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Cage-defining Ring: A Molecular Sieve Structural Indicator for Light Olefin Product Distribution from the Methanol-to-Olefins Reaction

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ABSTRACT: The methanol-to-olefins (MTO) process produces high value-added light olefins from non-petroleum sources. Acidic zeotypes containing cages bounded by 8-ring (small pore) windows can effectively catalyze the MTO reaction, since their cages can accommodate the necessary aromatic intermediates that produce the light olefin products that escape. While progress on the mechanisms of the MTO reaction continues, zeotype structure-reaction property relationships have yet to be elucidated. Here, we report MTO reaction results from various small pore, cage-containing SAPO/MAPOs and zeolites under the same reaction conditions. The MTO behaviors of microporous materials having the following topologies are investigated: LEV, ERI, CHA, AFX, SFW, AEI, DDR, RTH, ITE, SAV, LTA, RHO, KFI and UFI. The previous observation that light olefin product distributions from a series of small pore, cage-containing zeolites can be classified into four structural categories is further supported by the results shown here from zeolite structures not investigated in the previous study and SAPO and MAPO materials with isostructural frameworks to all the zeolites. Additionally, these data reveal that light olefin product distributions are essentially the same over a given topology independent of framework composition. In order to develop a structure-property relationship between the framework topology and the MTO light olefin product distribution, the concept of the cage-defining ring size is introduced. The cage-defining ring size is defined as the minimum number of tetrahedral atoms of the ring encircling the center of the framework cages in the molecular sieve topology. It is shown that the cage-defining ring size correlates with MTO light olefin product distribution.

Introduction

The light olefins are among the most important basic chemicals in the modern chemical industry.¹ Although most of the olefin demands are currently fulfilled by steam cracking and fluidized catalytic cracking of higher hydrocarbons, there remains a desire for alternative light olefin production technologies.² The methanol-to-olefins (MTO) reaction is one such technology. Methanol can be obtained from numerous carbon sources such as natural gas, coal, biomass, carbon dioxide, etc., and many MTO plants are currently operational or under construction, including the exemplary coal-to-olefin unit built in Dalian, China.³

The commercialized catalyst for the MTO process is SAPO-34 (silicoaluminophosphate-34) that has a chabazite (CHA: International Zeolite Association code for framework type) topology. The SAPO-34 molecular sieves

are known as excellent catalysts for the MTO reaction due to their acidity, thermal stability and cages with pores consisting of 8 tetrahedral atoms (8MR). The MTO reaction mechanism involves aromatic carbenium cation intermediates having multiple methyl and/or alkyl groups.⁴ The framework topology is critical to the commercial success of the SAPO-34 catalyst in that the *cha*-cages of SAPO-34 effectively trap these reaction intermediates (i.e., cage of sufficient size to accommodate) while allowing light olefin products to diffuse out. Small-pore, cage-possessing, high-silica zeolites and other metalloaluminophosphate (MAPO) materials are also capable of catalyzing the MTO reaction.

Among the numerous physicochemical catalyst properties that influence the MTO reaction behavior, the cage topology has been recognized as an important feature that has prominent influences on the olefin product distributions.⁵⁻⁷ From the viewpoint of the

reaction mechanism, the cage structure can limit the trapped polymethyl aromatic intermediate species, and it has been shown that each small-pore cage generates a unique set of these intermediates based on operando spectroscopic studies.⁷⁻¹¹ Previous work has focused on the elucidation of the influences of topology on the product distributions. Bhawe et al., for instance, investigated three zeolitic frameworks, LEV, CHA, and AFX, and isolated the effects of cage geometry by controlling the Si/Al molar ratio and other properties of the zeolites.¹² Pinilla-Herrero and co-workers studied SAPO-based catalysts having four cage topologies (LEV, AFX, SAV, and LTA) with several levels of acid-site density, and concluded that the influences of topology on the olefin product distributions dominated those of acid-site density.^{6, 13} The pore size that limits the diffusion of products was indicated as the primary parameter that attributes to the final selectivity patterns of light olefins.^{6, 13} The Liu group at the Dalian Institute of Chemical Physics (DICP) investigated the cage confinement effects that determine the polyaromatic intermediates during the MTO reaction over various SAPO-molecular sieves and their relationship to the products formed.^{7, 10} Although there has been significant research efforts on the MTO reactions, a general correlation linking cage dimensions to light olefin selectivity has yet been made.

Recently, we reported on the MTO reaction results of ten cage-containing zeolites having different small-pore (8MR) topologies (SSZ-13 (CHA), SSZ-16 (AFX), SSZ-52 (SFW), SSZ-98 (ERI), SSZ-105 (ERI/LEV intergrowth), SSZ-99, SSZ-104 (CHA/GME intergrowth), SSZ-27, ITQ-3 (ITE), and SSZ-28 (DDR)), and investigated the relationship between the cage topologies and light olefin product distributions.¹⁴ Together with other relevant previous results from our group,^{12, 15-18} we suggested that the MTO-active topologies can be classified into four types based on the light olefin selectivity distributions at the reaction temperature of 400 °C. The first group consisted of zeolites having CHA, AFX, SFW, and other GME-related ABC-6 family topologies. Catalysts in this group produced ethylene selectivity roughly equal to propylene with low butylenes. The second group of zeolites (LEV, ERI, and intergrowth of them) generated ethylene higher than propylene. Zeolites having cages wider than CHA such as AEI, DDR, RTH, ITE formed the third group that yielded more propylene than ethylene. The final group of zeolites having the wide *lta*-cages (LTA and RHO) gave high butylene selectivities comparable to those of ethylene and propylene.

In this work, we studied the MTO behavior of various AlPO_4 -based materials that are isostructural to those zeolites we reported on previously.¹⁴ SAPO-34, CoAPO-34,

MgAPO-34 (CHA), SAPO-56 (AFX), STA-18 (SFW), SAPO-18, CoAPO-18, MgAPO-18 (AEI), STA-7 (SAV), SAPO-42 (LTA), DNL-6 (RHO), STA-14 (KFI) were tested under the same reaction condition and compared to our previous results with zeolites of the same topology.¹⁴ Additionally, several more zeolites, SSZ-17 (Nu-3, LEV), SSZ-98, SSZ-39 (AEI), zeolite RTH, zeolite LTA, zeolite RHO, zeolite KFI, and UZM-5 (UFI) were synthesized and tested. The MTO light olefin selectivity results from the zeolites and molecular sieves are classified into the four categories we denoted previously.¹⁴ Additionally, we demonstrate that the MTO light olefin selectivity is a function of the framework topology and not its elemental composition (that influences acidity). In order to develop a molecular sieve framework-MTO product selectivity, structure-property relationship, we introduce the concept of a cage-defining ring size that represents a limiting dimension for the size of the polymethyl aromatic intermediate species. The cage-defining ring size concept proposed herein highlights the strong correlation existing between light olefin product distribution patterns and this structural indicator. The cage-defining ring size provides a useful structure-property metric, as it can be determined directly from the framework topology alone.

Experimental Section

Materials Preparation and Characterization

The small-pore cage-possessing molecular sieves demonstrated in this work were synthesized based on the previously reported protocols: SAPO-34,¹⁹⁻²⁰ CoAPO-34,²¹ MgAPO-34,²² SAPO-56,²³ STA-18,²⁴ SSZ-17¹² and lower-silica LEV zeolite,²⁵ SSZ-98,²⁶ SSZ-39,¹⁵ SAPO-18,²⁷ CoAPO-18 and MgAPO-18,²⁸ zeolite RTH,¹⁶ STA-7,²⁹ SAPO-42,⁶ DNL-6,³⁰ STA-14,²⁹ zeolite LTA,¹⁷ zeolite RHO,³¹ zeolite KFI,³² and UZM-5.³³ The methods to synthesize the other zeolites can be found in our previous paper.¹⁴ Detailed synthesis procedures for these molecular sieves and the OSDAs used to synthesize them are provided in Supporting Information.

The powder X-ray diffraction (PXRD, Rigaku Miniflex II bench-top diffractometer with Cu K α radiation λ = 1.54184 Å) profiles were obtained to identify the products from hydrothermal syntheses. The morphology and elemental composition were characterized using a ZEISS 1550VP field-emission scanning electron microscope (FE-SEM) equipped with an Oxford X-Max SDD energy dispersive spectrometer (EDS). The elemental compositions, PXRD profiles, and SEM images of the molecular sieves are provided in Table S1 and Figures S3–S5.

MTO Reaction Test

The methanol conversion reaction condition used in this work is the same to the condition used in our previous work.¹⁴ Specifically, the catalysts were transformed into their NH_4 -forms or H-forms by cycles of ion-exchange steps followed by a calcination. The detailed procedure for the ion-exchange and calcination is provided in the Supporting Information. For a single reaction, 200 mg of catalyst was loaded after being pelletized to be 0.18–0.60 mm in size. The catalyst bed was positioned between a pair of glass wool block in a fixed-bed tubular still reactor having dimensions of $\frac{1}{4}$ " in diameter and 6" in length. The bed was pretreated using an air flow at 580 °C for 12 hours (ramping rate: 1 °C min^{-1}). The dry weight of catalyst was estimated based on the thermogravimetric analysis (TGA, PerkinElmer STA 6000). The reaction was performed at strictly 400 °C with methanol (1.3 h^{-1}) in a carrier gas (5% Ar in 95% He, GC internal standard, 30 ml min^{-1}) flow. The sampling from the outlet flow was taken every 16 min. The selectivity values of products were calculated on the carbon-number basis, not on the molar or weight basis. The product distributions were obtained by averaging olefin product selectivities in the ranges of 98–100% methanol conversion.

Results and Discussion

MTO Light Olefin Product Distributions over Zeolites and Their AlPO_4 -analogous

We have been focusing on elucidating a relationship between the cage architectures of small-pore zeolites and the light olefin product distributions. Initially, the MTO behavior of SSZ-17, SSZ-13, and SSZ-16 having similar crystal sizes and Si/Al ratios were examined.¹² Also, we experimentally confirmed that there is a lower limit in sizes of zeolitic cages for the MTO reaction. The small cages in materials such as MCM-35 (MTF) and ERS-7 (ESV) do not have MTO activity due to their inability to accommodate aromatic hydrocarbon pool intermediates.³⁴ The MTO reactivities of several other zeolites have been reported,^{15–17} and we recently, published MTO results from 12 different cage-possessing small-pore zeolites.¹⁴ By analyzing these data, we identified four types of light olefin product distribution patterns that were closely related to the structures of the zeolite cages.

The first category of frameworks gave olefin selectivities similar to that of SAPO-34. SSZ-13, SSZ-16, SSZ-52 and other GME-related zeolites belonged to this category. Materials in this category had ethylene and propylene selectivities that were roughly similar, with low amounts of butylenes at 400 °C. The second category of materials included SSZ-17 and SSZ-98. Materials in this category yielded higher amounts of ethylene than propylene with

low butylenes at the same temperature. The third category of zeolites, SSZ-28, SSZ-39, ITQ-3, and zeolite RTH, produced higher propylene than ethylene with low-to-moderate levels of butylenes. The fourth and last category was a group of the *lta*-cage-possessing zeolites that were LTA and RHO. This fourth category was described as materials giving ethylene, propylene and butylene selectivities that roughly equal to each other.

The MTO product distributions are affected by many factors such as acid strength, acid-site density, i.e., Si/Al ratios of zeolites, and cage structures. For instance, it is known that molecular sieves having stronger acidity deactivate more quickly. This behavior has been confirmed numerous times, e.g., comparison of SAPO-34 to SSZ-13, two CHA isostructural materials having different acidities.²⁰ It was also shown that the proximity among acid sites substantially affected the initial alkane (propane) selectivity.²⁰ The formation of propane is closely related to the coke formation via the hydrogen transfer mechanism.^{35–36}

The reaction temperature is another important factor that has a significant influence on the MTO product distribution. Lighter olefins (e.g., ethylene) generally tend to be formed at higher temperature over both zeolites⁹ and SAPOs.¹⁰ The types of aromatic intermediates and coke species are primarily determined by the reaction temperature other than the cage geometry.^{3, 10} Therefore, we limited the reaction temperature to be at 400 °C in this work.

In order to further explore the structure-property relationships for the MTO reaction, we synthesized SAPO-34, CoAPO-34, MgAPO-34, SAPO-56, STA-18, SAPO-18, CoAPO-18, MgAPO-18, STA-7, SAPO-42, DNL-6, STA-14 and the zeolites, SSZ-17, SSZ-98, SSZ-39, zeolite RTH, zeolite LTA, zeolite RHO, zeolite KFI, and UZM-5. These microporous materials were tested for MTO reactivity

Figure 1. MTO product distributions when the methanol conversion is over 98%: (a) four isostructural molecular sieves having CHA topologies, and (b) two CHA-AFX-SFW series as SAPOs and zeolites. The selectivity data of DEA-SAPO-34, SSZ-13, SSZ-16, and SSZ-52 were reproduced from our previous work.¹⁴ All reactions are performed at $T = 400 \text{ }^{\circ}\text{C}$,

under the same reaction conditions, and the results are provided below in the category¹⁴ that best describes their light olefin product distribution.

Category I

Category I contained 9 materials (two SAPO-34s from different OSDAs, CoAPO-34, MgAPO-34, SSZ-13, SAPO-56, SSZ-16, STA-18, SSZ-52) with 3 cage topologies (CHA, AFX, and SFW). The MTO product distributions of these materials before deactivation are illustrated in Figure 1. The time-on-stream profiles are provided in the Supporting Information (Figure S10) and in our previous work.¹⁴ All of these molecular sieves gave similar ethylene and propylene selectivities and low butylenes selectivities (< 10%) at 400 °C despite differences in cage topology and elemental compositions.

Figure 1a shows the reaction results of four isostructural CHA-molecular sieves having different elemental compositions. These materials not only resulted in the highest overall light olefin (ethylene and propylene) product distributions amongst all tested small-pore/cage molecular sieves tested in this work, but their patterns were also very similar to each other. These data strongly supports the notion that light olefin product distributions are primarily controlled by the cage geometry as opposed to other parameters such as acid strength (although these parameters can influence other features such as initial propane selectivities, deactivation rate, etc.). Additionally, it has been reported that the product selectivity patterns of SAPO-34 are similar to those of lower silica chabazite zeolites.³⁷

In our previous work,¹⁴ we reported the MTO catalytic activities of zeolites SSZ-13, SSZ-16, and SSZ-52 having CHA, AFX, and SFW topologies, respectively. These three frameworks belong to the AABBC-6 family, and are exclusively composed of parallel stackings of double-6-ring (*d6r*) composite building units (CBUs). As a result, these three cage-type topologies share almost the same width of cages. All three zeolites gave ethylene-to-propylene product ratios close to one, and the size order (CHA < AFX < SFW) was the same to the propane selectivity order (12% for SSZ-13 < 47% for SSZ-16 < 71.5% for SSZ-52). Figure 1b illustrates data from an isostructural series of SAPO materials to the zeolites investigated previously (SAPO-34, SAPO-56, and STA-18). The SAPO-series gave behaviors similar to the zeolite-series. All three SAPO materials yielded ethylene selectivities close to those of propylene, and the initial propane selectivity order (8% for SAPO-34 < 15% for SAPO-56 < 20% for STA-18) was in the same sequence as with the zeolites.

Category II

Figure 2. MTO product distributions when the methanol conversion is over 98%. The selectivity data for SAPO-17 are at 375 °C and 425 °C, and were reproduced from Wilson and Barger.³⁸ All reactions are performed at T = 400 °C, WHSV(MeOH) = 1.3 h⁻¹ except for the two noted.

We grouped molecular sieves producing more ethylene than propylene into this category.¹⁴ Specifically, this category included materials having the following topologies: LEV and ERI. Figure 2 summarizes the MTO product distributions of Category II molecular sieves. The MTO reaction results of SAPO-17 (ERI) reported by Wilson and Barger in 1999 are reported for comparison.³⁸ The corresponding time-of-stream data are provided in Figure S11.

LEV has the smallest cage among all tested topologies that are known to be 'MTO-active'. Previously, we demonstrated that a few cages smaller than an LEV cage, such as ESV, MTF, ATN, and CDO, are not capable of catalyzing the methanol conversion via hydrogen pool intermediates.³⁴ The LEV topology has a minimum cage volume that can retain carbenium ions or neutral hydrocarbon species. The Liu group at DICP confirmed the presence of tri- and tetra-methylated hydrogen pool intermediates within the cages using an *in situ* solid-state ¹³C NMR technique; they reported that no significant amount of fully substituted aromatic intermediates or species having long side chains were formed within the cages of SAPO-35⁷ and RUB-50.¹¹ Given that aromatic intermediates having more and longer side chains generates higher olefins,³⁹ the steric confinement effect has been noted as the main reason why the LEV materials primarily generate ethylene and propylene.

Here, two LEV zeolites synthesized using two different OSDAs (N-methylquinuclidinium and N,N'-dimethyl-1,4-diazabicyclo[2.2.2]octanium) were tested. The LEV zeolite from N-methylquinuclidinium OSDA, that is known as either Nu-3 or SSZ-17, has a higher Si/Al ratio (EDS Si/Al = 17.7) than the other material (EDS Si/Al = 8.3).

Regardless of the synthesis method, the two LEV zeolites showed ethylene/propylene ratios that were significantly higher than one. Similar results were reported using a Nu-3 zeolite synthesized from another OSDA 1-adamantylamine.⁹ That said, the lifetime observed for the LEV zeolite (34 min) with the lower Si/Al ratio was significantly shorter than the one (259 min) with the higher Si/Al ratio. Indeed, these results are consistent with our previous findings for SSZ-13 CHA zeolites.²⁰

Although we ascribe SAPO-35 to Category II, we illustrate here a product distribution similar to those of SAPO-34 of Category I. SAPO-35 (EDS Si/T = 0.120) showed a slightly higher propylene selectivity than ethylene at 400 °C, contrary to the case for LEV zeolites. The ethylene/propylene ratios of SAPO-35 materials are known to depend upon the Si-distributions. Pinilla-Herrero and co-workers reported that an increase in Si-content for SAPO-35 resulted in higher ethylene/propylene ratios due to the decrease in acid-site density that was a consequence of the formation of Si-site islands, and that SAPO-35 samples with Si/T molar ratios higher than 0.140 yielded more ethylene than propylene.¹³ Additionally, the short lifetime of SAPO-35 can also contribute to the propylene selectivity higher than ethylene. Generally, SAPO-35 deactivates faster than other SAPO-based catalysts with similar Si-contents due to its lower-dimensional channel system (2D) combined with its large crystal sizes (~ 20–30 μm). Furthermore, most previous work reports short lifetimes for SAPO-35.^{6, 10, 13} As shown in Figure S11c and S14, the ethylene/propylene selectivity ratio for SAPO-35 increased with time on stream. Similar behaviors for SAPO-35 were observed in previously reported results.^{6, 10} Interestingly, this time-dependent increasing behavior of ethylene/propylene ratio was not only observed for SAPO-35, but also shown for all Category II materials, including zeolites. (Figure S14) This behavior of sharply increasing ethylene/propylene ratio was not seen in other categories, such as CHA or AEI. The trend in rising ethylene selectivity may be related to the diffusion process of products within the microporous material,⁴⁰ and are currently investigating the origins of the behavior.

The other topology member of Category II is ERI. ERI has a longer cage than LEV, but in terms of the maximum diameter of sphere that can be included within a cage, ERI (7.04 Å) is even narrower than LEV (7.10 Å) and much narrower than CHA (7.37 Å).⁴¹ The ERI-type catalysts showed higher ethylene/propylene ratios than LEV-type molecular sieves, for both zeolites and SAPOs. The SSZ-98 having a Si/Al ratio of 6.0 shown in this work (Figure 2 and Figure S11) gave an ethylene/propylene ratio as high as 2.1 at the onset of the catalyst deactivation. This result is

consistent with our previous work.¹⁴ Not only pure ERI-phase zeolites but also ERI-related intergrowth zeolites such as ZSM-34 (ERI/OFF intergrowth)⁴² and SSZ-105 (ERI/LEV intergrowth)¹⁴ showed high ethylene selectivities at 400 °C. These results demonstrate that ERI-cages are responsible for the high ethylene selectivities.

SAPO-17 (ERI) is known to give high ethylene selectivities.^{38, 43} Wilson and Barger reported that SAPO-17 gave ethylene/propylene ratios of 1.1 and 2.0 at 375 °C and 425 °C, respectively.³⁸ It has been shown that the ethylene/propylene ratio increases as the reaction temperature increases.⁹ It is therefore anticipated that SAPO-17 would show an ethylene/propylene ratio similar to that of SSZ-98 in this work.

Category III

Category III includes materials with topologies that give propylene selectivities that are higher than ethylene at 400°C. The MTO-product selectivity distributions and corresponding time-of-stream data are illustrated in Figure 3 and Figure S12, respectively. The MTO results from SSZ-28 (DDR) and ITQ-3 (ITE) are imported from our previous work for comparison.¹⁴

Figure 3. MTO product distributions when the methanol conversion is over 98%. (a) Molecular sieves with AEI topology. (b) Other category III results. The selectivity data from SSZ-28 and ITQ-3 were reproduced from our previous work.¹⁴ All reactions are performed at $T = 400\text{ }^{\circ}\text{C}$,

Zeolite SSZ-39 and three AlPO_4 -based molecular sieves (SAPO-18, CoAPO-18, MgAPO-18) were prepared and compared. The MTO product distributions from these materials were consistent with the previously reported results.^{15, 28, 44} Much like CHA materials (discussed previously), the AEI-series materials also showed impressively similar light olefin product distributions despite their completely different elemental compositions (Figure 3a). The data from the AEI as well as the CHA materials (*vide supra*) strongly support the conclusion that cage geometry primarily controls the light olefin product distribution. The alkane selectivities may be related to differences in acid-strength,^{28, 44–45} but we are not able to make that conclusion due to differences amongst the acid-site densities in the materials we investigated. It is noteworthy that the SSZ-39 shown in this work was synthesized from a sodium-free gel, and had a high Si/Al ratio of 10, inspired by a related work on SSZ-13.⁴⁶ However, its MTO behavior was not significantly different than conventional SSZ-39, which was prepared from sodium-containing gels.¹⁵ Unlike other AlPO_4 -based AEI materials, SSZ-39 showed a high initial alkane (propane) selectivity. We previously demonstrated that the proximity of acid sites, that is more rarely obtained with AlPO_4 -based catalysts, the reason for the high initial alkane selectivity with low-silica zeolites.²⁰

Figure 3b shows the product distributions of several molecular sieves belonging to Category III other than the AEI-type materials. The three frameworks—DDR, RTH, and ITE—have 5-membered ring silica units, thus, AlPO_4 -

based material do not exist with these topologies. Additionally, a zeolite having the SAV topology has yet to be discovered. Regardless of variations in structures and elemental compositions, the light olefin product distributions of these catalysts share a common feature: high propylene selectivities.

It was previously shown that SSZ-28 and ITQ-3 gave higher propylene than ethylene selectivity.¹⁴ Here, a zeolite RTH was added for comparison. The MTO behavior of the RTH zeolite having a Si/Al ratio of 13.2 concurred with our previous report¹⁶ and a study on RUB-13 recently reported by Corma et al.⁴⁷, showing a propylene selectivity that was higher than the other light olefins. It is also suggested that the cage structure of RTH is able to preferentially stabilize fully-substituted aromatic intermediates, that are responsible for the high propylene and butylene selectivity, while partially alkylated species are formed within the CHA cage which belongs to Category I.⁴⁷ RTH and ITE, the two frameworks having 2-dimensional channel systems, are crystallographically related to each other, and share key structural building units (connection are different, and RTH (16.1 T-atoms nm^{-3}) is slightly denser than ITE (15.7 T-atoms nm^{-3}) due to a small difference in bonding angles).⁴¹ The only major difference in the MTO reactivity between the two

Figure 4. MTO reaction results from category IV materials. (a) MTO product distributions when the methanol conversion is over 98%. (b) Ratios of light olefin selectivities (E: ethylene, P: propylene, B: butylenes) All reactions are performed at $T = 400\text{ }^{\circ}\text{C}$, WHSV(MeOH) = 1.3 h^{-1} except for these two.

materials was the C₂-C₄ alkane selectivity (mostly propane) that originated from the difference between the Si/Al ratios of the two materials. (The Si/Al ratio of ITQ-3 was 18.1.)

The two STA-7 molecular sieves gave very similar product distributions with high propylene levels regardless of Si-compositions. These results are consistent with previously reported results.^{6, 13, 29} The SAV topology has two cages, with one being much larger than the other.²⁹ In terms of the maximum diameter of a sphere that can be included, the minor cage of SAV (6.33 Å) is much smaller than an LEV- (7.10 Å) or an ERI-cage (7.04 Å), but similar to an MTF- (6.25 Å) or an ESV-cage (6.22 Å) that cannot accommodate a hydrogen pool intermediates.³⁴ Thus, it is reasonable to assume that the minor cage of SAV plays a negligible role during the hydrogen pool mechanism.

Category IV

All four topologies we classify under Category IV have *lta*-cages. Specifically, LTA, RHO, and KFI frameworks have cubic symmetries and 3-dimensionally connected *lta*-cages. Each pair of neighboring two *lta*-cages are connected directly, via a double-8-ring (*d8r*) unit, and via a minor *pau*-cage in LTA, RHO, and KFI frameworks, respectively. The UFI framework is the only member of Category IV that has a tetrahedral symmetry and a 2-dimensional channel system. It has *rth* composite building units, and as a result, has no phosphate counterpart. Each *lta*-cage in UFI has two 'caps' in the axial direction, and these caps are too small (max. sphere diameter of the caps = 5.92 Å) to accommodate independent MTO-intermediate aromatic molecules. These structural differences generate size differences in the *lta*-cages for the four aforementioned frameworks. The largest sphere that can be included in these cages (from the largest to smallest) is as follows: LTA (11.05 Å) > KFI (10.67 Å) > RHO (10.43 Å) > UFI (10.09 Å).

The MTO reaction product distributions and the corresponding MTO time-on-stream data for Category IV materials are shown in Figure 4 and Figure S13, respectively. The ratio of the sum of all C₄ olefins' selectivities to the average of ethylene and propylene selectivities, 2B/(E+P), was used as an indicator for the relative contributions of the butylenes. All catalysts in this category yielded high butylenes selectivities. The RHO zeolite (Si/Al = 5.4) showed the highest butylenes (2B/(E+P) = 0.99) among the tested catalysts. The lowest amount of butylenes was observed in STA-14 (0.49), which has a KFI topology, but this value was still higher than most of other SAPO molecular sieves from the other categories, such as SAPO-34 (0.29) or SAPO-18 (0.36), that

had smaller cages. Only a few SAPO-type catalysts having voluminous cages, such as STA-7 (SAV, 0.61) or STA-18 (SFW, 0.49), showed high butylenes, (i.e., higher than or comparable to STA-14).

Zeolites investigated in this work tended to show higher butylenes than their SAPO counterparts. All four zeolites from Category IV produced butylenes ratios that were higher than 0.66. The highest butylenes were observed for zeolite RHO, as mentioned previously, and the lowest was observed for zeolite KFI (0.66). The general order was RHO > LTA > (UFI) > KFI, but this order is different than the volume order based on the diameter of the maximum sphere (*vide supra*). Pinilla-Herrero et al. suggested that the butylene production is due to the wide pore (4.1 × 4.1 Å) of SAPO-42.⁶ However, the materials having the RHO topology (i.e., both zeolite rho and DNL-6, 3.6 × 3.6 Å pore window size) gave high butylene selectivities even though they have pore windows narrower than CHA (3.8 × 3.8 Å). Furthermore, the ethylene/propylene ratios of Category IV materials showed almost no regularity. Zeolite RHO and zeolite KFI showed high ethylene/propylene selectivity ratios, E/P = 1.92 and 1.56, respectively, while SAPO-42 and STA-14 preferred to produced more propylene, similar to Category III materials. We speculate that other parameters such as the distribution of acid-site also contribute to the olefin product distributions for Category IV catalysts having *lta*-cages, but the exact reasoning remains unclear to us at this time.

Definition of the Cage-defining Ring for Molecular Sieve Structure – MTO Light Olefin Product Distribution Structure-Activity Correlation

In the previous sections, we provided data to show that light olefin product distributions from small-pore, cage-containing molecular sieves are primarily a function of the framework topology and not the framework composition at a fixed temperature of reaction. Given this feature, we now develop a framework structural parameter to characterize each topology.

All of the MTO-active cages have unique structures that cannot simply be explained by heights, widths, and lengths. Consider a hypothetical cage having an ideal shape that is easy to deal with—an ellipsoid. An ellipsoid is defined by its three axes, *a*, *b*, and *c* where *a* ≤ *b* ≤ *c*. If a planar aromatic intermediate is residing in this ellipsoidal cage, the molecule will align parallel to the *bc* plane and perpendicular to the shortest *a* axis because it is the most energetically favorable orientation. Figure 5a shows an aromatic intermediate adopting such an orientation within an ellipsoidal cage. In this orientation, the limiting dimension that determines the maximum size of the intermediate molecule is the second longest axis *b*.

The longest axis c is less important in this view. Here, we define the ellipse ab as the cage-defining ring of this ellipsoidal cage, and the length of axis b which is the dimension that limits the size of the intermediate molecule is denoted as the cage-defining ring size.

Procedures analogous to that given above for an ellipsoid can be used for real cages. Using the crystallographic data for frameworks listed in the IZA database,⁴¹ cage dimensions can be calculated. There are many choices for [T-O-T...-O-] rings that circumscribe the cage. Among them, we find the smallest ring that is closest to the center of mass of the cage. This ring corresponds to the ellipse ab that is shown in Figure 5a, and defined as the cage-defining ring of the cage. Figure 5b depicts the case of a CHA-cage. In case of CHA, the '12-membered ring' that is perpendicular to the c axis is the cage-defining ring (red-colored in Figure 5b). It is possible to measure the size of this ring in the same manner as when measuring channel dimensions of zeolitic frameworks. In

Figure 6. Correlation chart of cage-defining ring size by cage structures and light olefin product distribution categories.

case of CHA, the dimension of the 12-membered ring is the cage-defining ring (7.45 × 7.05 Å). The length of the longer axis (7.45 Å) is what we denote as the cage-defining ring size for CHA. Here, the diameters of the T and O atoms are assumed to be 2.7 Å in accordance with the IZA convention.⁴¹ The selections of cage-defining rings and their sizes for all other cages used here are visualized in Figures S6-S9 in Supporting Information.

Figure 6 shows the correlation between the cage-defining ring sizes and the four categories of light olefin product distribution patterns. The three frameworks, CHA, AFX, and SFW, from the Category I have 12-membered cage-defining rings, and almost the same cage-defining ring size of 7.45 Å (these three small-pore frameworks are from the AABCC-6 family and are closely related to the structure of GME). The Category II frameworks (LEV and ERI) that give higher ethylene than propylene also have 12-membered cage-defining rings, but their sizes are smaller than those of Category I. The Category III frameworks produce higher propylene than ethylene, and

Figure 5. (a) An ellipsoidal model for the cage-defining ring and the cage-defining ring size. (b) The selection of the cage-defining ring from a CHA-cage.

have wider 14-membered cage-defining rings except for DDR that is the one exception. Lastly, Category IV frameworks that give high butylene selectivities have the widest 16-membered cage-defining rings that are derived from their LTA-cages, and their ring sizes are larger than 10 Å.

Conclusion

The MTO behavior of 30 different zeolitic and AlPO_4 -based molecular sieves with 14 small-pore cage-type topologies (CHA, AFX, SFW, LEV, ERI, DDR, AEI, RTH, ITE, SAV, LTA, RHO, KFI, UFI) at the same reaction condition were compared. The olefin product distributions from the MTO reactions over SAPO, MAPO and zeolite were placed into the four categories of product distributions reported previously. The AlPO_4 -based molecular sieves gave olefin

product distributions similar to their isostructural zeolitic counterparts. For two topologies, CHA and AEI, zeolites, SAPOs, CoAPOs and MgAPOs were prepared and the methanol conversion reactions were performed. The olefin product distributions obtained from these two sets of isostructural molecular sieves demonstrate that it is the cage geometry that mainly determines the light olefin product distributions. Furthermore, the MTO product distributions from the SAPO-versions of the three AABCC-6 family members (CHA, AFX, and SFW) which were isostructural to the zeolites support this conclusion.

A new geometric concept, the cage-defining ring, based on a simple assumption about the orientation of the hydrogen pool intermediates within the cages, was developed. The size of the cage-defining ring, which limits the sizes of polymethyl aromatic intermediate species, showed a strong correlation to light olefin product distributions. This structure-property relationship can provide guidance for further MTO investigations including the search for new topologies with anticipated MTO selectivities by design.

ASSOCIATED CONTENT

Supporting Information. Synthesis details, materials and catalysis characterization results, visualizations, time-on-stream profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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