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Methanol-to-Olefins Catalysis on ERI-Type Molecular Sieves: Towards Enhancing Ethylene Selectivity

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ABSTRACT:

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

KEYWORDS: Erionite, methanol-to-olefins, small-pore zeolites, SAPOs

1. Introduction

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

It is now widely accepted that the complex reaction network taking place within the small-pore, cages/cavities of MTO catalysts, following an initial induction period, proceeds through a dual-cycle mechanism that comprises of olefins-based chemistries of successive methylation and cracking steps and aromatic-based chemistries of methylation and dealkylation [4,5,8–10,35–44]. The two cycles are connected through hydrogen transfer and cyclization events. In small-pore, cage-containing molecular sieves with CHA, AEI, LEV, DDR, and RHO-type structures, it has been demonstrated that the hydrocarbon-pool (HP) species that remain entrapped inside the cavities of these microporous materials are primarily

comprised of cyclic organic species, with aromatic polymethylbenzenes and polymethylbenzenium ions recognized as key active HP compounds [1,5,6,12–15,22,25,29,45,46]. This is fundamentally different than what occurs in medium- and large-pore zeolites (e.g., MFI) (i.e., methanol-to-hydrocarbons (MTH)), for instance, where aromatic species can diffuse out of the molecular sieve and contribute to the product distribution as opposed to being trapped. The lack of larger molecule escape in small-pore, cage-type molecular sieves thus leads to improved light olefins selectivities and yields.

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

Our group recently proposed a new molecular sieve structural indicator, the cage-defining ring (CDR), that correlates light olefin product distributions in MTO with a geometric parameter of the molecular sieve cage architecture for a multitude of small-pore, cage-containing zeolites, SAPOs and metalloaluminophosphates (MAPOs) belonging to the following topology types: LEV, ERI, CHA, AFX, SFW, AEI, DDR, RTH, ITE, SAV, LTA, RHO, KFI, and UFI [31]. We showed that the CDR, defined as the minimum number of tetrahedral atoms of the ring encircling the center of the framework cages in a given molecular sieve topology, correlates with the MTO light olefins product distribution. Based on the product effluent, we classified the fourteen topologies to four overarching categories that are provided in **Figure S1**.

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

Table 1. Cages/materials studied in this work and their dimensions.

Framework	CHA	ERI
Channel Dimensionality	3	3
8-MR Pore Size (Å)	3.8 x 3.8	3.6 x 5.1
8-MR Pore Area (Å) ^[a]	11.34	14.42
Maximum Diameter of Sphere (Å)	7.37	7.04
Cage-defining Ring (CDR) (Å) ^[b]	7.45	6.75
Materials Tested	SAPO-34 SSZ-13	SAPO-17 SSZ-98

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

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

Here, we examine the catalytic behavior of several ERI-type materials (SSZ-98, UZM-12, ERI-type zeolite, and SAPO-17) synthesized using various OSDAs (**Figure 1**) that cover a wide range of Si/Al=5-9 and Si/T=0.034-0.12 (T=Si+Al+P), with the goal of identifying key material properties that enhance ethylene selectivity. We compare the performance of ERI-type materials to SSZ-13 (Si/Al=15) and SAPO-34 (Si/T=0.089), to discern any differences in reactivity and selectivity between these two framework types. All samples in this work were investigated with a battery of characterization techniques outlined in the next section. Partially reacted/deactivated samples from various reaction time-on-stream (TOS) were dissolved in acid to extract and analyze the occluded organic components in an effort to identify

differences between the composition and concentration of the entrained aromatics formed during reaction. These species assist in understanding the observed differences in MTO behavior (i.e., olefins product distribution) between CHA-type and ERI-type materials.

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

2. Experimental Section

2.1 Materials Syntheses

The small-pore, cage-containing molecular sieves shown in this work were synthesized based on previously reported (albeit with slight modifications) or newly developed procedures as outlined below. Detailed synthesis procedures of the organic structure-directing agents (OSDAs) used in this work are provided in the Supplemental Information (SI) Section. All materials, unless otherwise noted, were used as-received without further purification from the stated vendors. The moisture contents of the solid sources were determined by temperature-gravimetric analysis (TGA). In addition to the syntheses listed below, summaries of the zeolite and SAPO preparations are provided in **Tables S1** and **S2**, respectively.

2.1.1. SSZ-13 (CHA)

The synthesis gel molar composition for the SSZ-13 sample was $100 \text{ SiO}_2 : 3.33 \text{ Al}_2\text{O}_3 : 20 \text{ ROH} : 10 \text{ Na}_2\text{O} : 4400 \text{ H}_2\text{O}$, where ROH is N,N,N-trimethyl-1-adamantammonium hydroxide (OSDA 1) [69]. In a typical synthesis, desired amounts of sodium hydroxide solution (NaOH, 50%, Sigma-Aldrich), OSDA 1, and deionized (DI) water were added and stirred for approximately 0.5 hr. Aluminum isopropoxide (98%, Sigma-Aldrich) was then added as an aluminum source to this solution, and the mixture was stirred for at least 3 h. Finally, a colloidal silica solution (Ludox AS-40, Sigma-Aldrich) was added, and the gel was stirred until it was homogenous. The gel was placed in a Teflon-lined Parr reactor (23 cm^3) and heated in a static oven to 160°C at autogenous pressure for 6 days.

2.1.2. SAPO-34 (CHA)

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

2.1.3. SSZ-98-1 (ERI)

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

then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 150 °C at autogenous pressure for 6 days.

2.1.4. SSZ-98-2 (ERI)

SSZ-98-2 was prepared by converting commercial Y zeolite using N,N-dimethylpiperdinium hydroxide (OSDA 5; synthesis protocol in SI) [70]. The synthesis gel molar composition for SSZ-98-2 was 3.75 SiO₂ : 0.125 Al₂O₃ : 1.0 ROH (OSDA 5) : 1.9 KOH : 145 H₂O. In a typical synthesis, desired amounts of CBV720 (Si/Al=15, Zeolyst), KOH solution, OSDA 5, and DI water were added together and stirred for 24 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 150 °C at autogenous pressure for 7 days.

2.1.5. UZM-12 (ERI)

The synthesis gel molar composition for UZM-12 was 16 SiO₂ : 0.5 Al₂O₃ : 2.0 R(Br)₂ (OSDA 6) : 13 TEAOH (OSDA 2) : 1.5 KCl : 400 H₂O [60]. In a typical synthesis, desired amounts of OSDA 2 (TEAOH), OSDA 6 (hexamethonium bromide, Sigma), potassium chloride (Macron), Catapal B alumina (VISTA), and DI water were added and stirred for 0.5 h. Following this, colloidal silica (Ludox AS-40) was added and this solution was allowed to age for 24 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a rotating oven to 100 °C at autogenous pressure for 12 days. As will be shown later, this sample contained some defects. However, the defects in this sample are not representative of all UZM-12 materials. We included this sample in this study because it allows to study sub-standard features in ERI molecular sieves, and thus compare the performance of this sample to better crystallized ERI material.

2.1.6. ERI-type Zeolites-1, 2, and 3

The synthesis gel molar composition for what is denoted as ERI Zeolite-1 was 1 SiO₂ : 0.167 Al : 0.1 R(OH)₂ (OSDA 7) : 0.3 KOH : 20 H₂O [66]. In a typical synthesis, using a FAU-type zeolite as a T-atom

source, a mixture of OSDA 7 (butane-1,4-bis(trimethylammonium) dihydroxide; synthesis procedure outlined in the SI), NaOH, and DI water were stirred for 0.5 h. Then, Y zeolite (CBV712, Si/Al=6, Zeolyst) was added and this solution was stirred at room temperature for an additional 6 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 135 °C at autogenous pressure for 7 days. This sample is denoted as ERI Zeolite-1. ERI Zeolite-2 was synthesized using a similar procedure as ERI Zeolite-1; however, OSDA 7 was replaced with OSDA 8 (cyclohexane-1,4-bis(trimethylammonium) dihydroxide; synthesis procedure outlined in the SI). ERI Zeolite-3 was synthesized with a similar gel composition and procedure as ERI Zeolite-2 but with a lower aluminum content in the gel (0.067 rather than 0.167) (CBV720, Si/Al=15, Zeolyst).

2.1.7. SAPO-17-1

The synthesis gel molar composition was 0.1 SiO₂ : 1.0 Al₂O₃ : 1.0 P₂O₅ : 1.0 CHA (OSDA 9) : 50 H₂O [62]. In a typical synthesis, a desired amount of aluminum isopropoxide was mixed with DI water and stirred overnight. The following day, phosphoric acid (H₃PO₄; 85%, MACRON) was added to this mixture and the solution was stirred for 2 h. Next, colloidal silica (Ludox AS-30, Sigma-Aldrich) was added along with a small amount of AlPO₄-17 seed (2 wt%). (AlPO₄-17 was synthesized using the same gel composition and crystallization conditions as SAPO-17-1 just without any silicon). Lastly, cyclohexylamine (Aldrich; CHA; OSDA 9) was added to this mixture and the gel was stirred overnight. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a static oven to 200 °C at autogenous pressure for 2 days. (Note: vigorous stirring and seed addition were necessary to make SAPO-17 without impurity phases. These impurity phases do not form when lowering the Si content in the above gel composition.)

2.1.8. SAPO-17-2 and SAPO-17-3

The synthesis gel molar composition was 0.2 (or 0.8) SiO₂ : 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.35 R(OH)₂ : 70 H₂O [71]. In a typical synthesis, H₃PO₄ was diluted with DI water and mixed with pseudoboehmite

alumina (Catapal B, VISTA). This solution was stirred overnight and then digested for 1 h at 90 °C. Next, hexane-1,6-bis(trimethylammonium) dihydroxide (OSDA 6-(OH)₂) was added to this solution and stirred for 24 h. Lastly, tetraethyl orthosilicate (TEOS) (99.9%, Alfa Aesar) was added to this gel and stirred for 1 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a rotating oven to 180 °C at autogenous pressure for 4 days. The sample with the lower Si content was denoted as SAPO-17-2 (0.2Si) whereas the sample with the higher Si content (0.8 Si) was denoted as SAPO-17-3. SAPO-17 samples with lower Si content (i.e., lower than 0.2 in the gel) led to the formation of an impurity phase. This gel composition allows for the synthesis of SAPO-17 with up to 1.0 Si.

2.1.9. SAPO-17-4

The synthesis gel molar composition was 0.4 SiO₂ : 1.0 Al₂O₃ : 0.9 P₂O₅ : 0.37 R(OH)₂ (OSDA 10): 40 H₂O. In a typical synthesis, a desired amount of Barcroft aluminum hydroxide (containing 31% H₂O; 69% aluminum hydroxide) was mixed with DI water for 1 h, which was followed by the addition of H₃PO₄. This solution was stirred for 24 h and then fumed silica was added. Lastly, OSDA 10 was added to this mixture and stirred for another 24 h. The gel was then placed in a Teflon-lined Parr reactor (23 cm³) and heated in a rotating oven to 190 °C at autogenous pressure for 3 days.

2.1.10. SAPO-17-5 and SAPO-17-6

A similar procedure as the one used for the synthesis of SAPO-17-2 was used for the synthesis of SAPO-17-5 and SAPO-17-6. The only difference between these two latter samples was the choice of OSDA. For SAPO-17-5, the following gel composition was used: 0.3 SiO₂ : 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.35 R(OH)₂ (OSDA 7): 70 H₂O. For SAPO-17-6, the following gel composition was used: 0.3 SiO₂ : 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.35 R(OH)₂ (OSDA 8): 70 H₂O.

2.1.11 Product Recovery, Thermal Treatment, and Ammonium Exchange

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

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

2.2. Characterization

Powder X-ray diffraction patterns were obtained on a Rigaku MiniFlex II instrument using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) at a scan rate of 0.3 °/min to determine structure type and purity. Crystallite sizes were calculated using the Scherrer equation with a shape factor of 0.94. The reported crystallite sizes are the averaged value of five crystallite sizes calculated from five peaks (between 22 and 40° 2 θ). Morphology and elemental composition were determined via scanning electron microscopy/energy

dispersive spectroscopy (SEM/EDS) on a ZEISS 1550VP instrument equipped with an Oxford X-Max SDD energy dispersive X-ray spectrometer. Atomic ratios (atomic %) were reported as Si/Al for zeolites, or Si/T (where T=Si+Al+P) or Si/(Al+P) for SAPOs. To determine micropore volume using the t-plot method and ensure the absence of mesoporosity, N₂-adsorption/desorption experiments were performed on each sample at 77 K in a Quantachrome Autosorb iQ adsorption instrument using a constant-dose method. Prior to adsorption measurements, all samples were outgassed at 60 °C for 0.5 h, followed by holds of 0.5 h at 120 °C and 6 h at 350 °C (all ramping rates were 1 °C/min). Thermogravimetric analysis (TGA) measurements were performed on Perkin Elmer STA 6000. As-synthesized (prior to thermal treatment), partially-coked and fully-coked samples (0.02-0.06 g) were placed in an alumina crucible and heated at 10 °C/min in a flowing stream (0.33 cm³/s) of air to 800 °C. Liquid ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer whereas liquid ¹H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. All liquid NMR analyses, involving OSDAs, were performed in deuterium oxide (D₂O) (99.9%, Cambridge Isotope Laboratories, Inc.) or 10% D₂O (**Figure S2**).

All solid-state, magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy experiments were conducted on a Bruker 500 MHz spectrometer using a 4 mm ZrO₂ rotor. The number of Brønsted acid sites was measured using quantitative ¹H MAS NMR spectroscopy. In a typical experiment, the thermally treated samples were dehydrated under vacuum (10⁻² Torr) at 400 °C for 10 hours at a ramp rate of 2 °C/min in a dehydration manifold after being pre-packed in an uncapped NMR rotor. The rotor was then capped while under vacuum and inside the dehydration manifold (to minimize sample exposure to moisture) and then loaded into the spectrometer. Spectra were collected at 500.1 MHz and a spinning rate of 12 kHz using a 90° high power pulse length of 4 μs. Cycle delay time was varied depending on the relaxation time of the samples. Signal intensities were referenced to hexamethylbenzene and normalized by the mass packed into the rotor for quantification. The spectra were deconvoluted using DMFit, as shown in the Supplemental Information (SI). For ²⁹Si MAS NMR spectroscopy, oxygen was introduced to

the dehydrated sample to reduce the relaxation time. The ^1H -decoupled ^{29}Si MAS NMR spectra were then acquired at 99.3 MHz and a spinning rate of 8 kHz using a 90° pulse length of 4 μs and a cycle delay time of 10 s. The acquired spectra were deconvoluted using the DMFit software as described in the SI to identify different Si environments in the tested samples and calculate the framework Si/Al values for the zeolites. It is important to note here that zeolites with an ERI-type framework consist of two crystallographically distinct T (tetrahedral atom) sites. The presence of 24 T1 sites and 12 T2 sites in ERI topology results in two separate resonances with a 2:1 ratio in ^{29}Si MAS NMR [73]. Thus, the ^1H -decoupled ^{29}Si MAS NMR spectra of the ERI-type samples were deconvoluted by maintaining the 2 (down-field): 1 (up-field) ratio for each set of Q^4 resonances ($\text{Si}(\text{OSi})_n(\text{OAl})_{4-n}$, $n = 0, 1, 2$, and 3) and Q^3 resonance ($\text{Si}(\text{OSi})_3(\text{OH})$) with the assumption that Al and silanol defect uniformly occupy the two different T sites. ^{27}Al MAS NMR spectra were acquired on the proton-form of the samples without undergoing any dehydration at 130.2 MHz at a spin rate of 12 kHz, a 10° pulse length of 0.5 μs , and a cycle delay time of 0.5 s.

2.3. Catalytic Testing

Catalyst evaluation was carried out in a fixed-bed reactor at ambient pressure. In a typical experiment, approximately 200 mg of dried catalyst (35–60 mesh size) was loaded between two layers of quartz wool in a $0.25'' \times 6''$ stainless steel (or quartz) tube reactor as a part of a BTRS Jr. continuous flow reactor (Parker Autoclave Engineers). The dry weight of the catalyst was estimated on the basis of thermogravimetric analysis (TGA; PerkinElmer STA 6000). All catalysts were first pretreated by heating to 150°C at $1^\circ\text{C}/\text{min}$, held for 3 hours, and then heated further to 580°C at $1^\circ\text{C}/\text{min}$ and held for 12 h under flowing air (breathing-grade D, AirGas). Methanol was introduced via a liquid syringe pump (Harvard Apparatus Pump 11 Elite) at 4.0–5.0 $\mu\text{L}/\text{min}$ into a gas stream of an inert blend (95% He and 5% Ar; GC internal standard) at a volumetric flow rate of 30 cm^3/min . The methanol flow rate was adjusted, depending on the actual weight of the dried catalyst loaded in the reactor, to achieve a weight hourly

space velocity (WHSV) of 1.3 h^{-1} . Unless otherwise noted, all reactions were performed at a WHSV of 1.3 h^{-1} and a temperature of 400°C . Effluent gases were evaluated using an on-stream Agilent GC-MS (GC 6890N/MSD5793N) equipped with a Plot-Q capillary column. Aliquots of product flow were analyzed every 16 minutes. All selectivity values were calculated on carbon-number basis.

In experiments where the content of the entrained hydrocarbons was of interest, the reaction was quenched rapidly (-10°C/s) and a portion of the catalyst bed (15 mg) was transferred to a Teflon tube and suspended in 1.0 cm^3 of 48% aqueous hydrofluoric acid (Sigma Aldrich). The solution was stirred for 2 h to allow the framework to dissolve. Following dissolution, the organic material was extracted into 1 cm^3 of dichloromethane ($2 \times 0.5 \text{ cm}^3$). Hexachloroethane (Aldrich, 99%) was used as an internal standard. The speciation of aromatics in the organic layer was then identified using a mass spectrometer (Varian CP-3800/Saturn 2200) and a DB-5MS UI column ($30 \text{ m} \times 0.25 \text{ mm}$) and quantified using a gas chromatograph (Agilent 7890B) connected to a Polyarc. The organic compounds extracted were identified in comparison with the NIST database as well as standards.

3. Results and Discussion

3.1. Characterization

A total of fourteen small-pore, cage-containing molecular sieves were synthesized and characterized in this work: six ERI-type zeolite samples, six SAPO-17s and two CHA-type materials (one zeolite (SSZ-13) and one SAPO (SAPO-34)). Below, the characterizations of these materials are discussed in detail, and the results are summarized in **Table 2** for the zeolites and **Table 3** for the SAPOs.

Figures S3-S5 contain the TGA profiles of the fresh CHA-type materials (SSZ-13 and SAPO-34) as well as the fresh ERI-type samples. The corresponding mass losses due to the OSDA removal from heating in air (calculated from the mass losses between 300 and 800 °C) demonstrate that all catalysts contained ca. 10-20% OSDA (**Tables 2 and 3**). These organics were fully removed by approximately 600 °C.

Table 2. Characterization data of the CHA-type and ERI-type zeolites tested.

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

[a] Measured by EDS on the thermally treated samples after undergoing ion-exchange. [b] Obtained by ²⁹Si NMR spectroscopy. [c] The UZM-12 sample contained a significant amount of extra-framework aluminum, thus, leading to a much higher framework Si/Al. [d] Measured from SEM. [e] Measured from XRD using Scherrer's equation. [f] Measured by TGA. This value reflects the mass loss between 300 and 800 °C in air either due to OSDA or coke removal. All MTO reactions were terminated once methanol conversion dropped below 85% or DME selectivity was higher than 50%. [g] Measured from N₂-physisorption. [h] Obtained by ¹H MAS NMR spectroscopy and referenced to hexamethylbenzene. [i] Residual K/Al after undergoing multiple ion exchanges as described in the Experimental Section.

Table 3. Characterization data of the SAPO-34 and SAPO-17 materials.

Sample ID	Gel		Product ^[a]			Particle Size (μm) ^[b]	Crystallite Size ($\text{\AA}$) ^[c]	OSDA mass loss (wt%) ^[d]	V_{micro} (cc/g) ^[e]	Brønsted Acid Site Density (ppm) ^[f]				Occluded Organics mass loss (wt%) ^[d]
	Si/T	Si/T ^[a]	Si	Al	P					3.6-3.7 (mmol/g)	3.9-4 (mmol/g)	4+ (mmol/g)	Total (mmol/g)	
SAPO-17-1	0.024	0.034	3.39	49.83	46.77	2x(2-10)	528	15.77	0.21	-	-	-	-	11.07
SAPO-17-2	0.048	0.042	4.19	49.38	46.43	1-3	385	17.36	0.26	0.068	0.056	0.069	0.192	10.05
SAPO-17-3	0.167	0.120	11.95	46.18	41.86	(0.1-0.4)x3	334	-	0.19	0.241	0.246	0.332	0.830	10.35
SAPO-17-4	0.095	0.103	10.32	49.51	39.90	2-4	277	20.03	0.18	0.479	0.291	0.162	0.927	11.16
SAPO-17-5	0.070	0.071	7.12	48.83	44.05	3-8	436	-	0.25	0.154	0.140	0.126	0.420	12.94
SAPO-17-6	0.070	0.073	7.32	48.48	44.21	1-10	443	18.49	0.26	0.154	0.160	0.131	0.445	10.49
SAPO-34	0.070	0.089	8.90	49.23	41.86	0.2-0.6	322	12.40	0.24	0.795	0.242	-	1.037	20.09

[a] Measured by EDS on the thermally treated samples. ($\text{Si/T} = \text{Si}/(\text{Si} + \text{Al} + \text{P})$) [b] Measured from SEM. [c] Measured from XRD using Scherrer's equation. [d] Measured by TGA. This value reflects the mass loss between 300 and 800 °C in air due to OSDA or coke removal. All MTO reactions were terminated once methanol conversion dropped below 85% or DME selectivity was higher than 50%. [e] Measured from N_2 -physisorption experiments. [f] Obtained by ^1H MAS NMR spectroscopy and referenced to hexamethylbenzene. [g] atomic percentages.

Figures S6 and **S7** show the powder XRD patterns for CHA-type and ERI-type materials, respectively. These patterns are in good agreement with simulated patterns (IZA database) as well as diffraction patterns reported previously for these two frameworks [25,60]. Minor shifts in the diffraction peaks are observed among the various ERI samples. These variations can be attributed to small differences in unit cell size caused by differences in composition in the final product and choice of OSDA in the synthesis procedure [25,60]. The Scherrer equation was used to calculate an averaged crystallite size (**Tables 2** and **3**). All ERI-type zeolite samples have crystallite sizes in the range of ca. 200 to 400 Å, which is slightly smaller than the crystallite size calculated for SSZ-13 (439 Å). The SAPO-17 samples have slightly larger crystallites (300-450 Å) than the zeolite samples, with SAPO-17-1 having the largest crystallite size at 528 Å.

All N₂ adsorption-desorption isotherms are shown in **Figures S8-S10**, and the obtained micropore volumes (V_{micro}) are shown in **Tables 2** and **3**. SSZ-13 (CHA) has a micropore volume of 0.29 cm³/g, which is larger than all the ERI-type zeolite samples (0.18-0.23 cm³/g). UZM-12, a sample with more defects (discussed further below), has a micropore volume of 0.15 cm³/g. All the SAPO samples tested in this work, irrespective of framework, have micropore volumes in the range of 0.18-0.26 cm³/g.

Particle/crystal size has been shown to be a parameter that affects MTO catalytic activity, as particle size reduction from micro to nano often leads to a delay in catalyst deactivation [74,75]. Therefore, SEM was used to determine particle sizes and morphological features (**Figure S11-13**, and **Tables 2** and **3**). **Figure S11** shows that the CHA-type samples (SSZ-13 and SAPO-34) consist of particles that are mostly cubic-like, with the SSZ-13 sample containing heavily overlapped cuboids. The specific particle sizes for the CHA-type materials are 3-6 µm and 0.2-0.6 µm for SSZ-13 and SAPO-34, respectively.

Figure S12 shows the SEM images of the ERI-type zeolite samples, revealing that they consist of particles that vary by size from a micron (SSZ-98 samples and ERI zeolite-1) to a nanometer range (UZM-12 and ERI zeolites-2 and 3) and by morphology from quasi-spherical (rice grain-like) to rod-like to needle-

like, depending on the gel composition (e.g., K/Al, Si/Al, [OH]⁻/Si, etc.) and the type of OSDA utilized for synthesis. Similar to the ERI-type zeolite materials, the SAPO-17 samples exhibited differences in particle size (albeit to lesser extent than their zeolitic counterparts; 1-10 μm) and morphology. Particularly, SAPO-17 samples with lower Si content formed elongated hexagonal-like structures, but with increasing Si content, the SAPO-17 morphology either shortened or transformed to appear more zeolite-like, consisting primarily of rod-like particles (e.g., SAPO-17-3) (**Figure S13**).

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

Table 3 shows the elemental composition of the SAPO-17 samples. The data show that increasing the Si content results in a simultaneous reduction in P and Al. SAPO materials are obtained by isomorphous replacement of P by Si (or Al and P for two Si atoms), depending on the Si incorporation mechanism. When a Si atom is incorporated into a P position (referred to as SM2), a Si(4Al) environment is formed [17,18]. This replacement of pentavalent P by tetravalent Si generates a negative charge which is compensated for by a proton in the thermally treated sample, thus, creating a Si-OH-Al bridging hydroxide which acts as a Brønsted acid site. On the other hand, the Si incorporation via SM3, in which the incorporation of Si occurs in an island, and quantitatively (but not mechanistically) substitution of two Si atoms for a pair of Al and P atoms occurs to preserve the charge neutrality of the framework [18]. Therefore, the concentration and strength of the Brønsted acid sites in the SAPO samples (discussed in more depth subsequently) depends on the relative contribution of each mechanism.

The elemental composition results listed in **Table 3** show that the choices of the OSDA, crystallization conditions, and starting gel (e.g., Si content) play a consequential role in influencing the

relative contribution of each Si substitution mechanism (SM2 and SM3). In particular, two observations can be made from the elemental composition data in **Table 3**: (i) in all cases, increasing the Si content results in a higher contribution from the SM3 mechanism, as evidenced from the reduction in Al in the product and an increase in the (Si+P)/Al ratio, which was greater than 1 for all the samples, and (ii) SAPO-17-4 favors the SM2 mechanism. Overall, the SAPO-17 samples synthesized in this work contained different Si/T values (up to 0.12), thus allowing us to investigate the effect of this parameter on MTO activity.

^{29}Si MAS NMR spectroscopy was used to identify the different silicon environments present in the thermally treated samples prior to undergoing reaction, and to calculate framework Si/Al for the zeolites. **Figure S14** shows the ^{29}Si MAS NMR spectra for SSZ-13 and SAPO-34. For the SSZ-13 sample, four primary resonances at -112, -106, -101 and -100 ppm are observed that correspond to Si(0Al), Si(1Al), Si-OH defects, and Si(2Al) [76,77]. Deconvolution of the spectra (an example of the deconvolution is shown in **Figure S15**) enabled the calculation of the framework Si/Al=15 (**Table 2**). Indeed, this value is within a close range of the bulk Si/Al obtained from EDS (Si/Al=12.11). On the other hand, the spectra for SAPO-34 shows five bands centered at -92, -97, -101, -106, and -111, corresponding to the presence of Si(4Al) (isolated Si atoms), Si(3Al), Si(2Al), Si(1Al) and Si(0Al) (silicon islands) (**Figure S14d**).

Figure 2 shows the ^{29}Si MAS NMR spectra for the ERI-type zeolite samples. Several peaks are observed corresponding to Si(0Al), Si(1Al), Si(2Al), Si-OH defects, and Si(3Al). The peak assignments and deconvolution of the ERI-type zeolites spectra were different than SSZ-13, as discussed in the Experimental Section. The deconvolution procedure for ERI-type materials led to the fits shown in **Figure S16** and the framework Si/Al values shown in **Table 2**. Deconvolution of ^{29}Si MAS NMR spectra and subsequent use of Löwenstein's rule to calculate the Si/Al for ERI-type materials led to significantly lower Si/Al values than those obtained by EDS, which has previously been observed for related frameworks (e.g., OFF and SWY) [72,78].

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

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

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

^{27}Al NMR analyses were performed on the ERI-type zeolite samples as well as SSZ-13. The spectra in **Figure 2b** for ERI-type zeolites and **Figure S14b** for SSZ-13 show that all samples tested in this work have a strong resonance at 58 ppm, which corresponds to tetrahedrally coordinated Al in the zeolite framework, and a weaker resonance near 0 ppm, indicative of extra-framework Al. UZM-12 is the only sample that contains a significant amount of extra-framework Al as demonstrated by ^{27}Al NMR, in agreement with the vast difference observed in **Table 2** between the bulk Si/Al from EDS and the framework Si/Al from ^{29}Si MAS NMR.

^1H MAS NMR experiments were performed on the dehydrated samples and the obtained spectra are shown in **Figure S14** for CHA-type materials and in **Figure S17** for selected ERI-type zeolites and SAPO-17 materials. Several examples of deconvolution representing each class of material are shown in **Figures S15** and **S16**. For all zeolite spectra, multiple resonances were observed. A resonance near 1.8 ppm that corresponds to protons in silanols (Si-OH) was detected in most samples [79,80]. Additionally, due to the high Al content of many of the samples tested in this work, resonances for protons in aluminum-rich (e.g.

extra-framework Al) environments were present between 2 and 3.5 ppm, in agreement with the ^{27}Al NMR measurements (discussed previously) [80]. A main resonance near 4 ppm (for zeolites) was present, that originates from bridging hydroxyl groups that form from tetrahedrally coordinated Al (i.e., Al incorporated into the framework). Another peak was present in ERI zeolites near 4.3 ppm. For zeolite samples, deconvolution of the 4 and 4.3 ppm peaks gave rise to the total Brønsted acid site density values shown in **Table 2**.

For the SAPO-17 and SAPO-34 samples, two main peaks consistent with two differently formed acid sites were present in ^1H MAS NMR spectra : a weaker acid site showing a dominant resonance at ca. 3.6-3.7 ppm which corresponds to SAPO domains, that is, Si substituting for P (SM2), and a stronger acid site showing a resonance at 3.9-4 ppm, which corresponds to zeolite-like domains (i.e., two Si atoms substituting for an Al and a P pair) (SM3) [81–83]. In addition to these two acid-site peaks, a third small peak was observed near 4.3 ppm in ERI. Deconvolution of all of these peaks gave rise to the total acid site density values in NMR shown in **Table 3** for the SAPO samples.

Figures S18-S20 show the organic mass losses of the deactivated catalysts (defined as when methanol conversion falls below 85% or DME selectivity surpasses 50%) as determined by TGA. The organic mass losses shown in **Tables 2** and **3** were calculated based on the mass losses between 300 and 800 °C in air. The TGA results show that mass losses for CHA-type materials (20%) were higher than the ERI-type zeolites (10-15%). Additionally, the SAPO-17 catalysts accumulated slightly lower organic content than the ERI-type zeolites (<13%).

3.2. MTO Catalytic Activity

The reaction results for the two CHA-type and twelve ERI-type samples are summarized in **Table 4**. **Figure 4** shows the MTO product distributions of the evaluated materials before deactivation (when methanol conversion is greater than 97%). The time-on-stream (TOS) profiles are also provided in the SI section (**Figures S21-S23**).

Table 4. Reaction results of the molecular sieves investigated.

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

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

To establish a benchmark for the product distributions analysis, SSZ-13 and SAPO-34 were both tested for MTO at identical reaction conditions as those for ERI-type materials. Both SSZ-13 and SAPO-34 showed results consistent with literature data for those materials. SAPO-34 shows high stability (i.e., long lifetime), low alkane products, and high combined ethylene (35%) and propylene (41%) selectivities while SSZ-13 gives a shorter lifetime than SAPO-34, high initial propane (due to paired acid sites),^[25] and a slightly lower cumulative ethylene (33%) and propylene (40%) selectivities than SAPO-34 [25]. Additionally, results in **Table 4** and **Figure S21** show that both SSZ-13 and SAPO-34 form ca. 10% butenes and 7% C₅+

Figure 4 illustrates the product distributions of the ERI-type materials tested. The data show that ERI-type zeolite materials and SAPO-17 behave very differently, with the zeolite samples (stronger acid sites as demonstrated in the previous section via ¹H MAS NMR) registering significantly higher E/P values. In fact, E/P increases monotonically, irrespective of other material properties, from 1.12 for ERI Zeolite-3 (Si/Al=9) to an E/P maximum of 1.86 for SSZ-98-1 (framework Si/Al=5). Thus, the olefins product distributions from ERI-type zeolites appear to be highly sensitive to the framework Si/Al.

Figure 4. MTO product distributions for ERI- and CHA-type molecular sieves. (a) MTO product distributions when methanol conversion is over 97% for ERI zeolites (top) and SAPO-17 (bottom). (b) Relationship between framework Si/Al (as determined by ^{29}Si MAS NMR) and ethylene-to-propylene selectivities ratio (E/P) for the zeolites tested in this work. (c) Relationship between (Al+P)/Si (as determined by EDS) and E/P for SAPOs tested in this work.

Closer inspection of the data in **Figure 4a** shows that the apparent change in E/P as a function of framework Si/Al for ERI-type zeolites is primarily the result of changes in the ethylene selectivity. Indeed, over the tested range (Si/Al=5-9), the propylene selectivity marginally changes as a function of Si/Al, increasing only from 22 to 26% with decreasing Al content, whereas the ethylene selectivity decreases from 41% to 29%. Furthermore, paralleling the loss in ethylene selectivity are increases in the selectivity to C₅+ and decreases in the selectivities to light alkanes (mainly, propane). The latter could be due to the decrease in paired acid sites [25]. The only material that slightly deviates from this trend is UZM-12, a sample that registers slightly elevated C₅+ in comparison to ERI Zeolite-1 and ERI Zeolite-2. However, it is

worth noting that the UZM-12 sample tested in this work contained quite a bit of extra-framework aluminum and a comparatively lower pore volume, as discussed previously.

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

The promising behavior of ERI-type zeolites in enhancing the ethylene selectivity in MTO prompted us to investigate SAPO-17 as a molecular sieve that is isostructural to ERI-type zeolites but with milder acid sites. The data in **Figure 4a** (bottom), however, shows that the improved E/P exhibited in the ERI-type zeolites did not carry over to the SAPO-17 materials. In fact, the low acid site density combined with the low acid strength of several SAPO-17 samples ($Si/T < 0.07$) eliminated the ethylene enhancement effect observed for ERI-type zeolites, resulting in an $E/P < 0.9$. For instance, SAPO-17-1 ($Si/T = 0.034$) formed almost three times more C_5+ than SSZ-98-1 and almost half the amount of ethylene. To improve these selectivity numbers in favor of lighter olefins and less bulkier molecules, acid site density in SAPO-17 was systematically increased by increasing the Si/T as permitted by the gel composition. As shown in **Table 4**, increasing Si/T results in a gradual increase in the E/P, irrespective of other material properties. Particularly, in the samples with low Si content ($Si/T < 0.04$), a combined increase in ethylene and a decrease in propylene is observed. On the other hand, samples with higher Si content ($Si/T > 0.04$) appeared to improve the E/P mainly by decreasing the propylene selectivity.

A closer look at the TOS data shown in **Figure S23** demonstrates that increasing Si/T (or decreasing $(Al+P)/Si$) improves the E/P by allowing the olefins product distribution to switch from a C_3+ rich regime, where ethylene is low but other hydrocarbons are high, to a C_2 -rich regime, where ethylene is the

predominant product. Allowing this switch to occur quicker by manipulating the Si content in SAPO-17 (and therefore the catalyst acid site density, as discussed previously) results in higher initial (minimum) and final (maximum) E/P and an overall lower C_5^+/C_2^+ .

In spite of their slightly longer lifetimes, the SAPO-17 catalysts tested in this work were incapable of enhancing the ethylene selectivity in MTO to the extent that ERI-type zeolites with low Si/Al were able to. Indeed, the best performing ERI-type SAPO catalyst in this work, in terms of having the highest ethylene to propylene selectivity, was SAPO-17-3 ((Al+P)/Si=7.4), which also happens to be the catalyst with the highest Si/T=0.12. This catalyst gave an E/P of 1.1 and an overall product distribution that was almost identical to that of ERI Zeolite-3 (framework Si/Al=9.25), the worst performing zeolite in this work (**Table 4**).

To test if further reduction in acid site density of ERI-type zeolites would form materials that resemble SAPO-17s with lower Si contents ($0.06 < \text{Si/T} < 0.12$), two additional experiments were performed. Specifically, instead of performing seven ion exchanges on ERI Zeolite-2 and ERI Zeolite-3 to lower the K/Al to the lowest possible value, only two ion exchanges were performed. These two samples are denoted as ERI Zeolite-2-IE2 and ERI Zeolite-3-IE2. By reducing the number of times a sample is ion exchanged, we aimed to retain a higher amount of potassium ions and thus effectively reduce the number of protons in the framework (i.e., acid site density). The EDS results for these two samples show that ERI Zeolite-2-IE2 has a K/Al of 0.31 whereas ERI Zeolite-3-IE2 has a K/Al of 0.34. The MTO reaction TOS data for these two catalysts are shown in **Figure S25**. As expected, these two catalysts behaved like SAPO-17 with low Si content, resulting in high C_3^+ and low ethylene, especially in early stages of the reaction. Particularly, the averaged E/P measured for ERI Zeolite-2-IE2 and ERI Zeolite-3-IE2 were 0.98 and 0.71, respectively. The experimental results in this section clearly indicate that in order to improve the E/P in ERI-type molecular sieves over CHA both acid site density and strength ought to be controlled.

3.3. Relationships between Effluent Product and Retained Hydrocarbons Selectivity

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

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

Figure 5. GC-MS distribution of the extracted hydrocarbon species grouped by ring number/type for six molecular sieves (two CHA-type and four ERI-type materials are shown) after 30 minutes of reaction with methanol at 400 °C and WHSV of 1.3 h⁻¹. (a) Overall hydrocarbon distribution and relative concentration

of the aromatic species retained at TOS=30 mins. All concentrations measured were relative to the aromatics concentration measured for SAPO-34 after 30 minutes of reaction (dashed yellow line). (b) Distribution of methylbenzenes and 1-ring hydrocarbons. (d) Distribution of naphthalenes, methylnaphthalenes and 2-ring hydrocarbons. Legend: MB, methylbenzenes; N, naphthalenes; MN, methylnaphthalenes; the number before an abbreviation denotes the number of methyl groups.

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

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

the reaction data showed large quantities of C_5^+ , led us to consider the possibility of a contribution from the olefin cycle.

Figure 5a shows the relative concentration of the soluble aromatics for the six aforementioned catalysts. The aromatics concentration measured for SAPO-34 at TOS=30 mins was used as a basis for comparison against the extracted aromatics concentrations for the other catalysts (reported as relative concentration). The data show that materials with low acid site density, that is, ERI Zeolite-3 and SAPO-17-2, have low relative aromatic concentrations (i.e., lower than SAPO-34), with SAPO-17-2 having the lowest aromatic concentrations of all tested catalysts. SAPO-17-2 also has the second lowest E/P = 0.73 of all catalysts tested. On the other hand, SSZ-98-1, the catalyst with the highest acid site density and strength, had the highest aromatic concentration and the highest E/P (**Figure 5**). In addition to the differences observed in the relative concentration of the aromatic species, the ERI samples (particularly those with higher Si/Al or low Si/T) formed a more diverse set of 1-ring and 2-ring species and in larger quantities. These 1- and 2-ring species are denoted in the data of **Figure 5** as other 1-ring and other 2-rings, respectively. Species belonging to these two categories contained bulkier alkyl groups than methyl (e.g., ethyl, isopropyl, or isobutyl). Often, these intermediates contained 0-3 methyl groups and 1-2 alkyl (excluding methyl) groups.

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

monotonically increases as a function of TOS. Similar to the MBs, the concentration of the MNs also decreases with increasing TOS. Of the MN formed, tetra-methylnaphthalene (4MN) is the predominant naphthalene-type product recovered via this analysis.

Interestingly, the SAPO-17-2 behaved very differently than SSZ-98-1. As the reaction proceeds, the composition of the entrained MBs in SAPO-17-2 does not dramatically change as in SSZ-98-1. In fact, the 4MB/(5MB+6MB) ratio is fairly constant for all three TOS measurements (despite changes in the E/P and the overall concentration of the MBs). Since 4MB, 5MB, and 6MB are associated with the aromatics cycle (but not the olefins cycle), the fact that the 4MB/(5MB+6MB) ratio falls short in predicting the E/P observed in SAPO-17-2 is very likely due to a substantial contribution from the olefins cycle. Moreover, as the MBs levels are reduced with increasing TOS for SAPO-17-2, the amount of naphthalenes and MN increases. Significant amounts of alkylated benzenes and naphthalenes with groups larger than methyl are also present in the SAPO-17-2 sample, and in much larger quantities than in SSZ-98-1. These intermediates, at least in part, could be contributing towards the observed low C_2/C_3 and high C_5+/C_2 in SAPO-17 with low Si/T by splitting off larger product molecules upon their dealkylation. The narrower yet longer ERI cage (compared to CHA) and the absence of the double-6-rings (d6r) separating the ERI cages from each other like in CHA are likely the main reasons behind the formation of these species in SAPO-17 and ERI-type zeolites (**Figure S26**).

The aromatic concentrations at each TOS for SAPO-17-2 are about half of that of SSZ-98-1, thus, the accumulation of aromatics is lower in the SAPO-17 materials with low Si/T than in the ERI-type zeolites with low framework Si/Al. These differences in the aromatics concentrations and identities influence the olefins products distributions during the reaction period, leading to different deactivation profiles. **Figure S27** shows the GC-MS distribution of the deactivated catalysts. All the ERI-type materials contained a wide host of 3-rings and 4-ring compounds with up to 3 methyl groups. The distribution of the 3- and 4-ring hydrocarbons (primarily, anthracene-, phenanthrene-, and pyrene-type) accounted for approximately 40+

mol% of the retained aromatics for ERI-type molecular sieves. Interestingly, the SSZ-98-1 catalyst with the lowest framework Si/Al contained less than 10 mol% MBs upon deactivation and approximately 20 mol% MNs. This value was much lower than the other catalysts tested in this work and is five times lower than CHA, both SSZ-13 and SAPO-34.

The results herein combined with the reaction data in the previous section demonstrate that changes in acidity have a substantial role in controlling the rate of formation of aromatic compounds in ERI-type materials and their corresponding compositions. These effects together influence the E/P in ERI-type molecular sieves. Indeed, ERI-type materials with higher acid strengths and densities are required to suppress the olefins cycle and to shift the MTO product distribution in favor of ethylene (**Scheme 1**).

Figure 6. GC-MS distribution of the extracted hydrocarbon species grouped by ring number/type for two molecular sieves (SSZ-98-1 and SAPO-17-2) after 15, 30, and 60 minutes of reaction with methanol at 400 °C and WHSV of 1.3 h⁻¹. (a,d) Overall hydrocarbon distribution and relative concentration of the aromatic species retained for SSZ-98-1 and SAPO-17-2. All concentrations measured were relative to the aromatics concentration measured for SAPO-34 after 30 minutes of reaction. (b,e) Distribution of methylbenzenes and 1-ring hydrocarbons. (c,f) Distribution of naphthalenes, methyl naphthalenes and 2-ring hydrocarbons. Legend: MB, methylbenzenes; N, naphthalenes; MN, methyl naphthalenes; the number before an abbreviation denotes the number of methyl groups.

Scheme 1. Reaction mechanism in ERI-type Catalysts.

4. Conclusion

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

distributions that contained either high C_3+ or high $C_2=$. Specifically, it has been shown in this work that in addition to topological features, ERI-type zeolites with low framework Si/Al (<7), and thus specific acid strengths and densities, enhance the E/P over CHA-type materials.

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

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The Caltech authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. S.I. Zones is an employee of the Chevron Corporation.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dr. Zones is an employee of Chevron. Caltech investigators have not competing financial interests.

Methanol-to-Olefins Catalysis on ERI-Type Molecular Sieves: Towards Enhancing Ethylene Selectivity

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Highlights

- ERI-type molecular sieves enhance ethylene selectivity in MTO.
- Acidity significantly influences ethylene-to-propylene ratio in ERI-type materials.
- Changes in acidity alter hydrocarbon-pool species concentration and composition.
- Low acid site densities hinder the formation of aromatics (thus, ethylene) in ERI.

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