Synthesis and characterization of zincosilicate and pure-silica SSZ-42 and SSZ-71

C. Y. Chen\textsuperscript{a}, S. I. Zones\textsuperscript{b}, S.-J. Hwang\textsuperscript{b}, A. W. Burton\textsuperscript{a} and A. J. Liang\textsuperscript{a,e}

\textsuperscript{a}Chevron Energy Technology Company, Richmond, CA 94802, USA
\textsuperscript{b}Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA
\textsuperscript{e}Department of Chemical Engineering and Materials Sciences, University of California, Davis, CA 95616, USA

ABSTRACT

In this paper we report, for the first time, the synthesis and characterization of new zincosilicate Zn-SSZ-42. New method of synthesizing pure-silica SSZ-42 via the OH\textsuperscript{−} route without using F\textsuperscript{−} anions is presented. Furthermore, the synthesis and characterization of the novel layered zincosilicate and pure-silica designated as SSZ-71 are discussed.

1. INTRODUCTION

Zincosilicate and pure-silica zeolites have unique properties with regard to their use as catalysts and adsorbents [1-4]. Today over 170 zeolite structures have been discovered [5]. Theoretical studies indicate that this number represents only a small fraction of possible zeolite structures. The major roadblock in tailoring and utilizing zeolites for specific applications remains the development of synthesis methods to produce desirable structures with desirable framework compositions.

The framework structure of zeolite SSZ-42 is characterized by an undulating, one-dimensional 12-ring channel system [6,7]. According to the Structure Commission of the International Zeolite Association [5], pure-silica ITQ-4 (synthesized using F\textsuperscript{−} anions) [8,9] and aluminosilicate MCM-58 [10] are isostructural with borosilicate SSZ-42. The structure code of this zeolite is IFR. It has been reported that this zeolite can be also prepared in ferrosilicate and titanosilicate forms [11,12]. SSZ-71 is a layered material [13] and under certain conditions SSZ-42 can be synthesized using SSZ-71 as precursor.

Here we report, for the first time, the synthesis and characterization of new zincosilicate Zn-SSZ-42 as well as layered materials Zn-SSZ-71 and Si-SSZ-71. As the second topic, we will discuss our new method of synthesizing Si-SSZ-42 via the OH\textsuperscript{−} route without using F\textsuperscript{−} anions, in contrast to ITQ-4 which is one of the examples among pure-silica zeolites synthesized by Cambor et al. via the fluoride route. They pointed out that “the key parameter for the synthesis of ITQ-4 is the presence of F\textsuperscript{−} anions, with a wide tolerance existing toward changes in pH” [8].
2. EXPERIMENTAL

SSZ-42 and SSZ-71 were synthesized in both zicosilicate and pure-silica forms by using the hydroxide solution of N-benzyl-1,4-diazabicyclo[2.2.2]octane (i.e., benzyl-DABCO) as structure directing agent (SDA). The structure of this SDA is depicted in Fig. 1. The synthesis procedures are similar to those outlined in our previous publications [13,14]. The SSZ-42 products were calcined in diluted air at 868 K for 5 hours.

The synthesis products were characterized using powder XRD, SEM, N₂ adsorption, solid state NMR and elemental analyses. NMR experiments were performed using a Bruker DSX-500 spectrometer with the operating frequencies at 125.79 and 99.38 MHz for ¹³C and ²⁹Si nuclei, respectively. A Bruker 4mm CP/MAS probe was employed to run Block Decay and cross polarization MAS NMR experiments at various contact times. Sample packed in a 4 mm rotor was spun at 6-8 kHz for ¹³C and ²⁹Si MAS NMR. The chemical shifts were referenced to TMS for both nuclei. Details about these physicochemical characterizations are described elsewhere [7,15].

![Fig. 1. N-benzyl-1,4-diazabicyclo[2.2.2]octane hydroxide used as the SDA for the synthesis of Zn-SSZ-42, Si-SSZ-42, Zn-SSZ-71 and Si-SSZ-71.](image)

3. RESULTS AND DISCUSSION

3.1. Zn-SSZ-42

As an example, one Zn-SSZ-42 material was synthesized at 423 K under static conditions for 8 days. The composition of the synthesis gel was as follows: 0.018Na₂O:0.15R₂O:0.03 Zn(CH₃COO)₂:SiO₂:43H₂O, where R stands for SDA. The synthesis was carried out by adding 2 wt.% as-synthesized Zn-SSZ-42 as seeds (on the SiO₂ base) into the synthesis gel.

The XRD data shown in Fig. 2 indicate that both as-synthesized and calcined samples possess the XRD peaks characteristic of SSZ-42. The SEM image of the as-synthesized Zn-SSZ-42 depicted in Fig. 3 is consistent with the presence of a single phase. The micropore volume of the calcined Zn-SSZ-42 determined by N₂ adsorption is 0.205 ml/g, essentially the same value as obtained for B-SSZ-42 [7]. Based on elemental analyses, the molar bulk Si/Zn ratio of Zn-SSZ-42 amounts to 36.5, close to that in the synthesis gel (Si/Zn=33.3).

The ²⁹Si BD (Bloch Decay, non-CP) NMR spectrum of as-synthesized Zn-SSZ-42 (Fig. 4, left) shows a fairly clear signature at about -95 ppm (red line) which is interpreted as Zn incorporation into the framework although the presence of Q² sites (about -96 ppm) is overlapped in the region as Si-SSZ-42 shows a peak at the position. The ²⁹Si CP/MAS spectrum (Fig. 4, right) shows a better separation from the Q² sites. Removal of the organic SDA via calcination significantly improves the signal resolution so that all the 4 distinct Si T-atom sites present in the SSZ-42 structure [5-7,9] are now well resolved (Fig. 5). The distribution of the Si T-atom sites in Zn-SSZ-42 was calculated based on the average value of the total integration of the T-atom signals and is presented in Table 1, together with the results from Si-SSZ-42. The deviation from the theoretical 1:1:1:1 ratio is most likely related to the uneven distribution of Zn and/or Si-OH among these 4 T-atom sites. Broad signal between about -95 and -105 ppm indicates the presence of Q³ sites (Fig. 5). There is no clear sign of peak at about -95 ppm (red line), implying that Zn might have been removed upon calcination,
Fig. 2. Representative XRD patterns of as-synthesized and calcined Zn-SSZ-42 and Si-SSZ-42.

Fig. 3. SEM images of as-synthesized Zn-SSZ-42, Si-SSZ-42, Zn-SSZ-71 and Si-SSZ-71.
Fig. 4. $^{29}$Si MAS and CP/MAS NMR spectra of as-synthesized Zn-SSZ-42 and Si-SSZ-42.

Fig. 5. $^{29}$Si MAS NMR spectra of calcined Zn-SSZ-42 and Si-SSZ-42.

Fig. 6. $^{29}$Si CP/MAS NMR spectra of calcined Zn-SSZ-42 and Si-SSZ-42.
as also reported in [1-3]. The $^{29}$Si CP/MAS spectra after calcination also did not show the difference (Fig. 6). Extraction of the SDA with acids seems to be the next experiments for removing the SDA while maintaining Zn in the framework [1-3].

Table 1

<table>
<thead>
<tr>
<th>T-site</th>
<th>chemical shift, ppm</th>
<th>calcined Zn-SSZ-42</th>
<th>calcined Si-SSZ-42</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>-107.68</td>
<td>1.18</td>
<td>0.84</td>
</tr>
<tr>
<td>T2</td>
<td>-109.29</td>
<td>0.99</td>
<td>1.22</td>
</tr>
<tr>
<td>T3</td>
<td>-110.48</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>T4</td>
<td>-112.16</td>
<td>0.78</td>
<td>0.89</td>
</tr>
</tbody>
</table>

As evidenced by the results from elemental analyses and $^{13}$C MAS/NMR (not shown here, see [7] for information), SDA remains intact in as-synthesized Zn-SSZ-42 (as well as in as-synthesized Si-SSZ-42, Zn-SSZ-71 and Si-SSZ-71 that will be discussed in the next sections).

3.2. Si-SSZ-42

Two representative Si-SSZ-42 samples were synthesized at 423 K under static conditions for 30 days via the hydroxide route with the following gel compositions: (1) Sample A: 0.15R$_2$O:SiO$_2$:15H$_2$O and (2) Sample B: 0.15R$_2$O:SiO$_2$:43H$_2$O, respectively. Both samples show similar physicochemical properties and our discussion is focused on Sample A.

The XRD data and SEM image of Si-SSZ-42 are presented in Figs. 2 and 3, respectively, in association with discussions of Zn-SSZ-42. The micropore volume of the calcined Si-SSZ-42 determined by N$_2$ adsorption is 0.146 ml/g which is lower than ~0.20 ml/g for Zn-SSZ-42 and B-SSZ-42, most likely due to the presence of some Si-OH groups as defects and/or amorphous silica (see $^{29}$Si NMR data shown in Figs. 4-6). For some properties of Si-SSZ-42, please see section 3.1 for the discussions of Zn-SSZ-42.

Preliminary results from our more recent synthesis work show that, by using as-synthesized B-SSZ-42 as seeds, Si-SSZ-42 materials can be synthesized with higher micropore volume (0.212 ml/g) and significantly improved resolution of $^{29}$Si NMR signals of the Si T-atoms. This ongoing work will be reported shortly in a forthcoming publication.

Our results are important since (1) the synthesis medium consists only of silicon source and SDA solution and (2) aside from corrosion issues of the fluoride route; our method gives about double the yield of product per mole of silica.

3.3. Zn-SSZ-71

Zn-SSZ-71 can be synthesized at 150 °C under tumbling (43 rpm) for 17 days with the following synthesis gel compositions: 0.018X$_2$O:0.15R$_2$O:0.03Zn(CH$_3$COO)$_2$:SiO$_2$:43H$_2$O or 0.018YO:0.15R$_2$O:0.03Zn(CH$_3$COO)$_2$:SiO$_2$:43H$_2$O, where X stands for NH$_4$, Li, Na, K, Rb or Cs and Y does for Sr or Ba.

The distinct XRD patterns of the as-synthesized Zn-SSZ-71 samples are shown in Fig. 7, revealing that this new material can be synthesized in the presence of a variety of inorganic cations as well as NH$_4$$. The broadening of the XRD peaks reflects the layered nature of this material. The SEM image of the as-synthesized Na/Zn-SSZ-71 is depicted in Fig. 3, representing the morphology typical of layered materials.

The $^{29}$Si BD (Bloch Decay, non-CP) NMR spectrum of as-synthesized Zn-SSZ-71 (Fig. 8, left) with strong Q$^3$ peaks at -99.3 and -101.1 ppm (with ~1:1 intensity ratio) clearly represents the layered nature of this material. The ratio between the Q$^3$/Q$^4$ is approximately
1.4 (essentially the same for the as-synthesized Si-SSZ-71 depicted in Fig. 8, right). Note that the delay time for the $^{29}$Si Bloch Decay was 600 s and the relaxation of the $Q^4$ sites might need longer delay time for full relaxation, implying that this ratio could decrease. A small additional peak at -95 ppm is visible as indicated with a red line. As discussed with Zn-SSZ-42 above, this resonance can be associated with Zn site in the framework. Simulation of this spectrum renders the quantity of the -95 ppm peak, which is estimated to be about 5.6 % of the total Si ($Q^3+Q^4+Zn$-Si) sites. The framework Si/Zn ratio can be calculated based on the integration of the peaks: (i) assuming that Zn is incorporated into the zeolite framework with $Q^3$ Si sites, the molar framework Si/Zn ratio (i.e., $Q^3$/Zn-Si) amounts to 27.4; (ii) the molar framework Si/Zn ratio becomes smaller as 67.5 when $Q^4$ is also added for Si sites. Based on elemental analyses, the molar ratio of Si/Zn of this Zn-SSZ-71 sample is about 32.5 while the synthesis gel had a molar ratio of Si/Zn of 33.3. When comparing the bulk Si/Zn ratio (32.5) of this sample to its framework Si/Zn ratio (67.5) determined via $^{29}$Si NMR, it appears that not all Zn is incorporated in the framework. The presence of the resonance is unambiguously identified when $^{29}$Si CP/MAS NMR was employed with various CP contact times as represented in Fig. 9. More details will be discussed in a forthcoming publication.

Fig. 7. Representative XRD patterns of as-synthesized Zn-SSZ-71 and Si-SSZ-71.
Two representative Si-SSZ-71 samples were synthesized at 423 K under tumbling (43 rpm) for 15 days via the hydroxide route with the following gel compositions: (1) Sample A: 0.15R$_2$O:SiO$_2$:29H$_2$O and (2) Sample B: 0.15R$_2$O:SiO$_2$:43H$_2$O, respectively. Their XRD data are presented in Fig. 7, in association with discussions of Zn-SSZ-71. Both samples show similar physicochemical properties and our discussion is focused on Sample A. Similar to Zn-SSZ-71, the SEM image of the as-synthesized Si-SSZ-71 shows the morphology typical of layered materials (see Fig. 3). The $^{29}$Si MAS NMR (Figs 8 and 9) shows similar features between Si-SSZ-71 and Zn-SSZ-71 except for the incorporation of Zn in the framework of Zn-SSZ-71. For some properties of Si-SSZ-71, please see section 3.3 for the discussions of Zn-SSZ-71.
3.5. Conversion of Si-SSZ-71 to Si-SSZ-42

When an as-synthesized SSZ-71 sample (synthesized with the gel composition 0.018K$_2$O: 0.15R$_2$O:SiO$_2$:43H$_2$O at 423 K under static conditions for 14 days) was treated with a 0.93 M benzyl-DABCO solution at a 1:15 weight ratio of zeolite-to-solution at 423 K and 43 rpm for 11 days, it was completely converted to Si-SSZ-42. This phase transfer is not related to the dissolution of Si-SSZ-71 and the subsequent re-crystallization of Si-SSZ-42. Apparently the Si species are locally rearranged in the organic-inorganic composites during this phase transfer, as observed with the formation of mesoporous materials from layered material kanemite [16]. More work is in progress to elucidate the structure relationship between SSZ-42 and SSZ-71 and to determine the structure of SSZ-71.

4. SUMMARY

In this paper we have reported the synthesis of new zirconosilicates Zn-SSZ-42 and Zn-SSZ-71. They were characterized via $^{29}$Si NMR and other techniques. Analytical data indicate that zinc is located within the framework of both zeolite Zn-SSZ-42 and layered material Zn-SSZ-71. Pure-silica SSZ-42 and SSZ-71 have been successfully synthesized via the OH$^-$ route without using F$^-$ anions in the present work.

ACKNOWLEDGEMENTS

We thank Chevron Energy Technology Company for support of zeolite research, especially C.R. Wilson and G.L. Scheuerman.

REFERENCES