Chapter 1

Introduction to Part I: The Methanol-to-Olefins (MTO) Reaction and Small-Pore Microporous Materials

In this chapter, the topic of Part I of my thesis is introduced. First, I describe what the MTO reaction is and why it is an important process. Next, a brief introduction to the types of catalysts used for the MTO reaction will be provided. Then, the recent trend in mechanistic studies of the MTO reaction is summarized, particularly focusing on the hydrocarbon pool mechanism. Lastly, my motivations and objectives are outlined.

1.1. Background

Ethylene and propylene are the first and second most-produced petrochemicals in the world, respectively.[1-2] The majority (ca. 60–70 %) of total worldwide ethylene and propylene are used to produce polymer products—polyethylene and polypropylene.[1, 3] The remainder is used to produce more value-added specialty chemicals like ethylene oxide, propylene oxide, cumene, etc. In these days, it is very hard to find any commercial products in any field of industry which have nothing to do with these light olefins. Indeed, it is no exaggeration to say that they are chemicals supporting the human civilization itself.

The majority of ethylene has been produced from steam cracking (SC) of petroleum sources such as light naphtha, and it is currently the case.[4] Propylene can be also produced from the same SC process, but has more sources such as fluid catalytic cracking (FCC) of petroleum gas or dehydrogenation of propane.[5] All of these processes use various petroleum sources as feeds in common. During the 1970s energy crisis, the oil price skyrocketed from USD 10 to USD 60 per barrel.[6] Processes using non-petroleum sources such as natural gas or coal started to gather industrial interests. In the early 1970s, Mobil invented a revolutionary synthetic zeolite, ZSM-5, which shows excellent catalytic performances in a number of processes including the methanol-to-hydrocarbon (MTH) process.[7] The first methanol-to-gasoline (MTG) unit was commercialized in New Zealand by Mobil in 1985, and it produced approximately 30 % of the country's gasoline demand.[8-9] The original Mobil MTG process was composed of two steps: syngas-to-methanol and methanol-to-gasoline, as shown in Figure 1.1(a).[10] Syngas can be obtained from such as coal gasification and steam reforming of natural gas.

Scientists of UOP (at that time, Union Carbide) introduced a novel silicoaluminophosphate (SAPO) molecular sieve having a chabazite (CHA) topology which is called SAPO-34 in the early 1980s.[8, 11] In the MTH process, SAPO-34 converted methanol into ethylene and propylene with very high selectivity (80–90%) due to its narrow pore and cage dimension. The CHA cages of SAPO-34 bounded with 8-membered-ring pore openings allows reactants (methanol) and products (light olefins) to diffuse in and out, while traps bulky hydrocarbon intermediates within it. UOP and INEOS (Norsk Hydro) introduced the methanol-to-olefins (MTO) process in 1996; they adopted a combination of fluidized bed reactor and continuous regeneration unit to tackle the issue of limited catalytic lifetime of SAPO-34.[12] This process was further improved by combining the olefin cracking process (OCP) that converts higher olefins to propylene developed by Total.[8] (Figure 1.1(b))

In 2010, a major advancement was made by the Dalian Institute of Chemical Physics (DICP); the dimethyl ether/methanol-to-olefins (DMTO) process using SAPO-34 which recycles higher olefin to maximize the ethylene and propylene selectivity was developed by DICP which is shown in Figure 1.1(c).[8, 13] On the basis of this DMTO technology, Shenhua

Baotou Coal company and DICP constructed the first coal-to-olefin (CTO) unit (Figure 1.1(d)) in Inner Mongolia in 2010. This is now the largest commercialized CTO process unit in the world, producing 600,000 ton of ethylene and propylene per year. Although the majority of ethylene and propylene are currently produced from SC and FCC, for the last decade, the MTO process has attracted more and more attention from the industry not only because of the volatility of oil price but also because of the expected gap between olefin demand and capacity.[1]

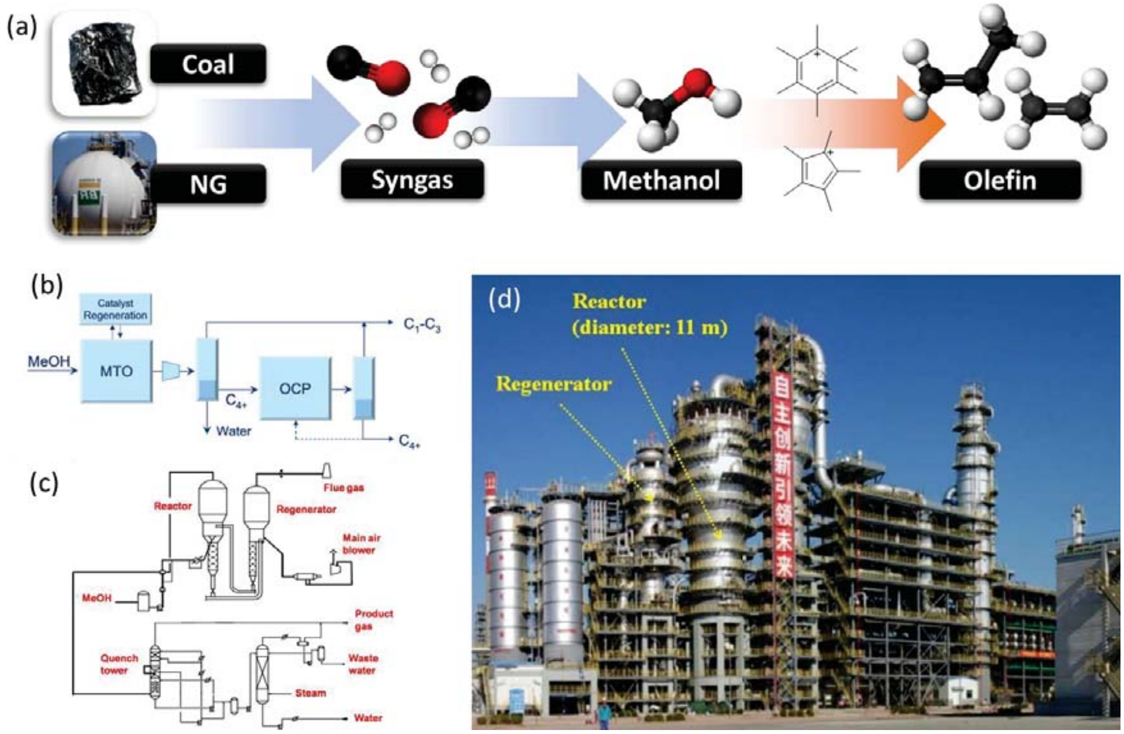

Figure 1.1. Overview of the MTO process. (a) Schematic description of the process. (b) UOP/INEOS MTO process with UOP/Total OCP process. Reproduced with Permission from Ref [8]. Copyright 2012 Wiley-VCH. (c) DICP DMTO process (d) DMTO commercial unit operating in Dalian, Jilin Province, PR China. Reproduced with Permission from Ref [13]. Copyright 2015 American Chemical Society.

1.1.1. Small-pore Molecular Sieves

Molecular sieves refer to crystalline and microporous solid state materials which can have any elemental compositions and any framework charge.[14] *Zeolites* are one class of molecular sieves. In the most rigorous definition, zeolites are the class of microporous crystalline aluminosilicates having alkali (Na^+, K^+, etc.) or alkali-earth (Mg^{2+}, Ca^{2+}, etc.) cations and water molecules within their pore systems. The cations can be replaced with protons, generating the Brønsted acid sites on the surface. Some heteroatoms (Ti^{4+}, Sn^{4+}, etc.) within silicate frameworks can exhibit the Lewis acidity. These acidities are the origin of catalytic abilities of zeolites. Up to date, thousands of synthetic zeolites and related metallosilicate molecular sieves have been introduced, particularly for catalytic purposes. For this reason, practically in these days, the terminology ‘zeolite’ is used in a broader meaning referring to any silicate-based molecular sieves. A new terminology ‘*zeotype*’ is used sometimes for this purpose.

Aluminosilicates are accomplished by substituting Al for Si within frameworks. In pure silica, the substitution of Al for Si results in negative charges within the framework due to the difference between the oxidation state of Al (III) and Si (IV) in oxide. This negative charge can hold a proton, thus enabling the material to play a role as a solid acid, as mentioned above. Any neighboring two tetrahedral silicon sites cannot be replaced with aluminum at the same time. In other words, a local tetrahedral structure such as -O-Al-O-Al-O- within silicate frameworks is not possible to exist. This is called the Loewenstein rule.[15] For this reason, the minimum value for Si/Al molar ratio of any zeolites is one. But two aluminum sites can be separated by only one silicon. This is called a *paired site*. Zeolites can have Si/Al ratios from 1 to ∞. Conventionally, *low-silica* zeolites refer to zeolites having Si/Al ratio close to 1. *High-silica* zeolites are aluminosilicates with small extents of Al-substitution (less than one or two aluminum sites per unit cell, typically $Si/Al > 10$).

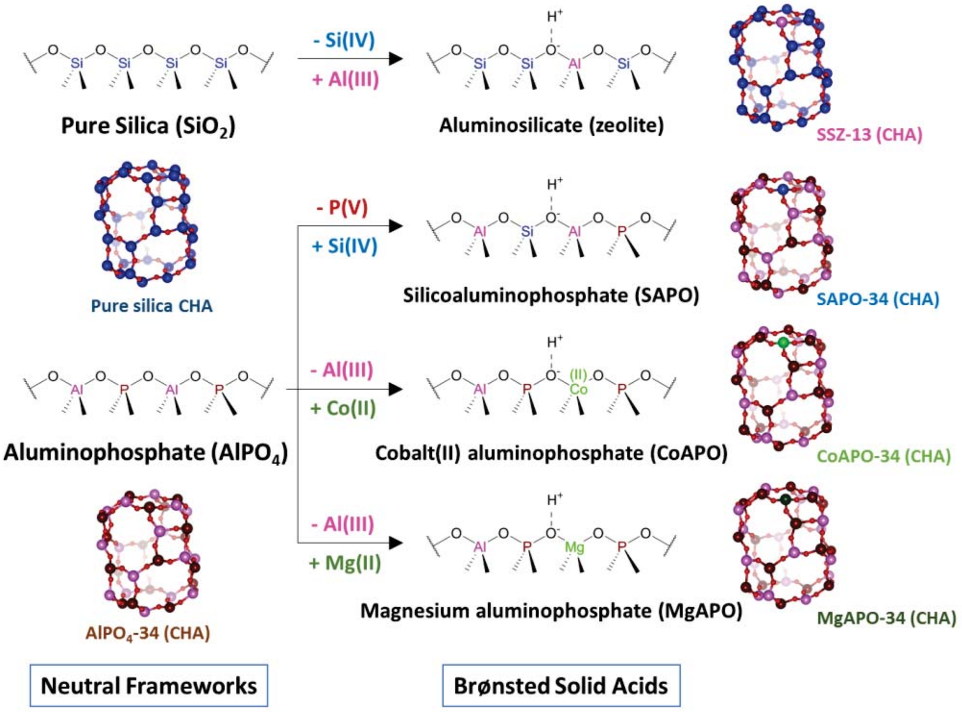

Figure 1.2. Schematic description of simplified structures of neutral frameworks and Brønsted acid sites composed of various elemental compositions. CHA cages having corresponding elemental compositions and acid sites.

The relation between neutral aluminophosphates (AlPOs) and silicoaluminophosphates (SAPO) is analogous to the case of aluminosilicates. In this system, Si (IV) replaces P (V) and generates one acid site. The substitution of Si for one isolated Al site is not possible due to the fact that the Si-O-P bonds cannot be formed in the SAPO systems.[11] Instead, in the SAPO system, a domain of $AlPO_4$ can be replaced with silica-domain having a boundary composed only of Al-O-Si bonds. This site is called an *islanded site*. For this reason, in SAPO materials having islanded sites, the numbers of Brønsted acid sites are not equal to the number of silicon sites. Also, metal ions which can have an oxidation state +2 with a tetrahedral coordination in solid oxides are able to replace Al (III) within the

$AlPO_4$-frameworks, resulting in metalloaluminophosphates (MAPOs). Magnesium, cobalt (II), manganese (II), and nickel (II) are such metals. Similarly to the cases of zeolites and SAPOs, this substitution generates a Brønsted acid site. However, since substituting M (II) for P (V) is not possible, these MAPOs can have isolated sites only.

Topology is a purely geometric concept, and refers to how the tetrahedral atoms are connected to each other to form the entire *framework*. In some contexts, 'topology' and 'framework' were used interchangeably. In 2019, the International Zeolite Association (IZA) structure database provides crystallographic data of 245 zeolite frameworks which have been discovered up to date.[16] One topology can have various elemental compositions. For example, the CHA (chabazite)-type framework can built with pure silica (SiO_2),[17] aluminosilicate (natural chabazite and SSZ-13),[18] aluminophosphate ($AlPO_4$-34),[19] silicoaluminophosphate (SAPO-34),[11] and many metalloaluminophosphates (MAPOs) including magnesium aluminophosphate (MgAPO-34)[20] and cobalt (II) aluminophosphate (CoAPO-34),[21] as shown in Figure 1.2. These CHA-type materials have different elemental compositions, thus having different chemical properties, but share crystallographically the same structure.

The frameworks are denoted using *three-letter codes*. These three-letter codes are abbreviations of the type materials that represents the frameworks. For example, three zeolite frameworks are shown in Figure 1.3. CHA is from the name of natural zeolite *cha*bazite. MFI is the abbreviation of ZSM-5 (Zeolite Socony *M*obil - *FI*ve). *BEA came from zeolite *BE*ta polymorph *A*. Asterisks (*) denote the presence of innate structural disorders within frameworks. Zeolite beta is always obtained as disordered crystals possessing intergrown domains of polymorphs A and B. Throughout my thesis, these three-letter codes will be used very frequently without providing any further explanation about name origins. In case of $AlPO_4$-based molecular sieves, the framework type is denoted as numbers.[11, 22] For example, SAPO-34 means silicoaluminophosphate molecular sieve having a CHA (-34) topology.

Conventionally, the dimension of pore openings of zeolite is denoted using the number of tetrahedral atoms (T-atoms, T = Si, Al, P, etc.). Most frequently observed pore openings are 8-, 10-, and 12-membered rings. These pore dimensions are conventionally referred to as *small-pore*, *medium-pore*, and *large-pore*, respectively. CHA, MFI, and *BEA shown in Figure 1.3 are representative examples. Pore openings larger than 14-membered rings are called *extra-large-pore*. Rings smaller than 6-membered rings are not considered as porous. For the MTO and MTG processes, small-pore (SAPO-34) and medium-pore (ZSM-5) molecular sieves are used, respectively. These pore sizes determine the product selectivity by limiting the intracrystalline diffusion of product molecules.

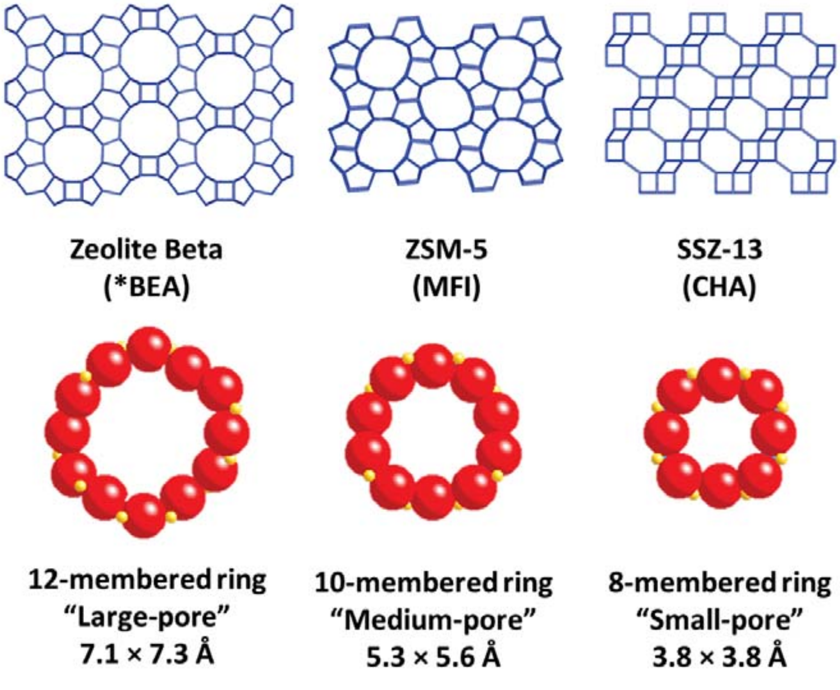

Figure 1.3. Examples of large-, medium-, and small-pore frameworks and their pore opening dimensions.

1.1.2. Mechanism of MTO Reaction

The formation mechanism of hydrocarbons including light olefins from methanol over solid acid molecular sieves has been studied extensively for decades.[8-9, 13, 23] There has been no doubt that the first step of mechanism is the acid-catalyzed dehydration of methanol via protonated surface methoxyl into dimethyl ether (DME).[9, 23] However, there has been many theories about the formation of C-C bonds after the formation of DME, such as the oxonium ylide mechanism,[24] the carbene mechanism,[7] the free radical mechanism,[25] etc. In the early 90s, Dahl and Kolboe suggested *the hydrocarbon pool mechanism* about the MTO reaction of SAPO-34 (Figure 1.4(a)).[26-28] The hydrocarbon pool intermediates do not have a specific chemical structure, but are aromatic hydrocarbons or carbocations having multiple ($n = 4$–7) methyl and alkyl groups. (Figure 1.4(b)) This mechanism has been widely accepted up to date, and the most of recent advancements of mechanistic studies about the MTO reaction have been made by further refining Dahl and Kolboe’s hydrocarbon pool mechanism.[8]

One of the most recognized mechanistic models for the MTH process is *the dual-cycle concept* suggested by Olsbye and co-workers.[8] (Figure 1.4(c)) The dual-cycle postulation is established by combining the mechanistic models for ZSM-5 and SAPO-34 into one.[8] This dual-cycle model has two cycles operating simultaneously: *the alkene cycle* and *the aromatic cycle*. These two cycles are connected with the hydrogen transfer reaction that produces paraffins. Svelle et al. reported that ethylene is exclusively formed from the aromatic cycle while the alkene cycle generates propylene with high selectivity on the basis of their carbon-isotope ($^{12}C/^{13}C$) switching experiments.[29] Sun et al. showed that both ethylene and propylene are formed from the aromatic cycle.[30]

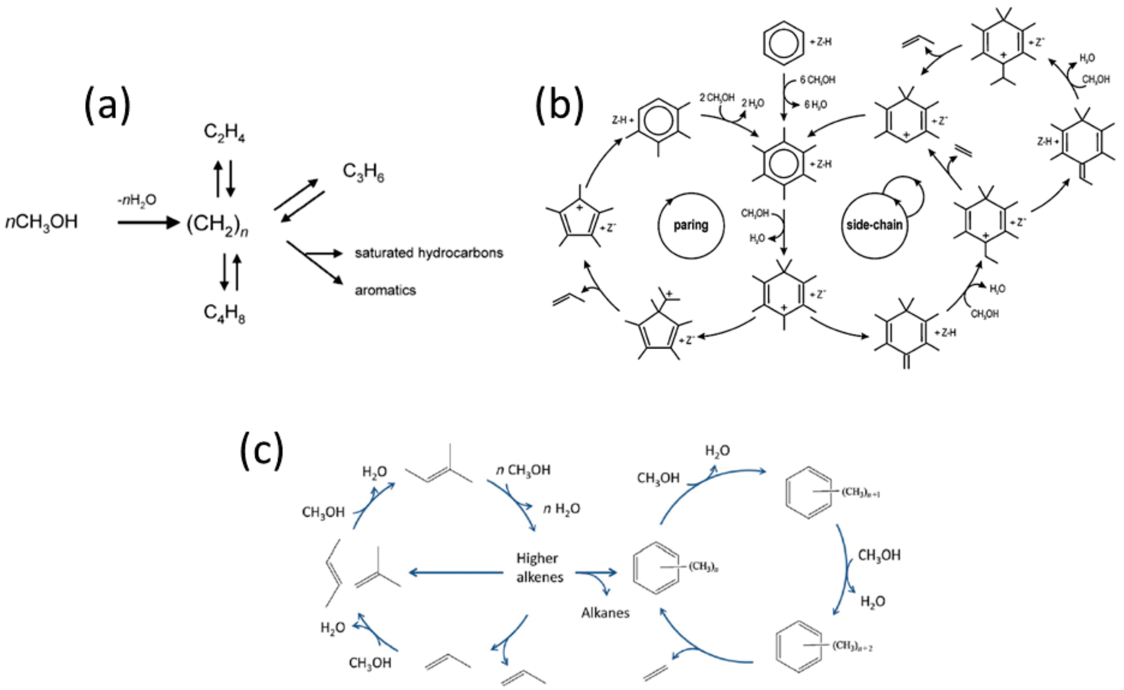

Figure 1.4. Proposed mechanisms of the MTO reaction. (a) The original hydrocarbon pool mechanism suggested by Dahl and Kolboe. Reproduced with Permission from Ref [27]. Copyright 1994 Elsevier. (b) The aromatic cycles showing the paring mechanism and side-chain mechanism by Lesthaeghe et al. on ZSM-5. Reproduced with Permission from Ref [31]. Copyright 2009 Wiley-VCH. (c) Dual cycle concept. Reproduced with Permission from Ref [8]. Copyright 2012 Wiley-VCH.

Most of the mechanistic studies introduced above are about the MTH reactions within the pore systems of ZSM-5 and SAPO-34. The topology is another important factor that determines the type of hydrocarbon pool intermediates. The formation of aromatic intermediates within molecular sieves could be investigated in real time using the *in situ* solid-state ^{13}C nuclear magnetic resonance spectroscopy[13] and the operando UV-Vis spectroscopy.[32] The Liu group of DICP investigated the confinement effects of cage structures on types of hydrocarbon pool intermediates formed during the MTO reactions within the cages having CHA (SAPO-34 and SSZ-13), LEV (RUB-50 and SAPO-35), and RHO (DNL-6) topologies.[13, 33-35] As shown in Figure 1.5(a), the larger the cage was, the more methyl groups the carbenium intermediate had.[13] Also, for each of the catalysts having different topologies, unique hydrocarbon pool cycles could be suggested.[34, 36]

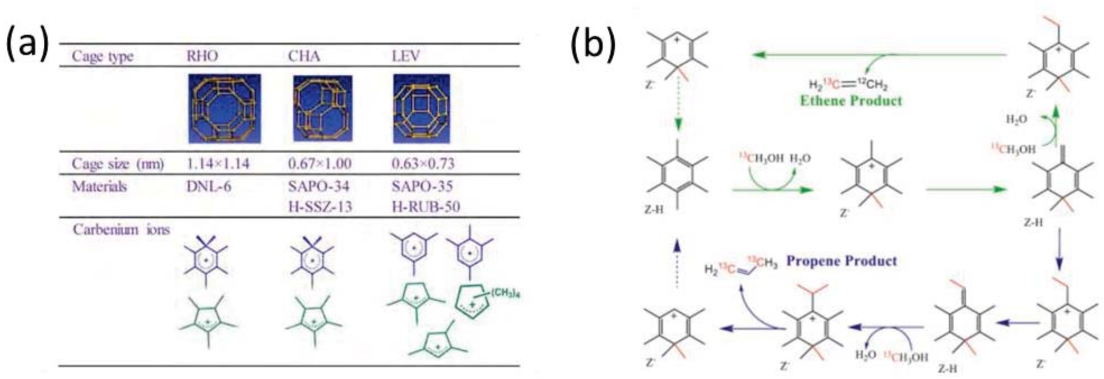

Figure 1.5. Dependence of hydrocarbon pool intermediate structures on cage structures. (a) Hydrocarbon pool carbenium cations which were formed in different topologies of cages. Reproduced with Permission from Ref [13]. Copyright 2015 American Chemical Society (b) Hydrocarbon pool mechanism suggested for DNL-6 having a RHO topology. Reproduced with Permission from Ref [36]. Copyright 2014 Elsevier.

1.2. Motivation

As explained in the previous section, there have been extensive studies regarding the mechanism of the MTO reaction and the structure-reaction intermediate relation. Haw et al. indicated that intermediates having more methyl groups are responsible for the formation of higher olefins.[37] Given that a catalyst having larger cages forms hydrocarbon pool intermediates having more methyl groups and eventually shows higher butylenes selectivities than catalyst having smaller cages,[13, 34-36] there must be a rule regarding the *intermediate shape selectivity*.

Also, there are many reports which compared olefin product distributions from MTO reactions over several small-pore molecular sieves having different topologies.[32, 38-45] Y. Bhawe who is one of the previous members of the Davis group also studied the shape selectivity problem by comparing three zeolites having LEV, CHA, and AFX topologies, concluding that the intermediate cage size of CHA is the main reason for its high light olefin selectivities.[41] Pinilla-Herrero et al. investigated four SAPO-based molecular sieves having LEV, AFX, SAV, and LTA topologies.[38-39] In these works, differences among olefin product distributions were attributed to different pore window sizes.[38] On the other hand, Castro and co-workers investigated the MTO reaction products of a set of SAPO-based materials having CHA, SAV, and KFI topology, and concluded that the olefin selectivity distribution is majorly dependent upon the cage topology which has a close relation with the distribution of hydrocarbon pool carbenium intermediates.[42] These works reached reasonable conclusions on the basis of their experimental results, but no general rule has yet been established.

There has been no reliable way to measure the size of a cage. Some previous reports actually provided dimensions of cages,[32, 41, 46] but there were large differences among the cage sizes evaluated by them. For example, for the same CHA cage, Bhawe et al.,[41] Chen et al.,[46] and Goetze et al.[32] gave 8.23 × 8.35 Å, 12.7 × 9.4 Å, and 10.9 × 6.7 Å, respectively, which are essentially all different from each other. Dimensions of cages were simply measured by calculating distances between the farthest pair of framework atoms (T or O) in a cage on the basis of crystallographic data provided in the IZA database.[16] But this way of measurements has a fundamental problem because these dimensions do not reflect the actual sizes which are ‘felt’ by methanol or hydrocarbon pool intermediate molecules.

Yokoi et al. used the free volume to estimate the cage size.[47] They gave free volumes of 408 Å^3 for an RTH cage and 415 Å^3 for a CHA cage, and stated that the former is smaller than the latter, which is essentially wrong. The size of maximum sphere diameter that can be occluded within an RTH cage is 8.18 Å which is much bigger than CHA of 7.37 Å. The 'tree ring plots' I contrived and provided in Chapter 3 also support that RTH is much larger than CHA. I speculate that they included dense layers of the RTH framework within their calculation.[48] The presence of these dense layers (CIT-10) makes the framework density of RTH (16.1 T-atoms nm^{-3}) higher than that of CHA (15.1 T-atoms nm^{-3}) despite the fact that an RTH cage is wider than a CHA cage. A statement that ERI is more spacious than CHA could be also found.[23] It is true that an ERI cage is longer than a CHA cage, but the former is apparently narrower than the latter as I will demonstrate in the following chapters. In summary, a reliable way to measure the actual sizes of cages that can have a correlation with the olefin product selectivity distributions should be established.

1.3. Objectives

The primary objective of this work is the creation of a rule regarding the shape selectivity of small-pore molecular sieve cages for the MTO reaction as illustrated in Figure 1.6. The rule must be on the basis of a solid way to measure the effective dimensions of cage structures. The evaluation of dimensions must be easy and straightforward enough to enable one to measure the size of cages without an assist of sophisticated computational tools. Also, the rule should have a predictive ability.

This rule must be deduced from real MTO data obtained at a strictly controlled reaction condition. Considering various non-linear shapes of known MTO-active cages, the reaction data must be obtained from multiple topologies having different elemental compositions (as many as possible). The synthesized catalysts must be as pure as possible to generate reliable reference data.

The following two chapters are about achievements of these goals. For the remainder of Part I of my thesis, in Chapter 2, the selection of topology, the syntheses of required organic-structure directing agents (OSDA) and molecular sieves, the characterization results, and the time-on-stream MTO data from them will be reported and discussed. In Chapter 3, the olefin product distributions, the categorization of topologies, the concept of cage-defining ring, which is a new way to evaluate the cage dimensions, and how my new concept of correlating the cage-defining ring to product olefin distributions will be discussed. Lastly, in Chapter 4, an overall summary will be provided and future work will be proposed.

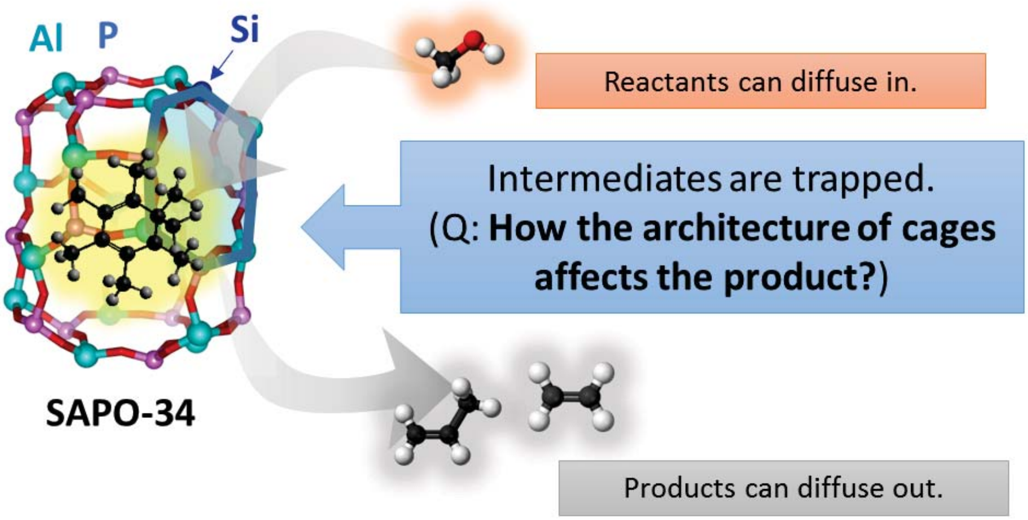

Figure 1.6. Schematic illustration of MTO reaction within a SAPO-34 cage and the main question to answer.