A mechanistic basis for the effect of aluminum content on ethene selectivity in methanol-to-hydrocarbons conversion on HZSM-5

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Abstract

Increasing crystallite size or aluminum content in MFI-type zeolites independently enhances the propagation of the aromatics-based methylation/dealkylation cycle relative to that of the olefins-based methylation/cracking cycle in methanol-to-hydrocarbons (MTH) conversion and consequentially results in higher ethene selectivity. We report that ethene selectivity increases monotonically with increasing aluminum content for ZSM-5 samples with nearly identical crystallite size as a follow-up to our recent report detailing the effects of crystallite size (J. Catal. 321 (2015) 23) on MTH selectivity. We also propose that the confected effects of crystallite size and acid site density on MTH selectivity can be correlated using a descriptor that represents the average number of acid sites that an olefin-precursor will interact with before elution.

Keywords: Methanol-to-hydrocarbons, methanol-to-olefins, zeolites, MFI, ZSM-5, silicon to aluminum ratio, ethene selectivity

1. Introduction

The catalytic conversion of methanol or dimethyl ether (DME), its dehydration product, irrespective of zeolite topology proceeds autocatalytically with olefins- and aromatics-based intermediates, constituting the so-called hydrocarbon-pool, acting as organic co-catalysts in carbon-carbon bond formation events[1–5]. The complex network of reactions for methanol conversion over microporous solid acid catalysts is summarized by dual catalytic cycles where the olefins-based chemistries of methylation and β -scission are coupled with aromatics-based chemistries of methylation and dealkylation by hydrogen transfer and cyclization events[6–12]. The product distribution in MTH conversion on MFI framework materials is sensitive to, e.g., reaction temperature[6,13], acid site density[14,15], textural properties[16,17], and feedstock identity[13,18–20]. Mechanistically these effects of catalyst composition and morphology and of process conditions can be rationalized as a consequence of the relative extents of propagation of the olefins- and the aromatics-based methylation/cracking cycles[13]. Previously we have ascribed the effects of temperature[13], feedstock composition[13,18,21], reaction conditions[22], and crystallite size [23] on MTH product selectivity to either an enhancement in the number of chain carries of the olefins- or aromatics-based cycles or to transport restrictions which selectively enhance the propagation of the aromatics-based cycle relative to that of the olefins-based cycle. A mechanistic basis relating zeolite morphology and composition to the complex hydrocarbon chemistry in MTH described by the dual-cycle schematic necessitates that:

- (i) we ascribe terminal products to the olefins- and aromatics-based cycles and relate the yield of these products to the relative propagation of the two catalytic cycles;
- (ii) we evaluate the catalyst under process conditions when the dual-cycle mechanism has been reported to propagate. Specifically, aromatic-dealkylation steps do not

occur in absence of methanol[22] implying that the dual-cycle mechanism only operates at sub-complete methanol/ dimethyl ether conversion; and

- (iii) we attribute a consequence of a material or process parameter on the selective propagation of the olefins- or aromatics-based cycles under conditions that isolate the effect of this material or process parameter.

Isotopic switching experiments by Svelle, Bjørngen, and coworkers [24–26] on HZSM-5 in which ^{12}C -methanol feed was switched with ^{13}C -methanol feed during steady state reaction showed that post-switch the ^{13}C -content of ethene closely matched that of MBs, and that of C_3^+ olefins matched each other. Ilias et al.[13] showed that ethene reacted ~ 20 times slower than DME for the reaction of $^{13}\text{C}_2$ -DME (~ 70 kPa) and 7 – 8 kPa of $^{12}\text{C}_2$ -ethene mixtures on HZSM-5 at 623 K. Additionally, kinetic measurements by Hill et al.[27–29] and Svelle et al.[30,31] have shown that the rate of ethene methylation is at least an order of magnitude slower than propene or butene methylation on HZSM-5 suggesting that ethene can be considered a terminal product of the aromatics-based catalytic cycle.

Isotopic switching experiments by Svelle, Bjørngen, and coworkers [24–26] also showed that the time-evolution of ^{13}C -incorporation in C_3^+ olefins was similar suggesting that olefins like isobutene and 2-methyl-2-butene are products of the olefins-based catalytic cycle. Min et al. [32] showed that the isotopic content in ethene was distinct from that in C_3^+ olefins when ^{14}C -methanol was co-processed with ^{12}C -labeled ethanol, 1-propanol, or 1-pentanol, on H-ZSM-5 at 453 – 573 K. Olefins (e.g. 2-methyl-2-butene) subsequently form alkanes (e.g. 2-methylbutane) via hydrogen transfer reactions. The selectivity to 2-methyl-2-butene and to 2-methylbutane in MTH is dependent on the extent of hydrogen transfer, however, we have shown that the sum of the yields of 2-methylbutane and 2-methyl-2-butene (2MBu) is largely independent of chemical

conversion[13] and, that ethene/2MBu varies systematically and predictably with reaction temperature[23], feedstock composition[13,21], and crystallite size[23].

Khare et al.[22] investigated the catalytic reaction of DME on a diffusion-free MFI zeolite at 723 K and showed that aromatics do not dealkylate in the absence of methanol or DME once complete DME/methanol conversion is achieved and the dominant chemistry under these reaction conditions is olefin inter-conversion. A mechanistic understanding of the influence of zeolite morphology or composition on MTH selectivity in terms of the dual cycle hydrocarbon-pool mechanism can therefore only be inferred from data acquired under reaction conditions where both the catalytic cycles are active i.e. sub-complete DME/methanol conversion conditions.

Here we report the effects of aluminum content in HZSM-5 on ethene selectivity for DME conversion at 623 K using five ZSM-5 samples with similar crystallite size (150 – 240 nm) with the underlying postulate that increasing the concentration of active sites will increase the propagation of the aromatics-based catalytic cycle. An increase in aluminum content will increase the number of interactions between methylbenzenes (which are precursors to light olefins) and Brønsted acid sites before these aromatics exit the zeolite crystallite. This increase in the number of interactions enables polymethylbenzenes (MBs) to undergo multiple methylation/dealkylation reaction cycles and produce light olefins, especially ethene, in the process, thereby increasing its selectivity in the product distribution. We also propose a single-value descriptor (N_{H+}), which conflates the effects of crystallite size and aluminum content on ethene selectivity for DME conversion on MFI-type zeolites.

2. Materials and methods

2.1. Synthesis of HZSM-5 zeolite samples

Five HZSM-5 samples with similar crystallite size (150 – 240 nm), and Si/Al varying between 55 and 1580 were synthesized via hydrothermal synthesis protocols according to a previously reported procedure [33,34]. These samples are referred to as HZSM-5-*X*, where *X* corresponds to Si/Al in the materials as determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The detailed synthesis procedure is described in the Supplementary Information section.

2.2. Structural and chemical characterization of ZSM-5 samples

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using Cu-K α radiation (1.54 Å) for 2θ between 5° and 35°. Transmission electron microscopy (TEM) was performed on a FEI-Tecnai T12 microscope operated at 120 KV. Elemental composition of the zeolite samples was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Thermo Fischer iCap 7000 instrument. The samples were digested in HF prior to the analysis and diluted 10 – 100 times to achieve concentrations of Si or Al between 1 – 10 ppm. NH₃ temperature programmed desorption (TPD) was performed to estimate the concentration of Brønsted acid sites. The detailed procedure and results for NH₃-TPD are reported in the Supplementary Information section.

Argon adsorption-desorption isotherms were measured on a Micromeritics 3 Flex Surface Characterization Analyzer at 87 K. Prior to the adsorption-desorption measurements, the samples were outgassed at 673 K for 8 h under high vacuum. The total surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Surface area of the micropores was estimated by the

NLDFT method. Total pore volume was measured at the absorption pressure $P/P_0 = 0.95$, and the micropore volume (<1.5 nm) was estimated using the NLDFT method.

Adsorption uptake of 2,2-dimethylbutane (2,2-dmb) was measured to estimate the effective diffusivity (D_{eff}) of 2,2-dmb in ZSM-5 at 298 K and the average crystallite size of the synthesized ZSM-5 samples. Adsorption of 2,2-dmb was performed on a Micromeritics ASAP 2020 surface area and porosity analyzer equipped with a vapor option using the rate of adsorption software. Prior to analysis, the catalyst samples (~25 mg) were outgassed at 723 K for 4 h under high vacuum. The adsorption data were collected at 298 K and 13 – 15 kPa 2,2-dmb pressure. The 2,2-dmb vapor source was kept at a temperature of 303 K.

2.3. Catalytic reactions on a packed-bed reactor

Catalytic reactions of DME were carried out in a 316/316L stainless steel packed-bed reactor (1/4 in OD; 0.035 in wall thickness) equipped with a concentric thermal well (1/16 in OD, 0.014 in wall thickness). Isothermal conditions were maintained in the catalyst bed using a heating coil (ARi Industries Inc., AeroRod[®] heating assembly) regulated by a Watlow 96 series temperature controller. A K-type thermocouple (Omega Engineering, 0.020 in probe diameter), inserted into the concentric thermal well, was used for measuring the temperature of the catalyst bed during the reaction. Reactions were performed using 13 – 45 mg catalyst diluted with ~100 mg quartz sand. Quartz sand (Acros Organics) was used as a diluent in the catalyst bed to prevent temperature rise due to the exothermic nature of MTH conversion. Prior to its use, the quartz sand was washed with 1 M nitric acid (Sigma-Aldrich), rinsed several times with deionized water, dried, and sieved between 40- and 80- mesh sieves to obtain uniformly sized particles. Prior to every reaction, the catalyst was pretreated in dry air ($1.67 \text{ cm}^3 \text{ s}^{-1}$, Minneapolis Oxygen, 20-21% O_2 , <10 ppm H_2O) at 823 K for 4 h. The temperature of the catalyst bed was

increased from ambient to 823 K in 8 h and was held at 823 K for 4 h before the sample was cooled to the reaction temperature. Following the pretreatment, the catalyst was flushed with helium ($1.67 \text{ cm}^3 \text{ s}^{-1}$, Minneapolis Oxygen, 99.995% purity) for 1 h.

The reactant stream constituted DME (Matheson Tri-Gas, 99.5% purity) and a mixture of CH_4 and Ar (Airgas, 10% CH_4 , 90% Ar) that was used as an internal standard. Gas flow rates were maintained using Brooks Instrument 5850S/SLA5850 series mass flow controllers. The space-velocity was varied between $0.3 - 2.5 \text{ mol C (mol Al-s)}^{-1}$ to achieve the desired chemical conversions (46 – 52%). Methanol was considered as a reactant in the calculation of net conversion. The total feed pressure was maintained at 103 – 106 kPa and all the reactions were carried out at 623 K. The temperature variation in the bed was less than 1 K during the reaction. The reactor effluent was analyzed using an online Agilent 7890A series GC (gas chromatograph) – Agilent 5975C series MS (mass spectrometer) equipped with a 100% dimethylpolysiloxane Agilent J&W HP-1 column ($50 \text{ m} \times 320 \text{ }\mu\text{m} \times 0.52 \text{ }\mu\text{m}$) connected to a flame ionization detector (FID) and a mass selective detector (MSD), and an Agilent J&W GS-GasPro column ($60 \text{ m} \times 320 \text{ }\mu\text{m}$) connected to a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Structural and chemical characterization

Table 1 shows Si/Al as determined from the ICP-OES elemental analysis and acid site density as determined from NH_3 -TPD measurements. The density of acid sites in each synthesized HZSM-5 sample is consistent with its Si/Al suggesting nearly complete incorporation of Al in the zeolite framework in these samples. The X-ray diffraction patterns of the synthesized HZSM-5 samples are presented in the Supplementary Information section and demonstrate that the synthesized samples are crystalline with an MFI-type framework. Figure 1

shows the TEM images of the ZSM-5 samples and confirms that the synthesized samples have nearly identical particle-size distributions despite the varying Al content. The particle sizes obtained from TEM images are reported in Table 1. Ar adsorption-desorption isotherms of the synthesized zeolite samples collected at 87 K are presented and the evaluated textural characteristics are summarized in the Supplementary Information section. The results show that the synthesized materials have similar total surface area ($412 - 443 \text{ m}^2 \text{ g}^{-1}$), micropore surface area ($379 - 415 \text{ m}^2 \text{ g}^{-1}$), total pore volume ($0.172 - 0.199 \text{ cm}^3 \text{ g}^{-1}$), and micropore volume ($0.125 - 0.140 \text{ cm}^3 \text{ g}^{-1}$).

3.2. Adsorption uptake measurements of 2,2-dimethylbutane

The average crystallite size for each of the synthesized HZSM-5 samples was estimated from the adsorption uptake of 2,2-dimethylbutane (2,2-dmb) at 298 K and 13 – 15 kPa 2,2-dmb pressure. The MFI-type zeolite framework consists of intersecting straight-channels ($0.51 \text{ nm} \times 0.55 \text{ nm}$) and sinusoidal-channels ($0.54 \text{ nm} \times 0.56 \text{ nm}$)[35,36]. The kinetic diameter of 2,2-dmb is 0.63 nm [37,38], which is close to the diameter of the pore-openings in MFI. The uptake rate of 2,2-dmb can therefore be used to estimate the crystallite size of zeolites with MFI-type framework[23,39]. The theoretical adsorption capacity of 2,2-dmb, which preferentially adsorbs in the channel intersections of MFI, is 4 molecules per unit cell or $\sim 60 \text{ mg g}^{-1}$ [39].

Figure 2 shows the adsorption uptake of 2,2-dmb on HZSM-5 samples at 298 K and 13 – 15 kPa 2,2-dmb pressure. The amount of 2,2-dmb adsorbed was normalized to the theoretical adsorption capacity of 2,2-dmb in ZSM-5. Assuming spherical crystallites (with diameter equal to the crystallite size of the zeolite), a simple Fickian diffusion model can be used to describe the uptake of 2,2-dmb in ZSM-5. For isothermal conditions and in the absence of other transport restrictions, the concentration profile inside the zeolite crystallite is given by Equation 1[40,41],

$$\frac{C(r,t)}{C_{\infty}} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \left[\frac{(-1)^n}{n} \sin\left(\frac{n\pi r}{R}\right) \exp\left(-\frac{D_{\text{eff}} n^2 \pi^2 t}{R^2}\right) \right] \quad (\text{Eq. 1}),$$

where $C(r,t)$ is the concentration of 2,2-dmb inside the spherical particle, r is the radial coordinate, t is the temporal coordinate, D_{eff} is the effective diffusivity of 2,2-dmb in MFI framework at 298 K, and C_{∞} is the saturation capacity of 2,2-dmb in ZSM-5 samples.

The amount of 2,2-dmb adsorbed inside the zeolite can be obtained from Equation 1 by integrating $C(r,t)$ between $r = 0$ and $r = R$ [40,41],

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{1}{n^2} \exp\left(-\frac{D_{\text{eff}} n^2 \pi^2 t}{R^2}\right) \right] \quad (\text{Eq. 2}),$$

where M_t and M_{∞} are the adsorbed amount at time t and at saturation, respectively. Equation 2 (from $n = 1$ to $n = 100$) was fitted to the experimental data and six parameters – the crystallite size of all ZSM-5 samples as well as the diffusivity of 2,2-dmb in ZSM-5 at 298 K – were estimated. The estimated crystallite sizes of the zeolite samples are reported in Table 1. The diffusivity of 2,2-dmb was calculated to be $3 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ on ZSM-5 at 298 K. This value is similar to the values reported previously by Khare et al.[23] $\sim 9 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$, Cavalcante and Ruthven [42] $\sim 1 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$, Xiao and Wei[43] $\sim 4 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$, and Yu et al.[38] $\sim 5 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$.

3.3. Effects of aluminum content on ethene selectivity in MTH conversion

DME (at 49 – 57 kPa pressure) was reacted on HZSM-5 samples at 623 K and 103 – 106 kPa total feed pressure. DME space-velocity was varied between 0.3 – 2.5 mol C (mol Al-s)⁻¹ to achieve iso-conversion (46 – 52% net DME conversion). The detailed product distribution is reported in the Supplementary Information section. Figure 3 shows ethene selectivity, propene selectivity, and ethene/2MBu, as a function of silicon-to-aluminum ratio. Ethene selectivity increased monotonically from 5.7% to 16% and the total light olefin selectivity increased from

23% to 38% as Si/Al decreased from 1580 to 55. Ethene/2MBu also increased monotonically from 0.80 to 2.4 with decreasing Si/Al indicating that preferential propagation of the aromatics-based catalytic cycle occurred in HZSM-5 samples with higher aluminum content. These results support our postulate that a decrease in Si/Al or an increase in Al content increases the propagation of the aromatics-based catalytic cycle and consequentially results in higher ethene selectivity. It must be noted that a higher concentration of acid sites within the zeolite may (i) increase the concentration of aromatics inside the zeolite mediated by a higher probability of sequential chain growth-ring closure-hydride transfer reactions required to form aromatics, and/or (ii) increase the probability that an aromatic will interact with an acid site before exiting the zeolite crystallite. Both these effects will result in higher propagation of the aromatics-based catalytic cycle and therefore an increased selectivity towards ethene.

3.4. A single-value descriptor of ethene selectivity in MTH conversion

We have previously reported that ethene selectivity in MTH conversion increases monotonically with increasing crystallite size of MFI-type zeolites[23]. The results presented in section 3.3 show that ethene selectivity also increased monotonically with increasing Al content or decreasing Si/Al. The underlying mechanistic basis for these effects is the enhanced propagation of the aromatics-based catalytic cycle due to an increase in the number of interactions between MBs and Brønsted acid sites before these MB molecules exit the zeolite crystallite. Increasing Al content (or decreasing Si/Al) enhances the number of interactions by increasing the concentration of the active sites. Increasing the crystallite size, on the other hand, increases the number of interactions by increasing the intra-crystalline residence time of MBs. These two effects can be combined into a single-value descriptor (referred to as N_{H^+}) of ethene

selectivity, which represents the average number of interactions between a MB molecule and a Brønsted acid site before the MB molecule exits the zeolite crystallite.

The average number of interactions between a MB molecule and an active site before it exits the zeolite crystallite will increase with increasing crystallite size and decrease with increasing Si/Al in the zeolite. N_{H^+} therefore must be proportional to the ratio of the crystallite size (in nm) of the zeolite and the Si/Al ratio of the material;

$$N_{H^+} = \frac{\text{Crystallite size (in nm)}}{\text{Si/Al}} \quad (\text{Eq. 3})$$

The assumptions involved in this formulation of the N_{H^+} parameter are presented in greater detail in the Supplementary Information section. Figure 4 shows ethene selectivity and 2MBu selectivity as a function of N_{H^+} for the reaction of DME on HZSM-5 samples at 623 K, 49 – 66 kPa DME pressure, and 46 – 59% net DME conversion. Ethene selectivity increases systematically with an increase in the value of N_{H^+} supporting our postulate that the effects of aluminum content and crystallite size on ethene selectivity can be described using a construct that posits that the aromatics-based catalytic cycle propagates to a greater extent due to an increase in the interactions between acid sites and MBs. The results shown in Figure 4 are based on crystallite sizes derived from 2,2-dimethylbutane adsorption uptake measurements for the calculation of N_{H^+} , however, the same trends are observed when crystallite sizes based on TEM data are used (Figure S4 of the Supplementary Information section) because of the nearly identical crystallite sizes (150 – 240 nm) of the zeolite samples used in this study.

The extent of propagation of the olefins-based catalytic cycle – represented by 2MBu selectivity – does not increase with increasing N_{H^+} . In general, olefins have a smaller kinetic diameter compared to MBs, for example, the kinetic diameter of isobutene is ~ 5.0 Å[44] while the kinetic diameter of 1,2,4-triMB is ~ 7.6 Å[45]. The average intra-crystalline residence time of

MBs is therefore longer than that for the olefins implying that an increase in crystallite size affects the intra-crystalline residence time of MBs to a greater extent than that of olefins. Correspondingly, the propagation of the aromatics-based cycle is enhanced relative to the propagation of olefins-based cycle with increasing N_{H^+} . In the olefins-based catalytic cycle, light olefins methylate or oligomerize to form higher olefins that undergo β -scission to form light olefins – these olefin-interconversion reactions render the selectivity of olefins largely invariant with the extent of propagation of the olefins-based catalytic cycle[22]. In the aromatics-based catalytic cycle, however, MBs undergo methylation/dealkylation reactions and form ethene (which is less reactive compared to C_3^+ olefins) [27,28,30,31] without getting consumed themselves. An increase in N_{H^+} enhances the propagation of both the catalytic cycles, however, the propagation of the aromatics-based catalytic cycle is enhanced relative to the propagation of the olefins-based catalytic cycle and therefore results in higher selectivity towards ethene, as observed experimentally.

4. Conclusions

Ethene selectivity, for DME conversion at 623 K and 46 – 52% DME iso-conversion on five HZSM-5 samples with similar crystallite sizes (150 – 240 nm) and Si/Al varying between 55 and 1580, increased from 5.7% on the HZSM-5 sample with low aluminum content (Si/Al = 1580) to 16% on the HZSM-5 sample with high aluminum content (Si/Al = 55). The mechanistic basis for this increase in ethene selectivity with increasing aluminum content is an increase in the number of interactions between active sites and MBs before these MB molecules exit the zeolite crystallite. Ethene/2MBu also increased monotonically from 0.8 on an HZSM-5 sample with low aluminum content (Si/Al = 1580) to 2.4 on an HZSM-5 sample with high aluminum content (Si/Al = 55). A single-value descriptor representative of the average number of active sites that a

MB molecule encounters before it exits the zeolite crystallite describes the combined effects of aluminum content and crystallite size on ethene selectivity for DME conversion on MFI-type zeolites.

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Tables

Table 1. Silicon-to-aluminum ratio, acid site density, and particle/crystallite size of HZSM-5 samples investigated in this work.

Zeolite sample	Si/Al ^a	Acid site density / $\mu\text{mol g}^{-1}$		Particle size ^c	Crystallite size ^d
		from ICP-OES ^b	from NH ₃ -TPD		
HZSM-5-55	55	298	308	179	210
HZSM-5-115	115	144	148	228	150
HZSM-5-651	651	25.6	27.3	218	180
HZSM-5-1119	1119	14.9	-	203	240
HZSM-5-1580	1580	10.5	-	213	230

^a Estimated from ICP-OES elemental analysis.

^b Assuming one Brønsted acid site per aluminum atom in the framework.

^c Estimated from TEM analysis.

^d Estimated from 2,2-dimethylbutane adsorption uptake measurements

Figures with captions

Figure 1. TEM images and particle-size distribution of (a) HZSM-5-55, (b) HZSM-5-115, (c) HZSM-5-257, (d) HZSM-5-1119, and (e) ZSM-5-1580.

Figure 2. Adsorption uptake of 2,2-dimethylbutane (2,2-dmb) on HZSM-5-55 ($\square$), HZSM-5-115 ($\triangle$), HZSM-5-651 ($\blacklozenge$), HZSM-5-1119 ($\circ$), and HZSM-5-1580 ($\blacktriangleright$), at 298 K and 13 – 15 kPa 2,2-dmb pressure. The adsorbed amount was normalized to the theoretical adsorption capacity of 2,2-dmb in ZSM-5. The solid lines represent the fits for the experimental data using Eq. 2.

Figure 3. Ethene selectivity (■), propene selectivity (■), and ethene/2MBu (◇), for DME conversion on HZSM-5 samples with similar crystallite size (150 – 240 nm) and Si/Al varying between 55 and 1580 at 623 K, 49 – 57 kPa DME pressure, and 46 – 52% iso-conversion.

Figure 4. Ethene selectivity (filled symbols) and 2MBu^a selectivity (open symbols) as a function of N_{H^+} – ratio of crystallite size (in nm) and Si/Al – for DME conversion on HZSM-5 samples investigated in this work (■, ◇) and zeolite samples investigated in reference [23] (◆, ◇) at 623 K, 49 – 66 kPa DME pressure, and 46 – 59% DME iso-conversion.

^a 2MBu = 2-methylbutane + 2-methyl-2-butene. A representative of the propagation of olefins-based catalytic cycle.