } 70 \text{ H}_2\text{O}$.

3.2.1.11 Product Recovery, Thermal Treatment, and Ammonium Exchange

Once the above syntheses were completed, each material was washed three times (minimum) with DI water (50 cm³ each time) and once with acetone. After each wash, materials were recovered by centrifugation at 3500+ rpm (Eppendorf model 5810 R). After washing, all samples were dried in air overnight at 100 °C. Following drying, all materials were thermally treated (in ceramic calcination boats) under flowing breathing-grade air in a Nabertherm DKN400 muffle furnace. Materials were initially heated to 150 °C at a heating rate of 1 °C/min and held for 3 h before being heated to 580 °C (again at a heating rate of 1 °C/min) and held for 12 h to ensure complete combustion of any remaining organic structure-directing agents (OSDAs).

ERI (SSZ-98s, UZM-12, and ERI-type Zeolites) and CHA (SSZ-13) zeolites were then converted to their ammonium-form by ion exchange, three to seven times with 1 M aqueous NH₄NO₃ solution at 70 °C for 6-8 h. Samples containing potassium generally required multiple ion exchanges to remove the majority of potassium (0.07-0.11 K/Al), as measured by energydispersive X-ray spectroscopy (EDS). A lower K/Al below 0.07 was not achievable for several of the samples, even after more than seven ion exchanges (data not shown). These results are likely due to the residual K⁺ ions residing in environments where they cannot be removed by ion exchange with NH₄⁺ (e.g., in the CAN cages) ⁷². The solid products after the last ion exchange were recovered by centrifugation, washed three times with water and once with acetone, and dried overnight at 100 °C. The dried samples were then thermally treated again using the method described above to convert them to the proton-form.

3.2.2 Characterization

Powder X-ray diffraction patterns were obtained on a Rigaku MiniFlex II instrument using Cu Ka radiation ($\lambda = 1.54184$ Å) at a scan rate of 0.3 °/min to determine structure type and purity. Crystallite sizes were calculated using the Scherrer equation with a shape factor of 0.94. The reported crystallite sizes are the averaged value of five crystallite sizes calculated from five peaks (between 22 and 40° 20). Morphology and elemental composition were determined via scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) on a ZEISS 1550VP instrument equipped with an Oxford X-Max SDD energy dispersive X-ray spectrometer. Atomic ratios (atomic %) were reported as Si/Al for zeolites, or Si/T (where T=Si+Al+P) or Si/(Al+P) for SAPOs. To determine micropore volume using the t-plot method and ensure the absence of mesoporosity, N₂-adsorption/desorption experiments were performed on each sample at 77 K in a Quantachrome Autosorb iQ adsorption instrument using a constant-dose method. Prior to adsorption measurements, all samples were outgassed at 60 °C for 0.5 h, followed by holds of 0.5 h at 120 °C and 6 h at 350 °C (all ramping rates were 1 °C/min). Thermogravimetric analysis (TGA) measurements were performed on Perkin Elmer STA 6000. As-synthesized (prior to thermal treatment), partially-coked and fully-coked samples (0.02-0.06 g) were placed in an alumina crucible and heated at 10 °C/min in a flowing stream (0.33 cm³/s) of air to 800 °C. Liquid ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer whereas liquid ¹H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. All liquid NMR analyses, involving OSDAs, were performed in deuterium oxide (D₂O) (99.9%, Cambridge Isotope Laboratories, Inc.) or 10% D₂O (**Figure A3.2**).

All solid-state, magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy experiments were conducted on a Bruker 500 MHz spectrometer using a 4 mm ZrO₂

rotor. The number of Brønsted acid sites was measured using quantitative ¹H MAS NMR spectroscopy. In a typical experiment, the thermally treated samples were dehydrated under vacuum (10⁻² Torr) at 400 °C for 10 hours at a ramp rate of 2 °C/min in a dehydration manifold after being pre-packed in an uncapped NMR rotor. The rotor was then capped while under vacuum and inside the dehydration manifold (to minimize sample exposure to moisture) and then loaded into the spectrometer. Spectra were collected at 500.1 MHz and a spinning rate of 12 kHz using a 90° high power pulse length of 4 µs. Cycle delay time was varied depending on the relaxation time of the samples. Signal intensities were referenced to hexamethylbenzene and normalized by the mass packed into the rotor for quantification. The spectra were deconvoluted using DMFit, as shown in the Supplemental Information (SI) (Appendix B). For ²⁹Si MAS NMR spectroscopy, oxygen was introduced to the dehydrated sample to reduce the relaxation time. The ¹H-decoupled 29 Si MAS NMR spectra were then acquired at 99.3 MHz and a spinning rate of 8 kHz using a 90° pulse length of 4 µs and a cycle delay time of 10 s. The acquired spectra were deconvoluted using the DMFit software as described in the SI (Appendix B) to identify different Si environments in the tested samples and calculate the framework Si/Al values for the zeolites. It is important to note here that zeolites with an ERI-type framework consist of two crystallographically distinct T (tetrahedral atom) sites. The presence of 24 T1 sites and 12 T2 sites in ERI topology results in two separate resonances with a 2:1 ratio in ²⁹Si MAS NMR ⁷³. Thus, the ¹H-decoupled ²⁹Si MAS NMR spectra of the ERI-type samples were deconvoluted by maintaining the 2 (down-field): 1 (up-field) ratio for each set of Q⁴ resonances (Si(OSi)_n(OAl)_{4-n}, n = 0, 1, 2, and 3) and Q³ resonance (Si(OSi)₃(OH)) with the assumption that Al and silanol defect uniformly occupy the two different T sites. ²⁷Al MAS NMR spectra were acquired on the proton-form of the samples without undergoing any dehydration at 130.2 MHz at a spin rate of 12 kHz, a 10° pulse length of 0.5 μ s, and a cycle delay time of 0.5 s.

3.2.3 Catalytic Testing

Catalyst evaluation was carried out in a fixed-bed reactor at ambient pressure. In a typical experiment, approximately 200 mg of dried catalyst (35-60 mesh size) was loaded between two layers of quartz wool in a $0.25^{\circ} \times 6^{\circ}$ stainless steel (or quartz) tube reactor as a part of a BTRS Jr. continuous flow reactor (Parker Autoclave Engineers). The dry weight of the catalyst was estimated on the basis of thermogravimetric analysis (TGA; PerkinElmer STA 6000). All catalysts were first pretreated by heating to 150 °C at 1 °C/min, held for 3 hours, and then heated further to 580 °C at 1 °C/min and held for 12 h under flowing air (breathing-grade D, AirGas). Methanol was introduced via a liquid syringe pump (Harvard Apparatus Pump 11 Elite) at 4.0-5.0 µL/min into a gas stream of an inert blend (95% He and 5% Ar; GC internal standard) at a volumetric flow rate of 30 cm³/min. The methanol flow rate was adjusted, depending on the actual weight of the dried catalyst loaded in the reactor, to achieve a weight hourly space velocity (WHSV) of 1.3 h⁻¹. Unless otherwise noted, all reactions were performed at a WHSV of 1.3 h⁻¹ and a temperature of 400 °C. Effluent gases were evaluated using an on-stream Agilent GC-MS (GC 6890N/MSD5793N) equipped with a Plot-Q capillary column. Aliquots of product flow were analyzed every 16 minutes. All selectivity values were calculated on carbon-number basis.

In experiments where the content of the entrained hydrocarbons was of interest, the reaction was quenched rapidly (-10 °C/s) and a portion of the catalyst bed (15 mg) was transferred to a Teflon tube and suspended in 1.0 cm³ of 48% aqueous hydrofluoric acid (Sigma Aldrich). The solution was stirred for 2 h to allow the framework to dissolve. Following dissolution, the organic material was extracted into 1 cm³ of dichloromethane (2 x 0.5 cm³). Hexachloroethane (Aldrich, 99%) was used as an internal standard. The speciation of aromatics in the organic layer was then

identified using a mass spectrometer (Varian CP-3800/Saturn 2200) and a DB-5MS UI column (30 m x 0.25 mm) and quantified using a gas chromatograph (Agilent 7890B) connected to a Polyarc. The organic compounds extracted were identified in comparison with the NIST database as well as standards.

3.3 Results and Discussion

3.3.1 Characterization

A total of fourteen small-pore, cage-containing molecular sieves were synthesized and characterized in this work: six ERI-type zeolite samples, six SAPO-17s, and two CHA-type materials (one zeolite (SSZ-13) and one SAPO (SAPO-34)). Below, the characterizations of these materials are discussed in detail, and the results are summarized in **Table 3.2** for the zeolites and **Table 3.3** for the SAPOs.

Figures A3.3-A3.5 contain the TGA profiles of the fresh CHA-type materials (SSZ-13 and SAPO-34) as well as the fresh ERI-type samples. The corresponding mass losses due to the OSDA removal from heating in air (calculated from the mass losses between 300 and 800 °C) demonstrate that all catalysts contained ca. 10-20% OSDA (**Tables 3.2** and **3.3**). These organics were fully removed by approximately 600 °C.

Figures A3.6 and **A3.7** show the powder XRD patterns for CHA-type and ERI-type materials, respectively. These patterns are in good agreement with simulated patterns (IZA database) as well as diffraction patterns reported previously for these two frameworks ^{25,60}. Minor shifts in the diffraction peaks are observed among the various ERI samples. These variations can be attributed to small differences in unit cell size caused by differences in composition in the final product and choice of OSDA in the synthesis procedure ^{25,60}. The Scherrer equation was used to calculate an averaged crystallite size (**Tables 3.2** and **3.3**). All ERI-type zeolite samples have

crystallite sizes in the range of ca. 200 to 400 Å, which is slightly smaller than the crystallite size calculated for SSZ-13 (439 Å). The SAPO-17 samples have slightly larger crystallites (300-450 Å) than the zeolite samples, with SAPO-17-1 having the largest crystallite size at 528 Å.

All N₂ adsorption-desorption isotherms are shown in **Figures A3.8-A3.10**, and the obtained micropore volumes (V_{micro}) are shown in **Tables 3.2** and **3.3**. SSZ-13 (CHA) has a micropore volume of 0.29 cm³/g, which is larger than all the ERI-type zeolite samples (0.18-0.23 cm³/g). UZM-12, a sample with more extra-framework Al (discussed further below), has a micropore volume of 0.15 cm³/g. All the SAPO samples tested in this work, irrespective of framework, have micropore volumes in the range of 0.18-0.26 cm³/g.

Particle/crystal size has been shown to be a parameter that affects MTO catalytic activity, as particle size reduction from micro to nano often leads to a delay in catalyst deactivation ^{74,75}. Therefore, SEM was used to determine particle sizes and morphological features (**Figure A3.11**-**A3.13**, and **Tables 3.2** and **3.3**). **Figure A3.11** shows that the CHA-type samples (SSZ-13 and SAPO-34) consist of particles that are mostly cubic-like, with the SSZ-13 sample containing heavily overlapped cuboids. The specific particle sizes for the CHA-type materials are 3-6 μ m and 0.2-0.6 μ m for SSZ-13 and SAPO-34, respectively.

	D	Dull Enomorical				OSDA			Brønsted Acid Site Density (ppm)		
Sample ID —	DUIK Framework		K/Al ^{[a][i]}	Particle	Crystallite	mass	Vmicro	[h]			Organics
	Si/Al ^[a]	Si /Al ^[b]	Size	Size (µm) ^[d]	Size (Å) ^[e]	Size (Å) ^[e] loss (wt%) ^[f]	(cc/g) ^[g]	3.9-4	4+	Total	mass loss
								(mmol/g)	(mmol/g)	(mmol/g)	(wt%) ^[f]
SSZ-98-1	3.96	5.06	0.084	(0.4-1)x10	272	8.8	0.18	0.29	0.10	0.40	14.4
SSZ-98-2	6.04	7.06	0.083	1-6	234	15.2	0.19	-	-	-	13.0
UZM-12	1.86	5.96 ^[c]	0.071	0.1-0.2	311	14.9	0.15	0.20	0.04	0.24	14.9
ERI zeolite-1	5.22	6.20	0.114	(0.3-0.6)x(2-3)	372	12.7	0.23	0.21	0.06	0.27	12.7
ERI zeolite-2	5.32	6.17	0.092	0.1-0.2	244	16.1	0.20	0.10	0.02	-	15.2
ERI zeolite-3	8.01	9.25	0.075	0.06-0.2	199	-	0.20	0.06	0.01	0.07	10.1
SSZ-13	12.11	15.49	-	3-6	439	18.7	0.29	1.03	-	1.03	20.0

Table 3.2. Characterization data of the CHA-type and ERI-type zeolites.

[a] Measured by EDS on the thermally treated samples after undergoing ion-exchange. [b] Obtained by ²⁹Si NMR spectroscopy. [c] The UZM-12 sample contained a significant amount of extra-framework aluminum, thus, leading to a much higher framework Si/Al. [d] Measured from SEM. [e] Measured from XRD using Scherrer's equation. [f] Measured by TGA. This value reflects the mass loss between 300 and 800 °C in air either due to OSDA or coke removal. All MTO reactions were terminated once methanol conversion dropped below 85% or DME selectivity was higher than 50%. [g] Measured from N₂-physisorption. [h] Obtained by ¹H MAS NMR spectroscopy and referenced to hexamethylbenzene. [i] Residual K/Al after undergoing multiple ion exchanges as described in the Experimental Section.
Sample ID	Gel Product ^[g]				Particle	Crystallite	OSDA		Brønsted Acid Site Density (ppm) ^[f]				Occluded	
	Si/T	Si/T ^[a]	Si	Al	Р	Size (µm) ^[b]	Size (Å) ^[c]	mass loss (wt%) ^[d]	V _{micro} (cc/g) ^[e]	3.6-3.7 (mmol/g)	3.9-4 (mmol/g)	4+ (mmol/g)	Total (mmol/g)	Organics mass loss (wt%) ^[d]
SAPO-17-1	0.024	0.034	3.39	49.83	46.77	2x(2-10)	528	15.77	0.21	-	-	-	-	11.07
SAPO-17-2	0.048	0.042	4.19	49.38	46.43	1-3	385	17.36	0.26	0.068	0.056	0.069	0.192	10.05
SAPO-17-3	0.167	0.120	11.95	46.18	41.86	(0.1-0.4)x3	334	-	0.19	0.241	0.246	0.332	0.830	10.35
SAPO-17-4	0.095	0.103	10.32	49.51	39.90	2-4	277	20.03	0.18	0.479	0.291	0.162	0.927	11.16
SAPO-17-5	0.070	0.071	7.12	48.83	44.05	3-8	436	-	0.25	0.154	0.140	0.126	0.420	12.94
SAPO-17-6	0.070	0.073	7.32	48.48	44.21	1-10	443	18.49	0.26	0.154	0.160	0.131	0.445	10.49
SAPO-34	0.070	0.089	8.90	49.23	41.86	0.2-0.6	322	12.40	0.24	0.795	0.242	-	1.037	20.09

Table 3.3. Characterization data of the SAPO-34 and SAPO-17 materials.

[a] Measured by EDS on the thermally treated samples. (Si/T=Si/(Si+Al+P)) [b] Measured from SEM. [c] Measured from XRD using Scherrer's equation. [d] Measured by TGA. This value reflects the mass loss between 300 and 800 °C in air due to OSDA or coke removal. All MTO reactions were terminated once methanol conversion dropped below 85% or DME selectivity was higher than 50%. [e] Measured from N₂-physisorption experiments. [f] Obtained by ¹H MAS NMR spectroscopy and referenced to hexamethylbenzene. [g] atomic percentages.

Figure A3.12 shows the SEM images of the ERI-type zeolite samples, revealing that they consist of particles that vary by size from a micron (SSZ-98 samples and ERI zeolite-1) to a nanometer range (UZM-12 and ERI zeolites-2 and 3) and by morphology from quasi-spherical (rice grain-like) to rod-like to needle-like, depending on the gel composition (e.g., K/Al, Si/Al, $[OH]^{-}$ /Si, etc.) and the type of OSDA utilized for synthesis. Similar to the ERI-type zeolite materials, the SAPO-17 samples exhibited differences in particle size (albeit to lesser extent than their zeolitic counterparts; 1-10 µm) and morphology. Particularly, SAPO-17 samples with lower Si content formed elongated hexagonal-like structures, but with increasing Si content, the SAPO-17 morphology either shortened or transformed to appear more zeolite-like, consisting primarily of rod-like particles (e.g., SAPO-17-3) (**Figure A3.13**).

The chemical compositions of the thermally treated samples were determined by EDS, and the results are shown in **Tables A3.2** and **A3.3**. For the ERI-type zeolites, the bulk Si/Al values measured by EDS are in the range of 4-6.5, consistent with prior reports on ERI-type zeolites 60,66 . The only exception is ERI zeolite-3, which has a Si/Al= ca. 8, the highest in this work. It is noteworthy that this value is lower than the one reported (Si/Al=11) by Boruntea et al. at an identical gel composition 66 .

Table 3.3 shows the elemental composition of the SAPO-17 samples. The data show that increasing the Si content results in a simultaneous reduction in P and Al. SAPO materials are obtained by isomorphous replacement of P by Si (or Al and P for two Si atoms), depending on the Si incorporation mechanism. When a Si atom is incorporated into a P position (referred to as SM2), a Si(4Al) environment is formed [17,18]. This replacement of pentavalent P by tetravalent Si generates a negative charge which is compensated for by a proton in the thermally treated sample, thus, creating a Si-OH-Al bridging hydroxide which acts as a Brønsted acid site. On the other

hand, the Si incorporation via SM3, in which the incorporation of Si occurs in an island, and quantitatively (but not mechanistically) substitution of two Si atoms for a pair of Al and P atoms occurs to preserve the charge neutrality of the framework [18]. Therefore, the concentration and strength of the Brønsted acid sites in the SAPO samples (discussed in more depth subsequently) depends on the relative contribution of each mechanism.

The elemental composition results listed in **Table 3.3** show that the choices of the OSDA, crystallization conditions, and starting gel (e.g., Si content) play a consequential role in influencing the relative contribution of each Si substitution mechanism (SM2 and SM3). In particular, two observations can be made from the elemental composition data in **Table 3.3**: (i) in all cases, increasing the Si content results in a higher contribution from the SM3 mechanism, as evidenced from the reduction in Al in the product and an increase in the (Si+P)/Al ratio, which was greater than 1 for all the samples, and (ii) SAPO-17-4 favors the SM2 mechanism. Overall, the SAPO-17 samples synthesized in this work contained different Si/T values (up to 0.12), thus allowing us to investigate the effect of this parameter on MTO activity.

²⁹Si MAS NMR spectroscopy was used to identify the different silicon environments present in the thermally treated samples prior to undergoing reaction, and to calculate framework Si/Al for the zeolites. **Figure A3.14** shows the ²⁹Si MAS NMR spectra for SSZ-13 and SAPO-34. For the SSZ-13 sample, four primary resonances at -112, -106, -101, and -100 ppm are observed that correspond to Si(0Al), Si(1Al), Si-OH defects, and Si(2Al) ^{76,77}. Deconvolution of the spectra (an example of the deconvolution is shown in **Figure A3.15**) enabled the calculation of the framework Si/Al=15 (**Table 3.2**). Indeed, this value is within a close range of the bulk Si/Al obtained from EDS (Si/Al=12.11). On the other hand, the spectra for SAPO-34 shows five bands

centered at -92, -97, -101, -106, and -111, corresponding to the presence of Si(4Al) (isolated Si atoms), Si(3Al), Si(2Al), Si(1Al), and Si(0Al) (silicon islands) (**Figure A3.14d**).

Figure 3.2 shows the ²⁹Si MAS NMR spectra for the ERI-type zeolite samples. Several peaks are observed corresponding to Si(0Al), Si(1Al), Si(2Al), Si-OH defects, and Si(3Al). The peak assignments and deconvolution of the ERI-type zeolites spectra were different than SSZ-13, as discussed in the Experimental Section. The deconvolution procedure for ERI-type materials led to the fits shown in **Figure A3.16** and the framework Si/Al values shown in **Table 3.2**. Deconvolution of ²⁹Si MAS NMR spectra and subsequent use of Löwenstein's rule to calculate the Si/Al for ERI-type materials led to significantly lower Si/Al values than those obtained by EDS, which has previously been observed for related frameworks (e.g., OFF and SWY) ^{72,78}.

Figure 3.3 shows the ²⁹Si MAS NMR spectra for the SAPO-17 samples. The SAPO-17 samples show five resonances, similar to SAPO-34 (discussed previously), that are consistent with presence of Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al) environments. All SAPO-17 samples, irrespective of OSDA, have a mixture of Si environments. However, SAPO-17-4 shows a distinctly high peak at -92, which corresponds to isolated Si atoms, Si(4Al), in agreement with the EDS data for this sample. Moreover, the results from the ²⁹Si MAS NMR experiments also demonstrate the effect that Si content has on the Si substitution mechanism, as samples with higher Si content (i.e., higher Si/T) formed more Si islands via SM3.



Figure 3.2. ²⁹Si (top) and ²⁷Al (bottom) MAS NMR spectra for SSZ-98-1, SSZ-98-2, UZM-12, ERI zeolite-1, ERI zeolite-2, and ERI-zeolite-3.



Figure 3.3. ²⁹Si MAS NMR spectra for SAPO-17-1, SAPO-17-2, SAPO-17-3, SAPO-17-4, SAPO-17-5, and SAPO-17-6.

²⁷Al NMR analyses were performed on the ERI-type zeolite samples as well as SSZ-13. The spectra in **Figure 3.2b** for ERI-type zeolites and **Figure A3.14b** for SSZ-13 show that all samples tested in this work have a strong resonance at 58 ppm, which corresponds to tetrahedrally coordinated Al in the zeolite framework, and a weaker resonance near 0 ppm, indicative of extra-framework Al. UZM-12 is the only sample that contains a significant amount of extra-framework Al as demonstrated by ²⁷Al NMR, in agreement with the vast difference observed in **Table 3.2** between the bulk Si/Al from EDS and the framework Si/Al from ²⁹Si MAS NMR.

¹H MAS NMR experiments were performed on the dehydrated samples and the obtained spectra are shown in **Figure A3.14** for CHA-type materials and in **Figure A3.17** for selected ERI-type zeolites and SAPO-17 materials. Several examples of deconvolution representing each class of material are shown in **Figures A3.15** and **A3.16**. For all zeolite spectra, multiple resonances

were observed. A resonance near 1.8 ppm that corresponds to protons in silanols (Si-OH) was detected in most samples ^{79,80}. Additionally, due to the high Al content of many of the samples tested in this work, resonances for protons in aluminum-rich (e.g. extra-framework Al) environments were present between 2 and 3.5 ppm, in agreement with the ²⁷Al NMR measurements (discussed previously) ⁸⁰. A main resonance near 4 ppm (for zeolites) was present, that originates from bridging hydroxyl groups that form from tetrahedrally coordinated Al (i.e., Al incorporated into the framework). Another peak was present in ERI zeolites near 4.3 ppm. For zeolite samples, deconvolution of the 4 and 4.3 ppm peaks gave rise to the total Brønsted acid site density values shown in **Table 3.2**.

For the SAPO-17 and SAPO-34 samples, two main peaks consistent with two differently formed acid sites were present in ¹H MAS NMR spectra : a weaker acid site showing a dominant resonance at ca. 3.6-3.7 ppm which corresponds to SAPO domains, that is, Si substituting for P (SM2), and a stronger acid site showing a resonance at 3.9-4 ppm, which corresponds to zeolite-like domains (i.e., two Si atoms substituting for an Al and a P pair) (SM3) ^{81–83}. In addition to these two acid-site peaks, a third small peak was observed near 4.3 ppm in ERI. Deconvolution of all of these peaks gave rise to the total acid site density values in NMR shown in **Table 3.3** for the SAPO samples.

Figures A3.18-A3.20 show the organic mass losses of the deactivated catalysts (defined as when methanol conversion falls below 85% or DME selectivity surpasses 50%) as determined by TGA. The organic mass losses shown in **Tables 3.2** and **3.3** were calculated based on the mass losses between 300 and 800 °C in air. The TGA results show that mass losses for CHA-type materials (20%) were higher than the ERI-type zeolites (10-15%). Additionally, the SAPO-17 catalysts accumulated slightly lower organic content than the ERI-type zeolites (<13%).

3.3.2 MTO Catalytic Activity

The reaction results for the two CHA-type and twelve ERI-type samples are summarized in **Table 3.4**. **Figure 3.4** shows the MTO product distributions of the evaluated materials before deactivation (when methanol conversion is greater than 97%). The time-on-stream (TOS) profiles are also provided in the SI section (**Appendix B**) (**Figures A3.21-A3.23**).

To establish a benchmark for the product distributions analysis, SSZ-13 and SAPO-34 were both tested for MTO at identical reaction conditions as those for ERI-type materials. Both SSZ-13 and SAPO-34 showed results consistent with literature data for those materials. SAPO-34 shows high stability (i.e., long lifetime), low alkane products, and high combined ethylene (35%) and propylene (41%) selectivities while SSZ-13 gives a shorter lifetime than SAPO-34, high initial propane (due to paired acid sites),²⁵ and a slightly lower cumulative ethylene (33%) and propylene (40%) selectivities than SAPO-34 ²⁵. Additionally, results in **Table 3.4** and **Figure A3.21** show that both SSZ-13 and SAPO-34 form ca. 10% butenes and 7% C₅+.

Figure 3.4 illustrates the product distributions of the ERI-type materials tested. The data show that ERI-type zeolite materials and SAPO-17 behave very differently, with the zeolite samples (stronger acid sites as demonstrated in the previous section via ¹H MAS NMR) registering significantly higher E/P values. In fact, E/P increases monotonically, irrespective of other material properties, from 1.12 for ERI Zeolite-3 (Si/Al=9) to an E/P maximum of 1.86 for SSZ-98-1 (framework Si/Al=5). Thus, the olefins product distributions from ERI-type zeolites appear to be highly sensitive to the framework Si/Al.

	Averaged Selectivities ^[a]										
Sample ID	C ₂ =	C3=	C 4	C5+	Total Alkanes	Averaged C ₂ =/C ₃ =	Minimum C ₂ =/C ₃ =	Maximum C ₂ =/C ₃ =	Averaged C ₂ =/C ₅ +	Deactivation (mins) ^[b]	
SSZ-13	0.33	0.40	0.10	0.069	0.100	0.82	0.60	1.23	4.76	242	
SAPO-34	0.35	0.41	0.13	0.074	0.013	0.85	0.77	0.92	4.73	777	
SSZ-98-1	0.41	0.22	0.10	0.100	0.167	1.86	1.28	2.37	4.11	126	
SSZ-98-2	0.34	0.24	0.12	0.153	0.147	1.45	0.96	1.93	2.25	105	
UZM-12	0.39	0.23	0.12	0.190	0.064	1.71	0.94	2.24	2.05	169	
ERI zeolite-1	0.39	0.25	0.12	0.169	0.060	1.55	0.87	2.06	2.33	231	
ERI zeolite-2	0.39	0.25	0.11	0.164	0.075	1.52	0.90	1.94	2.36	201	
ERI zeolite-3	0.29	0.26	0.14	0.245	0.049	1.12	0.79	1.54	1.18	168	
SAPO-17-1	0.23	0.33	0.14	0.283	0.006	0.70	0.41	1.00	0.81	362	
SAPO-17-2	0.25	0.35	0.15	0.214	0.014	0.73	0.33	1.04	1.18	171	
SAPO-17-3	0.30	0.27	0.13	0.230	0.038	1.12	0.77	1.29	1.32	153	
SAPO-17-4	0.30	0.31	0.11	0.174	0.033	0.98	0.47	1.20	1.75	188	
SAPO-17-5	0.29	0.34	0.14	0.190	0.031	0.86	0.48	1.16	1.55	206	
SAPO-17-6	0.28	0.33	0.13	0.186	0.025	0.85	0.50	1.11	1.53	185	

Table 3.4. Reaction results of the molecular sieves investigated.

[a] Evaluated at high methanol conversion (97-100%). [b] Defined as the time it takes for conversion to drop below 85% or DME selectivity to surpass 50%, whichever occurs first.



Figure 3.4. MTO product distributions for ERI- and CHA-type molecular sieves. (a) MTO product distributions when methanol conversion is over 97% for ERI zeolites (top) and SAPO-17 (bottom). (b) Relationship between framework Si/Al (as determined by ²⁹Si MAS NMR) and ethylene-to-propylene selectivities ratio (E/P) for the zeolites tested in this work. (c) Relationship between (Al+P)/Si (as determined by EDS) and E/P for SAPOs tested in this work.

Closer inspection of the data in **Figure 3.4a** shows that the apparent change in E/P as a function of framework Si/Al for ERI-type zeolites is primarily the result of changes in the ethylene selectivity. Indeed, over the tested range (Si/Al=5-9), the propylene selectivity marginally changes as a function of Si/Al, increasing only from 22 to 26% with decreasing Al content, whereas the ethylene selectivity decreases from 41% to 29%. Furthermore, paralleling the loss in ethylene selectivity are increases in the selectivity to C_{5+} and decreases in the selectivities to light alkanes (mainly, propane). The latter could be due to the decrease in paired acid sites ²⁵. The only material that slightly deviates from this trend is UZM-12, a sample that registers slightly elevated C_{5+} in comparison to ERI Zeolite-1 and ERI Zeolite-2. However, it is worth noting that the UZM-12

sample tested in this work contained quite a bit of extra-framework aluminum and a comparatively lower pore volume, as discussed previously.

As mentioned above, particle size has been previously shown to be a key parameter that influences lifetime. Here, we observed that samples with particle sizes in the nano-size range (but >100 nm) did in fact have slightly extended lifetimes over samples with micron-sized particles. However, crystal/particle size did not significantly alter E/P. Particle size did appear to cause the nano materials (for instance, ERI-zeolite 2) to behave slightly differently than the micron-sized particles in a couple of ways: by forming less initial propane and higher C_5 +, particularly in early stages of the reaction.

The promising behavior of ERI-type zeolites in enhancing the ethylene selectivity in MTO prompted us to investigate SAPO-17 as a molecular sieve that is isostructural to ERI-type zeolites but with milder acid sites. The data in **Figure 3.4a** (bottom), however, shows that the improved E/P exhibited in the ERI-type zeolites did not carry over to the SAPO-17 materials. In fact, the low acid site density combined with the low acid strength of several SAPO-17 samples (Si/T<0.07) eliminated the ethylene enhancement effect observed for ERI-type zeolites, resulting in an E/P<0.9. For instance, SAPO-17-1 (Si/T=0.034) formed almost three times more C₅+ than SSZ-98-1 and almost half the amount of ethylene. To improve these selectivity numbers in favor of lighter olefins and less bulkier molecules, acid site density in SAPO-17 was systematically increased by increasing the Si/T as permitted by the gel composition. As shown in **Table 3.4**, increasing Si/T results in a gradual increase in the E/P, irrespective of other material properties. Particularly, in the samples with low Si content (Si/T<0.04), a combined increase in ethylene and a decrease in propylene is observed. On the other hand, samples with higher Si content (Si/T>0.04) appeared to improve the E/P mainly by decreasing the propylene selectivity.

A closer look at the TOS data shown in **Figure A3.23** demonstrates that increasing Si/T (or decreasing (Al+P)/Si) improves the E/P by allowing the olefins product distribution to switch from a C_3 + rich regime, where ethylene is low but other hydrocarbons are high, to a C_2 -rich regime, where ethylene is the predominant product. Allowing this switch to occur quicker by manipulating the Si content in SAPO-17 (and therefore the catalyst acid site density, as discussed previously) results in higher initial (minimum) and final (maximum) E/P and an overall lower C_5 +/ C_2 =.

In spite of their slightly longer lifetimes, the SAPO-17 catalysts tested in this work were incapable of enhancing the ethylene selectivity in MTO to the extent that ERI-type zeolites with low Si/Al were able to. Indeed, the best performing ERI-type SAPO catalyst in this work, in terms of having the highest ethylene to propylene selectivity, was SAPO-17-3 ((Al+P)/Si=7.4), which also happens to be the catalyst with the highest Si/T=0.12. This catalyst gave an E/P of 1.1 and an overall product distribution that was almost identical to that of ERI Zeolite-3 (framework Si/Al=9.25), the worst performing zeolite in this work (**Table 3.4**).

To test if further reduction in acid site density of ERI-type zeolites would form materials that resemble SAPO-17s with lower Si contents (0.06<Si/T<0.12), two additional experiments were performed. Specifically, instead of performing seven ion exchanges on ERI Zeolite-2 and ERI Zeolite-3 to lower the K/Al to the lowest possible value, only two ion exchanges were performed. These two samples are denoted as ERI Zeolite-2-IE2 and ERI Zeolite-3-IE2. By reducing the number of times a sample is ion exchanged, we aimed to retain a higher amount of potassium ions and thus effectively reduce the number of protons in the framework (i.e., acid site density). The EDS results for these two samples show that ERI Zeolite-2-IE2 has a K/Al of 0.31 whereas ERI Zeolite-3-IE2 has a K/Al of 0.34. The MTO reaction TOS data for these two catalysts are shown in **Figure A3.24**. As expected, these two catalysts behaved like SAPO-17 with low Si

content, resulting in high C_{3+} and low ethylene, especially in early stages of the reaction. Particularly, the averaged E/P measured for ERI Zeolite-2-IE2 and ERI Zeolite-3-IE2 were 0.98 and 0.71, respectively. The experimental results in this section clearly indicate that in order to improve the E/P in ERI-type molecular sieves over CHA both acid site density and strength ought to be controlled.

3.3.3. Relationships between Effluent Product and Retained Hydrocarbons Selectivity

To rationalize the reaction differences observed in the olefins product distributions and overall MTO behavior of ERI-type molecular sieves with varying acid Brønsted site densities and strength, dissolution-extraction experiments were performed on six samples: SSZ-13, SAPO-34, SSZ-98-1 (sample with lowest framework Si/Al), ERI-zeolite-3 (sample with highest Si/Al), SAPO-17-2 (sample with second lowest Si/T), and SAPO-17-3 (sample with highest Si/T). Each of these catalysts was reacted with methanol and the reaction stopped after 30 mins. The reactor was then rapidly cooled to ambient conditions as described in the Experimental Section.

Figure 3.5 shows the extracted hydrocarbon distributions for each of these six catalysts after 30 minutes of reaction. The results in **Figure 3.5** illustrates that the extracted hydrocarbons from the CHA-type materials (SSZ-13 and SAPO-34) consist primarily of methylbenzenes (MB) with up to six methyl groups and methylnaphthalenes (MN) with up to four methyl groups. These data are consistent with prior reports ^{25,84}. Small amounts (<5 mol%) of 3-ring (anthracene and phenanthrene) and 4-ring (pyrenes) hydrocarbons are also detected, though the majority of these bulky compounds did not contain any methyl groups. Of the methylbenzenes, tetra-methylbenzene (4MB) is the primary MB extracted. Penta- and hexa-methylbenzenes (5MB and 6MB, respectively) also make up a sizable portion of the extracted species in CHA-type materials.



Figure 3.5. GC-MS distribution of the extracted hydrocarbon species grouped by ring number/type for six molecular sieves (two CHA-type and four ERI-type materials are shown) after 30 minutes of reaction with methanol at 400 °C and WHSV of 1.3 h⁻¹. (a) Overall hydrocarbon distribution and relative concentration of the aromatic species retained at TOS=30 mins. All concentrations measured were relative to the aromatics concentration measured for SAPO-34 after 30 minutes of reaction (dashed yellow line). (b) Distribution of methylbenzenes and 1-ring hydrocarbons. (c) Distribution of naphthalenes, methylnaphthalenes, and 2-ring hydrocarbons. Legend: MB, methylbenzenes; N, naphthalenes; MN, methylnaphthalenes; the number before an abbreviation denotes the number of methyl groups.

Unlike the CHA-type molecular sieves, the ERI-type materials formed significant amounts of 3-ring hydrocarbons at TOS=30 mins, with a notable portion of the 3-ring contribution coming from methylanthracenes species with 0-3 methyl groups. Materials with higher acid site densities and strengths also formed bulkier aromatics while also retaining higher concentrations of these compounds. The one exception was ERI Zeolite-3, which contained a significant amount of 3-ring hydrocarbons (60 mol%) that was larger than SSZ-98-1 (22 mol%). The ERI Zeolite-3 sample deactivated fairly quickly due to its nanocrystalline particle sizes (60-200 nm), which likely formed more external coke (i.e., polycyclic compounds), thus, inhibiting methanol diffusion, in agreement with a previous observation on nanocrystalline UZM-12⁶⁰. Indeed, it was previously suggested that UZM-12-type particles that are less than 100 nm in size may have a detrimental effect on MTO activity and stability ⁶⁰.

In addition to their propensity for retaining 3-ring compounds, the ERI-type molecular sieves tested also had higher 4MB/(5MB+6MB) ratios (1.8-2.8) than the CHA-type materials (1.2-1.5) after 30 minutes TOS, albeit the amount of MBs retained were far lower. 4MB/(5MB+6MB) has been previously used as an indicator to rationalize/correlate differences in E/P for AEI- and CHA-based materials (both frameworks are considered small-pore, cage-type) due to changes in reaction conditions ³. An elevated 4MB/(5M+6MB) suggests a higher E/P. It has been shown previously, too, both experimentally and theoretically, that 4MB undergoes dealkylation via the side-chain route of the aromatic cycle to yield ethylene, whereas 5MB and 6MB undergo dealkylation via the pairing route of the aromatic cycle to give propylene ^{3,40,44,85}. The presence of naphthalenes has also been associated with improved ethylene formation ⁸⁶. However, none of these conditions (concentration of naphthalenes or 4MB/(5MB+6MB)) alone explained the differences observed in product distributions. These results, coupled with fact that the reaction data showed large quantities of C_5+ , led us to consider the possibility of a contribution from the olefin cycle.

Figure 3.5a shows the relative concentration of the soluble aromatics for the six aforementioned catalysts. The aromatics concentration measured for SAPO-34 at TOS=30 mins was used as a basis for comparison against the extracted aromatics concentrations for the other catalysts (reported as relative concentration). The data show that materials with low acid site density, that is, ERI Zeolite-3 and SAPO-17-2, have low relative aromatic concentrations (i.e., lower than SAPO-34), with SAPO-17-2 having the lowest aromatic concentrations of all tested catalysts. SAPO-17-2 also has the second lowest E/P = 0.73 of all catalysts tested. On the other hand, SSZ-98-1, the catalyst with the highest acid site density and strength, had the highest aromatic concentration and the highest E/P (**Figure 3.5**). In addition to the differences observed

in the relative concentration of the aromatic species, the ERI samples (particularly those with higher Si/Al or low Si/T) formed a more diverse set of 1-ring and 2-ring species and in larger quantities. These 1- and 2-ring species are denoted in the data of **Figure 3.5** as other 1-ring and other 2-rings, respectively. Species belonging to these two categories contained bulkier alkyl groups than methyl (e.g., ethyl, isopropyl, or isobutyl). Often, these intermediates contained 0-3 methyl groups and 1-2 alkyl (excluding methyl) groups.

To investigate how the overall relative aromatics concentration changes as a function of TOS in general and how the alkylated aromatics concentration changes with this parameter in ERI-type materials, the two extreme ERI-type samples, SSZ-98-1 and SAPO-17-2, were further analyzed and the occluded intermediates retained in these catalysts were extracted after reaction for 15 and 60 minutes. The results are shown in **Figure 3.6**. The data from SSZ-98-1 (**Figure 3.6a-c**) shows that increasing the reaction time results in the formation of more 3-ring containing species and less MBs and MNs. As the reaction proceeds, the methylbenzenes composition changes to favor trimethylbenzene (3MB) and (4MB) while completely suppressing the presence of 5MB and 6MB. These compositional changes result in an improved 4MB/(5MB+6MB), which monotonically increases as a function of TOS. Similar to the MBs, the concentration of the MNs also decreases with increasing TOS. Of the MN formed, tetra-methylnaphthalene (4MN) is the predominant naphthalene-type product recovered via this analysis.

Interestingly, the SAPO-17-2 behaved very differently than SSZ-98-1. As the reaction proceeds, the composition of the entrained MBs in SAPO-17-2 does not dramatically change as in SSZ-98-1. In fact, the 4MB/(5MB+6MB) ratio is fairly constant for all three TOS measurements (despite changes in the E/P and the overall concentration of the MBs). Since 4MB, 5MB, and 6MB are associated with the aromatics cycle (but not the olefins cycle), the fact that the

4MB/(5MB+6MB) ratio falls short in predicting the E/P observed in SAPO-17-2 is very likely due to a substantial contribution from the olefins cycle. Moreover, as the MBs levels are reduced with increasing TOS for SAPO-17-2, the amount of naphthalenes and MN increases. Significant amounts of alkylated benzenes and naphthalenes with groups larger than methyl are also present in the SAPO-17-2 sample, and in much larger quantities than in SSZ-98-1. These intermediates, at least in part, could be contributing toward the observed low C₂/C₃ and high C₅+/C₂ in SAPO-17 with low Si/T by splitting off larger product molecules upon their dealkylation. The narrower yet longer ERI cage (compared to CHA) and the absence of the double-6-rings (d6r) separating the ERI cages from each other like in CHA are likely the main reasons behind the formation of these species in SAPO-17 and ERI-type zeolites (**Figure A3.25**).

The aromatic concentrations at each TOS for SAPO-17-2 are about half of that of SSZ-98-1, thus, the accumulation of aromatics is lower in the SAPO-17 materials with low Si/T than in the ERI-type zeolites with low framework Si/Al. These differences in the aromatics concentrations and identities influence the olefins products distributions during the reaction period, leading to different deactivation profiles. **Figure A3.26** shows the GC-MS distribution of the deactivated catalysts. All the ERI-type materials contained a wide host of 3-rings and 4-ring compounds with up to 3 methyl groups. The distribution of the 3- and 4-ring hydrocarbons (primarily, anthracene, phenanthrene-, and pyrene-type) accounted for approximately 40+ mol% of the retained aromatics for ERI-type molecular sieves. Interestingly, the SSZ-98-1 catalyst with the lowest framework Si/Al contained less than 10 mol% MBs upon deactivation and approximately 20 mol% MNs. This value was much lower than the other catalysts tested in this work and is five times lower than CHA, both SSZ-13 and SAPO-34.



Figure 3.6. GC-MS distribution of the extracted hydrocarbon species grouped by ring number/type for two molecular sieves (SSZ-98-1 and SAPO-17-2) after 15, 30, and 60 minutes of reaction with methanol at 400 °C and WHSV of 1.3 h⁻¹. (a,d) Overall hydrocarbon distribution and relative concentration of the aromatic species retained for SSZ-98-1 and SAPO-17-2. All concentrations measured were relative to the aromatics concentration measured for SAPO-34 after 30 minutes of reaction. (b,e) Distribution of methylbenzenes and 1-ring hydrocarbons. (c,f) Distribution of naphthalenes, methylnaphthalenes, and 2-ring hydrocarbons. Legend: MB, methylbenzenes; N, naphthalenes; MN, methylnaphthalenes; the number before an abbreviation denotes the number of methyl groups.

The results herein combined with the reaction data in the previous section demonstrate that changes in acidity have a substantial role in controlling the rate of formation of aromatic compounds in ERI-type materials and their corresponding compositions. These effects together influence the E/P in ERI-type molecular sieves. Indeed, ERI-type materials with higher acid strengths and densities are required to suppress the olefins cycle and to shift the MTO product distribution in favor of ethylene (**Scheme 3.1**).



Scheme 3.1 Reaction mechanism in ERI-type catalysts.

3.4 Conclusion

ERI-type molecular sieves were synthesized using a number of OSDAs to form materials with different Brønsted acid strengths and densities. The synthesized materials, both zeolites and SAPOs, were characterized and found to have different physiochemical properties (e.g., crystallite sizes, particle sizes, Si environments, etc.). These catalysts were tested in the MTO reaction and their product distributions were compared to SAPO-34 and SSZ-13 (both CHA-type molecular sieves). While the CHA-type molecular sieves gave an E/P of approximately 0.8, the E/P of ERI-type materials showed high sensitivity toward the acidity differences of the materials, leading to

the formation of olefins product distributions that contained either high C_{3+} or high $C_{2=}$. Specifically, it has been shown in this work that in addition to topological features, ERI-type zeolites with low framework Si/Al (<7), and thus specific acid strengths and densities, enhance the E/P over CHA-type materials.

To rationalize the differences observed in the MTO activity, organic species retained in the cavities of the partially reacted/deactivated catalysts were analyzed at different TOS via dissolution of the molecular sieve and extraction of organic components. The results from these experiments demonstrated that ERI-type materials with weak acid strengths and densities (i.e., SAPO-17s with low Si/T) accumulate aromatic intermediates at a slower rate than ERI-type zeolites while also forming a more diverse set of alkyl-containing benzenes and naphthalenes. As the concentration of these aromatics increases with reaction TOS, E/P continues to increase until the catalyst deactivates, with the ERI-type catalysts often reaching their maximum E/P right before they fully deactivate. The results herein highlight the promising MTO rection behavior of ERI-type molecular sieves as a possible methanol-to-ethylene catalysts while also demonstrating how cage geometry and acid site density play a vital role in influencing the olefins product distribution by regulating the HP intermediates that form as a part of the dual cycle.

3.5 Acknowledgements

The Chevron Energy and Technology Company provided financial support for this research. The authors gratefully acknowledge Dr. Nathan Dalleska (Resnick Water and Environment Laboratory at the California Institute of Technology) for assistance with the GC-MS experiments, Dr. Sonjong Hwang for assistance with solid-state NMR, and Dr. Donglong Fu for valuable technical discussions. F.H.A. would like to thank Aramco R&D for financially supporting

his graduate studies. Y.P. gratefully acknowledges financial support from Kwanjeong Educational Foundation.

3.6 References

 Dai, W.; Wang, C.; Dyballa, M.; Wu, G.; Guan, N.; Li, L.; Xie, Z.; Hunger, M. Understanding the Early Stages of the Methanol-to-Olefin Conversion on H-SAPO-34. *ACS Catal.* 2015, 5 (1), 317–326. https://doi.org/10.1021/cs5015749.

(2) Dahl, I. M.; Kolboe, S. On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: 2. Isotopic Labeling Studies of the Co-Reaction of Propene and Methanol. *Journal of Catalysis* **1996**, *161* (1), 304–309. https://doi.org/10.1006/jcat.1996.0188.

(3) Shi, Z.; Bhan, A. Tuning the Ethylene-to-Propylene Ratio in Methanol-to-Olefins Catalysis
 on Window-Cage Type Zeolites. *Journal of Catalysis* 2021, 395, 266–272.
 https://doi.org/10.1016/j.jcat.2021.01.015.

(4) Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B. The Mechanism of Methanol to Hydrocarbon Catalysis. *Acc. Chem. Res.* 2003, *36* (5), 317–326. https://doi.org/10.1021/ar0200060.

(5) Song, W.; Haw, J. F.; Nicholas, J. B.; Heneghan, C. S. Methylbenzenes Are the Organic Reaction Centers for Methanol-to-Olefin Catalysis on HSAPO-34. *J. Am. Chem. Soc.* 2000, *122* (43), 10726–10727. https://doi.org/10.1021/ja002195g.

(6) Hua, J.; Dong, X.; Wang, J.; Chen, C.; Shi, Z.; Liu, Z.; Han, Y. Methanol-to-Olefin Conversion over Small-Pore DDR Zeolites: Tuning the Propylene Selectivity via the Olefin-Based Catalytic Cycle. *ACS Catal.* **2020**, *10* (5), 3009–3017. https://doi.org/10.1021/acscatal.9b05521.

 Hwang, A.; Kumar, M.; Rimer, J. D.; Bhan, A. Implications of Methanol Disproportionation on Catalyst Lifetime for Methanol-to-Olefins Conversion by HSSZ-13. *Journal of Catalysis* 2017, 346, 154–160. https://doi.org/10.1016/j.jcat.2016.12.003.

(8) Hwang, A.; Prieto-Centurion, D.; Bhan, A. Isotopic Tracer Studies of Methanol-to-Olefins Conversion over HSAPO-34: The Role of the Olefins-Based Catalytic Cycle. *Journal of Catalysis* 2016, *337*, 52–56. https://doi.org/10.1016/j.jcat.2016.01.021.

(9) Olsbye, U.; Svelle, S.; Bjørgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity. *Angewandte Chemie International Edition* **2012**, *51* (24), 5810–5831. https://doi.org/10.1002/anie.201103657.

(10) Wang, C.-M.; Wang, Y.-D.; Xie, Z.-K.; Liu, Z.-P. Methanol to Olefin Conversion on HSAPO-34 Zeolite from Periodic Density Functional Theory Calculations: A Complete Cycle of Side Chain Hydrocarbon Pool Mechanism. *J. Phys. Chem. C* **2009**, *113* (11), 4584–4591. https://doi.org/10.1021/jp810350x.

(11) De Wispelaere, K.; Hemelsoet, K.; Waroquier, M.; Van Speybroeck, V. Complete Low-Barrier Side-Chain Route for Olefin Formation during Methanol Conversion in H-SAPO-34. *Journal of Catalysis* **2013**, *305*, 76–80. https://doi.org/10.1016/j.jcat.2013.04.015.

(12) Hemelsoet, K.; Van der Mynsbrugge, J.; De Wispelaere, K.; Waroquier, M.; Van Speybroeck, V. Unraveling the Reaction Mechanisms Governing Methanol-to-Olefins Catalysis by Theory and Experiment. *ChemPhysChem* 2013, *14* (8), 1526–1545. https://doi.org/10.1002/cphc.201201023.

(13) Li, J.; Wei, Y.; Chen, J.; Tian, P.; Su, X.; Xu, S.; Qi, Y.; Wang, Q.; Zhou, Y.; He, Y.; Liu,Z. Observation of Heptamethylbenzenium Cation over SAPO-Type Molecular Sieve DNL-6 under

Real MTO Conversion Conditions. J. Am. Chem. Soc. 2012, 134 (2), 836–839. https://doi.org/10.1021/ja209950x.

(14) Xu, S.; Zheng, A.; Wei, Y.; Chen, J.; Li, J.; Chu, Y.; Zhang, M.; Wang, Q.; Zhou, Y.; Wang, J.; Deng, F.; Liu, Z. Direct Observation of Cyclic Carbenium Ions and Their Role in the Catalytic Cycle of the Methanol-to-Olefin Reaction over Chabazite Zeolites. *Angewandte Chemie International Edition* **2013**, *52* (44), 11564–11568. https://doi.org/10.1002/anie.201303586.

(15) Zhang, W.; Chen, J.; Xu, S.; Chu, Y.; Wei, Y.; Zhi, Y.; Huang, J.; Zheng, A.; Wu, X.; Meng, X.; Xiao, F.; Deng, F.; Liu, Z. Methanol to Olefins Reaction over Cavity-Type Zeolite: Cavity Controls the Critical Intermediates and Product Selectivity. *ACS Catal.* 2018, 8 (12), 10950–10963. https://doi.org/10.1021/acscatal.8b02164.

(16) Bollini, P.; Chen, T. T.; Neurock, M.; Bhan, A. Mechanistic Role of Water in HSSZ-13
Catalyzed Methanol-to-Olefins Conversion. *Catal. Sci. Technol.* 2019, *9* (16), 4374–4383.
https://doi.org/10.1039/C9CY01015G.

(17) Kaiser, S. Production of Light Olefins. US Patent 4,499,327, 1985.

(18) Sierra de Saldarriaga, L.; Saldarriaga, C.; Davis, M. E. Investigations into the Nature of a Silicoaluminophosphate with the Faujasite Structure. *J. Am. Chem. Soc.* **1987**, *109* (9), 2686–2691. https://doi.org/10.1021/ja00243a022.

(19) Hasha, Dennis.; Sierra de Saldarriaga, Ligia.; Saldarriaga, Carlos.; Hathaway, P. E.; Cox,
D. F.; Davis, M. E. Studies of Silicoaluminophosphates with the Sodalite Structure. *J. Am. Chem. Soc.* 1988, *110* (7), 2127–2135. https://doi.org/10.1021/ja00215a020.

(20) Yarulina, I.; Goetze, J.; Gücüyener, C.; van Thiel, L.; Dikhtiarenko, A.; Ruiz-Martinez, J.; Weckhuysen, B. M.; Gascon, J.; Kapteijn, F. Methanol-to-Olefins Process over Zeolite Catalysts with DDR Topology: Effect of Composition and Structural Defects on Catalytic Performance. *Catal. Sci. Technol.* **2016**, *6* (8), 2663–2678. https://doi.org/10.1039/C5CY02140E.

(21) Ahn, N. H.; Seo, S.; Hong, S. B. Small-Pore Molecular Sieves SAPO-57 and SAPO-59:
Synthesis, Characterization, and Catalytic Properties in Methanol-to-Olefins Conversion. *Catal. Sci. Technol.* 2016, 6 (8), 2725–2734. https://doi.org/10.1039/C5CY02103K.

(22) Pinilla-Herrero, I.; Olsbye, U.; Márquez-Álvarez, C.; Sastre, E. Effect of Framework Topology of SAPO Catalysts on Selectivity and Deactivation Profile in the Methanol-to-Olefins Reaction. *Journal of Catalysis* **2017**, *352*, 191–207. https://doi.org/10.1016/j.jcat.2017.05.008.

(23) Li, C.; Paris, C.; Martínez-Triguero, J.; Boronat, M.; Moliner, M.; Corma, A. Synthesis of Reaction-adapted Zeolites as Methanol-to-Olefins Catalysts with Mimics of Reaction Intermediates as Organic Structure-directing Agents. *Nature Catalysis* **2018**, *1* (7), 547–554. https://doi.org/10.1038/s41929-018-0104-7.

(24) Zhang, L.; Wang, S.; Shi, D.; Qin, Z.; Wang, P.; Wang, G.; Li, J.; Dong, M.; Fan, W.; Wang,
J. Methanol to Olefins over H-RUB-13 Zeolite: Regulation of Framework Aluminum Siting and
Acid Density and Their Relationship to the Catalytic Performance. *Catal. Sci. Technol.* 2020, *10*(6), 1835–1847. https://doi.org/10.1039/C9CY02419K.

(25) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E.
Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction. *ACS Catal.* **2016**, *6* (2), 542–550. https://doi.org/10.1021/acscatal.5b01450.

(26) Martínez-Franco, R.; Li, Z.; Martínez-Triguero, J.; Moliner, M.; Corma, A. Improving the Catalytic Performance of SAPO-18 for the Methanol-to-Olefins (MTO) Reaction by Controlling the Si Distribution and Crystal Size. *Catal. Sci. Technol.* **2016**, *6* (8), 2796–2806. https://doi.org/10.1039/C5CY02298C. (27) Dusselier, M.; Deimund, M. A.; Schmidt, J. E.; Davis, M. E. Methanol-to-Olefins Catalysis with Hydrothermally Treated Zeolite SSZ-39. *ACS Catal.* **2015**, *5* (10), 6078–6085. https://doi.org/10.1021/acscatal.5b01577.

(28) Masih, D.; Imai, H.; Yokoi, T.; Kondo, J. N.; Tatsumi, T. Methanol Conversion to Lower Olefins over RHO Type Zeolite. *Catalysis Communications* **2013**, *37*, 1–4. https://doi.org/10.1016/j.catcom.2013.03.023.

(29) Goetze, J.; Meirer, F.; Yarulina, I.; Gascon, J.; Kapteijn, F.; Ruiz-Martínez, J.; Weckhuysen,
B. M. Insights into the Activity and Deactivation of the Methanol-to-Olefins Process over
Different Small-Pore Zeolites As Studied with Operando UV–Vis Spectroscopy. *ACS Catal.* 2017,
7 (6), 4033–4046. https://doi.org/10.1021/acscatal.6b03677.

(30) Park, J. W.; Lee, J. Y.; Kim, K. S.; Hong, S. B.; Seo, G. Effects of Cage Shape and Size of 8-Membered Ring Molecular Sieves on Their Deactivation in Methanol-to-Olefin (MTO) Reactions. *Applied Catalysis A: General* 2008, *339* (1), 36–44. https://doi.org/10.1016/j.apcata.2008.01.005.

(31) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. *ACS Catal.* **2019**, *9* (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.

(32) Bhawe, Y.; Moliner-Marin, M.; Lunn, J. D.; Liu, Y.; Malek, A.; Davis, M. Effect of Cage
Size on the Selective Conversion of Methanol to Light Olefins. *ACS Catal.* 2012, *2* (12), 2490–
2495. https://doi.org/10.1021/cs300558x.

(33) Deimund, M. A.; Schmidt, J. E.; Davis, M. E. Effect of Pore and Cage Size on the Formation of Aromatic Intermediates During the Methanol-to-Olefins Reaction. *Topics in Catalysis* 2015, *58*(7), 416–423. https://doi.org/10.1007/s11244-015-0384-y.

(34) Kang, J. H.; Walter, R.; Xie, D.; Davis, T.; Chen, C.-Y.; Davis, M. E.; Zones, S. I. Further Studies on How the Nature of Zeolite Cavities That Are Bounded by Small Pores Influences the Conversion of Methanol to Light Olefins. *ChemPhysChem* **2018**, *19* (4), 412–419. https://doi.org/10.1002/cphc.201701197.

(35) Ilias, S.; Bhan, A. Mechanism of the Catalytic Conversion of Methanol to Hydrocarbons.
 ACS Catal. 2013, 3 (1), 18–31. https://doi.org/10.1021/cs3006583.

(36) Wang, C.-M.; Wang, Y.-D.; Xie, Z.-K. Verification of the Dual Cycle Mechanism for Methanol-to-Olefin Conversion in HSAPO-34: A Methylbenzene-Based Cycle from DFT Calculations. *Catal. Sci. Technol.* **2014**, *4* (8), 2631–2638. https://doi.org/10.1039/C4CY00262H.

(37) Arstad, B.; Kolboe, S. The Reactivity of Molecules Trapped within the SAPO-34 Cavities in the Methanol-to-Hydrocarbons Reaction. *J. Am. Chem. Soc.* **2001**, *123* (33), 8137–8138. https://doi.org/10.1021/ja010668t.

(38) Svelle, S.; Joensen, F.; Nerlov, J.; Olsbye, U.; Lillerud, K.-P.; Kolboe, S.; Bjørgen, M.
Conversion of Methanol into Hydrocarbons over Zeolite H-ZSM-5: Ethene Formation Is
Mechanistically Separated from the Formation of Higher Alkenes. *J. Am. Chem. Soc.* 2006, *128*(46), 14770–14771. https://doi.org/10.1021/ja065810a.

(39) Yarulina, I.; Chowdhury, A. D.; Meirer, F.; Weckhuysen, B. M.; Gascon, J. Recent Trends and Fundamental Insights in the Methanol-to-Hydrocarbons Process. *Nature Catalysis* 2018, *1* (6), 398–411. https://doi.org/10.1038/s41929-018-0078-5.

(40) Ferri, P.; Li, C.; Paris, C.; Rodríguez-Fernández, A.; Moliner, M.; Boronat, M.; Corma, A. The Limits of the Confinement Effect Associated to Cage Topology on the Control of the MTO Selectivity. *ChemCatChem* **2021**, *13* (6), 1578–1586. https://doi.org/10.1002/cctc.202001760.

(41) Fečík, M.; Plessow, P. N.; Studt, F. Theoretical Investigation of the Side-Chain Mechanism of the MTO Process over H-SSZ-13 Using DFT and Ab Initio Calculations. *Catal. Sci. Technol.* **2021**, *11* (11), 3826–3833. https://doi.org/10.1039/D1CY00433F.

(42) Lesthaeghe, D.; Horré, A.; Waroquier, M.; Marin, G. B.; Van Speybroeck, V. Theoretical Insights on Methylbenzene Side-Chain Growth in ZSM-5 Zeolites for Methanol-to-Olefin Conversion. *Chemistry – A European Journal* 2009, *15* (41), 10803–10808. https://doi.org/10.1002/chem.200901723.

(43) Arstad, B.; Nicholas, J. B.; Haw, J. F. Theoretical Study of the Methylbenzene Side-Chain Hydrocarbon Pool Mechanism in Methanol to Olefin Catalysis. *J. Am. Chem. Soc.* 2004, *126* (9), 2991–3001. https://doi.org/10.1021/ja035923j.

(44) Ferri, P.; Li, C.; Paris, C.; Vidal-Moya, A.; Moliner, M.; Boronat, M.; Corma, A. Chemical and Structural Parameter Connecting Cavity Architecture, Confined Hydrocarbon Pool Species, and MTO Product Selectivity in Small-Pore Cage-Based Zeolites. *ACS Catal.* **2019**, *9* (12), 11542–11551. https://doi.org/10.1021/acscatal.9b04588.

(45) Hu, M.; Wang, C.; Gao, X.; Chu, Y.; Qi, G.; Wang, Q.; Xu, G.; Xu, J.; Deng, F. Establishing a Link Between the Dual Cycles in Methanol-to-Olefins Conversion on H-ZSM-5: Aromatization of Cycloalkenes. *ACS Catal.* 2020, *10* (7), 4299–4305. https://doi.org/10.1021/acscatal.0c00838.
(46) Li, J.; Wei, Y.; Chen, J.; Xu, S.; Tian, P.; Yang, X.; Li, B.; Wang, J.; Liu, Z. Cavity Controls the Selectivity: Insights of Confinement Effects on MTO Reaction. *ACS Catal.* 2015, *5* (2), 661–665. https://doi.org/10.1021/cs501669k.

(47) Chen, D.; Moljord, K.; Holmen, A. The Effect of the Particle Size on Methanol Conversion to Light Olefins. In *Studies in Surface Science and Catalysis*; Corma, A., Melo, F. V., Mendioroz,

S., Fierro, J. L. G., Eds.; Elsevier, 2000; Vol. 130, pp 2651–2656. https://doi.org/10.1016/S0167-2991(00)80870-8.

(48) Li, Z.; Martínez-Triguero, J.; Yu, J.; Corma, A. Conversion of Methanol to Olefins:
Stabilization of Nanosized SAPO-34 by Hydrothermal Treatment. *Journal of Catalysis* 2015, *329*, 379–388. https://doi.org/10.1016/j.jcat.2015.05.025.

(49) Bleken, F.; Bjørgen, M.; Palumbo, L.; Bordiga, S.; Svelle, S.; Lillerud, K.-P.; Olsbye, U. The Effect of Acid Strength on the Conversion of Methanol to Olefins Over Acidic Microporous Catalysts with the CHA Topology. *Topics in Catalysis* **2009**, *52* (3), 218–228. https://doi.org/10.1007/s11244-008-9158-0.

(50) Castellanos-Beltran, I. J.; Assima, G. P.; Lavoie, J.-M. Effect of Temperature in the Conversion of Methanol to Olefins (MTO) Using an Extruded SAPO-34 Catalyst. *Frontiers of Chemical Science and Engineering* **2018**, *12* (2), 226–238. https://doi.org/10.1007/s11705-018-1709-8.

(51) Inui, T.; Kang, M. Reliable Procedure for the Synthesis of Ni-SAPO-34 as a Highly Selective Catalyst for Methanol to Ethylene Conversion. *Applied Catalysis A: General* 1997, *164*(1), 211–223. https://doi.org/10.1016/S0926-860X(97)00172-5.

(52) Huang, H.; Wang, H.; Zhu, H.; Zhang, S.; Zhang, Q.; Li, C. Enhanced Ethene to Propene Ratio over Zn-Modified SAPO-34 Zeolites in Methanol-to-Olefin Reaction. *Catal. Sci. Technol.* **2019**, 9 (9), 2203–2210. https://doi.org/10.1039/C9CY00335E.

(53) De Wispelaere, K.; Wondergem, C. S.; Ensing, B.; Hemelsoet, K.; Meijer, E. J.; Weckhuysen, B. M.; Van Speybroeck, V.; Ruiz-Martínez, J. Insight into the Effect of Water on the Methanol-to-Olefins Conversion in H-SAPO-34 from Molecular Simulations and in Situ

Microspectroscopy. ACS Catal. 2016, 6 (3), 1991–2002. https://doi.org/10.1021/acscatal.5b02139.

(54) Arora, S. S.; Nieskens, D. L. S.; Malek, A.; Bhan, A. Lifetime Improvement in Methanolto-Olefins Catalysis over Chabazite Materials by High-Pressure H2 Co-Feeds. *Nature Catalysis* **2018**, *1* (9), 666–672. https://doi.org/10.1038/s41929-018-0125-2.

(55) Vogt, C.; Weckhuysen, B. M.; Ruiz-Martínez, J. Effect of Feedstock and Catalyst Impurities on the Methanol-to-Olefin Reaction over H-SAPO-34. *ChemCatChem* **2017**, *9* (1), 183–194. https://doi.org/10.1002/cctc.201600860.

(56) Borodina, E.; Sharbini Harun Kamaluddin, H.; Meirer, F.; Mokhtar, M.; Asiri, A. M.; Al-Thabaiti, S. A.; Basahel, S. N.; Ruiz-Martinez, J.; Weckhuysen, B. M. Influence of the Reaction Temperature on the Nature of the Active and Deactivating Species During Methanol-to-Olefins Conversion over H-SAPO-34. *ACS Catal.* 2017, 7 (8), 5268–5281. https://doi.org/10.1021/acscatal.7b01497.

(57) Pinilla-Herrero, I.; Márquez-Álvarez, C.; Sastre, E. Complex Relationship between SAPO Framework Topology, Content and Distribution of Si and Catalytic Behaviour in the MTO Reaction. *Catal. Sci. Technol.* **2017**, *7* (17), 3892–3901. https://doi.org/10.1039/C7CY01250K.

(58) Wang, M.; Kang, J.; Xiong, X.; Zhang, F.; Cheng, K.; Zhang, Q.; Wang, Y. Effect of Zeolite Topology on the Hydrocarbon Distribution over Bifunctional ZnAlO/SAPO Catalysts in Syngas Conversion. *Catalysis Today* **2021**, *371*, 85–92. https://doi.org/10.1016/j.cattod.2020.07.076.

(59) Yang, M.; Li, B.; Gao, M.; Lin, S.; Wang, Y.; Xu, S.; Zhao, X.; Guo, P.; Wei, Y.; Ye, M.;
Tian, P.; Liu, Z. High Propylene Selectivity in Methanol Conversion over a Small-Pore SAPO
Molecular Sieve with Ultra-Small Cage. *ACS Catal.* 2020, *10* (6), 3741–3749.
https://doi.org/10.1021/acscatal.9b04703.

(60) Lee, J. H.; Park, M. B.; Lee, J. K.; Min, H.-K.; Song, M. K.; Hong, S. B. Synthesis and Characterization of ERI-Type UZM-12 Zeolites and Their Methanol-to-Olefin Performance. *J. Am. Chem. Soc.* **2010**, *132* (37), 12971–12982. https://doi.org/10.1021/ja105185r.

(61) Nawaz, S.; Kolboe, S.; Stöcker, M. Conversion of Methanol to Light Olefins over Sapo-17
Molecular Sieve. In *Studies in Surface Science and Catalysis*; Curry-Hyde, H. E., Howe, R. F.,
Eds.; Elsevier, 1994; Vol. 81, pp 393–398. https://doi.org/10.1016/S0167-2991(08)63901-4.

(62) Lok, B.; Messina, C.; Patton, R.; Gajek, R.; Cannan, T.; Flanigen, E. Crystalline Silicoaluminophosphates. US 444,0871A, 1984.

(63) Lohse, U.; Jancke, K.; Löffler, E.; Schaller, T. The Influence of HF on the Incorporation of Silicon into the Erionite-like AlPO4-17 Molecular Sieve. *Crystal Research and Technology* 1994, 29 (2), 237–245. https://doi.org/10.1002/crat.2170290213.

(64) Zhong, S.; Song, S.; Wang, B.; Bu, N.; Ding, X.; Zhou, R.; Jin, W. Fast Preparation of ERI-Structure AlPO-17 and SAPO-17 in the Presences of Isomorphous and Heterogeneous Seeds. *Microporous and Mesoporous Materials* 2018, 263, 11–20.
https://doi.org/10.1016/j.micromeso.2017.11.034.

(65) Zibrowius, B.; Lohse, U. Multinuclear MAS NMR Study of the Microporous Aluminophosphate AlPO4-17 and the Related Silicoaluminophosphate SAPO-17. *Solid State Nuclear Magnetic Resonance* **1992**, *1* (3), 137–148. https://doi.org/10.1016/0926-2040(92)90014-Z.

(66) Boruntea, C.-R.; Sastre, G.; Lundegaard, L. F.; Corma, A.; Vennestrøm, P. N. R. Synthesis of High-Silica Erionite Driven by Computational Screening of Hypothetical Zeolites. *Chem. Mater.* 2019, *31* (22), 9268–9276. https://doi.org/10.1021/acs.chemmater.9b01229.

(67) Xie, D.; Chen, C.-Y. Synthesis of Aluminosilicate Zeolite SSZ-98. US 2016/0375428, 2016.

(68) Xie, D.; Zones, S.; Lew, C.; Davis, T. Molecular Sieve SSZ-98. US9,409,786 B2, 2016.

(69) Zones, S. I.; Van Nordstrand, R. A. Novel Zeolite Transformations: The Template-Mediated Conversion of Cubic P Zeolite to SSZ-13. *Zeolites* **1988**, *8* (3), 166–174. https://doi.org/10.1016/S0144-2449(88)80302-6.

(70) Xie, D.; Lew, C. Method for Preparing Zeolite SSZ-98. US 9,663,379, 2017.

(71) Valyocsik, E.; Ballmoos, R. Synthesis of Crystalline SAPO-17. US 4,778,780, 1988.

(72) Chitac, R. G.; Bradley, J.; McNamara, N. D.; Mayoral, A.; Turrina, A.; Wright, P. A.
Designed Synthesis of STA-30: A Small-Pore Zeolite Catalyst with Topology Type SWY. *Chem. Mater.* 2021. https://doi.org/10.1021/acs.chemmater.1c01329.

(73) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; Schutter, C. T. D.; Murphy, W. J.; Ozubko, R. S.; Slack, D. A. CHEMICAL SHIFT DISPERSION DUE TO CRYSTALLOGRAPHIC INEQUIVALENCE AND IMPLICATIONS REGARDING THE INTERPRETATION OF THE HIGH-RESOLUTION 29Si MAS NMR SPECTRA OF ZEOLITES. *Chem. Lett.* **1984**, *13* (2), 163–166. https://doi.org/10.1246/cl.1984.163.

(74) Li, Z.; Navarro, M. T.; Martínez-Triguero, J.; Yu, J.; Corma, A. Synthesis of Nano-SSZ-13 and Its Application in the Reaction of Methanol to Olefins. *Catal. Sci. Technol.* 2016, 6 (15), 5856–5863. https://doi.org/10.1039/C6CY00433D.

(75) Chen, G.; Sun, Q.; Yu, J. Nanoseed-Assisted Synthesis of Nano-Sized SAPO-34 Zeolites
Using Morpholine as the Sole Template with Superior MTO Performance. *Chem. Commun.* 2017, 53 (100), 13328–13331. https://doi.org/10.1039/C7CC07508A.

(76) Di Iorio, J. R.; Gounder, R. Controlling the Isolation and Pairing of Aluminum in Chabazite
Zeolites Using Mixtures of Organic and Inorganic Structure-Directing Agents. *Chem. Mater.* 2016, 28 (7), 2236–2247. https://doi.org/10.1021/acs.chemmater.6b00181.

(77) Barras, J.; Klinowski, J.; McComb, D. W. 27Al and 29Si Solid-State NMR Studies of Dealuminated Mordenite. *J. Chem. Soc., Faraday Trans.* **1994**, *90* (24), 3719–3723. https://doi.org/10.1039/FT9949003719.

(78) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; Graham, J. D.; Ozubko, R. S.; Murphy, W. J.; Bothner-By, A.; Dadok, J.; Chesnick, A. S. Detailed Interpretation of the 29Si and 27Al High-Field MAS n.m.r. Spectra of Zeolites Offretite and Omega. *Zeolites* **1985**, *5* (3), 179–183. https://doi.org/10.1016/0144-2449(85)90027-2.

(79) Gounder, R.; Davis, M. E. Beyond Shape Selective Catalysis with Zeolites: Hydrophobic
Void Spaces in Zeolites Enable Catalysis in Liquid Water. *AIChE Journal* 2013, *59* (9), 3349–
3358. https://doi.org/10.1002/aic.14016.

(80) Zhu, X.; Kosinov, N.; Hofmann, J. P.; Mezari, B.; Qian, Q.; Rohling, R.; Weckhuysen, B.
M.; Ruiz-Martínez, J.; Hensen, E. J. M. Fluoride-Assisted Synthesis of Bimodal Microporous SSZ-13 Zeolite. *Chem. Commun.* 2016, *52* (15), 3227–3230. https://doi.org/10.1039/C6CC00201C.

(81) Zibrowius, B.; Löffler, E.; Hunger, M. Multinuclear MAS n.m.r. and i.r. Spectroscopic Study of Silicon Incorporation into SAPO-5, SAPO-31, and SAPO-34 Molecular Sieves. *Zeolites* 1992, *12* (2), 167–174. https://doi.org/10.1016/0144-2449(92)90079-5.

(82) Sastre, G.; Lewis, D. W.; Catlow, C. R. A. Modeling of Silicon Substitution in SAPO-5 and SAPO-34 Molecular Sieves. *J. Phys. Chem. B* 1997, *101* (27), 5249–5262.
https://doi.org/10.1021/jp963736k.

(83) Lusardi, M.; Chen, T. T.; Kale, M.; Kang, J. H.; Neurock, M.; Davis, M. E. Carbonylation of Dimethyl Ether to Methyl Acetate over SSZ-13. *ACS Catal.* **2020**, *10* (1), 842–851. https://doi.org/10.1021/acscatal.9b04307.

(84) Xu, Z.; Ma, H.; Huang, Y.; Qian, W.; Zhang, H.; Ying, W. Synthesis of Submicron SSZ-13 with Tunable Acidity by the Seed-Assisted Method and Its Performance and Coking Behavior in the MTO Reaction. *ACS Omega* 2020, *5* (38), 24574–24583. https://doi.org/10.1021/acsomega.0c03075.

(85) Hwang, A.; Johnson, B. A.; Bhan, A. Mechanistic Study of Methylbenzene Dealkylation in Methanol-to-Olefins Catalysis on HSAPO-34. *Journal of Catalysis* **2019**, *369*, 86–94. https://doi.org/10.1016/j.jcat.2018.10.022.

(86) Zhou, J.; Gao, M.; Zhang, J.; Liu, W.; Zhang, T.; Li, H.; Xu, Z.; Ye, M.; Liu, Z. Directed Transforming of Coke to Active Intermediates in Methanol-to-Olefins Catalyst to Boost Light Olefins Selectivity. *Nature Communications* **2021**, *12* (1), 17. https://doi.org/10.1038/s41467-020-20193-1.

Chapter 4 | Synthesis and Characterization of Silicoaluminophosphate CIT-16P and its Transformation to SAPO-17

Information contained in Chapter 4 was originally published in:

Alshafei, F. H.; Kang, J. H.; Cho, S. J.; Davis, M. E. Synthesis and Characterization of Silicoaluminophosphate CIT-16P and its Transformation to SAPO-17, *accepted (Inorganic Chemistry)*.

Abstract

A silicoaluminophosphate molecular sieve, CIT-16P, is synthesized using butane-1,4bis(quinuclidinium) $[(C_7H_{13}N)-(CH_2)_4-(NC_7H_{13})]^{2+}$ dihydroxide (DiQ-C₄-(OH)₂) as an organic structure-directing agent (OSDA). Upon the removal of the OSDA, either by thermal treatment in air at temperatures exceeding 490 °C or extended ozone treatment at 150 °C, CIT-16P transforms to SAPO-17 (ERI topology). The structure solution of CIT-16P in its as-synthesized form is obtained using a Rietveld refinement of the powder X-ray diffraction pattern. The primary composite building units (CBUs) of CIT-16P are highly distorted cancrinite (*can*) CBUs that transform into stable *can* units of the ERI-type framework as a result of the OSDA removal. The distortion of *can* CBU is maintained without transformation by the presence of tightly bound DiQ-C₄ dications in the as-synthesized form of CIT-16P. The transformed material is characterized and evaluated as a catalyst in the methanol-to-olefins (MTO) reaction. The catalytic behavior of the formed SAPO-17 (Si/T-atom=0.021) (T=Si+Al+P) at 400 °C and WHSV of 1.3 h⁻¹ produces elevated C₃₊ olefin products (i.e., propylene, butenes, and pentenes) in early stages of the reaction. However, as the reaction proceeds, the C₃₊ fraction decreases in favor of more ethylene.

4.1 Introduction

Zeolites and related molecular sieves are crystalline microporous materials composed of tetrahedral units (TO₄, where T = Si⁴⁺, Al³⁺, P⁵⁺, etc.) with pore systems usually smaller than 2 nanometers.¹ Among them are microporous crystal structures with intracrystalline channels defined by 8-membered-ring (8MR) pore apertures (limited by 8 T-atoms) that are conventionally denoted as 'small-pore' molecular sieves.² Only molecules and ions smaller than 8MR pores (typically, 3–5 Å), such as light olefins, can diffuse within the channel systems of this class of molecular sieves. The pioneering work on silicoaluminophosphate (SAPO)-type molecular sieves by Flanigen et al.³⁻⁴ in the 1980s and the commercialization of the methanol-to-olefins (MTO) process thereafter stimulated a wide array of research in synthetic small-pore molecular sieves.

Brønsted acid sites in SAPO-based molecular sieves are created by replacing P⁵⁺ with Si⁴⁺, resulting in materials with milder acidity than their zeolitic counterparts; thus, the rate of coke formation is effectively attenuated in hydrocarbon-related catalytic reactions such as in the MTO reaction.⁵ This advantage can then be combined with the ability of small-pore molecular sieves with cages to efficiently retain aromatic hydrocarbon pool intermediates (e.g., methylated benzenes), which act as primary catalytic intermediates for the MTO reaction, to produce product streams rich with small molecules (primarily light olefins). The most successful commercialized MTO catalyst is SAPO-34, having a chabazite (CHA) topology,⁵⁻⁶ which is isostructural to the synthetic zeolite, SSZ-13.⁷⁻⁸ While CHA-type structures have been one of the most investigated frameworks in MTO, various small-pore zeolites and AlPO₄-based molecular sieves belonging to other frameworks have also been studied, in an effort to establish correlations between cage structure/geometry and the olefins product distribution.⁹⁻¹² We previously reported that the olefin selectivities in the MTO reaction over small-pore, cage-type molecular sieves are predominantly

influenced by cage topology, and we demonstrated that by correlating the cage-defining ring (CDR), a new structural parameter, to the observed olefins product distribution.⁹

For decades, catalytic 'shape selectivity' in molecular sieves has been a key driver for the discovery of new zeolite structures. In fact, about 60 new molecular sieve structures out of 255 structures enlisted in the IZA database have been reported in the last ten years alone. Many of the newly discovered materials are AlPO₄-based molecular sieves,¹³ such as AlPO₄-91 (ANO), AlPO₄-78 (AVE), PST-14 (POR), and STA-20 (SWY). Compared to their zeolitic counterparts, structures of AlPO₄-based molecular sieves can be more challenging to analyze based on X-ray or electron-beam diffractometry techniques due to their structural instability or complex coordination behaviors of T-sites. For instance, the Al- or P-sites of the AlPO₄ framework can form extra coordination bonds with OH⁻/H₂O¹⁴ or occluded organic molecules.¹⁵⁻¹⁶ One such example that demonstrates this difficulty is an organic-AlPO₄ hybrid material, PST-5, which transforms to PST-6 (PSI) following the removal of the organic structure-directing agent (OSDA).¹⁴

Here, we demonstrate the synthesis of a new SAPO material (designated herein as CIT-16P, **Figure 4.1(a)**) that transforms into SAPO-17 (ERI) when the OSDA is removed. Diquinuclidinium-based diquats with C_3 - or C_4 - linkers (**Figure 4.1(b**)), which are OSDAs known to crystallize ERI-,¹⁷ AFX-,¹⁸ and SAT-type¹⁹ molecular sieves, crystallized CIT-16P, albeit in a very narrow range of synthesis parameters. As a result of the OSDA-removal, regardless of the method of organic removal, the structure of the inorganic framework of CIT-16P is transformed into SAPO-17. CIT-16P is structurally related to the recently reported highly disordered framework, ECNU-38P, which also forms ECNU-38, an ERI-type material, by removing its OSDA, 1,1,6,6-tetramethyl-1,6-diazacyclododecane-1,6-diium hydroxide (TDDH) (**Figure**
4.1(c)).²⁰ The major structural difference between CIT-16P and ECNU-38P lies in the coordination of the Al-sites. Unlike ECNU-38P, which has a small population of octahedral Al sites, it was revealed that CIT-16P possesses a significant proportion of pentacoordinate Al-sites that condense into tetrahedral sites after the removal of the OSDA cations. The structure solution of the assynthesized CIT-16P, including the atomic positions of the DiQ-C₄ OSDA molecules, demonstrate that the organic cations are tightly bound within vacancies of the inorganic framework of CIT-16P. A SAPO-17 catalyst derived from CIT-16P by thermal treatment shows a longer lifetime with a higher initial methanol conversion in the MTO reaction than ECNU-38 (ERI), likely due to the large crystal size (1–5 μ m) of the parent material.

4.2 Experimental

4.2.1 Chemicals and Materials

All chemicals were used as-received without further purification: quinuclidine (97%, Alfa Aesar), 1,3-dibromopropane (99%, Sigma-Aldrich), 1,4-dibromobutane (99%, Sigma-Aldrich), diethyl ether (98%, VWR), acetone (99.5%, Sigma-Aldrich), acetone (Fisher), methanol (99.9%, Sigma-Aldrich), DOWEXTM MonosphereTM 550A hydroxide ion-exchange resin (Dow Chemical), deuterium oxide (D, 99.9%, Cambridge Isotope Laboratories, Inc.), methanol-d4 (99 atom% D, Sigma-Aldrich), dichloromethane-d₂ (99.5 atom% D, Aldrich), ethanolamine (99.5%, Sigma-Aldrich), phosphoric acid (85%, MACRON), hydrated alumina (Reheis F2000), aluminum hydroxide gel (Barcroft 250, SPI Pharma), pseudobohemite (Catapal B, VISTA), aluminum hydroxide (Pfaltz and Bauer), fumed silica (Cab-O-Sil®, ACROS), and hydrofluoric acid (48 wt%, Sigma Aldrich). The moisture contents of the solid sources involved in synthesis were determined by temperature-gravimetric analysis (TGA).



Figure 4.1. Structure representations of CIT-16P and related OSDAs. (a) Natural tiling of the idealized CIT-16P structure refined in the space group $P6_322$. (b) DiQ-C₃ and DiQ-C₄ OSDAs for CIT-16P. (c) TDDH for ECNU-38P.

4.2.2 Synthesis of the OSDAs

4.2.2.1 Bisquinuclidium-butane (DiQ-C₄)

DiQ-C₄ was prepared from the reaction of quinuclidine and 1,4-dibromobutane. In a typical synthesis, quinuclidine (100 mmol) was mixed with 150 cm³ of methanol and stirred at room temperature for a few minutes. The solution was then heated to 45 °C in an oil bath. After reaching 45 °C, 1,4-dibromobutane (35 mmol) was added dropwise to the quinuclidine-containing solution while stirring. After adding 1,4-dibromobutane, the reaction mixture was heated to 80 °C and refluxed for 6 days. Methanol was then evaporated using a rotary evaporator, and the solid product was filtered and washed with copious amounts of methanol, diethyl ether, and acetone. Following this, the solid was dried under vacuum at room temperature for 6-8 h. The ¹³C nuclear magnetic resonance (NMR) spectrum of DiQ-C₄ OSDA in its bromide form is shown in **Figure A4.1**.

The OSDA was then converted to its hydroxide form, and its concentration was determined by titration. The OSDA above was first ion-exchanged into its hydroxide form by dissolving the organic salt in deionized (DI) water and then adding DOWEXTM MonosphereTM 550A hydroxide ion-exchange resin. Specifically, for every 100 mmol of OSDA in the halide form, approximately 300 cm³ (by volume) of resin and 500 cm³ of DI water were added. The mixture was then stirred for 24 h at room temperature. After 24 h, the resin was separated by filtration, and the process was repeated a second time. The concentration of the OSDA, now in the hydroxide form, was quantified using a Mettler Toledo DL22 Potentiometric pH meter. Five readings were taken for each OSDA concentration, and these values were then averaged and used for gel calculations.

4.2.2.1 Bisquinuclidium-propane (DiQ-C₃)

DiQ-C₃ was prepared similarly to the DiQ-C₄ OSDA outlined above, with the only difference being the solvent used. Instead of methanol, acetone was used as a solvent for the synthesis of DiQ-C₃. The ¹³C NMR spectrum of DiQ-C₃ OSDA in its bromide form is also shown in **Figure A4.1**.

4.2.3 Synthesis of SAPO CIT-16P

In this work, the following gel composition was examined for the synthesis of CIT-16Ptype molecular sieves: $0.02-1.2 \text{ SiO}_2 : 0.45-0.50 \text{ Al}_2\text{O}_3 : 0.45-0.47 \text{ P}_2\text{O}_5 : 0.18-0.40 \text{ R}(\text{OH})_2 : 30 50 \text{ H}_2\text{O}$, where R=DiQ-C₄ or DiQ-C₃. All CIT-16P materials were prepared in 23 cm³ stainless steel autoclaves with Teflon liners. In a typical synthesis, a desired amount of H₃PO₄ was mixed with an appropriate amount of water, and the mixture was stirred for 10 mins. Next, the aluminum source (typically, BarcroftTM 0250 dried aluminum hydroxide gel, SPI Pharma) was weighed separately and added to this mixture. This gel was allowed to homogenize for 3-4 hours before adding fumed silica. Following the addition of silica, the OSDA (DiQ-C₃ or DiQ-C₄) was added, and the gel was aged at room temperature for 20-24 hours before being heated to 180-200 °C in a rotating oven (55-60 rpm) at autogenous pressure for 1-4 days. A complete summary of the attempted synthesis conditions and the resultant products is outlined in the Supplementary Information (**Appendix C**).

The best crystallized CIT-16P materials were prepared using the following gel: 0.03-0.04 SiO₂: 0.47-0.50 Al₂O₃ (Barcroft): 0.45 P₂O₅: 0.27-0.29 DiQ-C₄-(OH)₂: 40 H₂O (190 °C, rotating, 1-3 days). Note that even slight deviations in the amounts of Al- or Si-sources, phosphoric acid, water, or DiQ-C₄ from the above gel led to the formation of impurities or co-crystallization of CIT-16P with other frameworks (e.g., AFX and SAT), as will be further discussed in the Results and Discussion Section. A pure-phase SAPO-17 sample was synthesized according to a method previously reported and used in this work as a reference ERI-type material.¹⁷

4.2.4 Characterization

Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku MiniFlex II instrument using Cu K α radiation ($\lambda = 1.54184$ Å) at a scan rate of 0.3-0.6 °/min to determine structure type and purity. Morphology and elemental composition were determined via scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) on a ZEISS 1550VP instrument equipped with an Oxford X-Max S.D.D. energy dispersive X-ray spectrometer. Atomic ratios (atomic %) were reported as Si/T-atom (where T=Si+Al+P). To determine micropore volume using the t-plot method and detect the presence of mesoporosity, N₂-adsorption/desorption experiments were performed on each sample at 77 K in a Quantachrome Autosorb iQ adsorption instrument using a constant-dose method. Prior to adsorption measurements, all thermally treated samples (SAPO-17) were outgassed at 60 °C for 0.5 h, followed by holds of 0.5 h at 120 °C and 6 h at 350 °C (all ramping rates were 1 °C/min). In physisorption experiments that were performed

on the CIT-16P material (prior to thermal treatment), this outgassing procedure was slightly modified to avoid an inadvertent in-situ structural transformation (from CIT-16P to ERI). As such, the maximum degassing temperature was lowered from 350 °C to 200 °C, and the hold time was increased from 6 h to 12 h. TGA measurements were performed on Perkin Elmer STA 6000. Assynthesized (prior to thermal treatment) or thermally treated samples (0.02-0.06 g) were placed in an alumina crucible and heated at 10 °C/min in a flowing stream (0.33 cm³/s) of air to various temperatures. In experiments where the transformation of CIT-16P to SAPO-17 was of interest, samples were first heated in TGA at a heating rate of 5 °C/min (unless otherwise noted) in a flowing stream (0.33 cm³/s) of air (zero grade). Once the target temperature was reached, this temperature was held for a desired time (e.g., 0, 2, 5, or 10 minutes). The sample was then rapidly quenched and analyzed via PXRD. Liquid ¹³C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. All liquid NMR analyses, involving OSDAs, were performed in deuterium oxide (D₂O) or deuterated methanol (CD₃OD).

All solid-state, magic-angle spinning (MAS) and cross-polarization (CP) MAS NMR spectroscopy experiments were conducted on a Bruker 500 MHz spectrometer and a Bruker 4 mm MAS probe. CPMAS NMR experiments were performed on the as-synthesized CIT-16P-type molecular sieve and on the SAPO-17-like (ERI) material that formed following the removal of the OSDA. ²⁹Si CPMAS NMR spectra were acquired at 99.3 MHz and at a spinning rate of 8 kHz and using a recycle delay time of 6 s and 2 s for as-synthesized and thermally treated samples, respectively. ²⁷Al MAS NMR spectra were acquired at 130.2 MHz and at a spin rate of 13 kHz, a $\pi/18$ pulse length of 0.5 µs, and a cycle delay time of 0.5 s. ³¹P MAS NMR spectra were acquired at 202.4 MHz at a spin rate of 12 kHz, a $\pi/2$ pulse length of 4 µs, and a cycle delay time of 1000 s (T1~ 200 s) for the as-synthesized material and 4 s for thermally-treated material. ¹³C solid-state

NMR spectra were acquired on the as-synthesized samples at 125.7 MHz at a spin rate of 8 kHz, a CP contact time of 0.5 ms, and a cycle delay time of 6 s.

4.2.5 Catalytic Testing

Catalyst evaluation was carried out in a fixed-bed reactor at ambient pressure. In a typical experiment, approximately 200 mg of dried catalyst (35-60 mesh size) was loaded between two layers of quartz wool in a $0.25^{"} \times 6^{"}$ stainless steel reactor as a part of a BTRS Jr. continuous flow reactor (Parker Autoclave Engineers). The dry weight of the catalyst was estimated on the basis of TGA. The catalyst was first pretreated by heating to 150 °C at 1 °C/min, held for 3 hours, and then heated further to 580 °C at 1 °C/min and held for 12 h under flowing air (breathing-grade D, AirGas). Methanol was introduced via a liquid syringe pump (Harvard Apparatus Pump 11 Elite) at 4.0-5.0 µL/min into a gas stream of an inert blend (95% He and 5% Ar; G.C. internal standard) at a volumetric flow rate of 30 cm³/min. The methanol flow rate was adjusted, depending on the actual weight of the dried catalyst loaded in the reactor, to achieve a weight hourly space velocity (WHSV) of 1.3 h⁻¹. The reaction was performed at a WHSV of 1.3 h⁻¹ and a temperature of 400 °C. Effluent gases were evaluated using an on-stream Agilent GC-MS (gas chromatography – mass spectrometry; G.C. 6890N/MSD5793N) equipped with a Plot-Q capillary column. Aliquots of product flow were analyzed every 16 minutes. All selectivity values were calculated on a carbonnumber basis.

4.3 Results and Discussion

4.3.1 Synthesis

CIT-16P was first obtained as an impurity phase during the synthesis of SAPO-17 (ERI) using a gel composition of $0.1 \text{ SiO}_2 : 0.50 \text{ Al}_2\text{O}_3$ (Barcroft) $: 0.45 \text{ P}_2\text{O}_5 : 0.27 \text{ DiQ-C}_3\text{-}(\text{OH})_2 : 40 \text{ H}_2\text{O}$ and crystallization conditions of 190 °C for 72 h. Subsequently, it was found that the phase

associated with CIT-16P could be enhanced by altering the OSDA concentration and the silicon content (**Table A4.1** and **Figure A4.2**). Specifically, it was observed that the CIT-16P phase dominates the product when the OSDA concentration was in the range of 0.24-0.27 and the silicon content was low (0.06). Further increasing the OSDA or decreasing it outside of the aforementioned range led to the formation of ERI. In all our experiments with DiQ-C₃, ERI competitively formed either as the primary or secondary phase, which prompted us to consider a longer molecule, DiQ-C₄, in an attempt to suppress (or eliminate) the formation of ERI. The synthesis results and corresponding PXRD patterns are summarized in **Table A4.1** and **Figure A4.2** in the Supporting Information (**Appendix C**).

We performed a more thorough study on the DiQ-C₄ system as shown in **Table A4.2** and **Figure A4.3**, which showed more promise for the synthesis of CIT-16P. The gel compositions within the range of x (0.02-0.12) SiO₂ : y (0.45-0.50) Al₂O₃ : z (0.45-0.47) P₂O₅ : w (0.27-0.40) R(OH)₂ : 30-50 H₂O at 180–200 °C were tested to crystallize CIT-16P. As mentioned above, similar to the DiQ-C₃ system, the DiQ-C₄ OSDA crystallized a high-crystallinity CIT-16P phases within a narrow range of gel Si and OSDA contents, preferably x = 0.02-0.04 and w = 0.27-0.29 at 190 °C, respectively. The DiQ-C₄ system also featured the co-crystallization of other competing phases (e.g., AFX and SAT with longer or wider ABC-6 cages than ERI) in many tested conditions. These results suggest that the chain length of the diquaternary OSDA impacts the cage size of the impurity phases in the AIPO₄ system, as indicated by previous studies.^{18, 21} Through examining a wide range of conditions, we were able to eliminate the majority of the AFX and SAT phases, and identify a small region of synthesis parameters where CIT-16P forms either as a pure material or a nearly pure material (95+% CIT-16P; abbreviated as "vs" in Table A4.2 to indicate that the impurity phase is very small).

4.3.2 Characterization of CIT-16P

For the purpose of illustrating the characterization of CIT-16P, we selected the material that formed from Entry S50 in **Table A4.2**. While we did form other CIT-16P materials that had a higher degree of purity, this material exhibited a high degree of crystallinity, low Al-rich phases (due to the lower P/Al ratio in the gel), and relatively high silicon content (i.e., higher acid site density), which aided the MTO testing.

The CIT-16P (Entry S50 in Table A4.2) sample was characterized using a number of techniques, before and after thermal treatment, and the results of these analyses are shown in Figure 4.2. The PXRD profiles of the as-synthesized CIT-16P sample and that after the thermal treatment were compared to a reference SAPO-17 (ERI) (Figure 4.2(a)). The X-ray powder diffraction pattern of CIT-16P was partly consistent with that of ECNU-38P²⁰, supporting that the two organic-AlPO₄ hybrid materials are nearly isostructural except for the occluded OSDA. The diffraction peaks of CIT-16P were indexed on the basis of the structure solution from the Rietveld refinement (vide infra). It was confirmed that the structure of DiQ-C₄ OSDA molecules remain unchanged within the as-synthesized CIT-16P as shown in the ¹³C NMR spectrum (Figure A4.4). As a result of the elimination of the OSDA, CIT-16P was completely transformed into an ERI phase with a powder diffraction pattern that is perfectly consistent with the reference SAPO-17 that was prepared by direct synthesis. The 2-theta position of the (100) diffraction peak was shifted from 8.30° to 8.00° , while that of the (002) reflection was shifted from 10.42° to 12.06° , before and after the thermal treatment of as-synthesized CIT-16P, respectively. These shifts indicate that the hexagonal unit cell was stretched along the *a*-axis and contracted along the *c*-axis, as a result of the transformation from CIT-16P to SAPO-17, corresponding to ca. 22% reduction in the unit cell volume.

SEM analysis demonstrates that CIT-16P has a morphology vastly different from that of ECNU-38P, presumably due to the differences in the OSDA and crystallization conditions. The DiQ-C₄ OSDA for CIT-16P crystallized much larger crystals than the 1,1,6,6-tetramethyl-1,6-diazacyclododecane-1,6-diium (TDDH) OSDA for ECNU-38P.²⁰ A typical CIT-16P sample had crystal sizes of 1–5 μ m and a bullet-like or a rice-grain-like morphology, as seen in the scanning electron micrographs (**Figure 4.2(c)**). This morphology of CIT-16P crystals resembles that of UZM-12 zeolite²² having an ERI crystal structure despite the compositional difference between zeolites and SAPOs. AFX, the primary impurity phase usually encountered in a typical CIT-16P synthesis, has a planar morphology¹⁹ that is distinguishable from CIT-16P (see the Supplementary Information (**Appendix C**), **Figure 44.5(a–c**)).

The TGA profile of CIT-16P in its as-synthesized form (**Figure 4.2(d**)) showed a continuous mass loss curve extending from 25 °C to 500 °C. Due to the continuous nature of the mass loss curve, it was difficult to distinguish between the contribution of water loss and that of OSDA decomposition in this range. By 700 °C, approximately 26 percent of the total mass was lost. Considering the crystal structure revealed by the X-ray diffractometry analysis (*vide infra*), the ideal unit cell formula of as-synthesized CIT-16P assuming a full occupancy of OSDA is $Al_{18}P_{18}O_{72}[(DiQ-C4)^{2+}(OH)_2]$, which corresponds to 22.2% of OSDA content. The TG result indicated that the extra mass loss (26 compared to 22.2) is likely due to physically adsorbed moisture and/or the structural condensation of the framework.



Figure 4.2. Characterization of the as-synthesized and thermally treated CIT-16P samples (Entry S50 in **Table A4.2**). (a) PXRD patterns of as-synthesized and thermally treated CIT-16P compared to the reference SAPO-17. (b, c) SEM image of thermally treated and as-synthesized CIT-16P samples, respectively. (d) Thermogravimetric profile of CIT-16P.

The coordinations of Al, P, and Si in the as-synthesized CIT-16P and resultant SAPO-17 materials were investigated by solid-state CPMAS NMR spectroscopy (Figure 4.3(a-c)). Assynthesized CIT-16P showed two broad signals in its ²⁷Al MAS NMR spectrum at 41.5 ppm and 7.3 ppm that can be attributed to tetrahedral and pentacoordinated Al species, respectively.^{14, 16, 23-} ²⁴ The 7.3 ppm ²⁷Al signal survived cycles of extensive ethanolamine washing steps (Figure A4.6), suggesting that this signal is unlikely from extracrystalline Al-containing species, but rather from Al sites bound within the framework. The population of these non-tetrahedral Al sites is significant in the framework of CIT-16P.²⁵ This 7.3-ppm ²⁷Al resonance was not observed in the previously reported ECNU-38P sample²⁰, presumably due to different hydroxide-framework interactions. Unlike ECNU-38P, CIT-16P showed no small octahedral Al signal in the region from -20 to 0 ppm. However, this could be due to differences in the amount of hydration between the two materials. After thermal treatment, this 7.3-ppm²⁷Al resonance disappears. The resultant²⁷Al spectrum of the thermally treated CIT-16P sample was compatible with those of dehydrated SAPO-17.^{20, 24} Therefore, the 7.3-ppm peak is likely the result of extra-coordination of the Al site, which has been confirmed by the structural analysis based on the Rietveld powder pattern refinement of as-synthesized CIT-16P. The ²⁷Al NMR measurements on the hydration-rehydration cycle study outlined in the Supplemental Section after thermal treatment further confirms that the 7.3-ppm 27 Al signal originates from Al-sites coordinated to intracrystalline H₂O or OH (**Figure** A4.7).

The ³¹P MAS NMR spectrum of as-synthesized CIT-16P showed two groups of signals in the regions of -9 to -14 ppm and -20 to -30 ppm, the former, which disappear after thermal treatment, suggests the presence of partially OH-coordinated P-sites.¹⁴ The thermally treated CIT-16P showed only two resonances at -29.1 and -34.7 ppm in the ³¹P NMR spectrum, which is consistent with tetrahedrally connected and dehydrated AlPO₄- or SAPO-17 results.^{20, 24} The single resonance (**Figure 4.3(c)**) in the ²⁹Si CPMAS NMR spectrum at ca. -90 ppm indicates that the Sisites in the SAPO frameworks of the as-synthesized and thermally treated samples are isolated acid sites (P substitution by Si).



Figure 4.3. Multinuclear solid-state NMR results of CIT-16P (bottom) and its thermally treated form, SAPO-17 (top) :(a) ²⁷Al MAS, (b) ³¹P MAS, and (c) ¹H-²⁹Si CPMAS spectra.

4.3.3 Transformation of CIT-16P to SAPO-17 (ERI)

CIT-16P transforms to SAPO-17 (ERI) upon thermal treatment in air at 580 °C. Based on results from a separate ex-situ heating experiment using a TG instrument when taken together with data from powder X-ray diffractometry, it was discovered that the beginning of the CIT-16P-to-SAPO-17 transformation occurs at ca. 500 °C. (**Figures 4.4(a–b)**). By using a finer temperature increment, it was observed that the transformation of as-synthesized CIT-16P to SAPO-17 took approximately five minutes at 495 °C (**Figure A4.8**). As shown by the data in **Figure 4.2(d)**, at this temperature (about 500 °C), a large weight loss was observed. The temperature at which the onset of the steepest mass drop (as determined by TGA) that is observed is higher in the case of CIT-16P than ECNU-38P (< 450 °C).²⁰ It is worthy to note that the temperature of mass loss is not

solely determined by the type of OSDA. The same DiQ-C₄, for example, showed a lower decomposition temperature if the frameworks were AFX and SAT (**Figure A4.9**).



Figure 4.4. Characterizations of the transformation of CIT-16P to SAPO-17 induced by the removal of the OSDA. (a–b) PXRD profiles of CIT-16P samples after ex-situ heating to elevated temperatures (300–700 °C) displayed in the ranges of (a) 4–40° and (b) 6–9°. (c–d) PXRD profile of a CIT-16P sample before and after the 4-week ozone treatment displayed in the ranges of (c) 4–40° and (d) 6–9°. (e) N₂-adsorption-desorption isotherms of the ozone treated CIT-16P sample (Entry S50) compared to the thermally treated one. Treatment time was varied: 72 hours, 2 weeks, and 4 weeks.

The removal of OSDA was also attempted by treating the as-synthesized CIT-16P with an ozone flow (26–45 μ g O₃/cc O₂) at 150 °C in order to isolate the inorganic structure at a lower temperature. In the case of a large-pore GME-type CIT-9, one day (24 hours) of ozone treatment at 150 °C was sufficient to remove most of the occluded organics.²⁶ Isolating the inorganic framework in CIT-16P, on the other hand, failed even after a prolonged ozone treatment (1-2 weeks) at the same conditions (26 g O₃/cc O₂ at 150 °C). The micropore volume measured after 2 weeks of ozone treatment was only 0.037 cc/g (**Figure 4.4(e)**). After a 4-week of intensive ozone treatment with an increased ozone level (45 g O₃/cc O₂ at 150 °C), the organics were mostly eliminated, but the framework completely changed, transforming to SAPO-17, despite ca. 4.8 % of DiQ-C₄ OSDA surviving this long treatment, as shown by the data in **Figure 4.4(c–d)** and **Figure 4.4.10** in the Supporting Information (**Appendix C**). These results support the notion that the presence of OSDA is essential to the conservation of the inorganic framework of CIT-16P.

The aforementioned OSDA removal experiments at various oxidizing conditions and temperatures suggest that the inorganic framework of CIT-16P has a high lattice energy that can initiate the transformation once the OSDA is removed. Calculations were performed on the lattice energies of ERI and CIT-16P frameworks to estimate the lattice energy change associated with the transformation. According to the lattice-energy calculation using GULP (the General Utility Lattice Program Version 6) with the two force fields, *Catlaw* and *Reaxff*,²⁷ the transition from CIT-16P to SAPO-17 (ERI) stabilizes the lattice by -0.13 eV per T-atom, which is corresponds to -12.5 kJ·(mol T)⁻¹. This difference in lattice energy is significant when compared to the values obtained using the same GULP algorithm-based approach for other transformations such as *CTH-to-CFI, which corresponds to -3.56 kJ·(mol T)⁻¹.²⁸ We also performed the lattice energy calculation using the *Quantum Espresso Program suite*, ab-initio density functional theory (DFT) package in which

the projector augmented wave pseudopotentials (PAW) is utilized with the *PBEsol GGA* functional, and the resulting value for the lattice energy difference was comparable. The details of DFT calculation can be found in the Supporting Information (**Appendix C**). These results are summarized in **Table A4.3**.



Figure 4.5. Structure refinement of CIT-16P. (a) Dual-phase refinement for the main-phase CIT-16P and the AFX impurity. (b) Electron density map of the OSDA occluded within the CIT-16P cavities. (c) Idealized structure of CIT-16P occluded with DiQ-C₄ OSDA dications.

4.3.4 Structure Solution of CIT-16P

The structure solution of the as-synthesized CIT-16P was obtained from a powder diffraction method employing powder charge flipping algorithm (pCF). The high-resolution diffraction patterns of CIT-16P for the Rietveld refinement (Figure A4.11) was measured from a synchrotron radiation source at Pohang Accelerator Laboratory (PAL), Pohang, South Korea. The CIT-16P sample had a small amount of AFX impurity that was also identified based on the diffraction pattern acquired from the in-house X-ray diffractometer as well as SEM analysis. Although the amount of AFX impurity was small, the preliminary attempts for structural solutions using FOCUS and pCF failed due to the presence of impurity peaks which interfered with the correct partitioning of the PXRD peaks. The contribution of CIT-16P and AFX phases in the acquired diffraction patterns was analyzed based on a structureless refinement (Le Bail analysis), and the information from this analysis was used to solve for the structure solution of CIT-16P. Initially, each phase was identified by iterative indexing, using the *Dicvol06* indexing program implemented in the *Fullprof* program suite.²⁹ Subsequently, the structureless refinement of each phase was successfully performed employing Jana2006 program suite.³⁰ CIT-16P and AFX phases were refined in the $P6_3$ and $P\overline{6}2c$ space groups first, respectively. The structureless analysis of the resultant PXRD patterns resulted in reasonably acceptable R factors ($R_p = 0.0485$, $R_{wp} = 0.0728$, and $R_{exp} = 0.0829$). Finally, to obtain the electron density map from each PXRD pattern, the charge flipping method³¹ was employed for the structural solution.



Figure 4.6. Specification of DiQ-C₄ OSDA locations from refinement. Electron density maps of DiQ-C₄ OSDA molecules within inorganic frameworks of (a) CIT-16P and (b) AFX. (c) Isopycnic surfaces at different electron densities (2, 3, and 4 e^- Å⁻³) of as-synthesized CIT-16P with the occluded OSDA molecules.

The configuration of the DiQ-C₄ OSDA molecules within the pore system of CIT-16P phase were determined by utilizing the parallel templating method in which the previously obtained framework was considered as a rigid body and the flexible OSDA molecule was placed in the pore randomly.³²⁻³⁵ The same procedure was also used to identify the configuration of the organic molecules within the AFX phase, the major impurity. The Rietveld refinements on assynthesized CIT-16P with a small amount of AFX impurity were performed successfully in the space group of *P*3 for CIT-16P (**Figure 4.5**). The list of atomic locations, the lattice parameters of as-synthesized CIT-16P, and related refinement results are given in **Tables A4.4–4.7**. The electron density distribution of the OSDA molecules within the pores of CIT-16P was obtained based on the difference Fourier method (**Figure 4.6**). The 3D contour maps reveal the locations of atoms of

the OSDA molecules. The uncertainty in the positions of the OSDA atoms within CIT-16P (**Figure 4.6(a**)) were smaller than that within AFX (**Figure 4.6(b**)), which indicates that the OSDA cations are more tightly bound to the framework walls in CIT-16P. This strong interaction between OSDA molecules and framework may be one reason for the difficulty of removing the OSDA from assynthesized CIT-16P. The stabilization energy of the OSDA within the CIT-16P framework was estimated and summarized in **Table A4.8**. The visualizations of surfaces of equal electron density (**Figure 4.6(c**)) show well-defined positions of carbon atoms of the quinuclidinium end groups that make up the CIT-16P OSDA.

The framework structure of CIT-16P is closely related to that of ERI, which is the final product of the transformation. CIT-16P is composed of a "pre-can" composite building unit (CBU) of a high-strain that transforms into a *can* unit of ERI as a result of the OSDA removal (Figure **4.7(a)**). A can CBU is composed of 18 T-atoms of three layers that forms the ABA stacking sequence. In **Figure 4.7(b**), the top (A), middle (B), and bottom (A) layers are visualized in purple, blue and green colors, respectively. Within the *pre-can* unit of CIT-16P, the top-layer T-atoms are directly connected to the bottom-layer T-atoms via T-O-T (Al5-O16-P6) bridges, which may engender a "stress" within the framework. As a result, the connected T-sites (Al5 and P6) have O-T-O angles that highly deviate from the tetrahedral angle (109.5°) (Figure A4.12). Furthermore, an extra electron density was observed on the middle of the *pre-can* cage of CIT-16P, which is identified as an extra oxygen site (O26) in the refined structure (Figure 4.7(c)). This oxygen site forms an extra coordination to the closest Al site (Al5), which is likely the origin of the pentacoordinated Al-sites observed at 7.3 ppm in the ²⁷Al NMR spectrum of as-synthesized CIT-16P. The strain generated by the direct connection of the top and bottom layers could be partially stabilized by this extra coordination. The high potential energy of this structural unit is supported

by the presence of OSDA molecules within "*pre-eri cages*" surrounding *pre-can* units. In this respect, the transformation of CIT-16P into SAPO-17 can be understood as a rearrangement of T-O-T bonds, which forms a stable *can* unit, triggered by the removal of the OSDA.



Figure 4.7. Visualized structural characteristics of CIT-16P reproduced from the binary structure refinement result of CIT-16P and impurity AFX. (a) Wireframe side-views of visualizations of CIT-16P (left) compared to SAPO-17 (ERI) (right). (b) Side-views of a pre-can and a can CBU. The top A, middle B, and bottom A layers are denoted in purple, blue, and green colors, respectively. The oxygen site (O16) that directly connects the top and bottom layers is highlighted. (c) A top view of a pre-can CBU of CIT-16P revealing the position of the oxygen site (O26) that forms pentacoordinated Al-sites. (d) A perspective view that shows the highly-strained T-sites (Al5 and P6) of CIT-16P.

4.3.5 MTO Reaction

Some of us have investigated the MTO behavior of several ERI-type molecular sieves (e.g., ERI-type zeolites, SSZ-98, UZM-12, and SAPO-17).^{9-10, 17} We demonstrated that ERI-type zeolites give improved ethylene-to-propylene ratios (E/P=1.1-1.9) over CHA-based materials such as SSZ-13 and SAPO-34. On the other hand, SAPO-ERI samples (i.e., SAPO-17) produced an E/P of 0.7-1.1 and a generally high C_{4+} fraction. The differences observed in the olefins product distributions between the zeolites with low framework Si/Al and SAPO-17 with low Si/T-atom ratio were the result of slower maturation of aromatic hydrocarbon-pool (HP) species and the presence of aromatics with bulky alkyl-groups (C₃–C₄) in the SAPO-17 materials with low acid site densities.

The SAPO-17 sample that formed from the transformation of CIT-16P (Entry S50) via thermal treatment in air has a Si/T-atom of 0.022 (as determined by EDS). This is a fairly low Si/T value, and is indeed lower than the lowest value/material we tested in our previous work (SAPO-17-1, with a Si/T=0.034).¹⁷ **Figure 4.8** shows the MTO behavior of the SAPO-17 sample obtained from the thermal treatment of CIT-16P (Entry S50). The MTO reaction was conducted at 400 °C and a methanol WHSV of 1.3 h⁻¹, as described in the Experimental Section.

We observe from the reaction data that the thermally treated CIT-16P catalyst behaves similarly to the various low silicon content SAPO-17 catalysts we synthesized in our prior work. Specifically, the thermally treated CIT-16P material achieves 100% methanol conversion and forms primarily C_{3+} at the early stages of the reaction. However, as the reaction proceeds, the ethylene selectivity improves at the expense of the C_{3+} fraction.¹⁷ The averaged ethylene, propylene, and C_4 selectivities achieved on this catalyst when methanol conversion is greater than 97% are 21%, 33%, and 15.2%, respectively. These numbers lead to an E/P of about 0.66, which is slightly lower than the E/P achieved by SAPO-17-1 (Si/T=0.034; E/P=0.7) in our previous work.¹⁷ The MTO reaction result from SAPO-17 derived from CIT-16P was compared to several SAPO-17 samples having various Si/T ratios in **Table A4.9**. TGA experiments on the coked SAPO-17 sample derived from CIT-16P reveal that the coke content (determined in the temperature range of 300 to 850 °C) is approximately 11.2%.



Figure 4.8. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for SAPO-17 that forms following the transformation of CIT-16P (Entry S50).

Because the SAPO-17 catalyst derived from CIT-16P has larger crystal sizes (in the low micron range) than the nanosized ECNU-38 material reported by Wu et al.,²⁰ it has a better MTO activity and an extended lifetime. Indeed, ERI-type catalysts that appear to have crystal sizes (<100 nm) deactivate rather rapidly due to the fast buildup of external coke, as was previously observed on nanosized UZM-12 materials,²² nanosized ECNU-38,²⁰ and also nanosized ERI-type zeolites in our prior work (ERI-Zeolite-3).¹⁷ In spite of the improved lifetime that we are able to achieve

here by forming CIT-16P materials with crystal sizes that are more suitable for MTO than ECNU-38, the inherent low silicon content requirement for forming 'pure' CIT-16P invariably leads to the formation of ERI-SAPO materials with low acid site densities. This property leads the catalytic material to form low E/P, in agreement with our previous observations and trends on ERI-type materials.

4.4 Conclusion

CIT-16P, a SAPO framework that is stabilized by the presence of quinuclidinium-based diquat OSDAs, was synthesized and characterized. CIT-16P was crystallized using two OSDA systems, DiQ-C₃ and DiQ-C₄, within narrow ranges of synthetic parameters. CIT-16P transformed into SAPO-17, similarly to the recently reported case of ECNU-38P that was synthesized from TDDH. The onset temperature of the transformation of as-synthesized CIT-16P was 490–500 °C, which corresponds to the OSDA decomposition temperature as determined via TG analysis. The CIT-16P structure was also transformed to SAPO-17 as a result of the OSDA removal following an extensive ozone-treatment at a low temperature (150 °C). These observations indicated that the inorganic structure of CIT-16P was preserved without transformation by the presence of the organic cations.

The structure solution of as-synthesized CIT-16P was obtained from the Rietveld refinement of high-resolution PXRD pattern. The repeating building unit for the inorganic framework structure of CIT-16P was highly distorted *can* units, where the top and bottom T-sites are directly connected by T-O-T bonds. This distortion in connectivity of T-sites present within the *can* units was manifested by the pentacoordination of Al-sites of as-synthesized CIT-16P that was revealed in the ²⁷Al MAS NMR spectrum. The positions of DiQ-C₄ OSDA cations were also determined based on the different Fourier method. The inorganic framework of CIT-16P fixes the

atomic positions of the OSDA molecules in a tighter manner than that of the AFX phase, which is the major impurity phase encountered during the synthesis of CIT-16P. A thermally treated CIT-16P sample having Si/T = 0.022 showed an MTO behavior that is similar to that of SAPO-17 materials having a low Si content. Due to the crystal size of CIT-16P, which was larger than that of nanocrystalline ECNU-38P, the resultant SAPO-17 catalyst derived from CIT-16 showed longer lifetime and higher initial methanol conversion than that of ECNU-38 (ERI).

4.5 Acknowledgements

This work was supported by the New Faculty Startup Fund from Seoul National University (Grant Number 0668-20200245). The Chevron Energy and Technology Company also provided financial support for this research. The authors gratefully acknowledge Dr. Sonjong Hwang for assistance with solid-state NMR, and Dr. Stacey Zones and Dr. Dan Xie for valuable technical discussions. FHA would like to thank Aramco R&D for financially supporting his graduate studies. The authors acknowledge the Pohang Accelerator Laboratory (PAL) for beamline use. High resolution powder diffraction experiments at PAL were supported by the Ministry of Science & ICT, Republic of Korea.

4.6 References

Davis, M. E., Ordered porous materials for emerging applications, *Nature* 2002, *417*, 813-821.

(2) Dusselier, M.; Davis, M. E., Small-Pore Zeolites: Synthesis and Catalysis, *Chem. Rev.* **2018**, *118*, 5265-5329.

(3) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M., Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids, *J. Am. Chem. Soc.* **1982**, *104*, 1146-1147.

(4) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M., Silicoaluminophosphate molecular sieves: another new class of microporous crystalline inorganic solids, *J. Am. Chem. Soc.* **1984**, *106*, 6092-6093.

(5) Tian, P.; Wei, Y.; Ye, M.; Liu, Z., Methanol to Olefins (MTO): From Fundamentals to Commercialization, *ACS Catal.* **2015**, *5*, 1922-1938.

(6) Dahl, I. M.; Kolboe, S., On the reaction mechanism for propene formation in the MTO reaction over SAPO-34, *Catal. Lett.* **1993**, *20*, 329-336.

(7) Zones, S. I. Zeolite SSZ-13 and its method of preparation, US Patent 4,544,538. 1985.

(8) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E.,
Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction, *ACS Catal.*2016, *6*, 542-550.

(9) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E., Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction, *ACS Catal.* **2019**, *9*, 6012-6019.

(10) Kang, J. H.; Walter, R.; Xie, D.; Davis, T.; Chen, C.-Y.; Davis, M. E.; Zones, S. I., Further Studies on How the Nature of Zeolite Cavities That Are Bounded by Small Pores Influences the Conversion of Methanol to Light Olefins, *ChemPhysChem* **2017**, *19*, 412-419.

(11) Pinilla-Herrero, I.; Olsbye, U.; Márquez-Álvarez, C.; Sastre, E., Effect of framework topology of SAPO catalysts on selectivity and deactivation profile in the methanol-to-olefins reaction, *J. Catal.* **2017**, *352*, 191-207.

(12) Pinilla-Herrero, I.; Márquez-Álvarez, C.; Sastre, E., Complex relationship between SAPO framework topology, content and distribution of Si and catalytic behaviour in the MTO reaction, *Catal. Sci. Technol.* **2017**, *7*, 3892-3901.

(13) International Zeolite Association Structure Database (http://america.iza-structure.org/IZA-SC).

(14) Chang, S.; Jang, H.-G.; Lee, K.-Y.; Cho, S. J., Three-dimensional crystal structure of novel aluminophosphate PST-5 solved using a powder charge flipping method, *RSC Adv.* **2017**, *7*, 38631-38638.

(15) Lee, J. K.; Lee, J. H.; Ahn, N. H.; Cho, K. H.; Hong, S. B., Solid solution of a zeolite and a framework-bound OSDA-containing molecular sieve, *Chem. Sci.* **2016**, *7*, 5805-5814.

(16) Lee, J. K.; Shin, J.; Ahn, N. H.; Turrina, A.; Park, M. B.; Byun, Y.; Cho, S. J.; Wright, P. A.; Hong, S. B., A Family of Molecular Sieves Containing Framework-Bound Organic Structure-Directing Agents, *Angew. Chem. Int. Ed.* 2015, *54*, 11097-11101.

(17) Alshafei, F. H.; Park, Y.; Zones, S. I.; Davis, M. E., Methanol-to-olefins catalysis on ERItype molecular sieves: towards enhancing ethylene selectivity, *J. Catal.* **2021**, *404*, 620-633.

(18) Castro, M.; Seymour, V. R.; Carnevale, D.; Griffin, J. M.; Ashbrook, S. E.; Wright, P. A.; Apperley, D. C.; Parker, J. E.; Thompson, S. P.; Fecant, A.; Bats, N., Molecular Modeling, Multinuclear NMR, and Diffraction Studies in the Templated Synthesis and Characterization of the Aluminophosphate Molecular Sieve STA-2, *J. Phys. Chem. C* **2010**, *114*, 12698-12710.

(19) W. Noble, G.; A. Wright, P.; Kvick, Å., The templated synthesis and structure determination by synchrotron microcrystal diffraction of the novel small pore magnesium aluminophosphate STA-2, *J. Chem. Soc. Dalton. Trans.* **1997**, 4485-4490.

(20) Duan, Z.; Wang, N.; Xu, H.; Wu, P., Structural Transformation-Involved Synthesis of Nanosized ERI-Type Zeolite and Its Catalytic Property in the MTO Reaction, *Inorg. Chem.* 2022, *61*, 8066-8075. (21) Turrina, A.; Garcia, R.; Watts, A. E.; Greer, H. F.; Bradley, J.; Zhou, W.; Cox, P. A.; Shannon, M. D.; Mayoral, A.; Casci, J. L.; Wright, P. A., STA-20: An ABC-6 Zeotype Structure Prepared by Co-Templating and Solved via a Hypothetical Structure Database and STEM-ADF Imaging, *Chem. Mater.* **2017**, *29*, 2180-2190.

(22) Lee, J. H.; Park, M. B.; Lee, J. K.; Min, H.-K.; Song, M. K.; Hong, S. B., Synthesis and Characterization of ERI-Type UZM-12 Zeolites and Their Methanol-to-Olefin Performance, *J. Am. Chem. Soc.* **2010**, *132*, 12971-12982.

(23) Egan, J. M.; Wenslow, R. M.; Mueller, K. T., Mapping aluminum/phosphorus connectivities in aluminophosphate glasses, *J. Non-Cryst. Solids* **2000**, *261*, 115-126.

(24) Zibrowius, B.; Lohse, U., Multinuclear MAS NMR study of the microporous aluminophosphate AlPO4-17 and the related silicoaluminophosphate SAPO-17, *Solid State NMR* **1992**, *1*, 137-148.

(25) Fenzke, D.; Freude, D.; Fröhlich, T.; Haase, J., NMR intensity measurements of halfinteger quadrupole nuclei, *Chem. Phys. Lett.* **1984**, *111*, 171-175.

(26) Dusselier, M.; Kang, J. H.; Xie, D.; Davis, M. E., CIT-9: A Fault-Free Gmelinite Zeolite, *Angew. Chem. Int. Ed.* **2017**, *56*, 13475-13478.

(27) Gale, J. D., GULP: A computer program for the symmetry-adapted simulation of solids, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 629-637.

(28) Kang, J. H.; Xie, D.; Zones, S. I.; Davis, M. E., Transformation of Extra-Large Pore Germanosilicate CIT-13 Molecular Sieve into Extra-Large Pore CIT-5 Molecular Sieve, *Chem. Mater.* **2019**, *31*, 9777-9787.

(29) Boultif, A.; Louër, D., Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method, *J. Appl. Cryst.* **1991**, *24*, 987-993.

(30) Petříček, V.; Dušek, M.; Palatinus, L., Crystallographic Computing System JANA2006:
General features, Z. für Krist. – Cryst. Mater. 2014, 229, 345-352.

(31) Oszlányi, G.; Süto, A., Ab initio structure solution by charge flipping, *Acta Crystallogr. A* **2004**, *A60*, 134-141.

(32) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P., Optimization by Simulated Annealing, *Science* **1983**, *220*, 671-680.

(33) Deem, M. W.; Newsam, J. M., Framework crystal structure solution by simulated annealing: test application to known zeolite structures, *J. Am. Chem. Soc.* **1992**, *114*, 7189-7198.

(34) Chang, S.; Park, S. H.; Cho, S. J., Locating Structure Directing Agent and Al in CHA: Combined Study of Structure Determination of X-Ray Powder Diffraction and Classical Lattice Energy Calculation, *Bull. Korean Chem. Soc.* **2021**, *42*, 477-482.

(35) Park, J. H.; Sin, K. S.; Chang, S.; Park, S. H.; Cho, S. J., Structural analysis of Cu/Zeolite with controlled Si/Al ratio and the resulting thermal stability, *Catal. Today* **2022**

Chapter 5 | Improving the Propylene Selectivity in the Methanolto-Olefins Reaction over CIT-17, an SAT-Type Molecular Sieve

Abstract

Small-pore, cage-type molecular sieves exhibit high selectivities toward light olefins in the methanol-to-olefins (MTO) reaction. The ability to alter the olefin product selectivity for this complex reaction network while also achieving better carbon efficiency remains a challenge. Herein, we report the synthesis, characterization, and catalytic testing of several SAT-type molecular sieves: SAPO (CIT-17), MgAPO (STA-2), and CoAPO (STA-2). Several CHA- (e.g., SAPO-34, MgAPO-34, and CoAPO-34) and AEI-type (e.g., SAPO-18, MgAPO-18, and CoAPO-18) molecular sieves are also synthesized and tested for comparisons. The SAT materials exhibit high propylene selectivities (35-50%) in MTO. Propylene-to-ethylene ratios (P/E) of 1.64 to 4.17 are achieved and depend on the reaction conditions and material properties. These ratios are significantly higher than those from CHA- (P/E=0.91-1.31) and AEI-type (P/E=2.10-2.34) materials. The enhanced P/E ratio from the SAT framework (CIT-17 (Si/T-atom = 0.083), the best performing SAT material) is due to the delay in reaction time for the maturation of aromatic species, which are comprised of primarily tri- and tetra-methylbenzenes. These results demonstrate the subtle cooperativity between the narrow SAT cage (cage-defining ring (CDR) size of 6.6 Å) and low acidity of CIT-17, which creates a microenvironment for the conversion of methanol to propylene by promoting the olefins cycle and reducing the contribution of the aromatics cycle.

5.1 Introduction

Ethylene (E) and propylene (P) are two of the most important building blocks in the petrochemical industry as they are key in the synthesis of a wide array of polymers (e.g., polyethylene and polypropylene) and fine chemicals.^{1,2} However, a global propylene shortage is predicted as demand is expected to outstrip supply due to the rapidly growing demand for propylene along with the low propylene yields that are achieved in steam cracking and fluid catalytic cracking (FCC) processes.^{3–5} These market dynamics have paved the road for on-purpose propylene production technologies such as, propane dehydrogenation, butenes metathesis, Fischer-Tropsch-to-olefins, and methanol-to-olefins (MTO) to fill this widening gap between supply and demand.^{6–11}

MTO is one of the most promising non-petroleum routes to produce light olefins (e.g., ethylene, propylene and butenes (B)), owing to the ability to produce methanol from syngas (CO/CO₂/H₂), which can be obtained from several abundant feedstocks or alternative carbon raw materials, including natural gas, coal, biomass, CO₂, and municipal waste.^{12–15} In MTO (or more broadly, methanol-to-hydrocarbons (MTH)), molecular sieves containing Brønsted acid sites are the catalysts of choice, with ZSM-5 (MFI structure) and SAPO-34 (CHA) being the two materials deployed industrially.¹⁶ Molecular sieve topology is one of the most important parameters that influences the MTO catalytic performance and regulates product distribution.^{17–23} However, the strength, distribution/proximity, location, amount, and the nature of the acid sites can also contribute toward the observed catalytic behavior.^{24–31} Indeed, controlling product selectivity in MTO is a complex interplay of many parameters that are either inherent to the material or dictated by the reaction conditions (e.g., temperature, weight hourly space velocity (WHSV), etc.).^{32–35}

Due to the commercial significance of this reaction, considerable efforts have been devoted to understanding its mechanism. It is now widely accepted that methanol conversion reactions over acidic catalysts proceed via an indirect hydrocarbon pool (HP) mechanism, comprising of two competing catalytic cycles (i.e., dual cycle): an aromatics-based cycle and an olefins-based cycle.^{16,36–38} In the aromatics cycle, which typically predominates in small-pore, cage-type molecular sieves (e.g., CHA and AEI), poly-methylbenzenes (MB) act as active HP species that undergo repeated methylation and dealkylation reactions to form ethylene, propylene, and/or butenes, depending on the reaction pathway (paring or side-chain).^{20,39–42} On the other hand, in the olefins cycle, which is more prominent in channel-type molecular sieves (e.g., MFI and TON), olefins repeatedly undergo methylation and β -scission reactions to form primarily C₃₊.⁴³ These two cycles are connected via hydrogen transfer and cyclization reactions that convert the olefin-based species to aromatic species. Based on several previous studies, ethylene is recognized as a terminal product of the aromatics cycle, and as such, it can be used an indicator for the propagation of this cycle whereas the selectivity of 2-methylbutane and 2-methylbutene or the combined selectivities of higher aliphatics (e.g., C₄₊) are often used as indicators for the propagation of the olefins cvcle.29,44

Because propylene can form in both cycles, enhancing the propylene selectivity (i.e., improving the propylene-to-ethylene (P/E) ratio) in methanol conversion processes has been achieved either by utilizing 10- or 12-member ring (MR) zeolites with high Si/Al ratios (i.e., low acid sites) in order to suppress the formation of aromatic species and promote the olefins cycle, or 8-MR molecular sieves with cages larger than CHA (e.g., AEI, DDR, ITE, and RTH) to accommodate higher substituted methylbenzenes, which in turn are associated with enhanced propylene formation.^{17,20,22,45–49} Some of the top-performing MTH catalysts that have been

reported in the literature that form primarily propylene include, high-silica ZSM-5 (Si/Al=216), which registers a propylene selectivity of 51% and a P/E of 12.1;⁴⁸ high silica EU-1 zeolite (Si/Al=200), which achieves a propylene selectivity of 52% and a P/E of 15;⁵⁰ and high-silica beta zeolites (Si/Al=136-340), which affords a propylene selectivity of 49.7-58.3%.⁵¹ Even though each of these catalysts achieve a remarkably high P/E ratio coupled with a high propylene selectivity, because of their relatively large cavities and pore sizes, they also yield high amounts of various C₄₊ hydrocarbons (typically 30+%). A key advantage that small-pore, cage-type molecular sieves have over 10- or 12-MR zeotypes is that they are able to limit the size of the products that can diffuse out of their pores (though at the expense of faster deactivation) and thus achieve higher light olefins selectivities. Indeed, achieving a narrower product distribution could simplify downstream separations.

Our group has reported on several small-pore, cage-type materials that enhanced the propylene selectivity over CHA-type molecular sieves (e.g., SAPO-34 and SSZ-13), including SAPO-18 (AEI), steamed and unsteamed SSZ-39 (AEI), zeolite RTH, SSZ-28 (DDR), and ITQ-3 (ITE).^{17,18,27,28,52} However, none of these materials achieved a P/E ratio higher than 2.5 at our reaction conditions (temperature of 400 °C and WHSV of 1.3 h⁻¹). This is because even though larger cages accommodate higher substituted methylbenzenes (MBs) (e.g., penta- (5MB) and hexa-methylbenzenes (6MB)), once these MBs form, it becomes difficult to suppress (or regulate) the formation of lower substituted methylbenzenes (e.g., tri- and tetra-methylbenzenes), which are associated with the formation of ethylene.

Recently, Yang et al.⁵³ reported on the synthesis of a small-pore SAPO-14 (AFN) molecular sieve with low acid site density (Si/T=0.022) (T=Si+Al+P), which achieved a P/E ratio of 4.1 and a very short lifetime (~20 minutes). However, by employing a catalyst with an ultra-

small cage and a narrow 8-MR pore opening, the authors were able to better regulate the HP species formed (likely to enhance the contribution of the olefins cycle, which led to improved P/E ratios). We also recently investigated the MTO behavior of several ERI-type molecular sieves (e.g., SAPO-17, SSZ-98, UZM-12, ERI-type zeolites).²⁶ ERI has one of the narrowest cages active for MTO (cage-defining ring size of 6.75 Å), which can also accommodate polymethylbenzenes. We showed that increasing the acid site density and strength of ERI-type catalysts enhances the ethylene-to-propylene ratio (E/P=0.7-1.9). This enhancement correlated with how fast the ERI materials accumulated active HP aromatic species as a function of Si/Al or Si/T ratio. The acidity not only affected the catalytic behavior, but how quickly the catalysts transitioned from a C_{3+} rich regime in early stages of the reaction (indicative of the olefins cycle) to a $C_{2=}$ rich regime (indicative of the aromatics cycle).

Here, we investigate the catalytic behavior of several SAT-type molecular sieves with the aim of improving the P/E ratio in MTO. The SAT structure consists of double six-membered rings (D6Rs), cancrinite (CAN) cages, and elongated narrow cages (CDR size of 6.6 Å) that are interconnected via elliptical 8-MRs (**Figure A5.1**). SAT has been previously prepared by hydrothermal synthesis in the presence of bisquinuclidinium-butane (DiQ-C₄), bisquinuclidinium-pentane (DiQ-C₅), and bis-diazabicylcooctane-butane (DiDABCO-C₄), leading to the formation of several aluminophosphate-based materials, including, AlPO₄, MgAPO, and ZnAPO, which were denoted as STA-2.^{54–56} However, the silicoaluminophosphate (SAPO) version of SAT has not been synthesized in a pure form, as SAPO-SAT often crystallizes with AFX-impurities.⁵⁵ In this work, we demonstrate for the first time the synthesis of SAPO-SAT (CIT-17) without AFX impurities and characterize this material using a battery of characterization techniques outlined in the next section. We compare the performance of the SAT-type molecular sieves (e.g., CIT-17,

MgAPO, and CoAPO) to CHA- (e.g., SAPO-34, MgAPO-34, and CoAPO-34) and AEI-type (SAPO-18, MgAPO-18, and CoAPO-18) molecular sieves (**Figure 1**), to identify material properties that enhance propylene selectivity in small-pore, cage-type molecular sieves. Partially reacted samples (after 5 minutes of reaction) were dissolved in hydrofluoric (HF) acid to extract and analyze the occluded organic components to identify differences between the compositions and concentrations of the entrained HP species formed during reaction. The identification of these species assists in understanding the observed differences in MTO behavior between these three frameworks.



Figure 5.1. Cages studied in this work, their cage defining ring (CDR) sizes, and the organic structure-directing agents (OSDAs) used for the syntheses of these three frameworks.

5.2 Experimental Section

The CHA-, AEI-, and SAT-type molecular sieves investigated in this work were synthesized based on previously reported (albeit with slight modifications) or newly developed procedures as outlined below. Detailed synthesis procedures of the organic structure-directing agents (OSDAs) used in this work are also provided. The moisture contents of the solid sources were determined by temperature-gravimetric analysis (TGA).

5.2.1 Materials

All materials, unless otherwise noted, were used as-received without further purification from the stated vendors.: aluminum hydroxide (Barcroft 205, SPI Pharma), pseudoboehmite alumina (Catapal B, VISTA), phosphoric acid (H₃PO₄; Macron, 85%), colloidal silica Ludox AS-40 (Sigma Aldrich, 40%), fumed silica (Cab-O-Sil, ACROS), cobalt (II) acetate tetrahydrate (Sigma Aldrich, 98%), cobalt (II) sulfate hydrate (Sigma Aldrich), magnesium acetate tetrahydrate (Sigma Aldrich, 98%), 1,4-diazabicylco[2.2.2]octane (DABCO) (Sigma Aldrich, 99%), 1,4dibromobutane (Sigma Aldrich, 99%), 1,5-dibromopentane (Sigma Aldrich, 97%), quinuclidine (Alfa Aesar, 97%), diethyl either (VWR, 98%), methanol (Sigma Aldrich, 99.9%), and acetone (Fisher Chemical).

5.2.2 OSDA Syntheses

CHA-type molecular sieves (SAPO-34, CoAPO-34, MgAPO-34) were synthesized using morpholine (Thermo Scientific, 99%) and tetraethyl ammonium hydroxide (TEAOH) (Sigma Aldrich, 35% in H₂O) as OSDAs. A CHA/AEI intergrowth (or CHA/AEI mixture) molecular sieve (SAPO-34/18) was synthesized using triethylamine (Sigma Aldrich, 99.5%). AEI-type molecular sieves (SAPO-18, MgAPO-18, CoAPO-18) were synthesized using diisopropylethylamine (DIPEA) (Sigma Aldrich) and 1,1,3,5-tetramethylpiperdinium hydroxide (TMPOH, Sachem). SAT-type molecular sieves (CIT-17, MgAPO-SAT (STA-2), CoAPO-SAT (STA-2)) were synthesized using bisquinuclidinium-butane (DiQ-C₄), bisquinuclidinium-pentane (DiQ-C₅), and bis-diazabicylcooctane-butane (DiDABCO-C₄).

5.2.2.1 Bisquinuclidinium-butane (DiQ-C₄)

DiQ-C₄ was prepared from the reaction of quinuclidine and 1,4-dibromobutane. In a typical synthesis, quinuclidine (100 mmol) was mixed with 150 cm³ of methanol and stirred at room temperature for a few minutes. The solution was then heated to 45 °C in an oil bath. After reaching

45 °C, 1,4-dibromobutane (35 mmol) was added dropwise to the quinuclidine-containing solution while stirring. After adding 1,4-dibromobutane, the reaction mixture was heated to 80 °C and refluxed for 5-6 days. Methanol was then evaporated using a rotary evaporator, and the solid product was filtered and washed with methanol, diethyl ether, and acetone. Following this, the solid was dried under vacuum at room temperature for 6-8 h. The ¹³C NMR spectrum of DiQ-C₄ OSDA in its bromide form is shown in **Figure A5.2**. The OSDA was then converted to its hydroxide form, and its concentration was determined by titration as described in the Ion Exchange and Titration Section.

5.2.2.2 Bisquinuclidinium-pentane (DiQ-C5)

DiQ-C₅ was prepared from the reaction of quinuclidine and 1,5-dibromopentane. In a typical synthesis, quinuclidine (100 mmol) was mixed with 150 cm³ of acetone and stirred at room temperature for a few minutes. The solution was then heated to 45 °C in an oil bath. After reaching 45 °C, 1,5-dibromopentane (35 mmol) was added dropwise to the quinuclidine-containing solution while stirring. After adding 1,5-dibromopentane, the reaction mixture was heated to 80 °C and refluxed for 7 days. Acetone was then evaporated using a rotary evaporator, and the solid product was filtered and washed with diethyl ether and acetone. Following this, the solid was dried under vacuum at room temperature for 6-8 h. The ¹³C NMR spectrum of DiQ-C₅ OSDA in its bromide form is shown in **Figure A5.2**. The OSDA was then converted to its hydroxide form, and its concentration was determined by titration as described in the Ion Exchange and Titration Section.

5.2.2.3 Bis-diazabicylcooctane-butane (DiDABCO-C4)

DiDABCO-C₅ was prepared from the reaction of 1,4-diazabicyclo[2.2.2]octane (abbreviated as DABCO) and 1,4-dibromobutane. In a typical synthesis, DABCO (600 mmol) was mixed with 150 cm³ of methanol and stirred at room temperature for a few minutes. The solution

was then heated to 45 °C in an oil bath. After reaching 45 °C, 1,4-dibromobutane (75 mmol) was added dropwise to the DABCO-containing solution while stirring. After adding 1,4-dibromobutane, the reaction mixture was heated to 80 °C and refluxed for 6 days. Methanol was then evaporated using a rotary evaporator, and the solid product was filtered and washed with methanol, diethyl ether and acetone. Following this, the solid was dried under vacuum at room temperature for 6-8 h. The ¹³C NMR spectrum of DiDABCO-C₄ OSDA in its bromide form is shown in **Figure S5.2**. The OSDA was then converted to its hydroxide form, and its concentration was determined by titration as described in the Ion Exchange and Titration Section.

5.2.3 Ion Exchange and Titration

If required by the molecular sieve synthesis procedure, the OSDAs described above were ion exchanged into their hydroxide forms by first dissolving the organic salts in DI water and then adding DOWEXTM MonosphereTM 550A hydroxide ion-exchange resin (Dow chemical). Specifically, for every 100 mmol of OSDA in the halide form, approximately 300 cm³ (by volume) of resin and 500 cm³ of DI water were added. The mixture was then stirred for 24 h at room temperature. After 24 h, the resin was separated by filtration and the process repeated a second time. The quantification of the concentration of the OSDA, now in the hydroxide form, was performed using a Mettler Toledo DL22 Potentiometric pH meter. Five readings were taken for each OSDA concentration, and these values were then averaged and used for gel calculations. OSDAs in the hydroxide form are abbreviated as DiQ-C₄-(OH)₂ whereas OSDAs in the halide (bromide) form are abbreviated as DiQ-C₄-(Br)₂

5.2.4 Molecular Sieve Syntheses

5.2.4.1 CHA-type Molecular Sieves
Several CHA-type molecular sieves were synthesized or provided to us for comparison to the SAT samples. SAPO-34-1 was kindly provided by Mitsubishi and was thoroughly characterized in this work. SAPO-34-2 was synthesized according to a method outlined in our previous work with a gel molar composition of $1 \text{ Al}_2\text{O}_3$: $1 \text{ P}_2\text{O}_5$: 0.075 SiO_2 : 3 TEAOH : $50 \text{ H}_2\text{O}_{-}^{17,25}$ It's characterization data were shown previously.¹⁷ SAPO-34-3 was synthesized with a gel molar composition of $0.985 \text{ Al}_2\text{O}_3$: $1 \text{ P}_2\text{O}_5$: 0.4 SiO_2 : 2 morpholine : $60 \text{ H}_2\text{O}_{-}^{57}$ In a typical synthesis, a desired amount of pseudoboehmite was slurred in 50% of the required deionized (DI) water for approximately 3 h. Then, phosphoric acid was added dropwise to the alumina slurry and the solution was stirred for another 2 h. After stirring, fumed silica was added along with the remaining water. The mixture was left to stir for 1 hour before adding the OSDA (morpholine). This mixture was stirred overnight before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 200 °C for 48 hours. Both MgAPO-34 and CoAPO-34 were synthesized based on methods outlined in our previous work.^{17,58,59} Their characterization were also previously reported by our group.¹⁷

5.2.4.2 CHA/AEI-type Molecular Sieve

SAPO-34/18 was synthesized with a gel molar composition of $1 \text{ Al}_2\text{O}_3 : 0.9 \text{ P}_2\text{O}_5 : 0.05$ SiO₂ : 3.5 triethylamine : 40 H₂O.^{53,60} In a typical synthesis, a desired amount of pseudobohoemite and DI water were stirred for 3 h. Then, a desired amount of phosphoric acid was added along with fumed silica. This mixture was stirred for 3 h before triethylamine was added. Following the addition of the OSDA, the mixture was stirred for 2 h and then transferred to a stainless-steel Teflon-lined Parr reactor (23 cm³) and heated in a rotating oven to 180 °C for 24 hours.

5.2.4.3 AEI-type Molecular Sieves

Several AEI-type molecular sieves were synthesized for comparison to the SAT samples. SAPO-18-1 was synthesized with a gel molar composition of $1 \text{ Al}_2\text{O}_3 : 0.96 \text{ P}_2\text{O}_5 : 0.055 \text{ SiO}_2 :$ 1.62 diisopropylethylamine : 50 H₂O.⁶¹ In a typical synthesis, a solution of phosphoric acid in DI water was added to aluminum hydroxide hydrate (Barcroft) and the mixture was stirred overnight. Then, fumed silica was added to this mixture followed by the OSDA. The gel was stirred for an additional 2 h before being placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 160 °C for 10 days. SAPO-18-2 was synthesized using a similar procedure as SAPO-18-1, but with a slightly different gel composition (1 Al₂O₃ : 0.9 P₂O₅ : 0.2 SiO₂ : 1.6 diisopropylethylamine (DIPEA) : 50 H₂O). To obtain a pure AEI product, the H₃PO₄/OSDA ratio had to be adjusted. SAPO-18-3 was synthesized using a similar gel as SAPO-18-2 but with a higher Si content (1 SiO₂). Both MgAPO-18 and CoAPO-18 were synthesized based on methods outlined in our previous work.¹⁷ Their characterization were also previously reported by our group.¹⁷

5.2.4.4 SAT-type Molecular Sieves

MgAPO-SAT (STA-2) and CoAPO-SAT (STA-2) were synthesized with a gel molar composition of 0.45-0.5 Al₂O₃ : 0.45-0.5 P₂O₅ : 0.03-0.1 Mg (or Co) : 0.4 R(OH)₂ (R=DiQ-C₄ or DiDABCO-C₄) : 40 H₂O.^{54,55} In a typical synthesis, aluminum hydroxide (Barcroft), magnesium or cobalt (II) acetate, phosphoric acid, and DiQ-C₄ or DiDABCO-C₄ were sequentially added to a Teflon-liner containing deionized (DI) water. The prepared gel, following stirring overnight, was transferred to a stainless-steel autoclave and heated at 190 °C in a rotating (or a static) oven for 2-3 days. **Tables A5.1-3** include summary lists of the syntheses attempted for making SAT-type molecular sieves using the three aforementioned OSDAs and the resultant products as determined by Powder X-ray Diffraction (PXRD).

The synthesis of CIT-17 (SAPO-SAT) was attempted over a wide range of conditions: 0.45-0.5 Al₂O₃ : 0.45-0.5 P₂O₅ : 0.05-0.4 SiO₂ : 0.4-0.162 R(OH)₂ (R=DiQ-C₄, DiQ-C₅, or DiDABCO-C₄) : 0-0.11 R(Br)₂ : 40-75 H₂O. In a typical synthesis, a desired amount of phosphoric acid (H₃PO₄) was mixed with an appropriate amount of DI water, and the mixture was stirred for 10 mins. Next, the aluminum source (Barcroft) was weighed separately and added to this mixture. This gel was allowed to homogenize for 3-4 hours before adding fumed silica. Following the addition of silica, the OSDA was added, and the gel was aged at room temperature for 20-24 hours before being heated to 180-200 °C in a rotating (55-60 rpm) or a static oven at autogenous pressure for 3-5 days. All CIT-17 materials were prepared in 23 cm³ stainless steel Parr autoclaves with Teflon liners. In some cases (before loading), a CIT-17 seed (1 wt%) was added to the gel mixture (although the synthesis of CIT-17 does not require the presence of a seed). A complete summary of the attempted synthesis conditions and the resultant products is outlined in **Tables A5.1-3**.

The best crystallized CIT-17 materials were prepared using the following gel composition: 0.48-0.5 Al₂O₃ : 0.45-0.5 P₂O₅ : 0.05-0.15 SiO₂ : 0.17-0.23 R(OH)₂ (R=DiQ-C₄, DiQ-C₅, or DiDABCO-C₄) : 40 H₂O. Note that when the Al/P approaches 1 (by increasing the P content), the OSDA content needs to be on the higher end of the aforementioned range. Also, note that when DiQ-C₅ is used as an OSDA, the amount of OSDA (concentration) can be increased up to 0.27 in the above gel without forming impurities. The two major impurities encountered during the synthesis of CIT-17 are AFX (typically, when the Si content is high) and CIT-16P (typically, when the OSDA concentration is high). CIT-16P is a disordered SAPO phase that transforms to ERI following thermal treatment and the removal of the OSDA, which we recently reported on (refer to Chapter 4).

5.2.5 **Product Recovery and Thermal Treatment**

Once the above syntheses were completed, each material was washed three times (minimum) with DI water (50 cm³ each time) and once with acetone. After each wash, materials were recovered by centrifugation at 3500+ rpm (Eppendorf model 5810 R). After washing, all samples were dried in air overnight at 100 °C. Following drying, all materials were thermally treated (in ceramic calcination boats) under flowing breathing-grade air in a Nabertherm DKN400 muffle furnace. Materials were initially heated to 150 °C at a heating rate of 1 °C/min and held for 3 h before being heated to 580 °C (again at a heating rate of 1 °C/min) and held for 12 h to ensure complete combustion of any remaining organic structure-directing agents (OSDAs).

5.2.6 Characterization

Powder X-ray diffraction (PXRD/XRD) patterns were obtained on a Rigaku MiniFlex II instrument using Cu K α radiation ($\lambda = 1.54184$ Å) at a scan rate of 0.3-0.6 °/min to determine structure type and purity. Morphology and elemental composition were determined via scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) on a ZEISS 1550VP instrument equipped with an Oxford X-Max SDD energy dispersive X-ray spectrometer. Atomic ratios (atomic %) were reported as Si(M)/T-atom ratios, where T=Si(M)+Al+P and M is either Co or Mg, or Si(M)/(Al+P). To determine micropore volume using the t-plot method (or pore volume measured at P/P_0=0.01), N_2-adsorption/desorption experiments were performed on each sample at 77 K in a Quantachrome Autosorb iQ adsorption instrument using a constant-dose method. Prior to adsorption measurements, all samples were outgassed at 60 °C for 0.5 h, followed by holds of 0.5 h at 120 °C and 6 h at 350 °C (all ramping rates were 1 °C/min). Thermogravimetric analysis (TGA) measurements were performed on Perkin Elmer STA 6000. As-synthesized (prior to thermal treatment) or fully-coked samples (0.02-0.06 g) were placed in an alumina crucible and heated at 7-10 °C/min in a flowing stream (0.33 cm³/s) of air to 700-800 °C. Liquid ¹³C NMR

spectra were recorded on a Bruker 400 MHz spectrometer whereas liquid ¹H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. All liquid NMR analyses, involving OSDAs, were performed in deuterium oxide (D₂O) (99.9%, Cambridge Isotope Laboratories, Inc.).

All solid-state, magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy experiments were conducted on a Bruker Avance 500 MHz spectrometer using a 4 mm ZrO₂ rotor. The number of Brønsted acid sites was measured using quantitative ¹H MAS NMR spectroscopy. In a typical experiment, the thermally treated samples were dehydrated under vacuum (10⁻² Torr) at 400 °C for 10 hours at a ramp rate of 2 °C/min in a dehydration manifold after being pre-packed in an uncapped ZrO_2 rotor that is placed inside of a 5 mm glass NMR tube. The rotor was then capped while under vacuum and inside the dehydration manifold (to minimize sample exposure to moisture) and then loaded into the spectrometer. Spectra were collected at 500.20 MHz and a spinning rate of 12 kHz using a 90° pulse length of 4 µs. Recycle delay time was varied depending on the T_1 relaxation time of the samples. Signal intensities were referenced to hexamethylbenzene and normalized by the mass packed into the rotor for quantification. The spectra were deconvoluted using DMFit, as shown in our previous work.²⁶ For ²⁹Si MAS NMR spectroscopy, oxygen was introduced to the dehydrated sample to reduce the relaxation time. The ¹H-decoupled ²⁹Si MAS NMR spectra were then acquired at 99.38 MHz and a spinning rate of 8 kHz using a 90° pulse length of 4 μ s and a cycle delay time of 10 s. The acquired spectra were used to identify different Si environments in the tested samples. ²⁷Al MAS NMR spectra were acquired on the dehydrated samples (4 h at 400 °C at a ramp rate of 2 °C/min) at 130.2 MHz and at a spin rate of 13 kHz, a $\pi/18$ pulse length of 0.5 μ s, and a cycle delay time of 0.5 s. ³¹P MAS NMR spectra were also acquired on the dehydrated samples at 202.4 MHz at a spin rate of 12 kHz, a $\pi/2$ pulse length of 4 µs, and a cycle delay time of 4 s. ¹³C solid-state NMR spectra were acquired on the as-synthesized samples at 125.78 MHz at a spin rate of 8 kHz, a CP contact time of 0.5 ms, and a cycle delay time of 6 s.

5.2.7 Catalytic Testing

Catalyst evaluation was carried out in a fixed-bed reactor at ambient pressure. In a typical experiment, approximately 170-200 mg of dried catalyst (35-60 mesh size) was loaded between two layers of quartz wool in a 0.25" \times 6" stainless steel (or quartz) tube reactor as a part of a BTRS Jr. continuous flow reactor (Parker Autoclave Engineers). The dry weight of the catalyst was estimated on the basis of thermogravimetric analysis (TGA; PerkinElmer STA 6000). All catalysts were first pretreated by heating to 150 °C at 1 °C/min, held for 3 hours, and then heated further to 580 °C at 1 °C/min and held for 12 h under flowing air (breathing-grade D, AirGas). Methanol was introduced via a liquid syringe pump (Harvard Apparatus Pump 11 Elite) at 4.0-5.0 µL/min into a gas stream of an inert blend (95% He and 5% Ar; GC internal standard) at a volumetric flow rate of 30 cm³/min. The methanol flow rate was adjusted, depending on the actual weight of the dried catalyst loaded in the reactor, to achieve a weight hourly space velocity (WHSV) of $0.65-2.6 \text{ h}^{-1}$. Reactions were performed at 350-450 °C. Effluent gases were evaluated using an on-stream Agilent GC-MS (GC 6890N/MSD5793N) equipped with a Plot-Q capillary column. Aliquots of product flow were analyzed every 16 minutes. All selectivity values were calculated on carbonnumber basis.

In experiments where the content of the entrained hydrocarbons was of interest, the reaction was quenched rapidly (-7-10 °C/s) after 5 minutes of reaction and a portion of the catalyst bed (20 mg) was transferred to a Teflon tube and suspended in 1.0 cm³ of 48% aqueous hydrofluoric acid (Sigma Aldrich). The solution was stirred for 2 h to allow the framework to dissolve. Following dissolution, the organic material was extracted into 1 cm³ of dichloromethane

(2 x 0.5 cm³). Hexachloroethane (Aldrich, 99%) was used as an internal standard. The speciation of aromatics in the organic layer was then identified using a mass spectrometer (Agilent 6890N) and a ZB-5MS column (30 m x 0.25 mm) and quantified using a gas chromatograph (Agilent 7890B) connected to a Polyarc. The organic compounds extracted were identified in comparison with the NIST database as well as standards.

5.3 Results and Discussion

5.3.1 Synthesis and Characterization of CHA- and AEI-type Materials

Several CHA-, CHA/AEI-, and AEI-type molecular sieves were synthesized using various methods and OSDAs as outlined in the Experimental Section. Their characterization can be found in the Supplemental Section (**Appendix D**). The PXRD patterns of the CHA, CHA/AEI, and AEI samples synthesized in this work are shown in **Figures A5.3-5**. These patterns are in good agreement with simulated patterns (IZA database) as well as diffraction patterns reported previously for such materials.^{25,45,61} The PXRD pattern of SAPO-34/18 (CHA/AEI) indicates that this sample is made up primarily of CHA and only has as a small amount of AEI. We did not attempt in this work to thoroughly determine whether this sample contains a physical mixture of CHA and AEI phases or if both phases are present as an intergrowth. However, based on the PXRD patterns and SEM results, it is likely the latter.

The chemical composition of the various CHA, CHA/AEI, and AEI samples were determined by EDS and these results are shown in **Table A5.4**. In this work, we synthesized samples that covered a wide range of Si(M)/T-atom ratio, where T=Si(M)+Al+P and M is either Mg or Co, but focused mostly on the range from Si(M)/T=0.04-0.08, for comparison to the SAT samples.

Figure A5.6 shows the SEM images of a select group of CHA and AEI samples. SEM images of samples not provided in **Figure A5.6** were reported in our previous work.¹⁷ The SEM images show that the majority of the CHA , CHA/AEI and AEI samples have similar particle sizes (~0.5-2.5 microns). Only two materials have particle sizes that fall outside of this range: SAPO-34-3 and CoAPO-34. These materials have slightly larger particle sizes (~3-20 microns) likely because they were synthesized with morpholine as an OSDA. Morpholine is known to generally produce CHA-type materials with large particle sizes.⁶²

Due to the large number of CHA and AEI samples synthesized in this work, we designated SAPO-34-1, SAPO-34/18, and SAPO-18-1 as representative materials for each framework (or class of material) (i.e., CHA, CHA/AEI, and AEI). These materials were then further characterized using other techniques. **Figueres A5.7-9** show solid-state NMR results for these three samples.

The silicon distribution for these representative SAPO materials was studied by solid-state ²⁹Si MAS NMR spectroscopy. SAPO materials generally generate bands ranging from approximately -90 to -112 ppm, corresponding to the presence of Si(4Al) (isolated Si atoms), Si(3Al), Si(2Al), Si(1Al) and Si(0Al) (Si islands). The ²⁹Si MAS NMR spectra for SAPO-34-1 (**Figure A5.7**), SAPO-34/18 (**Figure A5.8**), and SAPO-18-1 (**Figure A5.9**) demonstrate that all samples have a main resonance at ~-95.4/95.5 ppm, with the SAPO-34-1 sample showing a slightly more diverse set of Si environments than the other two samples. However, all of the CHA, CHA/AEI and AEI representative samples are made up of mostly Si(4Al) and Si(3Al) environments, likely due to the low Si content of these materials. SAPO-18-1 had a very weak signal as a result of it having the lowest Si content of the three samples tested.

²⁷Al NMR analyses were performed on the three representative materials. The CHA (SAPO-34-1) and CHA/AEI (SAPO-34/18) materials had a strong resonance at approximately 35

ppm, which corresponds to tetrahedrally coordinated Al. The SAPO-18-1 sample showed a main resonance centered at 34.5 ppm (similar to what have been observed on AlPO-18 materials previously),⁶³ which corresponds to tetrahedrally coordinated Al, and a small peak at approximately 9 ppm, which is assigned to penta-coordinated Al species.³¹P NMR analyses were also performed. All of the samples had a single resonance at approximately -30/-31 ppm, which are consistent with tetrahedrally connected AlPO-18(34)/SAPO-18(34) materials.

¹H NMR experiments were performed on the dehydrated samples (SAPO-34-1, SAPO-34/18, and SAPO-18-1) and the obtained spectra are shown in **Figures A5.7-9**. Two main peaks were observed, which are consistent with two differently formed acid sites: a weaker acid site showing a dominant resonance at ca. 3.6-3.7 ppm and a stronger acid site showing a resonance at 3.9-4 ppm. Deconvolution of these peaks gave rise to the total acid site density values measured for these three samples. SAPO-34-1, SAPO-34/18, and SAPO-18-1 had Brønsted acid site densities of 1.09, 0.89, and 0.68 mmol/g.

 N_2 -adosprtion-desorption experiments were also performed on the three representative CHA, CHA/AEI, and AEI samples, and the obtained micropore volumes (V_{micro}) were 0.24, 0.25, and 0.18 cm³/g for SAPO-34-1, SAPO-34/18, and SAPO-18-1, respectively (**Figures A5.7-9**).

5.3.2 Synthesis and Characterization of SAT-type Molecular Sieves

MgAPO-SAT (STA-2) and CoAPO (STA-2) were synthesized based on methods that were reported previously. STA-2 materials have been thoroughly characterized in the literature.^{54–56} As such, for brevity, we only confirm the formation of these two products via PXRD and measure each sample's elemental composition for comparison as a part of the MTO work. No further characterization is performed on them.

Figure A5.10 shows the PXRD patterns of MgAPO-SAT as well as CoAPO-SAT, which are in agreement with the previously published patterns for STA-2. The elemental composition data show that MgAPO-SAT and CoAPO-SAT have a M/T-atom ratio of 0.071 and 0.063, respectively, as shown in **Table A5.4**.

STA-2 was first discovered in 1997 as a MgAPO (STA-2) using DiQ-C₄ as an OSDA.⁵⁴ The following gel led to the formation of MgAPO-SAT, which is the first reported SAT material: 0.45 Al₂O₃ : 0.5 P₂O₅ : 0.1 Mg : 0.4 R(OH)₂ (R=DiQ-C₄) : 40 H₂O. As a part of that work, the authors showed that increasing the Mg/P ratio (to 0.15 in the gel) led to the co-crystallization of MgAPO-56 (AFX), whereas in another set of experiments, they demonstrated that substituting R(OH)₂ with R(Br)₂ and sodium hydroxide (as the source of OH⁻) led to formation of AFX impurities as well. In 2010, Castro et al.⁵⁵ showed that DiQ-C₄ could be substituted for a less expensive molecule, DiDABCO-C₄, and still form STA-2.⁵⁵ In total, the authors proposed and examined three OSDAs for the synthesis of STA-2 (AlPO₄, MgAPO and SAPO): DiQ-C₄, DiDABCO-C₄, and DiDABCO-C₅. Slight changes were applied to the Al/P ratio in the new proposed gel (compared to the original gel), but otherwise, the OSDA concentration in the hydroxide form remained elevated (0.4-0.5) in all trials. The authors were able to obtain an AlPO₄-SAT as a pure phase in this new work. However, attempts to synthesize SAPO-SAT persistently led to the co-crystallization of SAPO-56 (AFX).

It does not appear that SAPO-SAT has crystallized in a pure form since the discovery of the first SAT material almost two decades ago. Recently, as a part of a program to synthesize small-pore, cage-type molecular sieves, we encountered a disordered phase, which we denoted as CIT-16P. CIT-16P, which is synthesized using DiQ-C₄, was found to have a somewhat similar structure to a recently reported material denoted as ECNU-38P (although each material is synthesized with a different OSDA and gel composition).⁶⁴ We showed that CIT-16P crystallizes in a gel that is very similar to STA-2, but only when the OSDA (DiQ-C₄) concentration was lower than 0.28. SAT appeared often as an impurity phase in that work when the OSDA concentration was higher than 0.28 in the gel or lower than 0.24. AFX was the other impurity phase appearing in that work (often when the Si content was high).

Following the discovery of CIT-16P and realizing that SAPO-SAT has not been synthesized in a pure form yet (i.e,. without SAPO-56), we hypothesized that the hydroxide ion content in the gel might be the differentiating factor that could lead to the formation of SAPO-SAT without AFX. **Tables A5.1-3** list the gel compositions that were attempted to synthesize various SAT-type molecular sieves with different OSDAs (DiDQ-C₄ in **Table A5.1**, DiDQ-C₅ in **Table A5.2**, and DiDABCO-C₄ in **Table A5.3**), but mainly SAPO-SAT. Once obtained, the pure SAPO-SAT product was denoted as CIT-17.

Our experimental results on the synthesis of CIT-17 demonstrate the importance of regulating the hydroxide content in the gel and keeping it between 0.17 and 0.22 (when H₂O is 40), particularly when DiQ-C₄ and DiDABCO-C₄ are used as OSDAs. Since CIT-16P does not form when using the longer OSDA (DiQ-C₅), the gel becomes more tolerant of the hydroxide content coming from the DiQ-C₅ OSDA (up to 0.27) while still leading to the formation of CIT-17. Our results show that the key factor to forming SAT is not necessarily the total amount or type of R^+ that is added to gel, but rather the hydroxide amount/concentration that is accompanying that OSDA (see Entries 20-22 and Entries 42 to 49 in **Tables A5.1-3**)). Specifically, one can increase the OSDA content, but also increase the water content simultaneously and still make CIT-17. Or, one could add the ideal amount of OSDA (in the hydroxide form) then add more OSDA in the bromide form and still make CIT-17.

Our experimental results show that there is some flexibility in terms of changing the Al/P ratio in the gel while making a relatively 'pure' product. Furthermore, CIT-17 can be made both in rotating and static conditions. Of all the parameters tested, Si content was the other parameter that had to be low (and in a narrow range) for CIT-17 to form without SAPO-56. It appears that once the Si content in the gel reaches approximately 0.2, AFX forms and the peaks associated with AFX increase as the Si content is further increased (see Entry 50 in **Table A5.3**).

Figure A5.11-12 shows the PXRD patterns of a select group of CIT-17 samples. Minor shifts in the diffraction peaks are observed among the various SAT samples, likely owing to small differences in unit cell size caused by differences in composition and choice of OSDA in the synthesis procedure. **Figure A5.13** shows the SEM images of all the CIT-17 samples that are later tested in this work in the MTO reaction. All the samples had particles that were comparable in size (~0.3-4 microns) and morphology (i.e., rhombohedral), irrespective of which OSDA was used in the synthesis stage. The DiDABCO-C₄ OSDA (CIT-17-3) did form particles that were on the lower end of this range (~0.3-1 microns). Additionally, the sample that had higher Si content (CIT-17-5) contained more amorphous-like phases and a small amount of AFX impurities. AFX has distinct hexagonal plate-like or disk-like morphologies, as reported previously.⁶⁵ Those were observed in the SEM images of CIT-17-5.

Due to the large number of CIT-17 samples synthesized in this work, we selected CIT-17-4 as a representative CIT-17 sample for further characterization. **Figure 5.2(a)** shows the PXRD pattern of the as-synthesized CIT-17-4 material, in agreement with the previously published pattern for STA-2. **Figure 5.2(b)** shows an SEM image of the as-synthesized form of CIT-17-4, revealing that it has particle sizes of ca. 0.5-2 microns.

TGA shows that the corresponding mass loss due to the OSDA (DiQ-C₅) removal from heating in air (calculated from the mass losses between 300 and 800 °C) was approximately 17.6% (**Figure 5.2(c)**). For CIT-17-4, the major weight loss starts at approximately 380 °C, with the biggest drop occurring near 500 °C due to the removal of the OSDA. We also performed TGA experiments (not shown) on two other samples that were synthesized using DiQ-C₄ (CIT-17-2) and DiDABCO-C₄ (CIT-17-3), and these materials had mass losses of approximately 18.1% and 16.4%. These values are in close accord with the value reported previously for STA-2 (ca. 17%).⁵⁵

¹³C solid-state NMR on the as-synthesized CIT-17-4 sample was compared to the solution ¹³C NMR of DiQ-C₅-(Br)₂, which shows that the OSDA was well preserved in the as-synthesized material following crystallization (Figure 5.2(d)). ¹H MAS NMR was performed on the thermally treated CIT-17-4 sample following dehydration as outlined in the Experimental Section (Figure 5.2(e)). Similar to the CHA and AEI materials discussed previously, two major resonances are detected: one at ca. 3.7 ppm and the other at 4 ppm. The broad resonance from 1-3 ppm is likely due to P-OH (at approximately 2.6 ppm) and Si-OH (at approximately 1.8 ppm).⁶⁶ The Brønsted acid site density of this sample was calculated to be 0.28 mmol/g (based on the 3.7 and 4 ppm peaks). ²⁹Si MAS NMR shows a mixture of Si environments from -90 to -112 ppm, with a clear peak at approximately -96.5 ppm (Figure 5.2(f)). This is consistent with the presence of various Si environments as described previously. ²⁷Al MAS NMR shows one broad peak centered at 36.1 ppm and the ³¹P MAS NMR shows two overlapping peaks at -28.8 and -31.6 ppm (Figure 5.2 (g) and (h)). It was previously reported by Castro et al.⁵⁵ that SAT AlPO₄-type materials have two distinct Al resonances (as determined via ²⁷Al MAS NMR) and two distinct P resonances (as determined via ³¹P MAS NMR) due to the structure of the SAT framework, which is built up of layers of CAN cages in which these cages share 4MRs (Figure A5.1). These layers are attached

204

to D6Rs, which are connected to the large SAT cage. One type of the Al and P set is located in the 4MRs whereas the other set is located in the planar 6MRs of the CAN cages.⁵⁵



Figure 5.2. Characterization on CIT-17-4. (a) PXRD pattern on the as-synthesized sample. (b) SEM image on the as-synthesized sample. (c) TGA profile of the as-synthesized sample. (d) solid-state ¹³C NMR of the as-synthesized sample compared to the solution ¹³C NMR spectrum (DiQ-C₅). (e) ¹H MAS NMR spectrum on the thermally treated sample (after dehydration). (f) ²⁹Si MAS NMR spectrum on the thermally treated sample (dehydrated then treated with oxygen). (g) ²⁷Al MAS NMR spectrum on the thermally treated sample (dehydrated). (h) ³¹P MAS NMR spectrum on the thermally treated sample (dehydrated).

Using N₂-physisorption, a pore volume was calculated for this sample (0.18 cm³/g at $P/P_0=0.01$). MgAPO-SAT (STA-2) was reported to have a void volume of 0.095 cm³/g.⁵⁴

5.3.3 MTO Reaction Testing

The reaction results for the various CHA-, CHA/AEI-, AEI-, and SAT-type molecular sieves that were characterized in the previous section are summarized in **Table 5.1**. **Figure 5.3** shows the averaged propylene-to-ethylene ratio of the evaluated catalysts (when methanol conversion is greater than 97%) for the three frameworks investigated. The time-on-stream (TOS) reaction profiles are provided in the supplemental section (**Appendix D**) (**Figures A5.14-19**).

To establish a benchmark for the product distribution analysis, several CHA-type molecular sieves with varying elemental compositions and Si(M)/T-atom ratios were tested for MTO at identical reaction conditions (temperature (T)=400 °C and WHSV of 1.3 h⁻¹). The SAPO-CHA-type materials (SAPO-34-series) showed results that were consistent with the literature data for such materials. The SAPO-34 samples, irrespective of Si/T ratio, exhibited high stability, low alkane products, and high combined ethylene (28-31%) and propylene (38-41%) selectivities. These ethylene and propylene selectivities give a P/E ratio of approximately 1.3 for all three SAPO-34 samples tested (SAPO-34-1, SAPO-34-2, and SAPO-34-3). The three SAPO-34 samples also produced a relatively low C₄₊ fraction. SAPO-34/18, which as mentioned earlier, is made up mostly of CHA phases (based on the PXRD), also behaved similarly to the SAPO-34 samples tested in this work (**Table 5.1**)

Parameter	Framework	Material ID	Si(M)/T	Temperature (°C)	WHSV (h⁻¹)	Averaged Selectivities (at 97-100% Conversion)					
						C2=	C3=	C₂+C₃ Alkanes	C 4	C 5+	C3=/C2=
Effect of Cage Size	СНА	SAPO-34-1	0.081	400	1.3	0.31	0.41	0.141	0.10	0.05	1.31
		SAPO-34-2	0.123	400	1.3	0.30	0.39	0.053	0.13	0.07	1.30
		SAPO-34-3	0.127	400	1.3	0.28	0.38	0.052	0.12	0.04	1.35
		MgAPO-34	0.015	400	1.3	0.41	0.40	0.034	0.10	0.04	0.97
		CoAPO-34	0.022	400	1.3	0.44	0.40	0.029	0.09	0.04	0.91
	CHA/AEI	SAPO-34/18	0.063	400	1.3	0.31	0.40	0.050	0.09	0.05	1.31
	AEI	SAPO-18-1	0.038	400	1.3	0.23	0.48	0.067	0.16	0.08	2.10
		SAPO-18-2	0.061	400	1.3	0.22	0.47	0.081	0.15	0.09	2.13
		SAPO-18-3	0.162	400	1.3	0.20	0.43	0.092	0.18	0.12	2.19
		MgAPO-18	0.031	400	1.3	0.17	0.40	0.134	0.19	0.09	2.34
		CoAPO-18	0.073	400	1.3	0.19	0.42	0.110	0.19	0.14	2.17
	SAT	CIT-17-1	0.068	400	1.3	0.14	0.48	0.031	0.17	0.15	3.40
		CIT-17-2	0.072	400	1.3	0.13	0.47	0.021	0.17	0.15	3.62
		CIT-17-3	0.073	400	1.3	0.15	0.47	0.038	0.16	0.13	3.23
		CIT-17-4	0.083	400	1.3	0.16	0.49	0.037	0.17	0.13	3.15
		CIT-17-5	0.094	400	1.3	0.19	0.47	0.047	0.16	0.12	2.47
		MgAPO-SAT	0.071	400	1.3	0.18	0.35	0.080	0.16	0.15	2.01
		CoAPO-SAT	0.063	400	1.3	0.18	0.42	0.063	0.16	0.13	2.33
Effect of Reaction Conditions	SAT	CIT-17-4	0.083	450	0.65	0.28	0.46	0.031	0.11	0.08	1.64
		CIT-17-4	0.083	400	0.65	0.18	0.40	0.033	0.17	0.09	2.22
		CIT-17-4	0.083	400	2.6	0.14	0.49	0.047	0.15	0.15	3.50
		CIT-17-4	0.083	350	1.3	0.12	0.45	0.050	0.19	0.18	3.75
		CIT-17-4	0.083	350	0.65	0.12	0.50	0.034	0.20	0.12	4.17

Table 5.1. Reaction results of the SAPO materials investigated.

We tested two MAPO-34 (M=Mg or Co) samples that were denotated as MgAPO-34 and CoAPO-34. These samples resulted in a slight reduction in the P/E ratio (from 1.3 for the SAPO-34-series samples down to 0.91-0.97 for the MAPO-34 samples) as each material enhanced primarily the ethylene selectivity (**Table 5.1**). We have reported previously on this behavior.¹⁷ The degree in improvement in the ethylene-to-propylene ratio (E/P) observed in the MAPO-34 materials is similar to the enhancement effect in the E/P ratio that we observed and reported on when testing various SSZ-13-type materials in MTO, a zeolite that is isostructural to SAPO-34. As we demonstrated in our previous work, the slight improvement in the E/P ratio exhibited by the various SSZ-13 samples, which had Si/Al ratios ranging from ca. 5 to 55, and the deviation in the catalytic performance of SSZ-13-type materials from SAPO-34 (in terms of alkane selectivities and lifetime) were due to differences in acidity (i.e., Brønsted acid site density, proximity, and strength).²⁵ While there are only a few reports on the use of MAPO materials in MTO, the substitution of Mg or Co into an AlPO₄-based structure results in the formation of acid sites that have different strengths (typically, stronger) than the sites generated by Si substitution, as demonstrated previously for several SAPO-18 and MAPO-18 materials.³⁰ As such, the olefins product distribution differences observed in this work between the MAPO-34 samples and the SAPO-34-series samples are likely rooted in differences in acid site strength. Nevertheless, all the CHA-type materials tested here, irrespective of composition, appear to give a propylene to ethylene ratio of approximately 1 (Figure 5.3).

AEI has received significant attention in the literature due to its ability to enhance the P/E ratio when compared to other small-pore, cage-type molecular sieves. Previously, we showed that both SAPO-18 (AEI) and SSZ-39 (AEI), its zeolitic analogue, can enhance the propylene selectivity in this reaction over CHA-type materials.^{17,27} In fact, of the 14 different small-pore,

cage type frameworks that we previously tested in MTO, AEI gave one of the highest P/E ratios combined with the lowest C_{4+} fractions.¹⁷

Due the ability of the AEI cage to significantly improve the propylene selectivity over CHA-type materials, several SAPO-18 (AEI) samples, with different Si/T-atom ratios, were compared. **Figure A5.16** shows the time-on-stream reaction data for the various AEI samples tested. Similar to our observations on SAPO-34 catalysts, all three of the SAPO-18 samples (SAPO-18-1, SAPO-18-2 and SAPO-18-3) had comparable P/E ratios (ca. 2). While the effect of changing the Si/T-atom ratio (thus, acidity) on the olefins product distribution was similar across the CHA- and AEI-SAPO-type materials, showing little to no effect, the effect of changing the significant, resulting in an improvement in the propylene selectivity. These improvements are reflected in the elevated P/E ratios reported in **Table 5.1** and shown in **Figure 5.2**.

Two AEI-type MAPOs were also investigated: MgAPO-18 and CoAPO-18. Our results show that changing the elemental composition (and hence acidity) of AEI-type molecular sieves does not result in significant changes in the light olefins selectivities, albeit the MAPO-18 catalysts generally deactivated much faster than the SAPO-18 catalysts, which was also the case with the CHA-type MAPOs when compared to SAPO-34.

The observations on CHA- and AEI-type matarials are consistent with what has been reported in the literature: that the effect of cage size is more significant in MTO than the effect of acidity, with larger cages such as, AEI forming more propylene and butenes than CHA. However, we also showed that in going to cages larger than AEI (e.g., KFI, LTA and RHO), the olefins product disturbution starts to shift to favor butenes formation, which are of far less value industrially than propylene. Since changing the acidity (both acid site strength and distrubtion) of both CHA and AEI-type molecular sieves does not appear to enhance the P/E ratio, we attempted to improve the P/E ratio by investigating SAT-type molecular sieves in MTO.



Figure 5.3. Propylene-to-ethylene (P/E) ratio of the various materials investigated.

SAT-type molecular sieves have not been tested in MTO previously. SAT, indeed, has one of the smallest cages (CDR size= 6.6Å) active for the formation of aromatic-type hydrocarbon pool species in MTO. When we originally planned to test SAT-type molecular sieves for MTO, we were more interested in improving the ethylene selectivity. Our logic was to design a catalyst that has a very narrow cage (narrower than ERI, which has a CDR size of 6.75Å). In doing so, based on our CDR prediction,¹⁷ we expected to see a higher E/P ratio out of such material. However, that did not happen. Rather, what we uncovered in our most recent MTO work on ERI-type molecular sieves was that the improvement in the E/P exhibited by the ERI samples was only possible when the Si/Al was low (Si/Al<7; higher acid site density) or the Si/T-atom ratio was high (Si/T>0.1).²⁶ Indeed, ERI-type molecular sieves showed a significant sensitivity toward acidity as a material property, which is something that we did not observe in CHA, AEI, AFX, and several other frameworks.^{17,19} Results from dissolution-extraction experiments on the molecular sieves after MTO reaction shed light on why ERI behaved so differently. ERI, likely due to its narrow cage, accumulated aromatic HP species at a much slower rate than CHA-type molecular sieves (SSZ-13 and SAPO-34). By increasing the Si/T ratio or lowering the Si/Al ratio, the ERI samples were able to accumulate aromatics at a much faster pace. These aromatic species favored the formation of partially methylated benzenes (1-4MB) and contained naphthalenes as well, which are species that are associated with the aromatics cycle. Thus, it was concluded that the slower maturation of aromatics species coupled with the high $C_{4+}/C_{2=}$ ratios detected early in the reaction are likely indicative of a higher contribution from the olefins cycle.

Since SAT materials can only form over a narrow Si(M)/T range, as demonstrated in the synthesis section, rather than try to improve the E/P ratio, we aimed to design materials that would do the opposite, that is, improve the P/E ratio. **Table 5.1** shows the MTO olefins product

distribution of several SAT-type molecular sieves, including the CIT-17 samples synthesized in this work. **Figure 5.3** shows that virtually all the CIT-17 materials gave improved P/E ratios over SAPO-34 (CHA). Also, the results show that lowering the Si/T ratio leads to higher P/E ratios. These data are consistent with the behavior and trends shown in our previous ERI work. Furthermore, no considerable differences between the olefins product distribution of the various CIT-17 samples synthesized with different OSDAs, but comparable Si/T ratios (CIT-17-1, CIT-17-2 and CIT-17-3) are observed (**Table 5.1**). The one difference between the MTO performance of SAT-type molecular sieves and CHA and AEI-type molecular sieves (beside the olefins product distribution) is lifetime. The TOS data for the CIT-17 samples show that they exhibit shorter lifetimes than the SAPO-34 and SAPO-18 samples. This effect is likely due to size of the SAT cage which is significantly narrower than CHA and AEI cages.

The CIT-17 samples generated a higher C_{4+} fraction (ca. 31%) than CHA (15%) and AEI (25%) (**Table 5.1**). The high C_{4+} fraction is not consistent with the cage size of SAT (one would expect a high ethylene selectivity) but is likely an indication of a possible contribution from the olefins cycle (discussed in more detail in the next section) due to the low Si/T ratio of the samples.

We investigated two MAPO-SAT materials, MgAPO-SAT and CoAPO-SAT. These materials gave improved E/P ratios over CIT-17 (P/E=2.1-2.33 compared to P/E=2.47-3.6 for CIT-17), consistent with the performance of other MAPO materials investigated in this work. That said, MAPO-SAT still gave P/E ratios that were higher than CHA. Furthermore, a closer look at the data in **Table 5.1** shows that substituting Mg or Co (instead of Si) in AlPO₄-structures results in an improvement in the ethylene selectivity and a reduction in the propylene selectivity. This improvement in the E/P ratio is more significant in the case of MAPO-SAT than in the case of MAPO-34 and MAPO-18.

5.3.4 Changing the Reaction Conditions to Further Enhance the P/E

All the reactions in the previous section were conducted at identical reaction conditions (400 °C and WHSV of 1.3 h⁻¹), to allow for comparisons between the various frameworks (cage size) and Si(M)/T ratios (acidity). In this section, results from changing the reaction temperature (300 °C to 450 °C) and WHSV (0.65 to 2.6 h⁻¹) on the P/E ratio of CIT-17-4 are described. Table 5.1 shows the reaction results of these experiments and Figure 5.3 shows the averaged P/E ratios of these various runs. Figure A5.19 shows the TOS data for these set of experiments. The data show that changing the reaction conditions has a profound effect not only on the olefins product distribution but also lifetime, in agreement with prior reports.^{32–34} While high temperatures are helpful for improving the ethylene selectivity, lower temperatures result in faster deactivations. Thus, a balance ought to be struck between these two effects. Also, lowering the reaction temperature down to 300 °C led to the formation of DME only (data not shown). Furthermore, we found through our experiments that it was necessary to lower the WHSV in order to better regulate and delay the catalyst deactivation, though that came at the expense of a slight reduction in the P/E ratio (Figure 5.3). Lowering the WHSV has been shown previously to alter the composition of HP species, steering them toward less methylated benzenes, which are associated with ethylene.³²

The results obtained suggest that T=350 °C and WHSV of 0.65 h⁻¹ are good reaction conditions for enhancing the propylene selectivity in CIT-17 while not significantly increasing the ethylene selectivity (i.e., maintaining a high P/E ratio) or significantly reducing the catalyst lifetime. **Figure 5.4** shows the TOS data for CIT-17-4 at these reaction conditions. At these conditions, we were able to obtain ethylene and propylene selectivities of 12% and 50%, resulting in a P/E ratio of approximately 4.17, which is factor of 2 times higher than AEI and a factor of 4 times higher than CHA-type molecular sieves. This P/E ratio is, indeed, one of the highest for this class of materials.



Figure 5.4. Representative MTO reaction data obtained at 350 °C and WHSV 0.65 h⁻¹ for CIT-17-4.

5.3.5 Relationships between Effluent Product and Retained Hydrocarbons

To rationalize the reaction differences observed in the olefins product distribution and overall MTO behavior between these three frameworks (CHA, AEI, and SAT), dissolution-extraction experiments were performed on five samples at identical reaction conditions (400 °C and WHSV of 1.3 h⁻¹): SAPO-18-1, SAPO-18-2, SAPO-34-1, SAPO-34-18, and CIT-17-4. These samples were chosen to represent two CHA and two AEI materials with different Si/T atom ratios. These four samples were then compared to CIT-17-4, one of the best performing SAT catalysts. For this analysis, each of these catalysts was reacted with methanol and the reaction stopped after 5 minutes to avoid the deactivation region and focus on the early region of reaction that is

associated with the propylene enhancement effect. The reactor was then rapidly cooled to ambient conditions as described in the Experimental Section.

Figure 5.5 shows the extracted hydrocarbons distribution for each of these five catalysts. Each of these catalysts contained primarily polymethylbenzenes (PMB) species. Of the total HP species recovered via this technique, 94+ mol% were polymethylbenzenes, with only a small amount of naphthalenes (<3 mol%) or alkylbenzenes (<1 mol%) detected via this technique. The SAPO-34 and SAPO-34/18 samples showed that they were made up primarily of tetra-, penta-, and hexamethylbenzenes (4MB, 5MB, and 6MB). Both catalysts had similar PMB distributions, with the SAPO-34/18 sample showing a slightly lower relative concentration, likely due to the lower Si/T ratio (thus, acid site density) of this sample.

On the other hand, both SAPO-18 samples had much higher concentrations of 5MB and 6MB species than the SAPO-34 samples, in agreement with prior results and the notion that AEI-type molecular sieves improve the propylene selectivity over CHA-type material due to their ability to better accommodate highly (or fully) methylated benzenes.^{20,21,32} Indeed, both of these frameworks are known to proceed via the aromatics cycle, with the differences in the product distribution often attributed to the type of entrapped species that form in both of these frameworks during reaction. Furthermore, **Figure 5.5** shows that SAPO-18-1 had a much lower concentration of aromatics than SAPO-18-2. This is likely due to its lower Si/T ratio, which is also demonstrated in the TOS reaction data (the catalyst does not immediately achieve 100% conversion) (**Figure A5.16**).

CIT-17-4 showed a high content of tri- and tetra-methylbenzenes (3MB and 4MB), which is consistent with the size of the SAT cage. However, this sample gave a high propylene selectivity in the beginning of this reaction (as opposed to high ethylene selectivity). 3MB and 4MB are associated with ethylene formation whereas 5MB and 6MB are associated with propylene formation.^{20,39,40} Therefore, we measured the concentration of the aromatics in this sample, which showed CIT-17-4 accumulated about half the amount of aromatics that SAPO-34-1 accumulated after 5 mins of reaction under similar conditions. As discussed previously, virtually all of the CIT-17 samples tested in this work had high C_{4+} selectivities and a low ethylene selectivity (particularly early in the reaction). This, as in the case of ERI, suggests a contribution from the olefins cycle.

Therefore, our data indicate that the high propylene selectivity (and low ethylene selectivity) exhibited by CIT-17 are the result of a much higher contribution from the olefins cycle whereas the high propylene observed in AEI-type materials are the result of changes in the identity of the entrapped HP species (i.e., more 5MB and 6MB). As such, the enhancement in propylene selectivity observed in AEI-type materials over CHA-type molecular sieves appear to be mechanistically different.



Figure 5.5. GC-MS distribution of the extracted hydrocarbon species after five minutes of reaction with methanol at 400 $^{\circ}$ C and WHSV of 1.3 h⁻¹ and their relative concentration (relative to SAPO-34-1).

5.3.6 Cyclic Testing

Due to the improved performance of CIT-17-4 in enhancing the propylene selectivity, this catalyst was reused for six consecutive MTO reactions (**Figure 5.6**). Without searching for an optimal catalyst regeneration strategy, a simple intermittent dry calcination in air was used (at 580 °C for 8 h at a ramp rate of 1 °C per minute). The results show that after each regeneration, we are able obtain a behavior and selectivities that are similar to the ones in the first run. Over six runs, the catalyst has efficiently converted methanol for about 10 hours on stream at 350 °C. TGA was performed on the coked sample (after the sixth run) revealing that the material had a mass loss of 6.36%, which is lower than the coke content that is typically recovered from CHA- and AEI-type materials (ca. 10-20%).^{26,27}



Figure 5.6. Time-on-stream (TOS) plot of six consecutive reactions with CIT-17-4 at the optimized reaction conditions ($350 \text{ }^{\circ}\text{C}$ and WHSV of 1.3 ^{h-1}).

5.4 Conclusion

SAT-type molecular sieves (SAPO, MgAPO, and CoAPO) were synthesized using a number of OSDAs to form materials with different Si/T-atom ratios. The synthesis of CIT-17 (a SAPO-SAT material) was achieved without AFX impurities for the first time. These SAT

materials were characterized using a myriad of techniques and tested as catalysts in the MTO reaction. The olefins product distribution of SAT-type molecular sieves were compared to CHAand AEI-type materials. Both SAPO-18 (AEI) and CIT-17 gave improved propylene selectivities (i.e., improved P/E ratios) over SAPO-34 (CHA). Specifically, SAPO-18 gave a P/E ratio of approximately 2 whereas CIT-17 gave a P/E of 2 to 3.5. Changing the Si(M)/T ratio did not enhance the olefins product distribution of CHA and AEI-type molecular sieves as much as it did with the SAT-type molecular sieves. Altering the reaction conditions by changing the temperature and methanol WHSV led to further improvements in the propylene selectivity for CIT-17. A P/E ratio of 4.17 was reported for CIT-17, which is one of the highest P/E ratios reported for this class of materials.

To rationalize the differences in the MTO behavior between these three frameworks, organic species retained in the cavities of the partially reacted catalysts were analyzed after 5 mins of reaction via dissolution of the molecular sieve and extraction of organic components. SAPO-34 samples retained mostly 4MB, 5MB, and 6MB whereas SAPO-18 retained mostly 5MB and 6MB. CIT-17, on the other hand, comprised mostly of 3MB and 4MB, which are typically associated with ethylene. Further investigations into the concentration of the aromatic species revealed that CIT-17 materials accumulate aromatic species at a much lower rate than CHA and AEI. Therefore, by regulating the cage size and acid site density as well as strength of small-pore, cage-type molecular sieves, an enhancement in propylene selectivity can be achieved in such materials by increasing the contribution of the olefins cycle.

5.5 Acknowledgements

The Chevron Energy and Technology Company provided financial support for this research. The authors gratefully acknowledge Dr. Sonjong Hwang for assistance with solid-state

NMR and Dr. Nathan Dalleska (Resnick Water and Environment Laboratory at the California Institute of Technology) for assistance with the GC-MS experiments. FHA would like to thank Aramco R&D for financially supporting his graduate studies.

5.6 References

 Hayes, G.; Laurel, M.; MacKinnon, D.; Zhao, T.; Houck, H. A.; Becer, C. R. Polymers without Petrochemicals: Sustainable Routes to Conventional Monomers. *Chem. Rev.* 2023, *123* (5), 2609– 2734. https://doi.org/10.1021/acs.chemrev.2c00354.

(2) Fernelius, C. W.; Wittcoff, H.; Varnerin, R. E. Ethylene: The Organic Chemical Industry's Most Important Building Block. J. Chem. Educ. 1979, 56 (6), 385. https://doi.org/10.1021/ed056p385.

(3) Yarulina, I.; Chowdhury, A. D.; Meirer, F.; Weckhuysen, B. M.; Gascon, J. Recent Trends and Fundamental Insights in the Methanol-to-Hydrocarbons Process. *Nature Catalysis* **2018**, *1* (6), 398–411. https://doi.org/10.1038/s41929-018-0078-5.

(4) Amghizar, I.; Vandewalle, L. A.; Geem, K. M. V.; Marin, G. B. New Trends in Olefin Production. *Engineering* **2017**, *3* (2), 171–178. https://doi.org/10.1016/J.ENG.2017.02.006.

(5) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. *Chemical Reviews* 2014, *114*(20), 10613–10653. https://doi.org/10.1021/cr5002436.

(6) Otroshchenko, T.; Zhang, Q.; Kondratenko, E. V. Enhancing Propene Formation in the Metathesis of Ethylene with 2-Butene at Close to Room Temperature over MoOx/SiO2 through Support Promotion with P, Cl, or S. *ACS Catal.* **2021**, *11* (22), 14159–14167. https://doi.org/10.1021/acscatal.1c04267.

(7) Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catal.* 2015, 5 (3), 1922–1938. https://doi.org/10.1021/acscatal.5b00007.

(8) Carrero, C. A.; Schloegl, R.; Wachs, I. E.; Schomaecker, R. Critical Literature Review of the Kinetics for the Oxidative Dehydrogenation of Propane over Well-Defined Supported Vanadium Oxide Catalysts. *ACS Catal.* **2014**, *4* (10), 3357–3380. https://doi.org/10.1021/cs5003417.

(9) Lin, T.; Gong, K.; Wang, C.; An, Y.; Wang, X.; Qi, X.; Li, S.; Lu, Y.; Zhong, L.; Sun, Y. Fischer–Tropsch Synthesis to Olefins: Catalytic Performance and Structure Evolution of Co2C-Based Catalysts under a CO2 Environment. *ACS Catal.* **2019**, *9* (10), 9554–9567. https://doi.org/10.1021/acscatal.9b02513.

(10) Chen, S.; Chang, X.; Sun, G.; Zhang, T.; Xu, Y.; Wang, Y.; Pei, C.; Gong, J. Propane Dehydrogenation: Catalyst Development, New Chemistry, and Emerging Technologies. *Chem. Soc. Rev.* **2021**, *50* (5), 3315–3354. https://doi.org/10.1039/D0CS00814A.

(11) Yamazaki, H.; Shima, H.; Imai, H.; Yokoi, T.; Tatsumi, T.; Kondo, J. N. Evidence for a "Carbene-like" Intermediate during the Reaction of Methoxy Species with Light Alkenes on H-ZSM-5. *Angewandte Chemie International Edition* **2011**, *50* (8), 1853–1856. https://doi.org/10.1002/anie.201007178.

(12) Torres Galvis, H. M.; de Jong, K. P. Catalysts for Production of Lower Olefins from Synthesis Gas: A Review. *ACS Catal.* **2013**, *3* (9), 2130–2149. https://doi.org/10.1021/cs4003436.

(13) Chen, J. Q.; Bozzano, A.; Glover, B.; Fuglerud, T.; Kvisle, S. Recent Advancements in Ethylene and Propylene Production Using the UOP/Hydro MTO Process. *Catalysis Today* 2005, *106* (1), 103–107. https://doi.org/10.1016/j.cattod.2005.07.178.

(14) Richardson, Y.; Drobek, M.; Julbe, A.; Blin, J.; Pinta, F. Chapter 8 - Biomass Gasification to Produce Syngas. In *Recent Advances in Thermo-Chemical Conversion of Biomass*; Pandey, A., Bhaskar, T., Stöcker, M., Sukumaran, R. K., Eds.; Elsevier: Boston, 2015; pp 213–250. https://doi.org/10.1016/B978-0-444-63289-0.00008-9.

(15) Ma, Z.; Porosoff, M. D. Development of Tandem Catalysts for CO2 Hydrogenation to Olefins. *ACS Catal.* **2019**, *9* (3), 2639–2656. https://doi.org/10.1021/acscatal.8b05060.

(16) Sun, X.; Mueller, S.; Liu, Y.; Shi, H.; Haller, G. L.; Sanchez-Sanchez, M.; van Veen, A.
C.; Lercher, J. A. On Reaction Pathways in the Conversion of Methanol to Hydrocarbons on
HZSM-5. *Journal of Catalysis* 2014, *317*, 185–197. https://doi.org/10.1016/j.jcat.2014.06.017.

(17) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. ACS Catal. 2019, 9 (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.

(18) Kang, J. H.; Walter, R.; Xie, D.; Davis, T.; Chen, C.-Y.; Davis, M. E.; Zones, S. I. Further Studies on How the Nature of Zeolite Cavities That Are Bounded by Small Pores Influences the Conversion of Methanol to Light Olefins. *ChemPhysChem* **2018**, *19* (4), 412–419. https://doi.org/10.1002/cphc.201701197.

(19) Bhawe, Y.; Moliner-Marin, M.; Lunn, J. D.; Liu, Y.; Malek, A.; Davis, M. Effect of Cage
Size on the Selective Conversion of Methanol to Light Olefins. *ACS Catal.* 2012, *2* (12), 2490–
2495. https://doi.org/10.1021/cs300558x.

(20) Ferri, P.; Li, C.; Paris, C.; Rodríguez-Fernández, A.; Moliner, M.; Boronat, M.; Corma, A. The Limits of the Confinement Effect Associated to Cage Topology on the Control of the MTO Selectivity. *ChemCatChem* **2021**, *13* (6), 1578–1586. https://doi.org/10.1002/cctc.202001760. (21) Ferri, P.; Li, C.; Paris, C.; Vidal-Moya, A.; Moliner, M.; Boronat, M.; Corma, A. Chemical and Structural Parameter Connecting Cavity Architecture, Confined Hydrocarbon Pool Species, and MTO Product Selectivity in Small-Pore Cage-Based Zeolites. *ACS Catal.* **2019**, *9* (12), 11542–11551. https://doi.org/10.1021/acscatal.9b04588.

(22) Ferri, P.; Li, C.; Millán, R.; Martínez-Triguero, J.; Moliner, M.; Boronat, M.; Corma, A.
Impact of Zeolite Framework Composition and Flexibility on Methanol-To-Olefins Selectivity:
Confinement or Diffusion? *Angewandte Chemie International Edition* 2020, *59* (44), 19708–19715. https://doi.org/10.1002/anie.202007609.

(23) Pinilla-Herrero, I.; Márquez-Álvarez, C.; Sastre, E. Complex Relationship between SAPO Framework Topology, Content and Distribution of Si and Catalytic Behaviour in the MTO Reaction. *Catal. Sci. Technol.* **2017**, *7* (17), 3892–3901. https://doi.org/10.1039/C7CY01250K.

(24) Dai, W.; Wang, X.; Wu, G.; Guan, N.; Hunger, M.; Li, L. Methanol-to-Olefin Conversion on Silicoaluminophosphate Catalysts: Effect of Brønsted Acid Sites and Framework Structures. *ACS Catalysis* **2011**, *1* (4), 292–299. https://doi.org/10.1021/cs200016u.

(25) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E.
Effect of Heteroatom Concentration in SSZ-13 on the Methanol-to-Olefins Reaction. *ACS Catal.* **2016**, *6* (2), 542–550. https://doi.org/10.1021/acscatal.5b01450.

(26) Alshafei, F. H.; Park, Y.; Zones, S. I.; Davis, M. E. Methanol-to-Olefins Catalysis on ERI-Type Molecular Sieves: Towards Enhancing Ethylene Selectivity. *Journal of Catalysis* 2021, *404*, 620–633. https://doi.org/10.1016/j.jcat.2021.10.025.

(27) Dusselier, M.; Deimund, M. A.; Schmidt, J. E.; Davis, M. E. Methanol-to-Olefins Catalysis with Hydrothermally Treated Zeolite SSZ-39. *ACS Catal.* **2015**, *5* (10), 6078–6085. https://doi.org/10.1021/acscatal.5b01577.

(28) Ji, Y.; Deimund, M. A.; Bhawe, Y.; Davis, M. E. Organic-Free Synthesis of CHA-Type Zeolite Catalysts for the Methanol-to-Olefins Reaction. *ACS Catal.* **2015**, *5* (7), 4456–4465. https://doi.org/10.1021/acscatal.5b00404.

(29) Hua, J.; Dong, X.; Wang, J.; Chen, C.; Shi, Z.; Liu, Z.; Han, Y. Methanol-to-Olefin Conversion over Small-Pore DDR Zeolites: Tuning the Propylene Selectivity via the Olefin-Based Catalytic Cycle. *ACS Catal.* **2020**, *10* (5), 3009–3017. https://doi.org/10.1021/acscatal.9b05521.

(30) Xie, J.; Firth, D. S.; Cordero-Lanzac, T.; Airi, A.; Negri, C.; Øien-Ødegaard, S.; Lillerud,
K. P.; Bordiga, S.; Olsbye, U. MAPO-18 Catalysts for the Methanol to Olefins Process: Influence of Catalyst Acidity in a High-Pressure Syngas (CO and H2) Environment. *ACS Catal.* 2022, *12*(2), 1520–1531. https://doi.org/10.1021/acscatal.1c04694.

(31) Cnudde, P.; Demuynck, R.; Vandenbrande, S.; Waroquier, M.; Sastre, G.; Speybroeck, V.
V. Light Olefin Diffusion during the MTO Process on H-SAPO-34: A Complex Interplay of Molecular Factors. *J. Am. Chem. Soc.* 2020, *142* (13), 6007–6017. https://doi.org/10.1021/jacs.9b10249.

(32) Shi, Z.; Bhan, A. Tuning the Ethylene-to-Propylene Ratio in Methanol-to-Olefins Catalysis on Window-Cage Type Zeolites. *Journal of Catalysis* **2021**, *395*, 266–272. https://doi.org/10.1016/j.jcat.2021.01.015.

(33) Castellanos-Beltran, I. J.; Assima, G. P.; Lavoie, J.-M. Effect of Temperature in the Conversion of Methanol to Olefins (MTO) Using an Extruded SAPO-34 Catalyst. *Frontiers of*

Chemical Science and Engineering **2018**, *12* (2), 226–238. https://doi.org/10.1007/s11705-018-1709-8.

(34) Borodina, E.; Sharbini Harun Kamaluddin, H.; Meirer, F.; Mokhtar, M.; Asiri, A. M.; Al-Thabaiti, S. A.; Basahel, S. N.; Ruiz-Martinez, J.; Weckhuysen, B. M. Influence of the Reaction Temperature on the Nature of the Active and Deactivating Species During Methanol-to-Olefins Conversion over H-SAPO-34. *ACS Catal.* 2017, 7 (8), 5268–5281. https://doi.org/10.1021/acscatal.7b01497.

(35) Zhong, J.; Han, J.; Wei, Y.; Liu, Z. Catalysts and Shape Selective Catalysis in the Methanol-to-Olefin (MTO) Reaction. *Journal of Catalysis* **2021**, *396*, 23–31. https://doi.org/10.1016/j.jcat.2021.01.027.

(36) Dahl, I. M.; Kolboe, S. On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: I. Isotopic Labeling Studies of the Co-Reaction of Ethene and Methanol. *Journal of Catalysis* **1994**, *149* (2), 458–464. https://doi.org/10.1006/jcat.1994.1312.

(37) Hu, M.; Wang, C.; Gao, X.; Chu, Y.; Qi, G.; Wang, Q.; Xu, G.; Xu, J.; Deng, F. Establishing a Link Between the Dual Cycles in Methanol-to-Olefins Conversion on H-ZSM-5:
Aromatization of Cycloalkenes. *ACS Catal.* 2020, *10* (7), 4299–4305.
https://doi.org/10.1021/acscatal.0c00838.

(38) Sun, X.; Mueller, S.; Shi, H.; Haller, G. L.; Sanchez-Sanchez, M.; van Veen, A. C.; Lercher, J. A. On the Impact of Co-Feeding Aromatics and Olefins for the Methanol-to-Olefins Reaction on HZSM-5. *Journal of Catalysis* **2014**, *314*, 21–31. https://doi.org/10.1016/j.jcat.2014.03.013.

(39) Hwang, A.; Prieto-Centurion, D.; Bhan, A. Isotopic Tracer Studies of Methanol-to-Olefins
Conversion over HSAPO-34: The Role of the Olefins-Based Catalytic Cycle. *Journal of Catalysis*2016, *337*, 52–56. https://doi.org/10.1016/j.jcat.2016.01.021.

(40) Hwang, A.; Johnson, B. A.; Bhan, A. Mechanistic Study of Methylbenzene Dealkylation in Methanol-to-Olefins Catalysis on HSAPO-34. *Journal of Catalysis* **2019**, *369*, 86–94. https://doi.org/10.1016/j.jcat.2018.10.022.

(41) Goetze, J.; Meirer, F.; Yarulina, I.; Gascon, J.; Kapteijn, F.; Ruiz-Martínez, J.; Weckhuysen, B. M. Insights into the Activity and Deactivation of the Methanol-to-Olefins Process over Different Small-Pore Zeolites As Studied with Operando UV–Vis Spectroscopy. *ACS Catal.*2017, 7 (6), 4033–4046. https://doi.org/10.1021/acscatal.6b03677.

(42) Peng, Q.; Wang, G.; Wang, Z.; Jiang, R.; Wang, D.; Chen, J.; Huang, J. Tuning Hydrocarbon Pool Intermediates by the Acidity of SAPO-34 Catalysts for Improving Methanolto-Olefins Reaction. *ACS Sustainable Chem. Eng.* **2018**, *6* (12), 16867–16875. https://doi.org/10.1021/acssuschemeng.8b04210.

(43) Teketel, S.; Skistad, W.; Benard, S.; Olsbye, U.; Lillerud, K. P.; Beato, P.; Svelle, S. Shape Selectivity in the Conversion of Methanol to Hydrocarbons: The Catalytic Performance of One-Dimensional 10-Ring Zeolites: ZSM-22, ZSM-23, ZSM-48, and EU-1. *ACS Catal.* **2012**, *2* (1), 26–37. https://doi.org/10.1021/cs200517u.

(44) Ilias, S.; Khare, R.; Malek, A.; Bhan, A. A Descriptor for the Relative Propagation of the Aromatic- and Olefin-Based Cycles in Methanol-to-Hydrocarbons Conversion on H-ZSM-5. *Journal of Catalysis* **2013**, *303*, 135–140. https://doi.org/10.1016/j.jcat.2013.03.021.

(45) Smith, R. L.; Svelle, S.; Campo, P. del; Fuglerud, T.; Arstad, B.; Lind, A.; Chavan, S.; Attfield, M. P.; Akporiaye, D.; Anderson, M. W. CHA/AEI Intergrowth Materials as Catalysts for the Methanol-to-Olefins Process. *Applied Catalysis A: General* **2015**, *505*, 1–7. https://doi.org/10.1016/j.apcata.2015.06.027.

(46) Martínez-Franco, R.; Li, Z.; Martínez-Triguero, J.; Moliner, M.; Corma, A. Improving the Catalytic Performance of SAPO-18 for the Methanol-to-Olefins (MTO) Reaction by Controlling the Si Distribution and Crystal Size. *Catal. Sci. Technol.* **2016**, *6* (8), 2796–2806. https://doi.org/10.1039/C5CY02298C.

(47) Martín, N.; Li, Z.; Martínez-Triguero, J.; Yu, J.; Moliner, M.; Corma, A. Nanocrystalline
SSZ-39 Zeolite as an Efficient Catalyst for the Methanol-to-Olefin (MTO) Process. *Chem. Commun.* 2016, *52* (36), 6072–6075. https://doi.org/10.1039/C5CC09719C.

(48) Hu, S.; Shan, J.; Zhang, Q.; Wang, Y.; Liu, Y.; Gong, Y.; Wu, Z.; Dou, T. Selective Formation of Propylene from Methanol over High-Silica Nanosheets of MFI Zeolite. *Applied Catalysis A: General* **2012**, *445–446*, 215–220. https://doi.org/10.1016/j.apcata.2012.08.032.

(49) Lin, L.; Fan, M.; Sheveleva, A. M.; Han, X.; Tang, Z.; Carter, J. H.; da Silva, I.; Parlett, C. M. A.; Tuna, F.; McInnes, E. J. L.; Sastre, G.; Rudić, S.; Cavaye, H.; Parker, S. F.; Cheng, Y.; Daemen, L. L.; Ramirez-Cuesta, A. J.; Attfield, M. P.; Liu, Y.; Tang, C. C.; Han, B.; Yang, S. Control of Zeolite Microenvironment for Propene Synthesis from Methanol. *Nature Communications* 2021, *12* (1), 822. https://doi.org/10.1038/s41467-021-21062-1.

(50) Hu, S.; Gong, Y.; Xu, Q.; Liu, X.; Zhang, Q.; Zhang, L.; Dou, T. Highly Selective Formation of Propylene from Methanol over High-Silica EU-1 Zeolite Catalyst. *Catalysis Communications* **2012**, *28*, 95–99. https://doi.org/10.1016/j.catcom.2012.08.011.

(51) Zhao, X.; Wang, L.; Li, J.; Xu, S.; Zhang, W.; Wei, Y.; Guo, X.; Tian, P.; Liu, Z. Investigation of Methanol Conversion over High-Si Beta Zeolites and the Reaction Mechanism of Their High Propene Selectivity. *Catal. Sci. Technol.* **2017**, *7* (24), 5882–5892. https://doi.org/10.1039/C7CY01804E.

Ji, Y.; Birmingham, J.; Deimund, M. A.; Brand, S. K.; Davis, M. E. Steam-Dealuminated,
OSDA-Free RHO and KFI-Type Zeolites as Catalysts for the Methanol-to-Olefins Reaction. *Microporous and Mesoporous Materials* 2016, 232, 126–137.
https://doi.org/10.1016/j.micromeso.2016.06.012.

(53) Yang, M.; Li, B.; Gao, M.; Lin, S.; Wang, Y.; Xu, S.; Zhao, X.; Guo, P.; Wei, Y.; Ye, M.;
Tian, P.; Liu, Z. High Propylene Selectivity in Methanol Conversion over a Small-Pore SAPO
Molecular Sieve with Ultra-Small Cage. *ACS Catal.* 2020, *10* (6), 3741–3749.
https://doi.org/10.1021/acscatal.9b04703.

(54) W. Noble, G.; A. Wright, P.; Kvick, Å. The Templated Synthesis and Structure Determination by Synchrotron Microcrystal Diffraction of the Novel Small Pore Magnesium Aluminophosphate STA-2[†]. *J. Chem. Soc., Dalton Trans.* **1997**, No. 23, 4485–4490. https://doi.org/10.1039/A705091G.

(55) Castro, M.; Seymour, V. R.; Carnevale, D.; Griffin, J. M.; Ashbrook, S. E.; Wright, P. A.; Apperley, D. C.; Parker, J. E.; Thompson, S. P.; Fecant, A.; Bats, N. Molecular Modeling, Multinuclear NMR, and Diffraction Studies in the Templated Synthesis and Characterization of the Aluminophosphate Molecular Sieve STA-2. *J. Phys. Chem. C* **2010**, *114* (29), 12698–12710. https://doi.org/10.1021/jp104120y.
(56) Seymour, V. R.; Eschenroeder, E. C. V.; Wright, P. A.; Ashbrook, S. E. An NMR
Crystallographic Approach to Monitoring Cation Substitution in the Aluminophosphate STA-2. *Solid State Nuclear Magnetic Resonance* 2015, 65, 64–74.
https://doi.org/10.1016/j.ssnmr.2014.10.007.

(57) Djieugoue, M.-A.; Prakash, A. M.; Kevan, L. Electron Spin Resonance and Electron Spin–Echo Modulation Studies of Synthesized NiAPSO-34 Molecular Sieve and Comparison with Ion-Exchanged NiH–SAPO-34 Molecular Sieve. *J. Phys. Chem. B* **1999**, *103* (5), 804–811. https://doi.org/10.1021/jp9823897.

(58)Ashtekar, S.; Chilukuri, S. V. V.; Prakash, A. M.; Chakrabarty, D. K. Small Pore Aluminum Phosphate Molecular Sieves with Chabazite Structure: Incorporation of Manganese in the Structures -34 and -44. J. Phys. Chem. 1996, 100 (9), 3665-3670. https://doi.org/10.1021/jp951800c.

(59) Ashtekar, S.; Chilukuri, S. V. V.; Prakash, A. M.; Harendranath, C. S.; Chakrabarty, D. K. Small Pore Aluminum Phosphate Molecular Sieves with Chabazite Structure: Incorporation of Cobalt in the Structures -34 and -44. *J. Phys. Chem.* **1995**, *99* (18), 6937–6943. https://doi.org/10.1021/j100018a027.

(60) Fan, D.; Tian, P.; Xu, S.; Xia, Q.; Su, X.; Zhang, L.; Zhang, Y.; He, Y.; Liu, Z. A Novel Solvothermal Approach to Synthesize SAPO Molecular Sieves Using Organic Amines as the Solvent and Template. *J. Mater. Chem.* **2012**, *22* (14), 6568–6574. https://doi.org/10.1039/C2JM15281A. (61) Chen, J.; Wright, P. A.; Thomas, J. M.; Natarajan, S.; Marchese, L.; Bradley, S. M.; Sankar,
G.; Catlow, C. R. A.; Gai-Boyes, P. L. SAPO-18 Catalysts and Their Broensted Acid Sites. J. *Phys. Chem.* 1994, 98 (40), 10216–10224. https://doi.org/10.1021/j100091a042.

(62) Bakhtiar, S. ul H.; Ali, S.; Wang, X.; Yuan, F.; Li, Z.; Zhu, Y. Synthesis of Sub-Micrometric SAPO-34 by a Morpholine Assisted Two-Step Hydrothermal Route and Its Excellent MTO Catalytic Performance. *Dalton Trans.* **2019**, *48* (8), 2606–2616. https://doi.org/10.1039/C8DT04559C.

(63) He, H.; Klinowski, J. Solid-State NMR Studies of the Aluminophosphate Molecular Sieve AlPO4-18. *J. Phys. Chem.* **1993**, *97* (40), 10385–10388. https://doi.org/10.1021/j100142a020.

(64) Duan, Z.; Wang, N.; Xu, H.; Wu, P. Structural Transformation-Involved Synthesis of Nanosized ERI-Type Zeolite and Its Catalytic Property in the MTO Reaction. *Inorg. Chem.* 2022, *61* (20), 8066–8075. https://doi.org/10.1021/acs.inorgchem.2c00914.

(65) Wilson, S. T.; Broach, R. W.; Blackwell, C. S.; Bateman, C. A.; McGuire, N. K.; Kirchner,
R. M. Synthesis, Characterization and Structure of SAPO-56, a Member of the ABC Double-SixRing Family of Materials with Stacking Sequence AABBCCBB. *Microporous and Mesoporous Materials* 1999, 28 (1), 125–137. https://doi.org/10.1016/S1387-1811(98)00293-5.

(66) Miletto, I.; Ivaldi, C.; Paul, G.; Chapman, S.; Marchese, L.; Raja, R.; Gianotti, E.
Hierarchical SAPO-34 Architectures with Tailored Acid Sites Using Sustainable Sugar Templates. *ChemistryOpen* 2018, 7 (4), 297–301. https://doi.org/10.1002/open.201800001.

Chapter 6 | Conclusions and Outlook

6.1 Conclusions

Small-pore, cage-type molecular sieves have received great attention in the last two decades due to the commercialization of the methanol-to-olefins (MTO) process. The MTO reaction can be accomplished using solid acid catalysts such as, zeolites (aluminiosilicates), silicoaluminophosphates (SAPOs), or metalloaluminophosphates (MeAPOs), thus, providing an alternative route for the production of light olefins (e.g., ethylene and propylene) from natural gas, coal, or biomass by using methanol as an intermediate. SAPO-34 (CHA), a molecular sieve with a chabazite (CHA) topology (three-dimensional cage structure with 8-membered ring pores), is the commercial catalyst for this process. Due its cage dimensions, structure, mild acidity, and pore size, SAPO-34 achieves complete conversion to methanol while providing exceptionally high ethylene and propylene selectivities (70+%).

In spite of the commercial success of SAPO-34, there is a growing interest in the field to developing strategies and catalysts that would augment the olefins product distribution to favor the formation of either more ethylene (i.e., increase the E/P) or more propylene (i.e., increase P/E), depending on market demand. Our group introduced the concept of a cage-defining ring (CDR), the minimum number of tetrahedral atoms of the ring encircling the center of the framework cage for a given molecular sieve topology, which correlated with the MTO olefins product distribution for 14 different frameworks (over 30 materials). As a part of this study, we also demonstrated for a few randomly selected frameworks that acidity (both acid site density and strength) appears to play a secondary role to the dominating influence of cage size/dimension on the olefins product distribution. As such, by simply regulating the size of the cage, we were able to control the olefins

product distribution (by either improving the E/P ratio or the P/E ratio) in a rather predictable manner.

Further investigations (outlined in Chapter 2) on the effect of acidity on MTO reveal that acidity could play a more significant role than what was previously shown and anticipated, in influencing the olefins product distribution. The extent to which acidity influences the product distribution depends on the framework/topology chosen and its cage size/geometry. Our experimental data show that frameworks that contain narrow cages (e.g., SAT, ERI, SWY, and LEV; all Category II materials) are more prone to the effects of acidity. The influence of acidity appears to be limited to frameworks/topologies that demonstrate a substantial contribution from the olefins cycle (as evidenced by high $C_{4+}/C_{2=}$) and accumulate aromatic species (i.e., aromatics cycle) at a slower rate (as determined via GC-MS studies) than CHA- and AEI-type molecular sieves. On the other hand, frameworks with larger cages (e.g., AEI and CHA) proceed primarily via the aromatics cycle as evidenced by the high concentration of aromatic species measured via dissolution-extraction experiments and low $C_{4+}/C_{2=}$. As such, changing the acidity by changing the Si/Al or Si/T-atom ratio of such materials, does not significantly influence the olefins product distribution. The results in Chapter 2 identify a missing (yet a very important) link between cage size and acidity.

Uncovering the missing link between acidity and cage size allowed for improving the MTO behavior of ERI-type molecular sieves (discussed in Chapters 3 and 4) and SAT-type molecular sieves (discussed in Chapter 5). Our results demonstrate that by tuning the Si/Al ratio in ERI-type zeolites (e.g., SSZ-98, UZM-12, and ERI-type zeolites), the ethylene-to-propylene ratio (E/P) in MTO can be greatly enhanced (E/P=1.5+), reaching a maximum E/P of approximately 2.4 for SSZ-98-1 (Si/Al=3.96) right before the catalyst deactivates. This is a factor of 2+ improvement

over SAPO-34, which typically gives E/P ratios of 0.7-0.8. While the ERI-zeolite samples showed improved E/P ratios, the SAPO-17 (ERI) samples gave E/P ratios of 0.7-1.1 and a generally high C_{4+} fraction, owing to a slower maturation of aromatic hydrocarbon-pool (HP) species and the presence of aromatics with bulky alkyl-groups. Therefore, enhancing the ethylene selectivity in ERI-type molecular sieves was accomplished only when the acid site density and strength was carefully regulated (i.e., in zeolite samples with low Si/Al).

Inspired by these results on ERI, we synthesized, for the first time, a pure SAPO-SAT sample (denoted as CIT-17). SAT has a cage size that is narrower than ERI, thus, making it one of the narrowest cages that can accommodate MTO active aromatic species (e.g., methylbenzenes). The MTO reaction data show that by controlling the cage environment (size and acid site density and strength), SAT-type molecular sieves can give a P/E of 2+ (and as high as 4.2 for CIT-17). Indeed, the combination of low acidity of CIT-17 and unique structural features of the narrow SAT-cage lead to a catalytic pathway and a mechanism (i.e., higher contribution from the olefins cycle) that predominantly favors propylene formation.

The results in this thesis demonstrate the delicate relationship that exists between acidity and cage size, and how this relationship can be utilized to manipulate the active and entrapped hydrocarbon pool species that form as a part of the dual cycle, thus, either enhancing the ethyleneto-propylene (or propylene-to-ethylene) ratio in MTO, in a significant improvement over CHAtype molecular sieves.

6.2 Outlook

Based on the results outlined in this thesis, there are a few areas that warrant further research. These are outlined in this section.

In Chapter 3, the dissolution-extraction experiments showed significant amounts of 3-ring compounds that formed over the course of the reaction, particularly near the deactivation region. Indeed, as the ERI-type catalysts deactivated, they all had varying (but high) amounts of 3-ring organics. It appears that 3-ring compounds are more unique to the ERI cage (due to its length) but what role, if any, do these 3-ring compounds play in enhancing the ethylene selectivity? Also, do these 3-ring compounds form inside the cages of ERI or on the external surface of the catalyst? More work on this topic will aid in further understanding how to enhance the ethylene selectivity in MTO.

In Chapter 3, virtually all of the reaction results (irrespective of Si/Al or Si/T) showed that ERI catalysts give more ethylene than propylene as the catalysts are about to deactivate and methanol conversions are about to drop. Given the data provided in Chapter 3, could one design a "pre-coked" ERI catalyst that is able to start with a high ethylene-to-propylene (E/P) and operate this catalyst in a fluidized bed reactor such that the re-generation of the catalyst does not burn off the entirety of the coke, thus, designing an ERI catalyst that is able to give a steady stream of ethylene with high selectivity (not just near deactivation)?

In Chapter 5, SAT-SAPO was synthesized and denoted as CIT-17. Attempts to synthesize CIT-17 with a higher Si/T-atom ratio (to improve the ethylene-to-propylene ratio in MTO) led to the formation of AFX (or other crystalline phases). I also attempted to make SAT-SAPO but with other OSDAs. However, I was not able to make the product with a higher Si/T ratio. Also, attempts to synthesize the zeolite form of SAT did not lead to the formation of an SAT phase. It would be interesting to prepare such materials (SAT-SAPO with high Si content and SAT zeolite) and investigate them in MTO.

Appendices

Appendix A | Supplemental Information – Chapter 2

Table A2.1. Sample IDs of the ERI-type molecular sieves tested in this work and their corresponding IDs in our previous work, where they were also characterized (refer to the Materials Section).

Sample ID (This Work)	Sample ID (Previous Work)
SAPO-17-0.1Si	SAPO-17-1
SAPO-17-0.2Si	SAPO-17-2
SAPO-17-0.3Si-1	SAPO-17-5
SAPO-17-0.3Si-2	SAPO-17-6
SAPO-17-0.4Si-1	-
SAPO-17-0.4Si-2	SAPO-17-4
SAPO-17-0.6Si	-
SAPO-17-0.8Si	SAPO-17-3
SSZ-98-(4)	SSZ-98-1
SSZ-98-(6)	SSZ-98-2
UZM-12-1(2)	UZM-12
UZM-12-2-(6)	-
ERI Zeolite-1-(5)	ERI Zeolite-1
ERI Zeolite-2-(5)	ERI Zeolite-2
ERI Zeolite-3-(8)	ERI Zeolite-3



Figure A2.1. Powder XRD patterns of AEI-type molecular sieves. (a) SAPO samples and (b) zeolites.



Figure A2.2. Powder XRD patterns of CHA-type molecular sieves. (a) SAPO samples and (b) zeolites.



Figure A2.3. Powder XRD patterns of LEV-type molecular sieves. (a) SAPO samples and (b) zeolites.



Figure A2.4. Powder XRD patterns of ERI-type molecular sieves. (a) SAPO samples and (b) zeolites.



Figure A2.5. Powder XRD patterns of SWY-type molecular sieves. (a) SAPO samples (STA-20) and (b) zeolite (STA-30).



Figure A2.6. ²⁹Si MAS NMR for selected SAPOs and zeolites (proton-form).



Figure A2.7. ¹H MAS NMR spectra for dehydrated SAPOs and zeolites (proton-form).



Figure A2.8. MTO reaction on SAPO-18 obtained at T=400 °C.



Figure A2.9. MTO on AEI zeolites obtained at T=400 °C.



Figure A2.10. MTO reaction on SAPO-34 obtained at T=400 °C.



Figure A2.11. MTO on CHA zeolites obtained at T=400 °C.



Figure A2.12. MTO on SAPO-LEV materials obtained at T=400 °C.



Figure A2.13. MTO on LEV-type zeolites obtained at T=400 °C.



Figure A2.14. MTO on SAPO-ERI materials obtained at T=400 °C.



Figure A2.15. MTO on ERI zeolites obtained at T=400 °C.



Figure A2.16. MTO on SAPO-SWY obtained at T=400 °C.



Figure A2.17. MTO on STA-30-(8) (SWY Zeolite) obtained at T=400 °C.

Appendix B | Supplemental Information – Chapter 3



Figure A3.1. 3-D plot of ethylene-to-propylene (E/P) ratio versus butenes (butylenes) and ethylene selectivities (averaged when the methanol conversion is >98%), showing the MTO catalytic performance of various molecular sieves at 400 °C and WHSV=1.3 h⁻¹. The plot was produced using data reported in our previous publication ¹. Category I (CHA, AFX, and SFW) comprises materials that form roughly equal amounts of ethylene and propylene, Category II (ERI and LEV; smallest CDR) comprises materials that form more ethylene than propylene (as well as low butenes), Category III (DDR, AEI, RTH, ITE, and SAV) comprises materials that form more propylene than ethylene, and lastly, Category IV (KFI, LTA, UFI, and RHO; largest CDR) comprises materials that form large amounts of butenes relative to ethylene and propylene. The sample marked as "SSZ-98-1" is from this work, which achieves the highest E/P of any material we tested at our experimental conditions.

A3.1 Synthesis of Organic Structure-Directing Agents (OSDAs)

A.3.1.1 Materials

A11 materials as-received without further purification. were used N.N.Ntrimethyladamantylammonium hydroxide (OSDA 1) (Sachem), tetraethylammonium hydroxide solution (OSDA 2) (40%, Aldrich), 1.4-diazabicyclo[2.2.2]octane (DABCO, 99%, Sigma-Aldrich), iodomethane (methyl iodide) (99.5%, Cu stabilized, Sigma-Aldrich), chloroform (99.8+%, Alfa Aesar), diethyl ether (98%, VWR), N-methylpiperidine (99%, Aldrich), 1,4dibromobutane (99%, Sigma Aldrich), trimethylamine solution (25% in water, Sigma-Aldrich), formic acid (95%, Sigma-Aldrich), sodium bicarbonate (99.7%, Mallinckrodt Chemicals), trans-1,4-diaminocyclohexane (98%, Aldrich), formaldehyde (36.5-38%, Sigma), hydrochloric acid (2 N, J.T. Baker), sodium hydroxide (pellets, EMD milipore), quinuclidine (97%, Alfa Aesar), 1,3dibromopropane (99%, Sigma-Aldrich), 18-crown-6 (OSDA 4) (99%, Sigma-Aldrich), hexamethonium bromide (**OSDA 6**; was also converted to its hydroxide form and used, Sigma), and cyclohexylamine (OSDA 9) (Sigma-Aldrich).

A3.1.2 OSDA Syntheses

A3.1.2.1 OSDA 3

OSDA 3 was prepared from the reaction of DABCO and iodomethane (methyl iodide) ¹. In a typical synthesis, DABCO (250 mmol) was dissolved in 350 cm³ of chloroform in a 1000 cm³ round-bottom flask. The round bottom flask was cooled using dry ice and acetone due to the exothermic nature of the reaction with iodomethane. Iodomethane (1000 mmol) was then added dropwise to the DABCO-containing solution. After completion of the addition of iodomethane, the reaction mixture was stirred at room temperature for approximately 4 days. Chloroform and iodomethane were removed by a rotary evaporator. (Note: Iodomethane vapor is toxic). The solid product was washed with a copious amount of diethyl ether and dried under vacuum at room temperature for 6 h. The OSDA was then converted to its hydroxide form and its concentration determined by titration as described in detail below in the Ion Exchange and Titration Section.

A.3.1.2.2 OSDA 5

OSDA 5 was prepared from the reaction of N-methylpiperidine and iodomethane ¹. In a typical synthesis, N-methylpiperidine (200 mmol) was dissolved in 400 cm³ of chloroform. This solution was cooled using dry ice and acetone due to the exothermic nature of the reaction with iodomethane. Iodomethane (600 mmol) was then added dropwise to the N-methylpiperidine-containing solution. After completion of the addition of iodomethane, the reaction mixture was stirred at room temperature for 4 days. The chloroform and excess iodomethane were removed by a rotary evaporator. (Note: Iodomethane vapor is toxic). The solid product was washed with a copious amount of diethyl ether and dried under vacuum at room temperature for 6 h. The OSDA was then converted to its hydroxide form and its concentration determined by titration as described in detail below in the Ion Exchange and Titration Section.

A3.1.2.3 OSDA 7

OSDA 7 (butane-1,4-bis(trimethylammonium) dihydroxide) was synthesized by mixing 40 mmol of 1,4-dibromobutane and excess trimethylamine (25%, Sigma Aldrich) (1:7 mol ratio). This mixture was vigorously stirred at room temperature for 10 days. Following the reaction, the unreacted trimethylamine and water were removed using a rotary evaporator. The obtained solid was further purified by washing with a small amount diethyl ether and then dried under vacuum at room temperature for 6 h. The OSDA was then converted to its hydroxide form and its

concentration determined by titration as described in detail below in the Ion Exchange and Titration Section.

A3.1.2.4 OSDA 8

OSDA 8 (cyclohexane-1,4-bis(trimethylammonium) dihydroxide) was synthesized according to the method described by Boruntea et al.² The OSDA was then converted to its hydroxide form and its concentration determined by titration as described in the Ion Exchange and Titration Section.

A3.1.2.5 OSDA 10

OSDA 10 was prepared from the reaction of quinuclidine and 1,3-dibromopropane. In a typical synthesis, quinuclidine (90 mmol) was mixed with acetone (125 cm³) and stirred at room temperature for a few minutes. This mixture was then heated to 45 °C and 1,3-dibromopropane (30 mmol) was added slowly (over a 30 min window) to this mixture while stirring. After completion of the addition of 1,3-dibromopropane, the reaction mixture was heated to 75 °C, and refluxed for 6 days. Acetone was then evaporated using a rotary evaporator, and the solid product was washed with copious amounts of diethyl either (1 L) and acetone. Following this, the solid was dried under vacuum at room temperature for 6 h. The OSDA was then converted to its hydroxide form and its concentration determined by titration as described in detail below in the Ion Exchange and Titration Section.

A3.1.3 Ion Exchange and Titration

If required by the molecular sieve synthesis procedure, the OSDAs described above were ion exchanged into their hydroxide forms by first dissolving the organic salts in DI water and then adding DOWEXTM MonosphereTM 550A hydroxide ion-exchange resin (Dow chemical). Specifically, for every 100 mmol of OSDA in the halide form, approximately 300 cm³ (by volume) of resin and 500 cm³ of DI water were added. The mixture was then stirred for 24 h at room temperature. After 24 h, the resin was separated by filtration and the process repeated a second time. The quantification of the concentration of the OSDA, now in the hydroxide form, was performed using a Mettler Toledo DL22 Potentiometric pH meter. Five readings were taken for each OSDA concentration and these values were then averaged and used for gel calculations.

A3.1.4 ¹³C NMR Spectra for OSDAs

All OSDAs were characterized using ¹³C and ¹H NMR. The ¹³C NMR results are shown in

Figure A3.2.



Figure A3.2. ¹³C-NMR of the OSDAs used in this work. 10% D_2O (with the remaining being water) was used as an NMR solvent for OSDAs 1-3, 5, 7-8, and 10. The other OSDAs were dissolved in D_2O .

A3.2 Molecular Sieve Synthesis

In addition to the ERI-type zeolite materials outlined in the main text, which were tested for MTO reactivity, listed below in **Table A3.1** are other gel compositions that were explored for the synthesis of ERI-type zeolites. Also, in addition to the SAPO-17s synthesized in the main text, each gel composition was examined over a wide range of Si content. Selected results are shown in **Table A3.2**.

Table A3.1. Products and chemical compositions of selected syntheses for ERI-type zeolites. These gels were slightly modified from the references ^{2–5}.

Gel Composition							Cryst. Conditions				Matarial		
Method ^[a]	SiO ₂	Al ₂ O ₃	кон	OSDA A	OSDA A Number	OSDA B	OSDA B Number	H ₂ O	Temp. (°C)	Oven	Time (days)	(XRD) ^[b]	
2.1.3	1.00	0.100	0.46	0.30	OSDA 3	0.10	OSDA 4	22	150	static	6	SSZ-98	
2.1.3	1.00	0.050	0.40	0.15	OSDA 3	0.00	N/A	16.5	150	static	6	amorph.	
2.1.3	1.00	0.035	0.40	0.15	OSDA 3	0.00	N/A	16.5	150	static	6	amorph.	
2.1.3	1.00	0.043	0.40	0.15	OSDA 3	0.00	N/A	16.5	150	static	6	amorph.	
2.1.3	1.00	0.100	0.46	0.20	OSDA 3	0.10	OSDA 4	22	150	static	6	SSZ-98	
2.1.3	1.00	0.100	0.46	0.30	OSDA 3	0.10	OSDA 4	25	150	static	5	amorph.	
2.1.4	3.75	0.125	1.90	1.00	OSDA 5	0.00	N/A	145	150	static	4	SSZ-98	
2.1.4	3.75	0.063	1.90	1.00	OSDA 5	0.00	N/A	145	150	static	7	amorph.	
2.1.4	3.75	0.047	1.90	1.00	OSDA 5	0.00	N/A	145	150	static	7	amorph.	
2.1.4	3.75	0.125	1.90	1.00	OSDA 5	0.00	N/A	145	150	static	7	SSZ-98	
2.1.6	1.00	0.084	0.30	0.10	OSDA 7	0.00	N/A	20	135	static	7	ERI	
2.1.6	1.00	0.084	0.30	0.08	OSDA 7	0.00	N/A	20	135	static	7	ERI	
2.1.6	1.00	0.084	0.30	0.06	OSDA 7	0.00	N/A	20	135	static	7	ERI	
2.1.6	1.00	0.084	0.30	0.12	OSDA 7	0.00	N/A	20	135	static	7	ERI	
2.1.6	1.00	0.084	0.35	0.10	OSDA 7	0.00	N/A	20	135	static	7	ERI	
2.1.6	1.00	0.084	0.25	0.10	OSDA 7	0.00	N/A	20	135	static	7	ERI	

[a] Refers to the synthesis procedure section in the main text. [b] "amorph." stands for amorphous. Legend: Cryst., crystallization.

Gel Composition						Cry						
[a]	SiO ₂	Al ₂ O ₃	P ₂ O ₅	OSDA	OSDA Number	H ₂ O	seed	Temp. (°C)	Oven	Time (days)	Material (XRD) ^[b]	
2.1.7	0.0	1.0	1.0	1.00	OSDA 9	50	Ν	200	static	2	AlPO-17	
2.1.7	1.0	1.0	1.0	1.00	OSDA 9	50	Ν	200	static	2	SAPO-17+Im.	
2.1.7	1.0	1.0	1.0	1.00	OSDA 9	50	Y	200	static	2	SAPO-17	
2.1.8	0.1	1.0	1.0	0.35	OSDA 6-(OH)2[c]	70	Ν	180	rot.	4	SAPO-17+Im.	
2.1.8	0.2	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.8	0.3	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.8	0.4	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.8	0.5	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.8	0.6	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.8	0.8	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.8	1.0	1.0	1.0	0.35	OSDA 6-(OH) ₂	70	Ν	180	rot.	4	SAPO-17	
2.1.9	0.2	1.0	0.9	0.37	OSDA 10	40	Ν	190	rot.	3	SAPO-17	
2.1.9	0.3	1.0	0.9	0.37	OSDA 10	40	Ν	190	rot.	3	SAPO-17	
2.1.9	0.4	1.0	0.9	0.37	OSDA 10	40	Ν	190	rot.	3	SAPO-17	
2.1.10	0.3	1.0	1.0	0.35	OSDA 7	70	Ν	180	rot.	4	SAPO-17	
2.1.10	0.5	1.0	1.0	0.35	OSDA 7	70	Ν	180	rot.	4	SAPO-17	
2.1.10	0.8	1.0	1.0	0.35	OSDA 7	70	Ν	180	rot.	4	SAPO-17	
2.1.10	0.3	1.0	1.0	0.35	OSDA 8	70	Ν	180	rot.	4	SAPO-17	
2.1.10	0.5	1.0	1.0	0.35	OSDA 8	70	Ν	180	rot.	4	SAPO-17	
2.1.10	0.8	1.0	1.0	0.35	OSDA 8	70	Ν	180	rot.	4	SAPO-17	

Table A3.2. Products and chemical compositions for SAPO-17.

[a] Refers to the synthesis procedure section outlined in the main text, which contains the specific chemicals used. [b] "im." Indicates the presence of an impurity. [c] OSDA-6(OH)₂ indicates OSDA-6 (from **Figure 3.1**) was converted to its hydroxide form prior to use. Gels using methods 2.1.7 and 2.1.8 are based on these references ^{6,7}. Legend: Cryst., crystallization; rot., rotational/tumbling; N, no; Y, yes.

A3.3 Characterizations of Molecular Sieves



Figure A3.3. TGA profiles of the fresh (as-synthesized) CHA-type materials: (a) SSZ-13 and (b) SAPO-34. (10 °C/min in air).



Figure A3.4. TGA profiles of the fresh (as-synthesized) ERI-type zeolite catalysts: (a) SSZ-98-1, (b) SSZ-98-2, (c) UZM-12, (d) ERI zeolite-1, and (e) ERI zeolite-2. ERI zeolite-3 is not shown. (10 °C/min in air).



Figure A3.5. TGA profiles of the fresh (as-synthesized) SAPO-17 catalysts: (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-4, (d) SAPO-17-5, and (e) SAPO-17-6. SAPO-17-3 is not shown. (10 °C/min in air).



Figure A3.6. XRD patterns of SSZ-13 (CHA-type) and SAPO-34 (CHA-type).



Figure A3.7. XRD patterns of (a) ERI-type zeolites and (b) SAPO-17 samples.



Figure A3.8. N₂-adsorption-desorption isotherms of thermally treated CHA-type materials. (a) SAPO-34 and (b) SSZ-13. Circles (darker) correspond to adsorption and triangles (lighter) to desorption.



Figure A3.9. N₂-adsorption-desorption isotherms of thermally treated ERI-type zeolites. (a) SSZ-98-1, (b) SSZ-98-2, (c) UZM-12, (d) ERI zeolite-1, (e) ERI zeolite-2, and (f) ERI zeolite-3. Circles (darker) correspond to adsorption and triangles (lighter) to desorption.


Figure A3.10. N₂-adsorption-desorption isotherms of thermally treated SAPO-17s. (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-3, (d) SAPO-17-4, (e) SAPO-17-5, and (f) SAPO-17-6. Circles (darker) correspond to adsorption and triangles (lighter) to desorption.



Figure A3.11. SEM images at 5k magnification of the CHA samples, SSZ-13 (left) and SAPO-34 (right) (scale bar = $10 \ \mu$ m).



Figure A3.12. SEM images at 20k magnification as of the ERI-type zeolites (scale bar = $1 \mu m$).

Figure A3.13. SEM images of the ERI SAPO-17s (scale bar = $10 \mu m$).

Figure A3.14. (a-c) ²⁹Si, ²⁷Al, and ¹H MAS NMR spectra for SSZ-13 (CHA-type) and (d-e) ²⁹Si and ¹H MAS NMR spectra for SAPO-34 (CHA-type).

Figure A3.15. (a-b) ²⁹Si and ¹H MAS NMR spectra for SSZ-13 and (c) ¹H MAS NMR for SAPO-34. All NMR spectra for CHA-type materials were plotted with the model fit using DMFit.

Figure A3.16. (a) ²⁹Si MAS NMR spectrum of ERI Zeolite-1 plotted with the model fit using DMFit as described in the main text. (b-c) ¹H MAS NMR spectra for SSZ-98-2 (middle) and SAPO-17-3 (right) plotted with the model fit using DMFit.

Figure A3.17. (a) ¹H MAS NMR spectra of selected ERI-type zeolites. (b) ¹H MAS NMR spectra of selected SAPO-17s.

Figure A3.18. TGA profiles of the spent (deactivated) CHA-type catalysts: (a) SSZ-13 and (b) SAPO-34. ($10 \text{ }^{\circ}\text{C/min}$ in air).

Figure A3.19. TGA profiles of the spent (deactivated) ERI-type zeolite catalysts: (a) SSZ-98-1, (b) SSZ-98-2, (c) UZM-12, (d) ERI zeolite-1, (e) ERI zeolite-2, and (f) ERI zeolite-3. (10 °C/min in air).

Figure A3.20. TGA profiles of the spent (deactivated) SAPO-17 catalysts: (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-3, (d) SAPO-17-4, (e) SAPO-17-5, and (f) SAPO-17-6. (10 °C/min in air).

Figure A3.21. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for (a) SAPO-34 and (b) SSZ-13.

Figure A3.22. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for ERI-type zeolite materials: (a) SSZ-98-1, (b) SSZ-98-2, (c) UZM-12, (d) ERI Zeolite-1, (e) ERI Zeolite-2, and (f) ERI Zeolite-3.

Figure A3.23. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for SAPO-17 materials: (a) SAPO-17-1, (b) SAPO-17-2, (c) SAPO-17-3, (d) SAPO-17-4, (e) SAPO-17-5, and (f) SAPO-17-6.

Figure A3.24. MTO reaction data obtained at 400 °C and WHSV of 1.3 h⁻¹ for ERI Zeolite-2-IE2 (left) and ERI Zeolite-3-IE2 (right).

Figure A3.25. ERI (left) and CHA (right) topologies (obtained from IZA).

Figure A3.26. GC-MS distribution of the extracted hydrocarbon species grouped by ring number/type for six molecular sieves (two CHA-type and four ERI-type) after reaction with methanol at 400 °C and WHSV of 1.3 h⁻¹. All catalysts shown are deactivated (reached 85% conversion or formed 50% DME). (a) Overall hydrocarbon distribution of the aromatic species retained after the catalyst deactivated. (b) Distribution of methylbenzenes and 1-ring hydrocarbons. (d) Distribution of naphthalenes, methylnaphthalenes, and 2-ring hydrocarbons. Legend: MB, methylbenzenes; N, naphthalenes; MN, methylnaphthalenes; the number before an abbreviation denotes the number of methyl groups.

A.3.4 References

- (1) Kang, J. H.; Alshafei, F. H.; Zones, S. I.; Davis, M. E. Cage-Defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction. *ACS Catal.* **2019**, *9* (7), 6012–6019. https://doi.org/10.1021/acscatal.9b00746.
- (2) Boruntea, C.-R.; Sastre, G.; Lundegaard, L. F.; Corma, A.; Vennestrøm, P. N. R. Synthesis
- of High-Silica Erionite Driven by Computational Screening of Hypothetical Zeolites. Chem.
- Mater. 2019, 31 (22), 9268–9276. https://doi.org/10.1021/acs.chemmater.9b01229.
- (3) Xie, D.; Chen, C.-Y. Synthesis of Aluminosilicate Zeolite SSZ-98. US 2016/0375428, 2016.
- (4) Xie, D.; Lew, C. Method for Preparing Zeolite SSZ-98. US 9,663,379, 2017.
- (5) Xie, D.; Zones, S.; Lew, C.; Davis, T. Molecular Sieve SSZ-98. US9,409,786 B2, 2016.
- (6) Valyocsik, E.; Ballmoos, R. Synthesis of Crystalline SAPO-17. US4778780A, 1987.
- (7) Lok, B.; Messina, C.; Patton, R.; Gajek, R.; Cannan, T.; Flanigen, E. Crystalline

Silicoaluminophosphates. US 444,0871A, 1984.

Appendix C | Supplemental Information – Chapter 4

Figure A4.1. ¹³C-NMR of the OSDAs used in this work in their bromide form: (a) $DiQ-C_3$ and (b) $DiQ-C_4$. The OSDAs were dissolved in D_2O for (a) and (b).

	Gel Compositions and Synthesis Conditions							Quality
Entry	Al ₂ O ₃ ^[a]	P ₂ O ₅	SiO2	R(OH)₂ (DiQ-C₃)	H₂O	Conditions	XRD ^[b]	of CIT-16P ^[c]
S1	0.50	0.45	0.11	0.37	40	190 °C 72 h /rotation	ERI	-
S2	0.50	0.45	0.10	0.37	40	190 °C 72 h /rotation	ERI	-
S3	0.50	0.45	0.10	0.33	40	190 °C 72 h /rotation	ERI+impurity	-
S4	0.50	0.45	0.12	0.27	40	190 °C 72 h /rotation	CIT-16P+ERI	2
S5	0.50	0.45	0.10	0.27	40	190 °C 72 h /rotation	CIT-16P+ERI	2
S6	0.50	0.45	0.08	0.27	40	190 °C 72 h /rotation	CIT-16P+ERI	2
S7	0.50	0.45	0.10	0.24	40	190 °C 72 h /rotation	CIT-16P+ERI	2
S8	0.50	0.45	0.06	0.24	40	190 °C 72 h /rotation	CIT-16P+ERI	3
S9	0.50	0.45	0.10	0.21	40	190 °C 72 h /rotation	CIT-16P+ERI	2
S10	0.50	0.45	0.06	0.21	40	190 °C 72 h /rotation	CIT-16P+ERI	2
S11	0.50	0.45	0.10	0.18	40	190 °C 72 h /rotation	ERI+CIT-16P	1
S12	0.50	0.45	0.06	0.18	40	190 °C 72 h /rotation	ERI+CIT-16P	1

Table A4.1. Products and gel chemical compositions for the synthesis of CIT-16P/ERI using DiQ- C_3 -(OH)₂ as an OSDA.

[a] Aluminum source: Barcroft SPI Pharma 0250TM. [b] First phase listed is the major phase whereas the second phase listed is the secondary phase. [c] Refers to the crystallinity of the material formed; 3 indicates best crystallinity and 1 is poorest.

Figure A4.2. XRD patterns of the SAPO materials that were synthesized using $DiQ-C_3-(OH)_2$ as an OSDA. These results demonstrate the effect of decreasing the OSDA concentration as well as the effect of Si in the gel on the formation of CIT-16P.

The results in **Figure A4.2** show that high OSDA concentration in the gel (0.37) leads to pure SAPO-17 (ERI) formation. However, by decreasing the OSDA concentration, the peaks associated with CIT-16P start to emerge. The peaks are highest when the OSDA concentration is about (0.24-0.27), but they decrease as the OSDA concentration is lowered even further (<0.24). The results also demonstrate that reducing the Si content (by comparing Entry S7 to S8) in the gel while maintaining the OSDA concentration at identical levels enhances the crystallization of CIT-16P, thus, leading to improved peak intensities. Note that the peak intensities associated with ERI were relatively the same irrespective of the gel composition.

		G	el Comp	ositions and Sy	ynthesi	s Conditions		Quality	
Entry	Al ₂ O ₃ ^[a]	P2O5	SiO ₂	R(OH)₂ (DiQ-C₃)	H ₂ O	Conditions ^[d]	XRD ^[b]	of CIT- 16P ^[c]	
Effect of OSDA Concentration and Silicon Content									
S13	0.50	0.45	0.08	0.40	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(vs)	1	
S14	0.50	0.45	0.08	0.36	40	190 °C 72 h / Rot.	CIT-16P+AFX(s)+SAT(vs)	1	
S15	0.50	0.45	0.08	0.32	40	190 °C 72 h / Rot.	CIT-16P+AFX(s)+SAT(vs)	1	
S16	0.50	0.45	0.09	0.30	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	2	
S17	0.50	0.45	0.12	0.28	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(s)	2	
S18	0.50	0.45	0.10	0.28	40	190 °C 72 h / Rot.	CIT-16P+AFX(s)	3	
S19	0.50	0.45	0.06	0.28	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S20	0.50	0.45	0.04	0.28	40	190 °C 24 h / Rot.	CIT-16P	3	
S21	0.50	0.45	0.04	0.28	40	190 °C 72 h / Rot.	CIT-16P	3	
S22	0.50	0.45	0.03	0.28	40	190 °C 24 h / Rot.	CIT-16P	3	
S23	0.50	0.45	0.03	0.28	40	190 °C 48 h / Rot.	CIT-16P	3	
S24	0.50	0.45	0.03	0.28	40	190 °C 72 h / Rot.	CIT-16P	3	
S25	0.50	0.45	0.02	0.28	40	190 °C 72 h / Rot.	CIT-16P+impurity(s)	3	
S26	0.50	0.45	0.12	0.27	40	190 °C 72 h / Rot.	CIT-16P+SAT(s)+AFX(s)	2	
S27	0.50	0.45	0.11	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S28	0.50	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S29	0.50	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S30	0.50	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S31	0.50	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S32	0.50	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)+SAT(vs)	3	
S33	0.50	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)+SAT(vs)	3	
S34	0.50	0.45	0.09	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S35	0.50	0.45	0.08	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S36	0.50	0.45	0.06	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S37	0.50	0.45	0.10	0.24	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(s)	2	
S38	0.50	0.45	0.08	0.24	40	190 °C 72 h / Rot.	CIT-16P+SAT(vs)+AFX(vs)	2	
S39	0.50	0.45	0.06	0.24	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	2	
					Effe	t of Temperature			
S40	0.50	0.45	0.10	0.27	40	180 °C 96 h / Rot.	CIT-16P+AFX(vs)	3	
S41	0.50	0.45	0.10	0.27	40	200 °C 72 h / Rot.	CIT-16P+AFX(vs)+SAT(vs)	3	
	Effect of	f Changi	ng Al So	urce and Mani	pulatin	g the AI/P, R/P, and R/H2O a	around the Optimal Conditions		
S42	0.50 ^v	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(vs)	2	
S43	0.50 ^R	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(s)	2	
S44	0.50 ^R	0.47	0.10	0.27	40	190 °C 72 h / Rot.	SAT+ CIT-16P +AFX(s)	2	
S45	0.50	0.45	0.10	0.27	30	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S46	0.50	0.45	0.10	0.27	50	190 °C 72 h / Rot.	CIT-16P+AFX(vs)+SAT	2	
S47	0.48 ^R	0.45	0.08	0.28	40	190 °C 72 h / Rot.	CIT-16P+AFX(s)+SAT	2	
S48	0.48 ^R	0.45	0.10	0.28	40	190 °C 72 h / Rot.	CIT-16P+AFX(s)+SAT	2	
S49	0.47	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)+SAT(vs)	3	
S50	0.47	0.45	0.04	0.29	40	190 °C 72 h / Rot.	CIT-16P+AFX(vs)	3	
S51	0.47	0.44	0.10	0.29	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(s)	2	
S52	0.46 ^p	0.45	0.10	0.27	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(s)	2	
S54	0.46 ^P	0.45	0.06	0.27	40	190 °C 72 h / Rot.	CIT-16P+SAT+AFX(s)	2	
S54	0.45	0.45	0.10	0.27	40	190 °C 72 h / Rot.	SAT+ CIT-16P +AFX(s)	2	
S55	0.45 ^R	0.45	0.10	0.28	40	190 °C 72 h / Rot.	CIT-16P+AFX	1	

Table A4.2. Products and gel chemical compositions for the synthesis of CIT-16 using DiQ-C₄-(OH)₂ as an OSDA.

[a] Aluminum source was Barcroft unless otherwise noted. "R" indicates Reheis F2000, "P"= Pfaltz and Bauer, and "V"= Vista. [b] First phase is the major phase: "vs"= very small, "s" small, as reference to the secondary or impurity phases [c] Refers to the crystallinity of the material formed; 3 indicates best crystallinity and 1 is poorest. [d] "Rot" is short for rotational.

Figure A4.3. XRD patterns of the SAPO materials that were synthesized using $DiQ-C_4-(OH)_2$ as an OSDA.

The results in **Figure A4.3** show that there is an optimal OSDA concentration (similar to the DiQ-C₃ system; 0.27-0.29) that allows for the synthesis of CIT-16P with relatively high crystallinity. However, by decreasing the OSDA concentration or increasing it such that the gel OSDA concentration is outside this range, the peaks associated with CIT-16P start to dramatically decrease and peaks associated with AFX and SAT phases start to emerge or increase in intesisties. SAT and AFX are known to form using DiQ-C₄₋₅. The results above also demonstrate that CIT-16P favors gels with low silicon content (0.02-0.04), in agreement with our results on the DiQ-C₃ OSDA.

Figure A4.4. 8k MAS solid-state ¹³C NMR spectrum of as-made CIT-16P compared to the solution ¹³C NMR spectrum of DiQ-C₄ OSDA. For the solution NMR spectrum, CD₃OD was used as the solvent.

Figure A4.5. SEM images at 20k magnification as of selected CIT-16P samples (from **Table A4.2**) (scale bar = 2 μ m). S17 represents a sample that contained CIT-16P, SAT, and AFX. S21 represents a sample that contained only CIT-16P (with Al-rich regions that are not detectible by XRD). S25 represents a sample that contained CIT-16P and an impurity peak (as shown in **Figure A4.3**).

CIT-16P synthesized using DiQ-C₄ has a distinct morphology (rice grain or bullet-like particles that are 1-5 microns in size) that differs from AFX and SAT. In the aluminophosphate system, AFX and SAT typically show distinct morphologies that are different from that of CIT-16P. SAPO-56 (AFX) crystals typically manifest a planar-type morphology, whereas STA-2-type crystals (SAT) typically manifest a rhomb-like morphology.¹ Changing the gel composition results in slight changes in the particle (crystal) sizes, but the morphology remains the same for CIT-16P.

Figure A4.6. Characterization on the as-synthesized CIT-16P sample (Entry S50) and following treatment with ethanolamine. (a) XRD patterns. (b, c) SEM images of the as-synthesized and treated CIT-16P samples, respectively. (d, e) N₂-adsorption-desorption isotherms of the thermally treated CIT-16P (now SAPO-17) and ethanolamine-treated CIT-16P sample (also now SAPO-17). (f) 27 Al MAS NMR spectra.

To examine if the peak at 7.3 ppm in the ²⁷Al NMR spectrum is of extraframework aluminum species, the as-synthesized CIT-16P was treated with ethanolamine. The structure and morphology of CIT-16P remained unchanged after the ethanolamine treatment, as illustrated in **Figures A4.6(a** and **b**). Also, no change was observed in the N₂-adsorption isotherms (**Figures A4.6(c** and **d**)) before and after the ethanolamine treatment. The ethanolamine treatment only reduced the 7.3-ppm signal in the ²⁷Al NMR spectra slightly, but most importantly, it did not eliminate it. These results suggest that the 7.3-ppm ²⁷Al resonance does not originate from extraframework aluminum species.

Figure A4.7. The dehydration–hydration cycle observed based on 27 Al MAS NMR spectroscopy. (A: as-made CIT-16P (Sample = Entry S50) with occluded OSDA, B: the sample freshly calcined and dehydrated, C: the sample after a long exposure (ca. 1–2 months) to ambient moisture, D: the sample after the second calcination/dehydration, E: the sample one day after the second dehydration under ambient moisture).

On the basis of ²⁷Al MAS NMR spectroscopy, the nature of the coordination states of Alsites within the frameworks of as-synthesized (as-made) parent CIT-16P and resultant SAPO-17 were examined. The as-synthesized CIT-16P sample with occluded OSDA cations shows two signals at 41.5 ppm and 7.3 ppm (**Spectrum A**). After thermal treatment (calcination), the dehydrated SAPO-17 derived from CIT-16P showed only one strong signal at 34.3 ppm (**Spectrum B**). After prolonged exposure to ambient moisture, two upfield resonances at 6.3 ppm and -14.3 ppm emerged (**Spectrum C**). The line shape of **Spectrum B** was restored after the second thermal treatment (**Spectrum D**). After one day of ambient moisture exposure, the two upfield signals seen in **Spectrum C** were restored (**Spectrum E**).

Figure A4.8. Structural changes of the CIT-16P sample (Entry S50) during ex-situ heating under air. (a) The temperature program associated with the ex-situ heating experiment. Each point denotes the temperature and time at which the sample was quenched. (b) PXRD profiles of samples after the ex-situ heating experiments.

The temperature of the transformation of as-synthesized CIT-16P to SAPO-17 was determined based on ex-situ heating experiments using a TG instrument and a powder X-ray diffractometer. Small portions of sample were heated under air in the TG instrument according to the temperature program shown in **Figure A4.8(a)**. At each point, the sample was quickly cooled down to the ambient temperature and subjected to PXRD analysis. The resultant PXRD profiles are shown in **Figure A4.8(b**). The sample series **A**, **B**, **C**, and **D** were collected "during" the temperature ramping at a rate of 5 °C/min. At 490 °C, no sign of (100) peak of ERI was observed (**A**). At 495 °C, a weak diffraction began to develop at the (100) diffraction site of ERI (**B**). Over 500 °C, the (100) diffraction of CIT-16P diminished dramatically, whereas the (100) of ERI grew significantly (**C** and **D**).

With these observations, the kinetics of the transformation was analyzed at 495 °C (the sample series **B**, **B2**, **B3**, and **B4**). With only 2 minutes of isotherm at 495 °C, the (100) diffraction intensity of ERI grew considerably (**B2**). After 5 minutes, the sample structure was completely transformed to ERI due to the elimination of the OSDA (**B3** and **B4**). As such, it is possible to deduce that the transition of as-synthesized CIT-16P to SAPO-17 occurs within 5 minutes at temperatures ranging from 490 to 500 °C.

Figure A4.9. TGA profiles of as-synthesized materials crystallized from DiQ-C4 OSDA: (top) AFX+SAT mixture, free of CIT-16P; (bottom) pure CIT-16P.

Structure	Package	Forcefield/Pseudopotential	Energy (eV ¹ ,	$\Delta E (eV/T)^3$
			Ry ²)	
ERI	GULP6	Catlow	-4823.073912	
		Reaxff6	-929.603122	
	Quantum Espresso	PAW, GGA-PBEsol	-4693.933504	
CIT-16P	GULP6	Catlow	-4818.557541	-0.1255
		Reaxff6	-924.2484823	-0.1487
	Quantum Espresso	PAW, GGA-PBEsol	-4693.514886	-0.1582

Table A4.3. Framework energy of ERI and CIT-16P obtained from GULP or DFT calculations.

¹GULP6.

²Quantum Espresso. ³ $\Delta E = E_{ERI} - E_{UNK}$ for per T site.

Figure A4.10. TGA profile of the CIT-16P sample after 4 weeks of ozone treatment. The amount of OSDA remaining in the sample following 4 weeks of ozone treatment is about 4.8%.

Structure Determination of CIT-16P with Rietveld Refinement

Synchrotron diffraction data of CIT-16P was measured using beamlines 9B at the Pohang Accelerator Laboratory (Pohang, Korea) where the wavelength of the highly collimated monochromatic synchrotron radiation was λ =1.5298 Å. The detector arm of the vertical scan diffractometer consisted of seven sets of Soller slits, flat Ge(111) crystal analyzers, anti-scatter baffles, and scintillation detectors, with each set separated by 20°. Data were obtained on the sample at room temperature in flat-plate mode, with a step size of 0.01° for a scan time of 2 s per step, and overlaps of 2° to the next detector bank over the 2 θ range of 5 - 100°.

Diffraction patterns obtained were indexed using the DICVOL06 program² implemented in the FullProf program suite.³ The initial structure of the occluded DiQ-C₄-(OH)₂ in the pore was obtained by the MM2 method implemented in ChemBio3D.⁴ Subsequently, the parallel tempering algorithm implemented in the Free Objects for Crystallography program⁵ was applied to determine the framework structure containing OSDA. Then, profile refinement of the structure model, comprising the framework and the included organic molecules, was performed using the Rietveld method in the JANA2006 package.⁶ During Rietveld refinement, a pseudo-Voigt function and microscopic broadening, together with a manually interpolated background, were used to describe the peak shapes. The framework was modeled as completely siliceous. Isotropic displacement parameters for all T atoms were constrained to be equal in order to minimize the number of parameters, as were those of all O atoms, and the TLS method⁷ was used to describe the thermal motion of OSDA molecule. The framework T(Al, P)-O distances were soft-restrained to 1.62 Å with the standard uncertainty of 0.005 Å.

Theoretical Calculations using Ab-initio DFT Method

The CIT-16P structure from the Rietveld refinement was subject to lattice energy minimization calculations using the General Utility Lattice Program (GULP).⁸ All atomic coordinates and cell parameters were optimized to zero force using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization method. Calculations were performed at constant pressure using a zeolite shell model as the potential model in which a Buckingham function was used to describe the short-range interactions and a three-body (bond bending) term was included to accurately model O-T-O angles. A shell model was also used to simulate the polarizability of the oxygen atoms. The Newton-Raphson optimizer was employed during an energy minimization, with maximum function and gradient tolerances of 0.0001 and 0.001 eV Å⁻¹, respectively; the symmetry was constrained and the cell parameters varied. A gradient-norm convergence criterion of 0.001 eV Å⁻¹ was used for all optimizations.

Also, the geometry optimization using DFT method⁹ were performed using the Quantum-Espresso code, using the ultrasoft pseudo potential with the Perdew-Burke-Ernzerh of exchange-correlation functional to treat the electronic structure within the generalized gradient approximation to density functional theory. Plane-wave basis set cutoffs were set to 30 and 420 Ry for the smooth part of the wave functions and the augmented charge, respectively; *k*-sampling was restricted to the gamma point only.

Figure A4.11. Binary structure refinement for CIT-16P and AFX. (Reproduction of Figure 4.5(a)).

Table A4.4. Lattice parameters and reliability factors obtained from the Rietveld refinement.

Phase		S	tructural paramete	ers	Reliability factor				
	SG	a(Å)	c(Å)	volume(Å ³)	GOF	<u>R</u> g(%)	<u>Rwp</u> (%)	<u>R_{exp}(%)</u>	
CIT-16P	P ₃	12.2899(6)	16.9714(11)	2220.0(2)	1.66	8.96	12.61	7.58	

vstematic
sum 'C66.49 Al18 N8.054 O72 P18'
12 2899(6)
12.2809(6)
12.2079(0) 16 0714(11)
10.9/14(11)
90
90
120
2220.0(2)
ting trigonal
group_name_H-M 'P 3'
group_name_Hall 'P 3'
bles_number 143
op_id
op_operation_xyz
ymbol
ne
or equiv
mmetry multiplicity
ncy
ag
nent_flags
er_assembly
r_group
0.389(7) 0.697990(4) Uiso 0.24(4) 3 1 d
0.431(8) 0.197960(4) Uiso 0.24(4) 3 1 d
0.099(7) 0.375100(4) Uiso 0.24(4) 3 1 d
) 0.295(9) 0.875120(4) Uiso 0.24(4) 3 1 d
0.492(9) 0.433920(4) Uiso 0.24(4) 3 1 d
7 0.466(6) 0.933950(4) Uiso 0.24(4) 3 1 d
).427(8) 0.510560(3) Uiso 0.027(6) 3 1 d
0.427(8) 0.510560(3) Uiso 0.027(6) 3 1 d 0.457308 0.010590(3) Uiso 0.027(6) 3 1 d

Table A4.5. Crystallographic Information File (atomic positions and anisotropic tensors of atoms) of CIT-16P acquired by the Rietveld refinement.

P4	P 0.412(7) 0.344(8) 0.333333(3) Uiso 0.027(6) 3 1 d
P5	P 0.374(6) 0.481(7) 0.774640(3) Uiso 0.027(6) 3 1 d
P6	P 0.155(6) 0.485(7) 0.274610(3) Uiso 0.027(6) 3 1 d
01	O 0.289769 0.029(5) 0.743482(10) Uiso 0.088(16) 3 1 d
O2	O 0.386(14) 0.347(15) 0.243442(10) Uiso 0.088(16) 3 1 d
O3	O 0.428(13) 0.038(7) 0.465096(10) Uiso 0.088(16) 3 1 d
O4	O 0.275(11) 0.359(7) 0.965126(10) Uiso 0.088(16) 3 1 d
O5	O 0.090(17) 0.524(10) 0.708582(10) Uiso 0.088(16) 3 1 d
06	O 0.176(11) 0.412(10) 0.208551(10) Uiso 0.088(16) 3 1 d
07	O 0.189(8) 0.400(9) 0.499978(10) Uiso 0.088(16) 3 1 d
08	O 0.080(12) 0.597(6) 0.000006(10) Uiso 0.088(16) 3 1 d
09	O 0.271(7) 0.447(18) 0.705634(10) Uiso 0.088(16) 3 1 d
010	O 0.156918 0.567(7) 0.205604(10) Uiso 0.088(16) 3 1 d
011	O 0.145(17) 0.572(8) 0.502918(10) Uiso 0.088(16) 3 1 d
012	O(0.125(9)(0.433(15)(0.002944(10)))) U iso $O(0.088(16)(3)(10,10))$
013	O 0 061(7) 0 280(16) 0 854290(10) Uiso 0 088(16) 3 1 d
014	O(0.584(11)) 0.135(12) 0.354260(10)) U iso $O(0.088(16)) 3.1 d$
015	O 0 053(11) 0 561(7) 0 854286(10) Uiso 0 088(16) 3 1 d
016	$O(0.227(8) \ 0.512(14) \ 0.354260(10) \ Uiso \ 0.088(16) \ 3.1 \ d$
017	O = 0.011(17) O 325(5) O 885296(10) U so 0.088(16) 3.1 d
018	O 0 340(17) 0 388(18) 0 385260(10) Uiso 0 088(16) 3 1 d
019	O = 0.042(7) = 0.0000(10) = 0.00000(10) = 0.000(10) = 0.000(10)
020	O 0 256(7) 0 435(9) 0 823295(10) Uiso 0 088(16) 3 1 d
021	O 0 271(8) 0 19774 0 854290(10) Uiso 0 088(16) 3 1 d
022	O(0.395(14)) O(215(10)) O(354260(10)) Uiso O(088(16)) 3.1 d
023	O = 0.067(11) = 0.000(10) =
023	O = 0.0007(11) = 0.007(12) = 0.007(10) = 0.0007(10) = 0
025	O 0 333333 0 666667 0 938273(10) Uiso 0 12 1 1 d
026	O 0 333333 0 666667 0 441489(10) Uiso 0 12 1 1 d
027	O 0 637614 0 265(16) 0 478058(10) Uiso 0 12 3 1 d
028	O 0.6666667 0.333333 0.458414(10) Uiso 0.12 1 0.0986 d
C1	C 0.252(4) 0.136(5) 0.256446(18) Uani 1.1(2) 3 1.17 d
C2	C 0.160(4) 0.138(5) 0.317836(18) Uani 0.71(16) 3 1.17 d
C3	C 0.188(4) 0.111(5) 0.402296(18) Uani 0.59(18) 3 1.17 d
C4	C 0 182(4) 0 110(5) 0 463946(18) Uani 0 6(2) 3 1 17 d
N1	N 0.228(4) 0.159(5) 0.170846(18) Uani 1.1(2) 3 1.17 d
N2	N 0 134(4) 0 091(5) 0 549056(18) Uani 0 6(4) 3 1 17 d
C5	C 0 154(4) 0 092(5) 0 141796(18) Uani 0 6(3) 3 1 17 d
C6	C 0 168(4) 0 128(5) 0 057206(18) Uani 0 8(4) 3 1 17 d
C7	C 0 199(4) 0 198(5) 0 025316(18) Uani 1 6(5) 3 1 17 d
C8	C 0 308(4) 0 173(5) 0 033556(18) Uani 2 2(6) 3 1 17 d
C9	C 0 233(4) 0 285(5) 0 163256(18) Uani 2 9(5) 3 1 17 d
C10	C 0 227(4) 0 313(5) 0 075586(18) Uani 3 8(8) 3 1 17 d
C11	C 0 333(4) 0 161(5) 0 121066(18) Uani 2 5(5) 3 1 17 d
C12	C 0 240(4) 0 190(5) 0 599396(18) Uani 0 9(4) 3 1 17 d
C13	C 0 201(4) 0 169(5) 0 686606(18) Uani 0 7(6) 3 1 17 d
C14	C 0.265(4) 0.148(5) 0.662856(18) Uani 1.0(6) 3.1.17 d
C15	C 0.252(4) 0.189(5) 0.554816(18) Uani 1.0(3) 3 1.17 d
C16	C = 0.285(4) = 0.223(5) = 0.642136(18) Uani = 1.6(5) = 1.17 d
C17	C 0.505(6) 0.170(6) 0.768256(18) Uani 1.1(2) 3 1.17 d
C18	C 0.625(6) 0.260(6) 0.814516(18) Uani 0.99(17) 3 1.17 d
-	$\langle \cdot \rangle$

C19 C 0.601(6) 0.256(6) 0.904316(18) Uani 1.01(17) 3 1.17 d . . . C20 C 0.722(6) 0.344(6) 0.950766(18) Uani 0.9(2) 3 1.17 d . . . N3 N 0.521(6) 0.170(6) 0.678476(18) Uani 1.1(3) 3 1.17 d . . . N4 N 0.705(6) 0.347(6) 1.040176(18) Uani 0.9(3) 3 1.17 d . . . C21 C 0.554(6) 0.298(6) 0.644086(18) Uani 0.9(4) 3 1.17 d . . . C22 C 0.574(6) 0.296(6) 0.554736(18) Uani 1.0(5) 3 1.17 d . . . C23 C 0.536(6) 0.163(6) 0.527406(18) Uani 1.1(6) 3 1.17 d . . . C24 C 0.401(6) 0.074(6) 0.554486(18) Uani 1.1(6) 3 1.17 d . . . C25 C 0.622(6) 0.139(6) 0.656776(18) Uani 1.3(4) 3 1.17 d . . . C26 C 0.622(6) 0.122(6) 0.567036(18) Uani 1.4(6) 3 1.17 d . . . C27 C 0.395(6) 0.070(6) 0.644916(18) Uani 1.2(4) 3 1.17 d ... C28 C 0.833(6) 0.442(6) 1.074006(18) Uani 0.9(4) 3 1.17 d . . . C29 C 0.826(6) 0.442(6) 1.164346(18) Uani 0.9(6) 3 1.17 d . . . C30 C 0.689(6) 0.362(6) 1.190676(18) Uani 1.0(6) 3 1.17 d . . . C31 C 0.641(6) 0.226(6) 1.165646(18) Uani 1.3(5) 3 1.17 d . . . C32 C 0.611(6) 0.390(6) 1.058966(18) Uani 1.0(4) 3 1.17 d . . . C33 C 0.661(6) 0.219(6) 1.076876(18) Uani 1.2(4) 3 1.17 d... C34 C 0.612(6) 0.411(6) 1.148326(18) Uiso 0.0127 3 1.17 d . . . loop _atom_site_aniso_label _atom_site_aniso_type_symbol _atom_site_aniso_U_11 _atom_site_aniso_U_22 _atom_site_aniso_U_33 _atom_site_aniso_U_12 atom site aniso U 13 _atom_site_aniso_U_23 C 0.0(3) 1.2(2) 1.9(3) 0.1(2) -0.05(19) -0.86(16) C1 C2 C 0.38(13) 0.1(2) 1.8(3) 0.22(13) 0.67(18) 0.67(15) C3 C - 0.1(2) 0.04(16) 1.8(3) - 0.01(16) - 0.1(2) - 0.06(16)C4 C -0.1(3) 0.0(3) 1.8(3) 0.0(3) -0.1(2) -0.01(19) N1 N 0.3(3) 0.4(3) 1.8(3) -0.3(3) 0.6(2) -0.2(2) N2 N -0.1(4) 0.1(5) 1.8(3) -0.1(4) -0.1(3) 0.6(3) C5 C 0.0(4) 0.1(4) 1.8(3) 0.1(3) 0.1(3) 0.5(2)C6 C 0.4(5) 0.2(6) 1.8(3) 0.1(5) 0.6(3) 0.6(3) C7 C 2.1(6) 0.2(7) 1.8(3) 0.3(6) 1.5(3) 0.7(3) C8 C 0.1(6) 3.0(9) 1.9(3) -0.4(7) 0.3(3) -1.4(3) C9 C 5.6(8) 0.2(4) 1.9(3) 0.7(5) 2.5(3) 0.8(2) C10 C 8.4(13) 0.5(7) 1.9(3) 1.7(8) 3.0(3) 1.2(3) C11 C 0.1(5) 4.5(9) 1.9(3) 0.4(6) -0.2(3) -2.0(3)C12 C 0.3(5) 0.1(5) 1.9(3) - 0.4(5) 0.7(3) - 0.4(3)C13 C 0.1(7) -0.1(8) 1.8(3) -0.1(7) 0.6(4) 0.0(3) C14 C -0.1(7) 1.1(8) 1.9(3) 0.1(7) -0.3(4) -1.2(3) C15 C 0.2(4) 0.3(4) 1.9(3) -0.4(4) 0.6(3) -0.6(2)C16 C 0.4(6) 0.6(7) 1.9(3) -0.7(6) 0.8(3) -0.9(3) C17 C 0.0(2) 0.2(2) 3.1(4) 0.0(2) 0.0(3) 0.5(2) C18 C -0.02(14) 0.15(18) 2.8(3) 0.01(14) 0.2(2) 0.02(19) C19 C 0.03(14) 0.25(18) 2.8(3) 0.08(14) 0.3(2) 0.52(19) C20 C 0.1(2) 0.2(2) 2.5(4) 0.1(2) 0.5(3) 0.1(2) N3 N 0.0(4) 0.1(4) 3.1(4) 0.0(4) -0.1(3) 0.0(3)

N4	N 0.2(4) 0.3(4) 2.5(4) 0.2(4) 0.6(3) 0.5(3)
C21	C 0.2(5) 0.0(5) 2.4(4) 0.0(5) 0.6(3) 0.1(3)
C22	C 0.2(7) 0.0(7) 2.5(3) -0.1(7) 0.5(4) -0.4(3)
C23	C 0.1(8) 0.0(8) 3.2(4) 0.0(8) -0.4(5) -0.7(4)
C24	C 0.1(7) -0.1(7) 3.4(5) 0.0(7) -0.6(5) 0.1(4)
C25	C 0.1(5) 0.3(4) 3.5(4) 0.2(5) -0.8(3) -1.1(3)
C26	C 0.2(8) 0.5(7) 3.6(4) 0.3(7) -1.0(4) -1.5(3)
C27	C 0.0(5) 0.1(5) 3.4(5) -0.1(5) -0.5(4) 0.5(4)
C28	C 0.4(5) 0.2(5) 2.3(5) 0.2(5) 0.8(4) 0.0(4)
C29	C 0.5(7) 0.2(8) 2.3(5) 0.4(7) 0.8(5) 0.4(4)
C30	C 0.5(8) 0.5(7) 2.4(4) 0.5(8) 0.9(5) 1.2(4)
C31	C 0.4(7) 0.4(7) 3.0(3) 0.2(7) 0.0(4) 1.1(3)
C32	C 0.6(5) 0.8(4) 2.1(4) 0.7(4) 1.2(3) 1.4(3)
C33	C 0.3(5) 0.2(5) 3.1(4) 0.1(5) -0.1(3) 0.5(3)

295

Bond va	alence					
Al1 2	2.9(4)					
Al2 3	3.1(6)					
Al3 3	3.2(6)					
Al4 3	3.1(5)					
Al5 3	3.4(6)					
Al6 2	2.8(3)					
P1 5	.0(8)					
P2 4	.8(7)					
P3 4	.6(5)					
P4 5	.1(12)					
P5 4	.7(5)					
P6 5	.1(6)					
Bond di	istance	for specific po	osition			
Al5-07		1.73(8)	2nd: O7	x,y,z		
Al5-01	1	1.76(9)	2nd: O11#s2t1,1,0	-y+1,x-	z-y+1,z	
Al5-01	6	1.76(12)	2nd: O16	x,y,z		
Al5-O1	8	1.7(3)	2nd: O18		x,y,z	
A15-O2	6	2.01(11)	2nd: O26		x,y,z	
P2-O4		1.50(1	1) 2nd: O4#t0,0,-	-1	x,y,z-1	
P2-08		1.58(12)	2nd: O8#s2t1,1,0	-y+1,x-	z-y+1,z	
P2-O12		1.59(15)	2nd: O12	x,y,z		
P2-O24	_	1.60(3)	2nd: O24	x,y,z		
P2-O25		2.581(11)	2nd: O25#t0,0,-1	x,y,z-1	l	

 Table A4.6. Bond valences and bond distances for specific positions.

Table A4.7. Topological analysis results for CIT-16P.

Material name					CIT-	CIT-16P									
Framework type found				Con g co	Congratulation: you seem to have a new framework (no existin g code was found for your structure)										
Number of unique topological T-atoms				З (о	ut of 3	T-ato	ms in	your s	tructu	re)					
Atom	type	T-atom ^a				Co	ordinat	tion Se	quence	N ₁ to I	N ₁₂				Vertex Symbol ^b
Si1	Si	T1	4	10	18	29	47	75	101	121	149	193	240	284	4·6·4·6·6 ₃ ·10 ₅
Si2	Si	T2	4	9	18	32	49	64	86	125	165	195	227	273	$4 \cdot 6 \cdot 4 \cdot 10_3 \cdot 4 \cdot 10_4$
Si3	Si	тз	4	9	17	29	48	71	97	124	150	182	236	297	$4 \cdot 4 \cdot 4 \cdot 6_2 \cdot 6_2 \cdot 8_2$

^a Topologically equivalent atom positions have the same "T-type" symbol

^b Size and number of smallest ring on each angle of the T-atom (M. O'Keeffe and S.T. Hyde, *Zeolites* **19**, 370 (1997)) * = no closed ring at this angle

^c A specific Coordination Sequence can also occur in a different framework structure (partial match). This is listed here if it w as found for an atom in the submitted structure. The T-atom given refers to the one listed under Framework > List of T-atom s for the given code.

System	Package	Forcefield/Pseudopotential	Energy (eV^1 ,	$\Delta E (eV^{1}/T,$
			Ry^2)	$Ry^2/T)^3$
OSDA	GULP6	Reaxff6	-496.1632459	
	CASTEP2022	OTFG (USPP, GGA, PBE)	-7867.397368	
	Quantum	PAW, GGA-PBEsol	-842.8238412	
	Espresso	PAW, GGA-PBE	-856.7954766	
CIT-16P	GULP6	Reaxff6	-924.2484823	
(framework only)	CASTEP2022	OTFG (USPP, GGA, PBE)	-37729.15418	
	Quantum	PAW, GGA-PBEsol	-4648.265406	
	Espresso	PAW, GGA-PBE	-4721.086683	
CIT-16P +OSDA	GULP6	Reaxff6	-1436.629825	-16.2181 eV/T
	CASTEP2022	OTFG (USPP, GGA, PBE)	-45611.98080	-15.4293 eV/T
	Quantum Espresso	PAW, GGA-PBEsol	-5493.262132	-29.5635 Ry/T
		PAW, GGA-PBE	-5580.049439	-29.4873 Ry/T

Table A4.8. Stabalization energy of CIT-16P obtained from GULP or DFT calculations.

¹GULP6. ²Quantum Espresso. ³ $\Delta E = E_{CIT-16P+OSDA} - (E_{CIT-16P} + E_{OSDA})$ per T site.

	pre-can	
As-made	$DiQ-C_4$	CIT-16

As-made Piperidine AIPO₄-17

Al5 site (P)	0-T-0 (°)	Al3 site (T)	O-T-O (°)
O11-Al5-O18	107(11)	O3-A13-O22	126(22)
O11-Al5-O7	98(4)	O3-Al3-O19	98(5)
O16-Al5-O18	95(8)	O3-Al3-O14	94(9)
O16-Al5-O7	104(7)	O19-Al3-O14	99(9)
O18-Al5-O7	105(8)	O14-Al3-O22	116(8)
O11-Al5-O16	144(11)	O22-Al3-O19	118(8)
011-Al5- <mark>026</mark>	73(8)		
016-Al5- <mark>026</mark>	73(7)		
07-Al5- <mark>026</mark>	107(7)		
026-Al5-O18	148(6)		

(Note: O26 is the extra oxygen site. AI5 is the pentacoordinated AI site)

All site (P)	0-T-0 (°)	Al2 site (T)	0-T-0 (°)
O4-Al1-O3	98.89	01-Al2-O1	112.97
04-Al1-O11	93.48	01-Al2-O5	110.13
O4-Al1-O2	97.77	01-Al2-O6	107.76
O3-Al1-O11	114.98	O5-Al2-O6	107.90
O11-Al1-O2	121.53		
O2-Al1-O3	119.43		
07-Al1-O3	86.35		
07-Al1-O11	83.50		
07-Al1-O2	80.22		
04-Al1- <mark>07</mark>	174.70		

(Note: O7 is the extra oxygen site. Al1 is the pentacoordinated Al site)

T1 site (T)	O-T-O (°)	T2 site (T)	O-T-O (°)
O1-T1-O2	109.56	O2-T2-O2	109.43
O1-T1-O3	109.52	O2-T2-O5	109.55
O1-T1-O4	109.52	O2-T2-O6	109.26
O2-T1-O3	109.43	O5-T2-O6	109.78
O3-T1-O4	109.37		
O4-T1-O2	109.42		

Figure A4.12. A list of selected O-T-O angles of the structure solutions of (1) as-synthesized CIT-16P with DiQ-C4 (this work), (2) as-synthesized SAPO-17 with piperidine, and (3) idealized ERI framework.

In order to visualize the geometric distortions of tetrahedral (T)-sites in the frameworks, we compared the O-T-O angles of various pentacoordinated and tetracoordinated aluminum sites in SAPO-17, as reported in the literature, to those of CIT-16P. **Figure A4.12(a)** depicts a pentacoordinate aluminum site (A15) and a selected tetrahedral aluminum site (A13) on the side of
the pre-can unit in the as-synthesized CIT-16P. The angles were measured based on the structure solution of CIT-16P. The tabulated O-T-O angles of CIT-16P reveal that most of the angles significantly deviate from the ideal tetrahedral angle of 109.5°, thereby supporting the conclusion that CIT-16P exhibits a certain degree of "distortion."

Similar distortion was also observed in the structure of as-synthesized piperidine SAPO-17, as demonstrated in **Figure A4.12(b)**. This material also features additional bridging oxygen sites (Al1-O7-Al1) with partial occupancies within the can units, which confer fifth coordination upon neighboring aluminum sites, thereby forming pentacoordinated Al-sites (Al1). Similar to CIT-16P, the Al1 site also exhibited significant deviation from the ideal tetrahedral angle of 109.5°. However, the degree of distortion observed in the tetrahedral site (Al2 of **Figure A4.12(b**)) of piperidine SAPO-17 was less pronounced compared to the corresponding site in CIT-16P.

It is notable that the idealized ERI framework, absent of OSDA cations, exhibits all O-T-O angles that closely approximate the ideal tetrahedral angle of 109.5° (**Figure A4.12(c)**).

Samula ID	S:/T	_	Defenence					
Sample ID	51/1	C ₂₌	C ₃₌	C ₄	C_{5+}	Total Alkanes	$C_{2=}/C_{3=}$	Kelerence
SAPO-17-A	0.022	21	33	15	22	1.7	0.65	This Work
SAPO-17-B	0.034	23	33	14	28	0.6	0.70	(10)
SAPO-17-C	0.042	25	35	15	21	1.4	0.73	(10)
SAPO-17-D	0.071	29	34	14	19	3.1	0.86	(10)
SAPO-17-E	0.073	28	33	13	19	2.5	0.85	(10)
SAPO-17-F	0.103	30	31	11	17	3.3	0.98	(10)
SAPO-17-G	0.120	30	27	13	23	3.8	1.12	(10)

Table A4.9. MTO reaction results of various SAPO-17 samples with different Si/T-atom ratios at identical reaction conditions (400 $^{\circ}$ C, 1.3 h⁻¹ WHSV).¹⁰

^[a] Evaluated at high methanol conversion (97–100%).

References:

(1) W. Noble, G.; A. Wright, P.; Kvick, Å. The templated synthesis and structure determination by synchrotron microcrystal diffraction of the novel small pore magnesium aluminophosphate STA-2[†]. J. Chem. Soc. Dalton. Trans. **1997**, (23), 4485-4490, 10.1039/A705091G. DOI: 10.1039/A705091G.

(2) Boultif, A.; Louër, D. Powder pattern indexing with the dichotomy method. *J. Appl. Crystallogr.* **2004**, *37*, 724-731.

(3) Rodríguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B* **1993**, *192*, 5569.

(4) Dudek, M. J.; Ponder, J. W. Accurate modeling of the intramolecular electrostatic energy of proteins. *Journal of Computational Chemistry* **1995**, *16* (7), 791-816, https://doi.org/10.1002/jcc.540160702. DOI: https://doi.org/10.1002/jcc.540160702 (accessed 2022/11/13).

(5) Favre-Nicolin, V.; Černý, R. FOX, 'free objects for crystallography': a modular approach to ab initio structure determination from powder diffraction. *J. Appl. Cryst.* **2002**, *35* (6), 734-743, https://doi.org/10.1107/S0021889802015236. DOI: https://doi.org/10.1107/S0021889802015236 (accessed 2022/11/13).

(6) Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic Computing System JANA2006:
General features. *Zeitschrift für Kristallographie - Crystalline Materials* 2014, 229 (5), 345-352.
DOI: doi:10.1515/zkri-2014-1737 (accessed 2022-10-07).

(7) Urzhumtsev, A.; Afonine, P. V.; Adams, P. D. TLS from fundamentals to practice. *Crystallography Reviews* **2013**, *19* (4), 230-270. DOI: 10.1080/0889311X.2013.835806. Winn, M.

D.; Isupov, P. V.; Murshudov, G. N. Use of TLS parameters to model anisotropic displacements in macromolecular refinement. *Acta Crystallogr.* **2001**, *57*, 122.

(8) Gale, J. D. GULP: A computer program for the symmetry-adapted simulation of solids. J. Chem. Soc. Faraday Trans. 1997, 93 (4), 629-637, 10.1039/A606455H. DOI: 10.1039/A606455H. Nguyen, C. M.; De Moor, B. A.; Revniers, M.-F.; Marin, G. B. Physisorption and Chemisorption of Linear Alkenes in Zeolites: A Combined QM-Pot(MP2//B3LYP:GULP)-Statistical Thermodynamics Study. J. Phys. Chem. C 2011, 115 (48), 23831-23847. DOI: 10.1021/jp2067606. Girard, S.; Tuel, A.; Mellot-Draznieks, C.; Férey, G. Computational Prediction of the Phase Transformation of Two As-Synthesized Oxyfluorinated Compounds into the Zeotype CHA Forms. Angew. Chem. Int. Ed. 2002, 41 (6), 972-975, https://doi.org/10.1002/1521-3773(20020315)41:6<972::AID-ANIE972>3.0.CO;2-5. DOI: https://doi.org/10.1002/1521-3773(20020315)41:6<972::AID-ANIE972>3.0.CO;2-5 (accessed 2022/11/13).

(9) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: a modular and opensource software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* **2009**, *21* (39), 395502. DOI: 10.1088/0953-8984/21/39/395502.

(10) Alshafei, F. H.; Park, Y.; Zones, S. I.; Davis, M. E. Methanol-to-olefins catalysis on ERI-type molecular sieves: towards enhancing ethylene selectivity. *J. Catal.* **2021**, *404*, 620-633. DOI: https://doi.org/10.1016/j.jcat.2021.10.025.

Appendix D | Supplemental Information – Chapter 5



Figure A5.1. Molecular sieve topologies (obtained from IZA) for SAT (left), CHA (middle), and AEI (right).



Figure A5.2. ¹³C-NMR of the OSDAs used for the synthesis of SAT-type molecular sieves. (a) $DiQ-C_4$, (b) $DiQ-C_5$, and (c) $DiDABCO-D_4$.

Table A5.1. Products and gel chemical compositions of SAT-type molecular sieves using DiQ-C₄ as an OSDA. [a] "N" indicates no, whereas "Y" indicates yes. Entries highlighted in orange are samples that were tested in MTO. Entry 5 refers to CIT-17-2. Entry 25 refers to MgAPO-SAT.

Entry	Internal ID	Al ₂ O ₃	P ₂ O ₃	SiO2	Co	Mg	OSDA	R(Br) ₂	R(OH)₂	H₂O	Temperature (°C)	Time (h)	Rotation ^[a]	Seed (1wt%) ^[a]	Product XRD	Reference
1	FHS0329	0.45	0.50	0.10	0.00	0.00	DiQ-C4	0.00	0.40	40	190	48	N	N	CIT-16P+SAT	This Work
2	FHS0154	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.00	0.24	40	190	72	Y	N	CIT-16P+SAT	CIT-16P
3	FHS0156	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.24	40	190	72	Y	N	CIT-16P+SAT	CIT-16P
4	FSAT1	0.50	0.45	0.15	0.00	0.00	DiQ-C4	0.00	0.21	40	190	72	Y	N	SAT+impurity	This Work
5	FHS0155	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.00	0.21	40	190	72	Y	N	CIT-17 (SAT)	This Work
6	FHS0157	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.21	40	190	72	Y	N	CIT-17 (SAT)	This Work
7	FHS0169	0.50	0.45	0.06	0.00	0.00	DiQ-C4	0.00	0.21	40	190	72	Y	N	CIT-17 (SAT)	This Work
8	FHS0186	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.21	40	180	96	Y	N	CIT-17 (SAT)	This Work
9	FHS0187	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.21	40	200	72	Y	N	CIT-17 (SAT)	This Work
10	FHS0170	0.50	0.45	0.12	0.00	0.00	DiQ-C4	0.00	0.19	40	190	72	Y	N	SAT+impurity	This Work
11	FHS0172	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.00	0.19	40	190	72	Y	N	CIT-17 (SAT)	This Work
12	FSAT2	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.19	40	190	72	Y	N	CIT-17 (SAT)	This Work
13	FHS0171	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.00	0.17	40	190	72	Y	N	CIT-17 (SAT)	This Work
14	FSAT3	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.17	40	190	72	Y	N	CIT-17 (SAT)	This Work
15	FHS0344	0.50	0.50	0.10	0.00	0.00	DiQ-C4	0.00	0.27	40	190	72	N	N	SAT+AFX	This Work
16	FSAT4	0.50	0.48	0.10	0.00	0.00	DiQ-C4	0.00	0.25	40	190	72	N	N	CIT-17 (SAT)	This Work
17	FSAT9	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.00	0.26	60	190	72	N	N	CIT-17 (SAT)	This Work
18	FSAT7	0.50	0.45	0.08	0.00	0.00	DiQ-C4	0.00	0.33	75	190	96	Y	Y	CIT-17 (SAT)	This Work
19	FSAT8	0.50	0.50	0.08	0.00	0.00	DiQ-C4	0.00	0.33	75	190	96	Y	Y	CIT-17 (SAT)	This Work
20	FHS0282	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.05	0.22	40	190	72	Y	N	CIT-17 (SAT)	This Work
21	FHS0283	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.08	0.19	40	190	72	Y	N	CIT-17 (SAT)	This Work
22	FHS0284	0.50	0.45	0.10	0.00	0.00	DiQ-C4	0.11	0.16	40	190	72	Y	N	CIT-17 (SAT)	This Work
23	FHS0342	0.45	0.50	0.00	0.00	0.10	DiQ-C4	0.00	0.40	40	190	48	N	N	MgAPO-SAT	This Work (STA-2)
24	F0816	0.45	0.50	0.00	0.00	0.10	DiQ-C4	0.00	0.40	40	190	72	N	N	MgAPO-SAT	This Work (STA-2)
25	F0819	0.45	0.50	0.00	0.00	0.10	DiQ-C4	0.00	0.40	40	190	72	Y	N	MgAPO-SAT	This Work
26	FHS0282	0.45	0.50	0.00	0.10	0.00	DiQ-C4	0.00	0.27	40	190	72	N	N	CoAPO-SAT+CIT-16P	This Work
27	FHS0285	0.50	0.45	0.08	0.025	0.00	DiQ-C4	0.00	0.27	40	190	72	Y	N	CoSAPO-SAT	This Work
28	FHS0286	0.50	0.45	0.05	0.05	0.00	DiQ-C4	0.00	0.27	40	190	72	Y	N	CoAPO-SAT	This Work
29	F0996	0.45	0.53	0.00	0.08	0.00	DiQ-C4	0.00	0.40	75	190	72	Y	Y	CoAPO-SAT	This Work
30	F0997	0.45	0.55	0.00	0.08	0.00	DiQ-C4	0.00	0.40	75	190	72	Y	Y	CoAPO-SAT	This Work

Table A5.2. Products and gel chemical compositions of SAT-type molecular sieves using DiQ-C₅ as an OSDA. [a] "N" indicates no, whereas "Y" indicates yes. Entries highlighted in orange are samples that were tested in MTO. Entry 31 refers to CIT-17-5. Entry 32 refers to CIT-17-4. Entry 33 refers to CIT-17-1. [b] "vs" indicates that the impurity phase is very small (<5%).

Entry	Internal ID	Al ₂ O ₃	P ₂ O ₃	SiO ₂	Co	Mg	OSDA	R(Br) ₂	R(OH) ₂	H ₂ O	Temperature (°C)	Time (h)	Rotation ^[a]	Seed (1wt%) ^[a]	Product XRD ^[b]	Reference
31	FHS0250	0.50	0.45	0.20	0	0	DiQ-C5	0	0.27	40	190	72	Y	N	SAT+impurity(vs)	This Work
32	FHS0249	0.50	0.45	0.15	0	0	DiQ-C5	0	0.27	40	190	72	Y	N	CIT-17 (SAT)	This Work
33	FHS0212	0.50	0.45	0.10	0	0	DiQ-C5	0	0.27	40	190	72	Y	N	CIT-17 (SAT)	This Work
34	FHS0211	0.50	0.45	0.10	0	0	DiQ-C5	0	0.23	40	190	72	Y	N	CIT-17 (SAT)	This Work
35	FSAT5	0.50	0.45	0.08	0	0	DiQ-C5	0	0.23	40	190	72	Y	N	CIT-17 (SAT)	This Work
36	FSAT6	0.50	0.45	0.06	0	0	DiQ-C5	0	0.23	40	190	72	Y	N	CIT-17 (SAT)	This Work
37	FSAT20	0.50	0.46	0.40	0	0	DiQ-C5	0	0.23	40	190	72	Y	Y	SAT+AFX	This Work
38	FHS0240	0.50	0.49	0.05	0	0	DiQ-C5	0	0.23	40	190	72	Y	N	SAT+impurity	This Work
39	FHS0242	0.50	0.49	0.20	0	0	DiQ-C5	0	0.23	40	190	72	Y	N	CIT-17 (SAT)	This Work

Table A5.3. Products and gel chemical compositions of SAT-type molecular sieves using DiDABCO-C₄ as an OSDA. [a] "N" indicates no, whereas "Y" indicates yes. Entries highlighted in orange are samples that were tested in MTO. Entry 45 refers to CIT-17-3. Entry 41 refers to CoAPO-SAT. [b] "vs" indicates that the impurity phase is very small (<5%).

Entry	Internal ID	Al ₂ O ₃	P ₂ O ₃	SiO2	Co	Mg	OSDA	R(Br)2	R(OH)₂	H₂O	Temperature (°C)	Time (h)	Rotation ^[a]	Seed (1wt%) ^[a]	Product XRD ^(b)	Reference
40	F1102	0.45	0.50	0.00	0.03	0.00	DiDABCO-C4	0	0.40	75	190	96	Y	N	CoAPO-SAT	This Work
41	F1101	0.45	0.50	0.00	0.05	0.00	DiDABCO-C4	0	0.40	75	190	96	Y	N	CoAPO-SAT	This Work
42	F1006	0.50	0.50	0.08	0.00	0.00	DiDABCO-C4	0	0.33	75	190	120	Y	Y	SAT+AFX (vs)	This Work
43	FHS0779	0.50	0.47	0.10	0.00	0.00	DIDABCO-C4	0	0.33	75	190	120	Y	Y	CIT-17 (SAT)	This Work
44	FHS0780	0.50	0.50	0.10	0.00	0.00	DIDABCO-C4	0	0.33	75	190	120	Y	Y	CIT-17 (SAT)	This Work
45	FHS0774	0.50	0.45	0.10	0.00	0.00	DIDABCO-C4	0	0.20	40	190	48	Y	Y	CIT-17 (SAT)	This Work
46	FHS0775	0.48	0.45	0.10	0.00	0.00	DiDABCO-C4	0	0.20	40	190	48	Y	Y	CIT-17 (SAT)	This Work
47	FHS0776	0.46	0.45	0.10	0.00	0.00	DiDABCO-C4	0	0.20	40	190	48	Y	Y	CIT-17 (SAT)	This Work
48	FHS0777	0.45	0.44	0.10	0.00	0.00	DiDABCO-C4	0	0.20	40	190	48	Y	Y	CIT-17 (SAT)	This Work
49	FHS0778	0.44	0.45	0.10	0.00	0.00	DiDABCO-C4	0	0.20	40	190	48	Y	Y	CIT-17 (SAT)	This Work
50	FHS0843	0.44	0.45	0.40	0.00	0.00	DIDABCO-C4	0	0.20	40	190	48	Y	Y	AFX+SAT	This Work



Figure A5.3. PXRD patterns of the CHA-type molecular sieves. (Note: SAPO-34-1 is a sample that was provided to us and was already thermally treated, hence the shift in the peak positions.)



Figure A5.4. PXRD patterns of the CHA/AEI-type molecular sieve (SAPO-34/18). The sample is mostly CHA, with a small amount of AEI. CHA/AEI intergrowth materials typically display this shoulder (shown with an arrow) due to the presence of AEI.



Figure A5.5. PXRD patterns of the AEI-type molecular sieves.

Framework	Sample ID	Entry Number ^[a]	Si(M)/T ^[b]
	SAPO-34-1	-	0.081
	SAPO-34-2	-	0.123
СНА	SAPO-34-3	-	0.127
	MgAPO-34	-	0.015
	CoAPO-34	-	0.022
CHA/AEI	SAPO-34/18	-	0.063
	SAPO-18-1	-	0.038
	SAPO-18-2	-	0.061
AEI	SAPO-18-3	-	0.162
	MgAPO-18	-	0.031
	CoAPO-18	-	0.073
	CIT-17-1	33	0.068
	CIT-17-2	5	0.072
	CIT-17-3	45	0.073
SAT	CIT-17-4	32	0.083
	CIT-17-5	31	0.094
	MgAPO-SAT (STA-2)	25	0.071
	CoAPO-SAT (STA-2)	41	0.063

Table A5.4. Elemental composition data for the various samples tested in this work. [a] Refers to the Entry numbers in **Tables A5.1** to **A5.3**. [b] Determined by EDS. T=Si(M)+Al+P and M is either Co or Mg.



Figure A5.6. SEM images of the CHA, CHA/AEI, and AEI-type samples. SEM images of samples not shown here can be found in our previous work as indicated in the Experimental Section.



Figure A5.7. Characterization on SAPO-34-1. (a) ²⁹Si MAS NMR spectrum. (b) ²⁷Al MAS NMR spectrum. (c) ³¹P MAS NMR spectrum. (d) ¹H MAS NMR spectrum.



Figure A5.8. Characterization on SAPO-34/18. (a) ²⁹Si MAS NMR spectrum. (b) ²⁷Al MAS NMR spectrum. (c) ³¹P MAS NMR spectrum. (d) ¹H MAS NMR spectrum.



Figure A5.9. Characterization on SAPO-18-1. (a) ²⁹Si MAS NMR spectrum. (b) ²⁷Al MAS NMR spectrum. (c) ³¹P MAS NMR spectrum. (d) ¹H MAS NMR spectrum.



Figure A5.10. PXRD patterns on MgAPO-SAT (black; bottom; Entry 25) and CoAPO-SAT (grey; top; Entry 41).



Figure A5.11. PXRD patterns on CIT-17-2 (synthesized using DiQ-C₄; bottom; Entry 5) and CIT-17-3 (synthesized using DiDABCO-C₄; top; Entry 45).



Figure A5.12. PXRD patterns of several CIT-17 samples with different Si/T-atom ratios synthesized using DiQ-C₅. CIT-17-1 (bottom; Entry 33), CIT-17-4 (middle; Entry 32; different batch than the one reported in the main-text), and CIT-17-5 (top; Entry 31).



Figure A5.13. SEM images of CIT-17 samples. CIT-17-1 and CIT-17-5 were synthesized using DiQ-C₅. CIT-17-2 was synthesized using DiQ-C₄. CIT-17-3 was synthesized using DiDABCO-C₄ (and shows slightly smaller particle sizes than samples prepared using the other two OSDAs). The few plate-like structures in the SEM image of CIT-17-5 are SAPO-56 (AFX).



Figure A5.14. MTO reaction data on CHA-type molecular sieves obtained at 400 °C and WHSV of 1.3 h⁻¹. (a) SAPO-34-1, (b) SAPO-34-2, (c) SAPO-34-3, (d) MgAPO-34, and (e) CoAPO-34.



Figure A5.15. MTO reaction data on CHA/AEI-type molecular sieves obtained at 400 $^{\circ}$ C and WHSV of 1.3 h⁻¹.



Figure A5.16. MTO reaction data on AEI-type molecular sieves obtained at 400 °C and WHSV of 1.3 h⁻¹. (a) SAPO-18-1, (b) SAPO-18-2, (c) SAPO-18-3, (d) MgAPO-18, and (e) CoAPO-18.



Figure A5.17. MTO reaction data on CIT-17-type molecular sieves obtained at 400 $^{\circ}$ C and WHSV of 1.3 h⁻¹. (a) CIT-17-1, (b) CIT-17-2, (c) CIT-17-3, (d) CIT-17-4, and (e) CIT-17-5.



Figure A5.18. MTO Reaction data on CIT-17-type molecular sieves obtained at 400 $^{\circ}$ C and WHSV of 1.3 h⁻¹. MgAPO-SAT is on the left whereas CoAPO-SAT is on the right.



Figure A5.19. MTO reaction on CIT-17-4 obtained at various reaction conditions: temperatures and weight hourly space velocities. (a) T=450 °C and WHSV=0.65 h⁻¹, (b) T=400 °C and WHSV=0.65 h⁻¹, (c) T=400 °C and WHSV=2.6 h⁻¹, (d) T=350 °C and WHSV=1.3 h⁻¹, and (e) T=350 °C and WHSV=0.65 h⁻¹. Experiments performed at T=300 °C led to the formation of DME only (data not shown).