H. S. Lee et al.

Effect of Mesoporosity on Methanol-to-Olefin Reactions over Organosilane-Directed Mesoporous SSZ-13 Zeolites

Hae Sol Lee,[†] Sung Chan Nam,^{‡,*} and Changbum Jo ^{(b)†,*}

[†]Department of Chemistry and Chemical Engineering, Inha University, Incheon 22212, South Korea. *E-mail: jochangbum@inha.ac.kr [‡]Greenhouse Gas Laboratory, Korea Institute of Energy Research, Daejeon 34129, South Korea. *E-mail: scnam@kier.re.kr Received February 19, 2020, Accepted April 22, 2020

Keywords: Methanol-to-olefin, Mesoporous zeolite, SSZ-13 zeolites, Chabazite, Deactivation

Methanol to olefin (MTO) reactions are among the most promising pathways in C1 chemistry, which provides value-added olefins from synthesis gas via methanol. Tremendous research efforts have been devoted to MTO reactions since they were proposed by Mobil in 1977.¹ In particular, significant progress has been made in understanding reaction kinetics and mechanisms, and in the developments of efficient catalysts. Currently, the MTO process has been demonstrated on plant scale, and a methanol-to-propene process, developed by Lurgi, is ready for commercialization.²

Zeolites are a class of crystalline microporous aluminosilicates and are widely used as solid acid catalysts in petrochemistry because they possess catalytically active acid sites onto micropores and high (hydro)thermal stabilities.³ Zeolites can exhibit shape-selective functionality in some acid-catalyzed reactions, and shape-selectivity can be controlled using zeolite pore size, shape, and connectivity.⁴⁻⁶ However, microporous networks can retard the diffusion rates of chemical reagents due to their too narrow pore diameters and this causes pre-cokes to remain in micropores and thereby accelerate deactivation.⁷ For example, SSZ-13 zeolite with chabazite structure (micropore diameter, $0.37 \text{ nm} \times 0.42 \text{ nm})^8$ is rapidly deactivated during MTO reaction due to the deposition of carbonaceous cokes, which prevent methanol accessing active sites.^{9,10} Therefore, MTO processes typically require frequent catalyst regeneration, and unfortunately, catalyst regeneration irreversibly damages active acid sites, which further reduces initial catalytic activities.^{11,12} To avoid this situation, zeolite structures should be investigated in detail to prevent coke deposition and catalyst deactivation.

Hierarchically mesoporous-microporous zeolites (hereafter, referred to as denoted by mesoporous zeolites) are aluminosilicates with the characteristics of secondary mesoporosity and crystalline microporous structures. Several routes such as postsynthetic modification¹³ and the use of multiammoniumsurfactants as crystal-growth inhibitors^{14,15} and organosilanes as mesopore-generating agents^{16,17} have been devised for the production of high-quality mesoporous zeolite.¹⁸ These zeolites have several advantages over conventional zeolites, which include the rapid diffusion of reactants through mesopores. For this reason, mesoporous zeolites can provide significantly enhanced catalytic lifetimes over conventional zeolites in some reactions, which include MTO.¹⁹ However, it has been recently reported that mesoporous zeolites typically possess framework defects that reduce acid strength and hydrothermal stability,^{20–21} and for MTO reactions, hydrothermal stability is important as it enhances catalyst lifetime because the water produced as a byproduct damages zeolites.^{22,23} From this point of view, the generation of mesoporosity does not guarantee enhanced MTO catalyst stability.

BULLETIN OF THE

KOREAN CHEMICAL SOCIETY

The present study was undertaken to investigate the effect of mesoporosity on the MTO catalyst lifetimes.^{20,24,25} Accordingly, mesoporous SSZ-13 zeolites were synthesized using organosilane surfactants (*i.e.*, $C_{18}H_{37}$ -N⁺(Me)₂- $C_{3}H_{6}$ -Si(OMe)₃) as the mesopore generator at a gel composition of 400 SiO₂: 10 Al₂O₃: *x* organosilane surfactant (*x* = 1, 2, 4, 6): 100 *N*,*N*, *N*-trimethyladamantan-1-ammonium hydroxide (TMAdOH): 9000 H₂O.²⁴ Amounts of organosilane surfactants were varied to produce SSZ-13 zeolites with different mesoporosities. The resultant zeolites are denoted by *x*-MP-SSZ, where *x* represents the amount of organosilane molecule in the gel composition. The catalytic lifetimes of these zeolites in MTO reactions were investigated for the textural properties of zeolites, which were derived from N₂ adsorption isotherms.

Figure 1 shows X-ray diffraction (XRD) patterns and N₂ adsorption–desorption isotherms of a *x*MP-SSZ-13 series. Bulk SSZ-13 zeolite is displayed for comparison purposes. As shown in Figure 1(a), a series of *x*MP-SSZ zeolites exhibited several reflection XRD peaks with positions identical to those of bulk SSZ-13 zeolite. Other than for these diffraction peaks, no other XRD peak was observed in the wide-angle region, which indicated the zeolite samples obtained in the present work were pure and highly crystal-line chabazite. Pore structures were investigated using N₂ adsorption–desorption isotherms (Figure 1(b)). Bulk SSZ-13 zeolite showed a sharp increase at $\langle P/P_0 \rangle$ of 0.01. This abrupt increase observed at such a low-relative pressure was attributed to N₂ condensation within micropores.



Figure 1. XRD patterns and N₂ adsorption–desorption isotherms of mesoporous SSZ-13 zeolites hydrothermally synthesized at 145°C with a gel composition of 400 SiO₂: 10 Al₂O₃: *x* organosilane surfactant (x = 1, 2, 4, 6): 100 SDA: 9000 H₂O. For comparison, the XRD pattern and N₂-isotherm of bulk SSZ-13 zeolite is also shown. The isotherms are offset by 250 cm³/g.

Similar to bulk SSZ-13 zeolite, a series of *x*MP-SSZ also demonstrated nitrogen adsorption below a P/P_0 of 0.01, indicating micropore accessibility. However, a significant difference was observed between bulk SSZ-13 and *x*MP-SSZ zeolites. The series of *x*MP-SSZ zeolites produced adsorbed a large amount of N₂ in the relative pressure range from 0.4 to 0.9, suggesting N₂ condensation in mesopores. The 1MP-SSZ zeolites had a mesopore volume of 0.20 mL/g and mesopore volume increased in the following order: 1MP-SSZ < 2MP-SSZ < 4MP-SSZ < 6MP-SSZ. The pore size distributions of the *x*MP-SSZ zeolites are displayed in Figure S1. This tendency was attributed to an increase in organosilane content, as organosilanes can generate mesopores during mesoporous SSZ-13 zeolite synthesis.

Figure 2 shows NH₃ temperature-programmed desorption (TPD) of bulk SSZ-13 zeolite and xMP-SSZ-13 zeolites. NH₃-TPDs are widely used to evaluate relative acid strengths and numbers of acid sites in solid samples. In Figure 2, peak areas correspond to numbers of acid sites, and temperatures at peak maxima correspond to the acid site strengths. NH₃-TPDs of all samples exhibited bimodal distribution with maxima at ~217 and ~500 °C, which are associated with weak and strong acid sites, respectively, catalyze MTO reactions. It has been reported that only strong acid sites effectively catalyze MTO reactions, and thus, we calculated relative amounts of catalytically active acid sites by calculating the peak areas of high-temperature desorption peaks. According to our calculations, strong acid sites decreased in the following order: bulk-SSZ-13 (0.43 mmol/g) > 6MP-SSZ-13 (0.29 mmol/g)> 4MP-SSZ-13 (0.27 mmol/g) > 1MP-SSZ-13 (0.26 mmol/ g) > 2MP-SSZ-13 (0.20 mmol/g). Overall, bulk SSZ-13



Figure 2. NH_3 temperature-programmed desorption of a series *xMP-SSZ-13* zeolites and bulk SSZ-13 zeolite.



Figure 3. Catalytic activities and olefin (ethylene + propylene) selectivities of methanol-to-olefin reactions over mesoporous SSZ-13 zeolites with different mesoporosities.

zeolite possessed the largest amount of strong acid sites as compared to mesoporous SSZ-13 zeolites.

A series of *x*MP-SSZ-13 zeolites with different mesoporosities were examined in MTO reactions at $350 \,^{\circ}$ C with a weight-hourly-space-velocity of 1.0 h⁻¹. Haw *et al.* proposed MTO reactions are catalyzed by 'hydrocarbon-pool' like mechanism, whereby methylated aromatics inside zeolite pores provide active centers for the generation of paraffin and olefin products.²⁶ According to this proposed mechanism, the primary products ethylene and propylene could be transformed into higher-hydrocarbons by polymerization, isomerization, hydrogenation, etc. In this regard, the facile diffusion of ethylene and propylene out of the zeolite matrices would be enhanced light-olefin selectivity and act to prevent progressive deactivation by bulky hydrocarbons inside zeolite micropores. Accordingly, mesopores provide pathways that facilitate hydrocarbon escape from the zeolite matrix.

Figure 3(a) shows plots of MeOH conversion and lightolefin (that is, ethylene and propylene) selectivity as functions of reaction time at a fixed space velocity of 1.0 h^{-1} for a series of xMP-SSZ-13 zeolite samples. We performed catalytic reactions two times and used average values. To compare catalyst stabilities, we defined half-life $(t_{1/2})$ as the time needed for the initial conversion to decrease to half of its initial value. Bulk-SSZ-13 zeolite had $t_{1/2}$ of 86 min, which was much lower than those of all xMP-SSZ-13 zeolite samples. Of the mesoporous SSZ-13 samples, 2MP-SSZ-13 exhibited the greatest catalytic stability with $t_{1/2}$ of 604 min. $T_{1/2}$ values of samples decreased in the following order: 2MP-SSZ-13 (604 min) > 1MP-SSZ-13 (484 min) > 4MP-SSZ-13 (437 min) > 6MP-SSZ-13 (243 min). Olefin productivities over 600 min of MTO are summarized in Figure S2. Selectivities for C_2H_4 plus C_3H_6 were also higher for 2MP-SSZ-13 than the other samples, which demonstrated that a suitable balance between microporosity and mesoporosity is required to achieve a long lifetime and high olefin selectivity.

Based on the findings of previous studies regarding the positive effects of mesoporosity, we expected that SSZ-13 zeolites with higher mesoporosities would have longer lifetimes and greater olefin selectivities, but this was not observed. To understand this departure from expectation, we investigated changes in zeolite microporosity after MTO reactions,^{27,28} because these are known to occur within micropores. Before N_2 adsorption measurements, the used catalysts were calcined at 550°C in flowing air to remove coke. Microporosities were calculated from adsorption branches of N2 isotherms using the t-plot method. As shown in Table 1, catalysts obviously differed with respect to loss of catalyst microporosities after MTO reactions (Table 1) in a mesoporosity dependent manner. 4MP- and 6MP-SSZ-13 catalyst exhibited significant microporosity loss, which was c degree of real 1MP- and 2 that SSZ-13 their intrinsic and, as a resu

Ta

onsistent with its short catalytic lifetime. Such a duction of microporosity is less conspicuous for MP-SSZ-13 zeolites. These observations suggest zeolites with higher mesoporosities lose more of a microporosities in the course of MTO reaction, alt, are more rapidly deactivated.	at 145 °C for 8 days under tumbling conditions (10 rp After crystallization, the solid material was filtered, was with distilled water, and dried at 90 °C. Catalysts produ- were then calcined at 550 °C under flowing air for 10 The characterization and catalytic activities of the catal produced are described in detail in Supporting Information					
ural property and acidity of a series of <i>x</i> MP-SSZ-13 zeolites.						

Table 1. Textural property and acidity of a series of xMP-SSZ-13 zeolites.						
Zeolite	$S_{BET}(m^2/g)^a$	$V_{tot} (cm^3/g)^b$	V _{meso} (cm ³ /g) ^c	V _{micro} (cm ³ /g) ^d	Acidity (mmol/g) ^e	
Bulk-SSZ-13	552	0.326	0.054	0.272	0.43	
1MP-SSZ-13	595	0.457	0.204	0.253	0.26	
2MP-SSZ-13	620	0.487	0.243	0.244	0.20	
4MP-SSZ-13	680	0.513	0.267	0.246	0.27	
6MP-SSZ-13	717	0.599	0.373	0.226	0.29	
Bulk-SSZ-13-regen ^f	233	0.123	0	0.123		
1MP-SSZ-13-regen ^f	595	0.409	0.168	0.241		
2MP-SSZ-13-regen ^f	600	0.460	0.230	0.230		
4MP-SSZ-13-regen ^f	580	0.432	0.219	0.213		

0.335

^aS_{BET} is a specific surface area calculated from BET equation at the relative pressure range (p/p_0) of 0.1–0.25.

^b V_{tot} is the total pore volume at $p/p_0 = 0.96$.

6MP-SSZ-13-regenf

^c V_{meso} is the mesopore volume calculated from BJH method.

671

 $^{d}\,V_{micro}$ is the micropore volume calculated from t-plot method.

^e Acidity is derived from the peak areas of NH₃ desorption peaks ranging from 350 to 600 °C.

^fThe SSZ-13 zeolite samples marked with asterisk are the regenerated SSZ-13 zeolites sample at 550 °C under air-flow.

0.526

In conclusion, we synthesized mesoporous SSZ-13 zeolites with different mesoporosities using organosilanes as mesopore-generating agents and investigated their MTO catalytic activities. Catalyst stability and olefin selectivity trends as a function of mesoporosity were observed using volcano plots. Mesoporosity was found to enhance catalyst lifetime, which we putatively attribute to the facile diffusions of ethylene and propylene. However, mesoporosity also reduced zeolite framework stability, and thus negatively affected catalyst lifetimes. Our results indicate a suitable balance between microporosity and mesoporosity is required to achieve MTO catalyst longevity with high olefin selectivity.

Experimental

Bulk-SSZ-13 zeolite and a series of xMP-SSZ-13 zeolites were synthesized as previously reported.²⁴ In a typical method, 3.1 g of 6 M NaOH solution was mixed with 7.04 g of TMAdOH, (25 wt.%, ZeoGen[™] SDA 2825, Austin, Texas). A specific amount of organosilane surfactant was added to this solution followed by 5 g of Ludox[®] (Sigma-Aldrich, AS-40), which was dropwised with vigorous stirring. A specific amount of organosilane exhibited in Table S1. After stirring at room temperature for 30 min, 2 g of distilled water containing 0.55 g of aluminum sulfate hydrate (Sigma-Aldrich, >97%) was poured, and the resulting mixture was stirred at room temperature for 2 h and then at 60 °C overnight. The final mixture was transferred into a Teflon-lined autoclave and heated in an oven om). hed iced 0 h. ysts on.

0.191

Communication

Acknowledgments. This work was supported by Inha University Research Grant (INHA-60131).

Supporting Information. Detailed description of characterization and catalytic experiment, textural properties of SSZ-13 zeolite.

Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

References

- 1. C. D. Chang, A. J. Silvestri, J. Catal. 1977, 47, 249.
- 2. H. Koempel, W. Liebner, Stud. Surf. Sci. Catal. 2007, 167, 261.
- 3. A. Primo, H. Garcia, Chem. Soc. Rev. 2014, 43, 7548.
- 4. X. Tang, A. Zhang, J. Liu, Stud. Surf. Sci. Catal. 2004, 154, 2754.
- S. Teketel, M. W. Erichsen, F. L. Bleken, S. Svelle, K. P. Lillerud, U. Olsbye, *Catalysis* 2014, 26, 179.
- 6. S. M. Csicsery, Zeolites 1984, 4, 202.
- 7. F. Xiao, J. Wei, Chem. Eng. Sci. 1992, 47, 1123.
- 8. L. S. Dent, J. V. Smith, Nature 1958, 181, 1794.
- 9. J. J. Spivey, G. F. Froment, W. J. H. Dehertog, A. J. Marchi, *Catalysis* **1992**, *9*, 1.
- A. J. J. Koekkoek, H. Xin, Q. Yang, C. Li, E. J. M. Hensen, *Micropor. Mesopor. Mat.* 2011, 145, 172.
- S. A. Hosseini, A. Niaei, R. Saeedi, *Adv. Ceramic Sci. Eng.* 2016, 5, 20.
- J. Zhang, H. Zhang, X. Yang, Z. Huang, W. Cao, J. Nat. Gas Chem. 2011, 20, 266.

 M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature* 2009, 461, 246.

BULLETIN OF THE

- W. Park, D. Yu, K. Na, K. E. Jelfs, B. Slater, Y. Sakamoto, R. Ryoo, *Chem. Mater.* 2011, 23, 5131.
- K. Zhang, C. Li, Z. Liu, M. Wang, X. Yang, H. Xi, *Chem. Asian J.* 2017, 12, 2711.
- M. Choi, H. S. Cho, R. Sricastava, C. Venkatesan, D. G. Choi, R. Ryoo, *Nat. Mater.* 2006, *5*, 718.
- A. J. J. Koekkoek, C. H. L. Tempekman, C. Degirmenci, M. Guo, Z. Feng, C. Li, E. J. M. Hensen, *Catal. Today* 2011, *168*, 96.
- L. H. Chen, X. Y. Li, J. C. Rooke, Y. H. Zhang, X. Y. Yang, Y. Tang, F. S. Xiao, B. L. Su, *J. Mater. Chem.* **2012**, *22*, 17381.
- 19. R. Bai, Y. Song, Y. Li, J. Yu, Trends Chem. 2019, 1, 601.
- L. Sommer, D. Mores, S. Svelle, M. Stöker, B. M. Weckhuysen, U. Olsbye, *Micropor. Mesopor. Mat.* 2010, 132, 384.
- A. H. Janssen, A. J. Koster, K. P. de Jong, *Angew. Chem. Int. Ed.* 2001, 40, 1102.
- 22. A. Lucas, P. Canizares, A. Duran, A. Carrero, *Appl. Catal. A Gen.* **1997**, *154*, 221.
- A. G. Gayubo, A. T. Aguayo, M. Olazar, R. Vivanco, J. Bilbao, *Chem. Eng. Sci.* 2003, 58, 5239.
- L. Wu, V. Degirmenci, P. C. M. M. Magusin, N. J. H. G. H. Lousberg, E. J. M. Hensen, J. Catal. 2013, 298, 27.
- L. Wu, V. Degirmenci, P. C. M. M. Magusin, B. M. Szyja, E. J. M. Hensen, *Chem. Commun.* **2012**, *48*, 9492.
- B. Arstad, J. B. Nicholas, J. F. Haw, J. Am. Chem. Soc. 2004, 126, 2991.
- 27. M. Moliner, C. Martínez, A. Corma, *Chem. Mater.* 2014, 26, 246.
- C. H. Christensen, I. Schmidt, A. Carlsson, K. Johannsen, K. Herbst, J. Am. Chem. Soc. 2005, 127, 8098.