Electronic Supplementary Information (ESI)

Dual template synthesis of highly mesoporous SSZ-13 zeolite with improved stability in the methanol-to-olefins reaction

Leilei Wu, Volkan Degirmenci, Pieter C.M.M. Magusin, Bartłomiej M. Szyja, Emiel J. M. Hensen*
Eindhoven University of Technology, Schuit Institute of Catalysis,
5600 MB Eindhoven, The Netherlands

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A. Materials and Methods

**Mesoprogen.** The surfactant \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9-\text{N}_3\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9\text{]}\text{Br}_2 \) was synthesized in two steps. Firstly, 4.1 g (0.01 mol) 1-bromodocosane (Aldrich, 96 %) was dissolved in 20 ml toluene and dropwisely added into the mixture of 10.3 g (0.07 mol) \( \text{N}, \text{N}, \text{N'}, \text{N'}-\text{tetramethyl-1,4-butanediamine (Aldrich, 98 %) and 20 ml acetonitrile solution. The solution was first stirred for 3 h at room temperature and then refluxed overnight in an oil bath kept at 70 °C. After cooling to room temperature, the solution was kept in a refrigerator at 4 °C for 1 h, filtered and washed with cold diethyl ether. The resulting solid was dried in a vacuum oven at room temperature. The product was \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9\text{]}\text{Br} \). Secondly, 3.7 g (0.007 mol) \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9\text{]}\text{Br} \) and 1.96 g (0.014 mol) 1-bromobutane (Aldrich, 98 %) were dissolved in 110 ml of acetonitrile and then refluxed overnight at 70 °C. After cooling to room temperature, the solid product was kept in refrigerator at 4 °C for 1 h, filtered, washed with cold diethyl ether and dried in a vacuum oven at room temperature. The resulting product was \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9\text{]}\text{Br}_2 \) (C22-4-4Br2).

The surfactant \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_6\text{H}_{12}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_{13}\]Br \) was synthesized according to a literature procedure.1 Firstly, 4.1 g (0.01 mol) 1-bromodocosane (Aldrich, 96 %) was dissolved in 50 ml toluene and dropwisely added into the mixture of 17.2 g (0.1 mol) \( \text{N}, \text{N}, \text{N'}, \text{N'}-\text{tetramethyl-1,6-hexanediamine (Aldrich, 99 %) and 50 ml acetonitrile solution. The solution was first stirred for 3 h at room temperature and then refluxed overnight in an oil bath kept at 70 °C. After cooling to room temperature, the solution was kept in a refrigerator at 4 °C for 1 h, filtered, washed with cold diethyl ether. The resulting solid was dried in a vacuum oven at 50 °C. The product was \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_6\text{H}_{12}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_{13}\]Br \) and 1.96 g (0.014 mol) 1-bromobutane (Aldrich, 98 %) were dissolved in 110 ml of acetonitrile and then refluxed overnight at 70 °C. After cooling to room temperature, the solid product was kept in refrigerator at 4 °C for 1 h, filtered, washed with cold diethyl ether and dried in a vacuum oven at room temperature. The resulting product was \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9\text{]}\text{Br} \).

The surfactant \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_6\text{H}_{12}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_{13}\]Br \) was synthesized in one step. 8.2 g (0.02 mol) 1-bromodocosane (Aldrich, 96 %) was dissolved in 40 ml toluene and dropwisely added into the mixture of 40 g (0.01 mol) \( \text{N}, \text{N}, \text{N'}, \text{N'}-\text{tetramethyl-1,6-hexanediamine (Aldrich, 99 %) and 40 ml acetonitrile solution. The solution was first stirred for 24 h at 70 °C. After cooling down, the solid product was kept in refrigerator at 4 °C for 1 h, filtered, washed with cold diethyl ether and dried in a vacuum oven at 50 °C. The resulting product was \( \text{[C}_{22}\text{H}_{45}-\text{N}^+\text{(CH}_3\text{)}_2-\text{C}_4\text{H}_9\text{]}\text{Br} \).

**Zeolite SSZ-13.** SSZ-13 was synthesized according to a published method.2 2 g 1 M NaOH solution, 4 g 0.5 M \( \text{N}, \text{N}, \text{N'}, \text{N'}-\text{trimethyl-1-adamantanammonium hydroxide (TMAdOH) and 2.0 g deionized water were mixed together. TMAdOH template was synthesized according to a literature procedure.}^3 0.05 g aluminum hydroxide (Sigma Aldrich) was added to this solution under vigorous stirring. After 30 min, 0.6 g fumed silica (Sigma) was added in. The resulting mixture was stirred at room temperature to obtain a homogeneous gel with the following composition: 20 TMAdOH : 10 Na2O : 3 Al2O3 : 100 SiO2 : 4400 H2O, which was then transferred into a Teflon-lined autoclave and kept in oven at 160 °C for 4 days. Afterward, the solid material was recovered by filtration. The catalyst was finally calcined at 550 °C for 10 h in static air. The proton form of the zeolite was obtained by triple ion exchange of the calcined zeolite with 1 M NH4NO3 at 70 °C for 2 h and calcination in static air at 550 °C for 4 h.

**Mesoporous SSZ-13.** Mesoporous SSZ-13(C22-4-4Br2) was synthesized using the following gel composition: 10 TMAdOH : 5 C22-4-4Br2 : 10 Na2O : 3 Al2O3 : 100 SiO2 : 5000 H2O prepared in the same manner as SSZ-13. C22-4-4Br2 was added into mixture before silica. The initial gel was subjected to crystallization in a Teflon-lined stainless-steel autoclave at 160 °C for 6 days. The solid product...
were collected by filtration, washed with deionized water, and dried at 110 °C. The catalysts were finally calcined at 550 °C for 10 hours in static air. The proton form of the zeolites were obtained by triple ion exchange of the calcined form zeolites with 1 M NH₄NO₃ at 70 °C and finally by calcination in static air at 550 °C for 4 h. Mesoporous SSZ-13(C₂₂-₆₆Br₂) was synthesized in a similar manner from the gel composition: 10 TMAOH : 5 C₂₂-₆₆Br₂ : 10 Na₂O : 3 Al₂O₃ : 100 SiO₂ : 5000 H₂O. Mesoporous SSZ-13(C₂₂-₄Br) was synthesized with the gel composition: 10 TMAOH : 10 C₂₂-₄Br : 10 Na₂O : 3 Al₂O₃ : 100 SiO₂ : 5000 H₂O.

Catalytic activity. Catalytic activity measurements were carried out in a quartz tubular fixed-bed reactor. The catalyst was placed as pressed and sieved particles in the 250-500 μm range between two quartz wool plugs. Prior to reaction, the catalyst was activated at 550 °C in artificial air (30 ml/min) for 2 h. The methanol-to-olefins (MTO) reaction was performed at 350 °C. Methanol (Merck, 99%) was introduced to the reactor by flowing He through a saturator containing the reactant. The WHSV was kept at 0.8 g·g⁻¹ h⁻¹ and the effluent was analyzed online gas chromatography (Compact GC Interscience) equipped with TCD and FID detectors with RT-Q-Bond and Al₂O₃/KCl columns.

The amount of coke in the spent catalysts was estimated by temperature programmed oxidation. The spent catalysts (48 h time on stream) were exposed to a flow of 6 vol.% O₂ in He at a total flow rate of 100 ml/min. The temperature was increased from room temperature to 850 °C at a rate of 5 °C/min. The amount of CO₂ was quantified by a Balzers mass-spectrometer. The mass signal due to CO₂ (m/e = 44) signal was calibrated by the thermal decomposition of a known amount of NaHCO₃.

Characterization methods. X-ray powder (XRD) analysis was performed on a Bruker D4 Endeavor powder diffraction system using Cu Kα radiation in the range of 5° to 60°. XRD crystallinities were determined using the Bruker TOPAS 3.0 software. Adsorption experiments were determined at 87.6 K on a Micromeritics ASAP 2020 instrument in static mode. The zeolite samples were outgassed at 400 °C for 8 h prior to the sorption measurements. Langmuir adsorption isotherm model was used to determine the total surface area (Sₐ) in the p/p₀ range between 0.05-0.20. The mesopore volume (Vₘeso) and mesopore size distribution was calculated from the adsorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. The micropore volume (Vₘicro) was determined by the t-plot method. The total pore volume (Vₜot) was calculated using the Horvath-Kawazoe (HK) method at p/p₀=0.97. Elemental analyses were carried out by ICP-OES (Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing). To extract the metals, the zeolites were dissolved in 1.5 ml of an acid mixture of HF/HNO₃/H₂O.

Scanning electron microscopy (SEM) pictures were taken on a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 3-5kV. The catalysts were coated with gold prior to measurements.

Transmission electron microscopy (TEM) pictures were taken on a FEI Tecnai 20 at 200 kV. The catalysts were suspended in ethanol and dispersed over a Cu grid with a holy carbon film prior to measurements. ¹H and ²⁹Si NMR spectra were recorded on a Bruker DMX500 spectrometer equipped with a 4-mm magic-angle spinning (MAS) probehead. The ¹H and ²⁹Si NMR frequencies were 500 and 99 MHz, respectively and the employed sample rotation rate was 10 kHz. Two-dimensional ²⁹Si{¹H} heteronuclear correlation (HETCOR) NMR spectra were recorded with a rectangular contact pulse of 3 ms with carefully matched amplitudes on both channels. Tetramethylsilane (TMS) was employed as an external reference for the chemical shift for ¹H and ²⁹Si NMR.
B. Computer Simulations

In order to estimate the interaction of the two candidate mesoporogens with the chabazite framework, molecular dynamics (MD) simulations were carried out. For this purpose, we employed the CVFF forcefield as implemented in the Discover v2010.1 module of the Materials Studio 5.5 package (Accelrys Inc.). A cutoff of 12.5 Å was employed for the van der Waals term of the atom-atom interactions. The Ewald summation was employed to compute the electrostatic energies of the system. The simulation cell consisted of 24 unit cells of CHA ($a \times b = 2 \times 4$ for the surface with a thickness of 3 unit cells). A vacuum of 20 Å was added perpendicular to the $a$ direction. To this model two TMAc cations were added in randomly chosen CHA cavities and one C$_{22-4-4}$, C$_{22-6-6}$ or C$_{22-4}$ cation. One further TMAc cation was placed in the cavity below the mesoporogen. Different configurations of the mesoporogen were compared. The oxygen atoms at the zeolite surface were protonated. The positive charge of the whole system due to the template molecules was compensated by application of a negative background. To equilibrate the system before evaluation of the interaction energies, a MD simulation was carried out in the $NVE$ ensemble at a temperature of 298 K for 10 ps. Subsequently, the geometry of the system was optimized and the final energy was taken as the total energy of the system. The template-framework interaction energy was determined as the difference in total energy with respect to the optimized system without the mesoporogen. The framework destabilization energy was determined in the following way. From the final optimized geometry of the model containing the zeolite, the three TMAc and mesoporogen cations, the latter was removed. The framework destabilization energy was determined as the difference between the energy of the latter system with that of the optimized system without mesoporogen.

References

C. Supplementary Figures and Tables

Figure S1. XRD patterns of (a) conventional SSZ-13 and (b-d) mesoporous SSZ-13 zeolites synthesized by combination of (b) C_{22-4,4Br2} and TMAdOH, (c) C_{22-6,6Br2} and TMAdOH and (d) C_{22-4Br} and TMAdOH. The XRD crystallinaties are also indicated.

Figure S2. (left) Ar adsorption-desorption isotherms and (right) pore size distribution of conventional (◊) and mesoporous SSZ-13 by templating with C_{22-4,4Br2} (○) and C_{22-6,6Br2} (□).
Figure S3. (a) 2D $^{29}$Si{$^1$H} HETCOR NMR spectrum of as-synthesized mesoSSZ-13 with the $^{29}$Si NMR) direct frequency axis in vertical direction, and $^1$H and $^{29}$Si NMR projections along the horizontal and vertical axis, respectively. (b) $^1$H MAS NMR spectrum of mesoSSZ-13 containing both N,N,N-trimethyl-1-adamantanammonium (TMAd) and C$_{22}$H$_{45}$-N$^+$-CH$_2$-N$^+$-CH$_3$-C$_4$H$_9$ (C$_{22}$-4-4) with molecular structures indicated above the spectrum; (c-d) $^1$H MAS NMR spectra of (c) conventional SSZ-13 with only TMAd and (d) amorphous silica synthesized in the presence of only C$_{22}$-4-4. (e-g) $^1$H NMR cross-sections from the 2D HETCOR spectrum at $^{29}$Si NMR shifts -110, -105 and -100 ppm, assigned to Q$^4$(0Al), Q$^4$(1Al) and Q$^3$(0Al) silicon atoms with respective coordination Si(OSi)$_4$, Si(OSi)$_3$(OAl), Si(OSi)$_3$(OH) in the zeolite framework. 2D $^{29}$Si{$^1$H} HETCOR correlates the $^{29}$Si and $^1$H NMR resonances of $^{29}$Si and $^1$H nuclear spins that are close (< 1 nm) in the template-aluminosilicate structure [K. Na, C. Jo, J. Kim, K. Cho, J. Jung, Y. Seo, R.J. Messinger, B.F. Chmelka and R. Ryoo, Science 2011, 333, 328-332.]. Compared to the overall $^1$H NMR spectrum of mesoSSZ-13, the $^1$H NMR resonances of the C$_{22}$ chains of the C$_{22}$-4-4 template are absent in the $^1$H NMR traces e-g. Thus, the alkyl chains are relatively distant from silicon atoms, which is consistent with their outside location predicted by computational modelling.
Figure S4. TPO profiles of spent (◊) microporous SSZ-13 and (○) mesoSSZ-13 zeolite catalysts after 48 h time on the stream in the MTO reaction.
Figure S5. The C$_{22}$-4-4 template in the CHA model with its two ammonium centers in the large cavities (configuration II) and the hydrophobic tail sticking out at the zeolite surface.

Figure S6. The C$_{22}$-6-6 template in configuration I showing the folding of the terminating hexyl chain back into the cavity leading to increased destabilization of the zeolite framework.
Figure S7. The $C_{22,4}$ template in the CHA model with its ammonium center in the large cavity below the surface (configuration II) and the hydrophobic tail sticking out at the zeolite surface.
Figure S8. TEM images of mesoporous SSZ-13 prepared in the presence of TMAdOH and C_{22,6,6}Br_2. The sample contains very small cubic shaped crystals as well as an amorphous phase with disordered mesopores smaller than 10 nm.
Table S1: Textural analysis by Ar physisorption and Si/Al molar ratios determined by ICP

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Templates</th>
<th>( S_{\text{Langmuir}} ) (m².g⁻¹)</th>
<th>( V_{\text{micro}} ) (cm³.g⁻¹)</th>
<th>( V_{\text{meso}} ) (cm³.g⁻¹)</th>
<th>( V_{\text{tot}} ) (cm³.g⁻¹)</th>
<th>Si/Al (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSZ-13</td>
<td>TMAOH</td>
<td>651</td>
<td>0.18</td>
<td>0.01</td>
<td>0.22</td>
<td>19</td>
</tr>
<tr>
<td>MesoSSZ-13</td>
<td>C22-4-4 TMAOH</td>
<td>815</td>
<td>0.21</td>
<td>0.21</td>
<td>0.46</td>
<td>17</td>
</tr>
<tr>
<td>MesoSSZ-13(C22-6-6)</td>
<td>C22-6-6 TMAOH</td>
<td>719</td>
<td>0.10</td>
<td>0.45</td>
<td>0.62</td>
<td>n.d. (^b)</td>
</tr>
</tbody>
</table>

\(^a\) determined by ICP; \(^b\) not determined.

Table S2. Lifetime and product distribution of SSZ-13 and mesoporous SSZ-13 catalysts for MTO reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lifetime (^a) (hour)</th>
<th>Ethylene (%)</th>
<th>Ethane (%)</th>
<th>Propylene (%)</th>
<th>Propane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSZ-13</td>
<td>2.8</td>
<td>46.4</td>
<td>0.8</td>
<td>44.9</td>
<td>4.6</td>
</tr>
<tr>
<td>MesoSSZ-13</td>
<td>6.8</td>
<td>44.5</td>
<td>0.7</td>
<td>47.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(^a\) Catalyst lifetime defined as the time passed to reach 50 % of the initial conversion.