

## REFERENCES

- (1) Plotkin, J. S. The Propylene Gap: How Can It Be Filled?, American Chemical Society. 2015.
- (2) Amghizar, I.; Vandewalle, L. A.; Van Geem, K. M.; Marin, G. B., New Trends in Olefin Production, *Engineering* **2017**, *3*, 171-178.
- (3) Plotkin, J. S. Beyond the Ethylene Steam Cracker, American Chemical Society. 2016.
- (4) Zimmermann, H.; Walzl, R., Ethylene. In *Ullmann's encyclopedia of industrial chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim: 2009.
- (5) Bricker, J. In *History and State of the Art of Ethane/Propane Dehydrogenation Catalysis.*, The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Proceedings of a Workshop, by Nat. Acad. Sci. Eng. and Med., Washington, DC, Washington, DC, 2016.
- (6) Annual Energy Review 2006, U.S. Energy Information Administration, Department of Energy. 2007.
- (7) Chang, C. D.; Silvestri, A. J., The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts, *J. Catal.* **1977**, *47*, 249-259.
- (8) 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, *Angew. Chem. Int. Ed.* **2012**, *51*, 5810-5831.
- (9) Stöcker, M., Methanol-to-hydrocarbons: catalytic materials and their behavior, *Micropor. Mesopor. Mater.* **1999**, *29*, 3-48.
- (10) Maiden, C. J., The New Zealand Gas-to-Gasoline Project, *Stud. Surf. Sci. Catal.* **1988**, *36*, 1-16.
- (11) 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.

(12)Vora, B. V.; Marker, T. L.; Barger, P. T.; Nilsen, H. R.; Kvisle, S.; Fuglerud, T., Economic route for natural gas conversion to ethylene and propylene, *Stud. Surf. Sci. Catal.* **1997**, *107*, 87-98.

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

(14)Szostak, R., *Molecular Sieves, Principles of Synthesis and Identification*. Van Nostrand Reinhold: New York, New York, the United States, 1989.

(15)Loewenstein, W., The distribution of aluminum in the tetrahedra of silicates and aluminates, *Am. Mineral.* **1954**, *39*, 92.

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

(17)Miyamoto, M.; Nakatani, T.; Fujioka, Y.; Yogo, K., Verified synthesis of pure silica CHA-type zeolite in fluoride media, *Micropor. Mesopor. Mater.* **2015**, *206*, 67-74.

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

(19)Marchese, L.; Frache, A.; Gianotti, E.; Martra, G.; Causà, M.; Coluccia, S., ALPO-34 and SAPO-34 synthesized by using morpholine as templating agent. FTIR and FT-Raman studies of the host-guest and guest-guest interactions within the zeolitic framework, *Micropor. Mesopor. Mater.* **1999**, *30*, 145-153.

(20)Ashtekar, S.; Prakash, A. M.; Chakrabarty, D. K.; Chilukuri, S. V. V., Small-pore aluminium phosphate molecular sieves with chabazite structure. Incorporation of magnesium in structures -34 and -44, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2481-2486.

(21)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*, 6937-6943.

(22)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.

(23)Yarulina, I.; Chowdhury, A. D.; Meirer, F.; Weckhuysen, B. M.; Gascon, J., Recent trends and fundamental insights in the methanol-to-hydrocarbons process, *Nat. Catal.* **2018**, *1*, 398-411.

(24)Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inaba, S.-i.; Ip, W. M.; Lammertsma, K.; Salem, G.; Tabor, D., Onium Ylide chemistry. 1. Bifunctional acid-base-catalyzed conversion of heterosubstituted methanes into ethylene and derived hydrocarbons. The onium ylide mechanism of the C1 to C2 conversion, *J. Am. Chem. Soc.* **1984**, *106*, 2143-2149.

(25)Chang, C. D.; Hellring, S. D.; Pearson, J. A., On the existence and role of free radicals in methanol conversion to hydrocarbons over HZSM-5: I. Inhibition by NO, *J. Catal.* **1989**, *115*, 282-285.

(26)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.

(27)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, *J. Catal.* **1994**, *149*, 458-464.

(28)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, *J. Catal.* **1996**, *161*, 304-309.

(29)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*, 14770-14771.

(30)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, *J. Catal.* **2014**, *314*, 21-31.

(31)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, *Chem. Eur. J.* **2009**, *15*, 10803-10808.

(32)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*, 4033-4046.

(33)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*, 661-665.

(34)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*, 10950-10963.

(35)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, *Angew. Chem. Int. Ed.* **2013**, *52*, 11564-11568.

(36)Li, J.; Wei, Y.; Xu, S.; Tian, P.; Chen, J.; Liu, Z., Heptamethylbenzenium cation formation and the correlated reaction pathway during methanol-to-olefins conversion over DNL-6, *Catal. Today* **2014**, *226*, 47-51.

(37)Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B., The Mechanism of Methanol to Hydrocarbon Catalysis, *Acc. Chem. Res.* **2003**, *36*, 317-326.

(38)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.

(39)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.

(40)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*, 2725-2734.

(41)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*, 2490-2495.

(42)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*, 15731-15741.

(43)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, *Appl. Catal. A* **2008**, *339*, 36-44.

(44)Wilson, S.; Barger, P., The characteristics of SAPO-34 which influence the conversion of methanol to light olefins, *Micropor. Mesopor. Mater.* **1999**, *29*, 117-126.

(45)Chen, J.; Wright, P. A.; Natarajan, S.; Thomas, J. M., Understanding The Brønsted Acidity of Sapo-5, Sapo-17, Sapo-18 and SAPO-34 and Their Catalytic Performance for Methanol Conversion to Hydrocarbons, *Stud. Surf. Sci. Catal.* **1994**, *84*, 1731-1738.

(46)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, *Catal. Commun.* **2014**, *46*, 36-40.

(47)Yokoi, T.; Yoshioka, M.; Imai, H.; Tatsumi, T., Diversification of RTH-Type Zeolite and Its Catalytic Application, *Angew. Chem. Int. Ed.* **2009**, *48*, 9884-9887.

(48)Schmidt, J. E.; Xie, D.; Davis, M. E., Synthesis of the RTH-type layer: the first small-pore, two dimensional layered zeolite precursor, *Chem. Sci.* **2015**, *6*, 5955-5963.

(49)Xiang, D.; Yang, S.; Liu, X.; Mai, Z.; Qian, Y., Techno-economic performance of the coal-to-olefins process with CCS, *Chem. Eng. J.* **2014**, *240*, 45-54.

(50)Smit, B.; Maesen, T. L. M., Towards a molecular understanding of shape selectivity, *Nature* **2008**, *451*, 671.

(51)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.

(52)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.

(53)Effenberger, H.; Giester, G.; Krause, W.; Bernhardt, H. J., Tschörtnerite, a copper-bearing zeolite from the Bellberg volcano, Eifel, Germany, *Am. Mineral.* **1998**.

(54)Low, J. J.; Lewis, G. J. Synthetic crystalline aluminosilicate zeolite having the tschörtnerite framework topology and uses thereof, US Patent 6,534,034 B1. 2003.

(55)McGuire, N. K.; Bateman, C. A.; Scott Blackwell, C.; Wilson, S. T.; Kirchner, R. M., Structure refinement, electron microscopy, and solid-state magic angle spinning nuclear magnetic resonance characterization of AlPO<sub>4</sub>-52: An aluminophosphate with a large cage, *Zeolites* **1995**, *15*, 460-469.

(56)Broach, R. W.; Greenlay, N.; Jakubczak, P.; Knight, L. M.; Miller, S. R.; Mowat, J. P. S.; Stanczyk, J.; Lewis, G. J., New ABC-6 net molecular sieves ZnAPO-57 and ZnAPO-59: Framework charge density-induced transition from two- to three-dimensional porosity, *Micropor. Mesopor. Mater.* **2014**, *189*, 49-63.

(57) Sedlmaier, S. J.; Döblinger, M.; Oeckler, O.; Weber, J.; Schmedt auf der Günne, J.; Schnick, W., Unprecedented Zeolite-Like Framework Topology Constructed from Cages with 3-Rings in a Barium Oxonitridophosphate, *J. Am. Chem. Soc.* **2011**, *133*, 12069-12078.

(58) Turrina, A.; Garcia, R.; Cox, P. A.; Casci, J. L.; Wright, P. A., Retrosynthetic Co-Templating Method for the Preparation of Silicoaluminophosphate Molecular Sieves, *Chem. Mater.* **2016**, *28*, 4998-5012.

(59) Zones, S. I.; Van Nordstrand, R. A., Further studies on the conversion of Cubic P zeolite to high silica organozeolites, *Zeolites* **1988**, *8*, 409-415.

(60) Xie, D. Method for Preparing Zeolite SSZ-98, US Patent 9,663,379B2. 2016.

(61) Xie, D. Synthesis of aluminosilicate LEV framework type zeolites, US Patent 9,708,193B2. 2017.

(62) Boal, B. W.; Schmidt, J. E.; Deimund, M. A.; Deem, M. W.; Henling, L. M.; Brand, S. K.; Zones, S. I.; Davis, M. E., Facile Synthesis and Catalysis of Pure-Silica and Heteroatom LTA, *Chem. Mater.* **2015**, *27*, 7774-7779.

(63) Boal, B. W.; Deem, M. W.; Xie, D.; Kang, J. H.; Davis, M. E.; Zones, S. I., Synthesis of Germanosilicate Molecular Sieves from Mono- and Di-Quaternary Ammonium OSDAs Constructed from Benzyl Imidazolium Derivatives: Stabilization of Large Micropore Volumes Including New Molecular Sieve CIT-13, *Chem. Mater.* **2016**, *28*, 2158-2164.

(64) 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.

(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-six-ring family of materials with stacking sequence AABBCB, *Micropor. Mesopor. Mater.* **1999**, *28*, 125-137.

(66) Corma, A.; Moliner, M.; Martínez, R. Synthesis of sa-po-18 and the catalytic applications thereof, US Patent Application 20170259253A1. 2017.

(67)Chen, J.; Thomas, J. M., MAPO-18 (M • Mg, Zn, Co): a new family of catalysts for the conversion of methanol to light olefins, *J. Chem. Soc. Chem. Commun.* **1994**, 603-604.

(68)Su, X.; Tian, P.; Li, J.; Zhang, Y.; Meng, S.; He, Y.; Fan, D.; Liu, Z., Synthesis and characterization of DNL-6, a new silicoaluminophosphate molecular sieve with the RHO framework, *Micropor. Mesopor. Mater.* **2011**, *144*, 113-119.

(69)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*, 6078-6085.

(70)Chatelain, T.; Patarin, J.; Fousson, E.; Soulard, M.; Guth, J. L.; Schulz, P., Synthesis and characterization of high-silica zeolite RHO prepared in the presence of 18-crown-6 ether as organic template, *Micropor. Mater.* **1995**, *4*, 231-238.

(71)Kim, J.; Cho, S. J.; Kim, D. H., Facile Synthesis of KFI-type Zeolite and Its Application to Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub>, *ACS Catal.* **2017**, *7*, 6070-6081.

(72)Archer, R. H.; Zones, S. I.; Davis, M. E., Imidazolium structure directing agents in zeolite synthesis: Exploring guest/host relationships in the synthesis of SSZ-70, *Micropor. Mesopor. Mater.* **2010**, *130*, 255-265.

(73)Xie, D.; McCusker, L. B.; Baerlocher, C.; Zones, S. I.; Wan, W.; Zou, X., SSZ-52, a Zeolite with an 18-Layer Aluminosilicate Framework Structure Related to That of the DeNO<sub>x</sub> Catalyst Cu-SSZ-13, *J. Am. Chem. Soc.* **2013**, *135*, 10519-10524.

(74) Xie, D. Synthesis of molecular sieve SSZ-105, US Patent 9,663,377. 2017.

(75)Zones, S. I.; Xie, D.; Chen, C.-Y.; Liang, A. J.-B. Method for making molecular sieve SSZ-99, US Patent 9,193,600 B1. 2015.

(76)Davis, T. M. Molecular sieve SSZ-104, its synthesis and use, US Patent 9,725,328 B1. 2017.



(77)Zones, S. I.; Xie, D.; Saxton, R. J. Method for making molecular sieve SSZ-27, US Patent 9,586,830 B2. 2017.

(78)Zones, S. I.; Holtermann, D. L.; Innes, R. A. Zeolite SSZ-28, US Patent 5,200,377 A. 1993.

(79)Lee, G. S.; Zones, S. I., Polymethylated [4.1.1] Octanes Leading to Zeolite SSZ-50, *J. Solid State Chem.* **2002**, *167*, 289-298.

(80)Bereciartua, P. J.; Cantín, Á.; Corma, A.; Jordá, J. L.; Palomino, M.; Rey, F.; Valencia, S.; Corcoran, E. W.; Kortunov, P.; Ravikovitch, P. I.; Burton, A.; Yoon, C.; Wang, Y.; Paur, C.; Guzman, J.; Bishop, A. R.; Casty, G. L., Control of zeolite framework flexibility and pore topology for separation of ethane and ethylene, *Science* **2017**, *358*, 1068.

(81)Nishiyama, N.; Kawaguchi, M.; Hirota, Y.; Van Vu, D.; Egashira, Y.; Ueyama, K., Size control of SAPO-34 crystals and their catalyst lifetime in the methanol-to-olefin reaction, *Appl. Catal. A* **2009**, *362*, 193-199.

(82)Bakhtiar, S. u. 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*, 2606-2616.

(83)Yang, G.; Wei, Y.; Xu, S.; Chen, J.; Li, J.; Liu, Z.; Yu, J.; Xu, R., Nanosize-Enhanced Lifetime of SAPO-34 Catalysts in Methanol-to-Olefin Reactions, *J. Phys. Chem. C* **2013**, *117*, 8214-8222.

(84)Chen, J. Q.; Bozzano, A.; Glover, B.; Fuglerud, T.; Kvisle, S., Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process, *Catal. Today* **2005**, *106*, 103-107.

(85)Borodina, E.; Meirer, F.; Lezcano-González, I.; 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-SSZ-13, *ACS Catal.* **2015**, *5*, 992-1003.

(86)Wang, C.-M.; Wang, Y.-D.; Du, Y.-J.; Yang, G.; Xie, Z.-K., Similarities and differences between aromatic-based and olefin-based cycles in H-SAPO-34 and H-SSZ-13

for methanol-to-olefins conversion: insights from energetic span model, *Catal. Sci. Technol.* **2015**, *5*, 4354-4364.

(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, *Top. Catal.* **2015**, *58*, 416-423.

(88)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 Brønsted Acid Sites, *J. Phys. Chem.* **1994**, *98*, 10216-10224.

(89)Wendelbo, R.; Akporiaye, D.; Andersen, A.; Dahl, I. M.; Mostad, H. B., Synthesis, characterization and catalytic testing of SAPO-18, MgAPO-18, and ZnAPO-18 in the MTO reaction, *Appl. Catal. A* **1996**, *142*, L197-L207.

(90)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*, 3268-3277.

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

(92)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.

(93)Djeugoue, 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, *J. Phys. Chem. B* **2000**, *104*, 6452-6461.

(94)Hereijgers, B. P. C.; Bleken, F.; Nilsen, M. H.; Svelle, S.; Lillerud, K.-P.; Bjørgen, M.; Weckhuysen, B. M.; Olsbye, U., Product shape selectivity dominates the Methanol-to-Olefins (MTO) reaction over H-SAPO-34 catalysts, *J. Catal.* **2009**, *264*, 77-87.

(95)Zhou, F.; Tian, P.; Liu, Z.; Liu, G.; Chang, F.; Li, J., Synthesis of ZSM-34 and Its Catalytic Properties in Methanol-to-Olefins Reaction, *Chinese J. Catal.* **2007**, *28*, 817-822.

(96)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 Process. Technol.* **2003**, *83*, 203-218.

(97)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*, 6072-6075.

(98)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*, 2236-2247.

(99)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, *Nat. Catal.* **2018**, *1*, 547-554.

(100)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*, 2663-2678.

(101) Field, L. A. Two-step reforming process, US Patent 4,443,326. 1984.

(102)Pinilla-Herrero, I.; Borfecchia, E.; Holzinger, J.; Mentzel, U. V.; Joensen, F.; Lomachenko, K. A.; Bordiga, S.; Lamberti, C.; Berlier, G.; Olsbye, U.; Svelle, S.; Skibsted, J.; Beato, P., High Zn/Al ratios enhance dehydrogenation vs hydrogen transfer reactions of Zn-ZSM-5 catalytic systems in methanol conversion to aromatics, *J. Catal.* **2018**, *362*, 146-163.

(103)Müller, S.; Liu, Y.; Kirchberger, F. M.; Tonigold, M.; Sanchez-Sanchez, M.; Lercher, J. A., Hydrogen Transfer Pathways during Zeolite Catalyzed Methanol Conversion to Hydrocarbons, *J. Am. Chem. Soc.* **2016**, *138*, 15994-16003.

(104)Martínez-Espín, J. S.; De Wispelaere, K.; Janssens, T. V. W.; Svelle, S.; Lillerud, K. P.; Beato, P.; Van Speybroeck, V.; Olsbye, U., Hydrogen Transfer versus Methylation: On the Genesis of Aromatics Formation in the Methanol-To-Hydrocarbons Reaction over H-ZSM-5, *ACS Catal.* **2017**, *7*, 5773-5780.

(105)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*, 1896-1905.

(106)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, *Micropor. Mesopor. Mater.* **2016**, *232*, 126-137.

(107)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.

(108)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.

(109)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.

(110)Lago, R. M.; Haag, W. O.; Mikovsky, R. J.; Olson, D. H.; Hellring, S. D.; Schmitt, K. D.; Kerr, G. T., Proceedings of the 7th Annual International Zeolite Conference. Murakami, Y.; Ijima, A.; Ward, J. W., Eds. Elsevier: Amsterdam, 1986; Vol. 28, pp 677-684.

- (111) 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*, 4456-4465.
- (112) Davis, M. E., Ordered porous materials for emerging applications, *Nature* **2002**, *417*, 813-821.
- (113) Zones, S. I., Translating new materials discoveries in zeolite research to commercial manufacture, *Micropor. Mesopor. Mater.* **2011**, *144*, 1-8.
- (114) Jiang, J.; Yu, J.; Corma, A., Extra-Large-Pore Zeolites: Bridging the Gap between Micro and Mesoporous Structures, *Angew. Chem. Int. Ed.* **2010**, *49*, 3120-3145.
- (115) Li, Y.; Yu, J., New Stories of Zeolite Structures: Their Descriptions, Determinations, Predictions, and Evaluations, *Chem. Rev.* **2014**, *114*, 7268-7316.
- (116) Paillaud, J.-L.; Harbuzaru, B.; Patarin, J.; Bats, N., Extra-Large-Pore Zeolites with Two-Dimensional Channels Formed by 14 and 12 Rings, *Science* **2004**, *304*, 990.
- (117) Shvets, O. V.; Kasian, N.; Zukal, A.; Pinkas, J.; Čejka, J., The Role of Template Structure and Synergism between Inorganic and Organic Structure Directing Agents in the Synthesis of UTL Zeolite, *Chem. Mater.* **2010**, *22*, 3482-3495.
- (118) Verheyen, E.; Joos, L.; Van Havenbergh, K.; Breynaert, E.; Kasian, N.; Gobechiya, E.; Houthoofd, K.; Martineau, C.; Hinterstein, M.; Taulelle, F.; Van Speybroeck, V.; Waroquier, M.; Bals, S.; Van Tendeloo, G.; Kirschhock, C. E. A.; Martens, J. A., Design of zeolite by inverse sigma transformation, *Nat. Mater.* **2012**, *11*, 1059.
- (119) Shvets, O. V.; Zukal, A.; Kasian, N.; Žilková, N.; Čejka, J., The Role of Crystallization Parameters for the Synthesis of Germanosilicate with UTL Topology, *Chem. Eur. J.* **2008**, *14*, 10134-10140.
- (120) Maesen, T., Chapter 1 - The Zeolite Scene – An Overview, *Stud. Surf. Sci. Catal.* **2007**, *168*, 1-12.
- (121) Schmidt, J. E.; Xie, D.; Rea, T.; Davis, M. E., CIT-7, a crystalline, molecular sieve with pores bounded by 8 and 10-membered rings, *Chem. Sci.* **2015**, *6*, 1728-1734.

(122)Roth, W. J.; Nachtigall, P.; Morris, R. E.; Wheatley, P. S.; Seymour, V. R.; Ashbrook, S. E.; Chlubná, P.; Grajciar, L.; Položij, M.; Zukal, A.; Shvets, O.; Čejka, J., A family of zeolites with controlled pore size prepared using a top-down method, *Nat. Chem.* **2013**, *5*, 628.

(123)Wheatley, P. S.; Chlubná-Eliášová, P.; Greer, H.; Zhou, W.; Seymour, V. R.; Dawson, D. M.; Ashbrook, S. E.; Pinar, A. B.; McCusker, L. B.; Opanasenko, M.; Čejka, J.; Morris, R. E., Zeolites with Continuously Tuneable Porosity, *Angew. Chem. Int. Ed.* **2014**, *53*, 13210-13214.

(124)Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C., VPI-5: The first molecular sieve with pores larger than 10 Ångstroms, *Zeolites* **1988**, *8*, 362-366.

(125)Davis, M. E.; Young, D., Further Studies on the Synthesis of VPI-5, *Stud. Surf. Sci. Catal.* **1991**, *60*, 53-62.

(126)Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C., A molecular sieve with eighteen-membered rings, *Nature* **1988**, *331*, 698-699.

(127)Maistriau, L.; Gabelica, Z.; Derouane, E. G.; Vogt, E. T. C.; van Oene, J., Solid-state n.m.r. study of the transformation of VPI-5/MCM-9 into AIPO4-8/SAPO-8, *Zeolites* **1991**, *11*, 583-592.

(128)Richardson, J. W.; Vogt, E. T. C., Structure determination and rietveld refinement of aluminophosphate molecular sieve AIPO4-8, *Zeolites* **1992**, *12*, 13-19.

(129)Estermann, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H., A synthetic gallophosphate molecular sieve with a 20-tetrahedral-atom pore opening, *Nature* **1991**, *352*, 320-323.

(130)Freyhardt, C. C.; Tsapatsis, M.; Lobo, R. F.; Balkus, K. J.; Davis, M. E., A high-silica zeolite with a 14-tetrahedral-atom pore opening, *Nature* **1996**, *381*, 295-298.

(131)Wagner, P.; Yoshikawa, M.; Tsuji, K.; E. Davis, M.; Wagner, P.; Lovallo, M.; Taspatsis, M., CIT-5: a high-silica zeolite with 14-ring pores, *Chem. Commun.* **1997**, 2179-2180.

(132)Yoshikawa, M.; Wagner, P.; Lovallo, M.; Tsuji, K.; Takewaki, T.; Chen, C.-Y.; Beck, L. W.; Jones, C.; Tsapatsis, M.; Zones, S. I.; Davis, M. E., Synthesis, Characterization, and Structure Solution of CIT-5, a New, High-Silica, Extra-Large-Pore Molecular Sieve, *J. Phys. Chem. B* **1998**, *102*, 7139-7147.

(133)Burton, A.; Elomari, S.; Chen, C.-Y.; Medrud, R. C.; Chan, I. Y.; Bull, L. M.; Kibby, C.; Harris, T. V.; Zones, S. I.; Vittoratos, E. S., SSZ-53 and SSZ-59: Two Novel Extra-Large Pore Zeolites, *Chem. Eur. J.* **2003**, *9*, 5737-5748.

(134)Martinez-Triguero, J.; Diaz-Cabañas, M. J.; Camblor, M. A.; Fornés, V.; Maesen, T. L. M.; Corma, A., The Catalytic Performance of 14-Membered Ring Zeolites, *J. Catal.* **1999**, *182*, 463-469.

(135)Sugi, Y.; Maekawa, H.; Mulla, S. A. R.; Ito, A.; Naitoh, C.; Nakagawa, K.; Komura, K.; Kubota, Y.; Kim, J.-H.; Seo, G., The Alkylation of Biphenyl over Fourteen-Membered Ring Zeolites. The Influence of Zeolite Structure and Alkylating Agent on the Selectivity for 4,4'-Dialkylbiphenyl, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1418-1428.

(136)Tontisirin, S.; Ernst, S., Zeolite SSZ-53: An Extra-Large-Pore Zeolite with Interesting Catalytic Properties, *Angew. Chem. Int. Ed.* **2007**, *46*, 7304-7306.

(137)Corma, A.; Díaz-Cabañas, M. J.; Rey, F.; Nicolopoulos, S.; Boulahya, K., ITQ-15: The first ultralarge pore zeolite with a bi-directional pore system formed by intersecting 14- and 12-ring channels, and its catalytic implications, *Chem. Commun.* **2004**, 1356-1357.

(138)Corma, A.; Díaz-Cabañas, M. J.; Jordá, J. L.; Martínez, C.; Moliner, M., High-throughput synthesis and catalytic properties of a molecular sieve with 18- and 10-member rings, *Nature* **2006**, *443*, 842-845.

(139)Moliner, M.; Díaz-Cabañas, M. J.; Fornés, V.; Martínez, C.; Corma, A., Synthesis methodology, stability, acidity, and catalytic behavior of the 18×10 member ring pores ITQ-33 zeolite, *J. Catal.* **2008**, *254*, 101-109.

(140)Sun, J.; Bonneau, C.; Cantín, Á.; Corma, A.; Díaz-Cabañas, M. J.; Moliner, M.; Zhang, D.; Li, M.; Zou, X., The ITQ-37 mesoporous chiral zeolite, *Nature* **2009**, *458*, 1154.

(141) Corma, A.; Díaz-Cabañas, M. J.; Jiang, J.; Afeworki, M.; Dorset, D. L.; Soled, S. L.; Strohmaier, K. G., Extra-large pore zeolite (ITQ-40) with the lowest framework density containing double four- and double three-rings, *Proc. Acad. Nat. Sci.* **2010**, *107*, 13997.

(142) Xu, H.; Jiang, J.; Yang, B.; Wu, H.; Wu, P., Effective Baeyer–Villiger oxidation of ketones over germanosilicates, *Catal. Commun.* **2014**, *55*, 83-86.

(143) Bnmner, G. O.; Meier, W. M., Framework density distribution of zeolite-type tetrahedral nets, *Nature* **1989**, *337*, 146-147.

(144) O'Keeffe, M.; Yaghi, O. M., Germanate Zeolites: Contrasting the Behavior of Germanate and Silicate Structures Built from Cubic T8O20 Units (T=Ge or Si), *Chem. Eur. J.* **1999**, *5*, 2796-2801.

(145) Morris, R. E.; Čejka, J., Exploiting chemically selective weakness in solids as a route to new porous materials, *Nat. Chem.* **2015**, *7*, 381.

(146) Corma, A.; Rey, F.; Valencia, S.; Jordá, J. L.; Rius, J., A zeolite with interconnected 8-, 10- and 12-ring pores and its unique catalytic selectivity, *Nat. Mater.* **2003**, *2*, 493-497.

(147) Corma, A.; Navarro, M. T.; Rey, F.; Rius, J.; Valencia, S., Pure Polymorph C of Zeolite Beta Synthesized by Using Framework Isomorphous Substitution as a Structure-Directing Mechanism, *Angew. Chem. Int. Ed.* **2001**, *40*, 2277-2280.

(148) Dorset, D. L.; Kennedy, G. J.; Strohmaier, K. G.; Díaz-Cabañas, M. J.; Rey, F.; Corma, A., P-Derived Organic Cations as Structure-Directing Agents: Synthesis of a High-Silica Zeolite (ITQ-27) with a Two-Dimensional 12-Ring Channel System, *J. Am. Chem. Soc.* **2006**, *128*, 8862-8867.

(149) Corma, A.; Puche, M.; Rey, F.; Sankar, G.; Teat, S. J., A Zeolite Structure (ITQ-13) with Three Sets of Medium-Pore Crossing Channels Formed by 9- and 10-Rings, *Angew. Chem. Int. Ed.* **2003**, *42*, 1156-1159.



(150)Cantín, A.; Corma, A.; Diaz-Cabanas, M. J.; Jordá, J. L.; Moliner, M., Rational Design and HT Techniques Allow the Synthesis of New IWR Zeolite Polymorphs, *J. Am. Chem. Soc.* **2006**, *128*, 4216-4217.

(151)Fu, W. H.; Yuan, Z.; Wang, Z.; Wang, Y.; Yang, W.; He, M.-Y., Direct synthesis of hydrothermally stable Ge-IWR zeolites, *Dalton. Trans.* **2017**, *46*, 6692-6699.

(152)Shamzhy, M. V.; Ochoa-Hernández, C.; Kasneryk, V. I.; Opanasenko, M. V.; Mazur, M., Direct incorporation of B, Al, and Ga into medium-pore ITH zeolite: Synthesis, acidic, and catalytic properties, *Catal. Today* **2016**, *277*, 37-47.

(153)Shamzhy, M. V.; Shvets, O. V.; Opanasenko, M. V.; Yaremov, P. S.; Sarkisyan, L. G.; Chlubná, P.; Zukal, A.; Marthala, V. R.; Hartmann, M.; Čejka, J., Synthesis of isomorphously substituted extra-large pore UTL zeolites, *J. Mater. Chem.* **2012**, *22*, 15793-15803.

(154)Xu, H.; Jiang, J.-g.; Yang, B.; Zhang, L.; He, M.; Wu, P., Post-Synthesis Treatment gives Highly Stable Siliceous Zeolites through the Isomorphous Substitution of Silicon for Germanium in Germanosilicates, *Angew. Chem. Int. Ed.* **2014**, *53*, 1355-1359.

(155)Shi, D.; Xu, L.; Chen, P.; Ma, T.; Lin, C.; Wang, X.; Xu, D.; Sun, J., Hydroxyl free radical route to the stable siliceous Ti-UTL with extra-large pores for oxidative desulfurization, *Chem. Commun.* **2019**, *55*, 1390-1393.

(156)Liu, X.; Xu, H.; Zhang, L.; Han, L.; Jiang, J.; Oleynikov, P.; Chen, L.; Wu, P., Isomorphous Incorporation of Tin Ions into Germanosilicate Framework Assisted by Local Structural Rearrangement, *ACS Catal.* **2016**, *6*, 8420-8431.

(157)Valtchev, V.; Majano, G.; Mintova, S.; Pérez-Ramírez, J., Tailored crystalline microporous materials by post-synthesis modification, *Chem. Soc. Rev.* **2013**, *42*, 263-290.

(158)Shamzhy, M. V.; Eliašová, P.; Vitvarová, D.; Opanasenko, M. V.; Firth, D. S.; Morris, R. E., Post-Synthesis Stabilization of Germanosilicate Zeolites ITH, IWW, and UTL by Substitution of Ge for Al, *Chem. Eur. J.* **2016**, *22*, 17377-17386.

(159)Gao, F.; Jaber, M.; Bozhilov, K.; Vicente, A.; Fernandez, C.; Valtchev, V., Framework Stabilization of Ge-Rich Zeolites via Postsynthesis Aluminations, *J. Am. Chem. Soc.* **2009**, *131*, 16580-16586.

(160)Shamzhy, M. V.; Opanasenko, M. V.; Ramos, F. S. d. O.; Brabec, L.; Horáček, M.; Navarro-Rojas, M.; Morris, R. E.; Pastore, H. d. O.; Čejka, J., Post-synthesis incorporation of Al into germanosilicate ITH zeolites: the influence of treatment conditions on the acidic properties and catalytic behavior in tetrahydropyranylation, *Catal. Sci. Technol.* **2015**, *5*, 2973-2984.

(161)Roth, W. J.; Shvets, O. V.; Shamzhy, M.; Chlubná, P.; Kubů, M.; Nachtigall, P.; Čejka, J., Postsynthesis Transformation of Three-Dimensional Framework into a Lamellar Zeolite with Modifiable Architecture, *J. Am. Chem. Soc.* **2011**, *133*, 6130-6133.

(162)Mazur, M.; Wheatley, P. S.; Navarro, M.; Roth, W. J.; Položij, M.; Mayoral, A.; Eliášová, P.; Nachtigall, P.; Čejka, J.; Morris, R. E., Synthesis of 'unfeasible' zeolites, *Nat. Chem.* **2015**, *8*, 58.

(163)IUPAC, *Compendium of Chemical Terminology, 2nd ed. (the "Gold Book")*. Blackwell Scientific Publication: 1997.

(164)Gao, Z.-H.; Chen, F.-J.; Xu, L.; Sun, L.; Xu, Y.; Du, H.-B., A Stable Extra-Large-Pore Zeolite with Intersecting 14- and 10-Membered-Ring Channels, *Chem. Eur. J.* **2016**, *22*, 14367-14372.

(165)Firth, D. S.; Morris, S. A.; Wheatley, P. S.; Russell, S. E.; Slawin, A. M. Z.; Dawson, D. M.; Mayoral, A.; Opanasenko, M.; Položij, M.; Čejka, J.; Nachtigall, P.; Morris, R. E., Assembly–Disassembly–Organization–Reassembly Synthesis of Zeolites Based on cfi-Type Layers, *Chem. Mater.* **2017**, *29*, 5605-5611.

(166)Schmidt, J.; Davis, M. E.; Boal, B. W.; Kang, J. H.; Xie, D. GERMANOSILICATE COMPOSITIONS AND METHODS OF PREPARING THE SAME, US Patent Application 20170252729. 2017.

(167)Liu, X.; Mao, W.; Jiang, J.; Lu, X.; Peng, M.; Xu, H.; Han, L.; Che, S.-a.; Wu, P., Topotactic Conversion of Alkali-Treated Intergrown Germanosilicate CIT-13 into

Single-Crystalline ECNU-21 Zeolite as Shape-Selective Catalyst for Ethylene Oxide Hydration, *Chem. Eur. J.* **2019**, *25*, 4520-4529.

(168)Lobo, R. F.; Tsapatsis, M.; Freyhardt, C. C.; Khodabandeh, S.; Wagner, P.; Chen, C.-Y.; Balkus, K. J.; Zones, S. I.; Davis, M. E., Characterization of the Extra-Large-Pore Zeolite UTD-1, *J. Am. Chem. Soc.* **1997**, *119*, 8474-8484.

(169)Davis, M. E.; Lobo, R. F., Zeolite and molecular sieve synthesis, *Chem. Mater.* **1992**, *4*, 756-768.

(170)Kang, J. H.; Xie, D.; Zones, S. I.; Smeets, S.; McCusker, L. B.; Davis, M. E., Synthesis and Characterization of CIT-13, a Germanosilicate Molecular Sieve with Extra-Large Pore Openings, *Chem. Mater.* **2016**, *28*, 6250-6259.

(171)van de Water, L. G. A.; van der Waal, J. C.; Jansen, J. C.; Cadoni, M.; Marchese, L.; Maschmeyer, T., Ge-ZSM-5: the Simultaneous Incorporation of Ge and Al into ZSM-5 Using a Parallel Synthesis Approach, *J. Phys. Chem. B* **2003**, *107*, 10423-10430.

(172)Smeets, S.; McCusker, L. B.; Baerlocher, C.; Elomari, S.; Xie, D.; Zones, S. I., Locating Organic Guests in Inorganic Host Materials from X-ray Powder Diffraction Data, *J. Am. Chem. Soc.* **2016**, *138*, 7099-7106.

(173)Saito, A.; Foley, H. C., Curvature and parametric sensitivity in models for adsorption in micropores, *AIChE J.* **1991**, *37*, 429-436.

(174)Shvets, O. V.; Shamzhy, M. V.; Yaremov, P. S.; Musilová, Z.; Procházková, D.; Čejka, J., Isomorphous Introduction of Boron in Germanosilicate Zeolites with UTL Topology, *Chem. Mater.* **2011**, *23*, 2573-2585.

(175)Vidal-Moya, J. A.; Blasco, T.; Rey, F.; Corma, A.; Puche, M., Distribution of Fluorine and Germanium in a New Zeolite Structure ITQ-13 Studied by <sup>19</sup>F Nuclear Magnetic Resonance, *Chem. Mater.* **2003**, *15*, 3961-3963.

(176)Kasian, N.; Tuel, A.; Verheyen, E.; Kirschhock, C. E. A.; Taulelle, F.; Martens, J. A., NMR Evidence for Specific Germanium Siting in IM-12 Zeolite, *Chem. Mater.* **2014**, *26*, 5556-5565.

(177)Rojas, A.; Arteaga, O.; Kahr, B.; Cambor, M. A., Synthesis, Structure, and Optical Activity of HPM-1, a Pure Silica Chiral Zeolite, *J. Am. Chem. Soc.* **2013**, *135*, 11975-11984.

(178)Kasian, N.; Vanbutsele, G.; Houthoofd, K.; Koranyi, T. I.; Martens, J. A.; Kirschhock, C. E. A., Catalytic activity and extra-large pores of germanosilicate UTL zeolite demonstrated with decane test reaction, *Catal. Sci. Technol.* **2011**, *1*, 246-254.

(179)Ritter, S. K., Where has all the sparteine gone?, *Chemical Engineering News* **2017**, *95*, 18.

(180)Gao, F.; Jaber, M.; Bozhilov, K.; Vicente, A.; Fernandez, C.; Valtchev, V., Framework Stabilization of Ge-Rich Zeolites via Postsynthesis Alumination, *J. Am. Chem. Soc.* **2009**, *131*, 16580-16586.

(181)Eliášová, P.; Opanasenko, M.; Wheatley, P. S.; Shamzhy, M.; Mazur, M.; Nachtigall, P.; Roth, W. J.; Morris, R. E.; Čejka, J., The ADOR mechanism for the synthesis of new zeolites, *Chem. Soc. Rev.* **2015**, *44*, 7177-7206.

(182)Mazur, M.; Kubů, M.; Wheatley, P. S.; Eliášová, P., Germanosilicate UTL and its rich chemistry of solid-state transformations towards IPC-2 (OKO) zeolite, *Catal. Today* **2015**, *243*, 23-31.

(183)McCusker, L. B.; Baerlocher, C.; Jahn, E.; Bülow, M., The triple helix inside the large-pore aluminophosphate molecular sieve VPI-5, *Zeolites* **1991**, *11*, 308-313.

(184)Lobo, R. F.; Davis, M. E., Synthesis and characterization of pure-silica and boron-substituted SSZ-24 using N(16) methylsparteinium bromide as structure-directing agent, *Micropor. Mater.* **1994**, *3*, 61-69.

(185)Ren, X.; Liu, J.; Li, Y.; Yu, J.; Xu, R., Hydrothermal synthesis of an ITH-type germanosilicate zeolite in a non-concentrated gel system, *J. Porous Mater.* **2013**, *20*, 975-981.

(186)Corma, A.; Chica, A.; Guil, J. M.; Llopis, F. J.; Mabilon, G.; Perdigón-Melón, J. A.; Valencia, S., Determination of the Pore Topology of Zeolite IM-5 by Means of

Catalytic Test Reactions and Hydrocarbon Adsorption Measurements, *J. Catal.* **2000**, *189*, 382-394.

(187)Matijasic, A.; Paillaud, J.-L.; Patarin, J., Synthesis, characterization and structure determination of Mu-15: a new fluorogallophosphate with fluoride as a specific template of the D4R units, *J. Mater. Chem.* **2000**, *10*, 1345-1351.

(188)Schmidt, J. E.; Deem, M. W.; Davis, M. E., Synthesis of a Specified, Silica Molecular Sieve by Using Computationally Predicted Organic Structure-Directing Agents, *Angew. Chem. Int. Ed.* **2014**, *53*, 8372-8374.

(189)Grünberg, B.; Emmler, T.; Gedat, E.; Shenderovich, I.; Findenegg, G. H.; Limbach, H.-H.; Buntkowsky, G., Hydrogen Bonding of Water Confined in Mesoporous Silica MCM-41 and SBA-15 Studied by <sup>1</sup>H Solid-State NMR, *Chem. Eur. J.* **2004**, *10*, 5689-5696.

(190)NIST Chemistry WebBook, SRD 69, Thermophysical Properties of Fluid Systems (<https://webbook.nist.gov/chemistry/fluid/>).

(191)Lu, P.; Gómez-Hortigüela, L.; Xu, L.; Cambor, M. A., Synthesis of STW zeolites using imidazolium-based dications of varying length, *J. Mater. Chem. A* **2018**, *6*, 1485-1495.

(192)Kosslick, H.; Tuan, V. A.; Fricke, R.; Peuker, C.; Pilz, W.; Storek, W., Synthesis and characterization of Ge-ZSM-5 zeolites, *J. Phys. Chem.* **1993**, *97*, 5678-5684.

(193)Blasco, T.; Corma, A.; Díaz-Cabañas, M. J.; Rey, F.; Vidal-Moya, J. A.; Zicovich-Wilson, C. M., Preferential Location of Ge in the Double Four-Membered Ring Units of ITQ-7 Zeolite, *J. Phys. Chem. B* **2002**, *106*, 2634-2642.

(194)Thomas, J. M.; Klinowski, J.; Ramdas, S.; Hunter, B. K.; Tennakoon, D. T. B., The evaluation of non-equivalent tetrahedral sites from <sup>29</sup>Si NMR chemical shifts in zeolites and related aluminosilicates, *Chem. Phys. Lett.* **1983**, *102*, 158-162.

(195)Henkelis, S. E.; Mazur, M.; Rice, C. M.; Bignami, G. P. M.; Wheatley, P. S.; Ashbrook, S. E.; Čejka, J.; Morris, R. E., A procedure for identifying possible products in

the assembly–disassembly–organization–reassembly (ADOR) synthesis of zeolites, *Nat. Protoc.* **2019**, *14*, 781-794.

(196)Burel, L.; Kasian, N.; Tuel, A., Quasi All-Silica Zeolite Obtained by Isomorphous Degermanation of an As-Made Germanium-Containing Precursor, *Angew. Chem. Int. Ed.* **2014**, *53*, 1360-1363.

(197)Chlubná-Eliášová, P.; Tian, Y.; Pinar, A. B.; Kubů, M.; Čejka, J.; Morris, R. E., The Assembly-Disassembly-Organization-Reassembly Mechanism for 3D-2D-3D Transformation of Germanosilicate IWW Zeolite, *Angew. Chem. Int. Ed.* **2014**, *53*, 7048-7052.

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

(199)Foster, M. D.; Rivin, I.; Treacy, M. M. J.; Delgado Friedrichs, O., A geometric solution to the largest-free-sphere problem in zeolite frameworks, *Micropor. Mesopor. Mater.* **2006**, *90*, 32-38.

(200)Shamzhy, M.; Opanasenko, M.; Tian, Y.; Konyshova, K.; Shvets, O.; Morris, R. E.; Čejka, J., Germanosilicate Precursors of ADORable Zeolites Obtained by Disassembly of ITH, ITR, and IWR Zeolites, *Chem. Mater.* **2014**, *26*, 5789-5798.

(201)Verheyen, E.; Jo, C.; Kurttepli, M.; Vanbutsele, G.; Gobechiya, E.; Korányi, T. I.; Bals, S.; Van Tendeloo, G.; Ryoo, R.; Kirschhock, C. E. A.; Martens, J. A., Molecular shape-selectivity of MFI zeolite nanosheets in n-decane isomerization and hydrocracking, *J. Catal.* **2013**, *300*, 70-80.

(202)Elangovan, S. P.; Hartmann, M., Evaluation of Pt/MCM-41//MgAPO-n composite catalysts for isomerization and hydrocracking of n-decane, *J. Catal.* **2003**, *217*, 388-395.

(203)Liu, X.; Ravon, U.; Bosselet, F.; Bergeret, G.; Tuel, A., Probing Ge Distribution in Zeolite Frameworks by Post-Synthesis Introduction of Fluoride in As-Made Materials, *Chem. Mater.* **2012**, *24*, 3016-3022.

(204)Liu, X.; Ravon, U.; Tuel, A., Evidence for F<sup>-</sup>/SiO<sup>-</sup> Anion Exchange in the Framework of As-Synthesized All-Silica Zeolites, *Angew. Chem. Int. Ed.* **2011**, *50*, 5900-5903.

(205)Liu, X.; Chu, Y.; Wang, Q.; Wang, W.; Wang, C.; Xu, J.; Deng, F., Identification of double four-ring units in germanosilicate ITQ-13 zeolite by solid-state NMR spectroscopy, *Solid State NMR* **2017**, *87*, 1-9.