Al-rich mesoporous FSM-16 materials: Synthesis, characterization and catalytic properties

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Al-rich mesoporous FSM-16 materials (Si/Al = 5-16) have been synthesized using CTMABr as a surfactant. Additional mechanistic insight into the formation of Al-FSM-16 materials is gained from careful characterization of the samples collected at various stages of the preparation procedure by means of XRD and MAS NMR (\textsuperscript{29}Si and \textsuperscript{27}Al). These results suggest that the single sheet structure of kanemite breaks up during the intercalation process and regains its structure upon the addition of Na-aluminate and then condensation occurs between the adjacent silicate layers, leading to the formation of mesoporous Al-FSM-16 materials. Fe-exchanged Al-FSM-16 samples were also prepared and their performance tested in the decomposition of N\textsubscript{2}O in a fixed bed reactor.

1. INTRODUCTION

Mesoporous materials have stimulated extensive research efforts because of their potential applications in catalytic, adsorption, separation and nanoscience processes [1]. In the past decade, a wide variety of mesoporous materials have been synthesized using different types of surfactants [2]. FSM-16 materials [3], in particular, have received considerable attention because of their higher thermal and hydrothermal stabilities than the most extensively studied MCM-41 (hexagonal, \textit{p6mm}) materials. The exceptional thermal and hydrothermal stabilities were attributed to their thicker pore walls. Therefore, these FSM-16 materials are of industrial significance for catalytic applications. The synthesis and characterization of FSM-16 and Al-FSM-16 materials are well documented in the literature [4-8]. In addition, the mechanism of the formation of FSM-16 materials has been extensively studied using various characterization techniques (XRD, EDXRD, MAS NMR and TEM), which have provided clearecut evidence for the topochemical folded sheet mechanism involving the condensation of the reactive silanol groups present on the adjacent silicate layers in CTMA-kanemite complex [4, 9-10]. This mechanism leads to the formation of a hexagonal array of channels with thicker pore walls. However, the intralayer condensation of the silicate sheets
leads to the formation of lamellar organoammonium (C16TMA) silicates [11]. A novel mesoporous silica (and aluminosilicate; KSW-2) with square channels has also been obtained by adjusting the pH of the layered C16TMA-kanemite complex to a pH of 4.0-6.0 with 1M acetic acid [12-13]. Recently, we have reported the synthesis of Al-substituted FSM-16 materials (Si/Al = 14-226), possessing a slightly disordered hexagonal packing of channels, by treating a mixture of kanemite, CTMABr and Na-aluminate (pH = 10.7-11.8) at room temperature followed by hydrothermal treatment at 100 °C [14]. In continuation of our previous work, herein, we present the results of our extensive study, which provides additional mechanistic insight into the formation of mesoporous Al-rich FSM-16 materials. In view of our interest in the hydroxylation of toluene to cresol using N2O over Fe-containing catalysts, Fe-exchanged Al-FSM-16 materials have been prepared and tested for their catalytic activity in the decomposition of N2O in a fixed bed reactor.

2. EXPERIMENTAL

2.1. Synthesis of mesoporous Al-rich FSM-16 materials from kanemite

The preparation procedure of Al-rich FSM-16 materials was the same as described in our previous publication [14]. A typical procedure for the synthesis of Al-rich FSM-16 materials was as follows: kanemite powder was dispersed in a beaker containing CTMABr (Aldrich, 99%) and deionized water, and stirred for 60 min. Then, the aluminum source (19.93% Al2O3 and 19.11% Na2O) was added and stirred for another 60 min. The final synthesis mixture had the following molar composition: 0.30 Na2O : SiO2 : 0.05 Al2O3 : 0.10 CTMABr : 100 H2O. The pH value of the initial synthesis mixture was ~12.9. The synthesis mixture was then transferred into a stainless steel autoclave and heated at 100 °C for 24 h under static conditions. The resultant product was filtered, washed repeatedly with deionized water, dried at room temperature and then calcined at 550 °C in air for 12 h. In order to obtain H-form of Al-FSM-16, the calcined sample was then ion-exchanged with 0.1 M NH4NO3 solution at 70 °C for 12 h, filtered, dried and recalcined at 550 °C for 12 h.

2.2. Preparation of Fe-exchanged Al-FSM-16 materials

Fe-exchanged Al-FSM-16 materials were prepared by using the conventional ion-exchange method. Fe(NO3)3.9H2O was used as the iron source. The H-form of Al-FSM-16 (Si/Al = 12) material was dispersed in aqueous Fe(NO3)3.9H2O solutions (0.025 M and 0.1 M) and stirred for 12 h at 70 °C. The resultant sample was filtered, washed with deionized water, dried at room temperature and calcined at 550 °C for 12 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns, Transmission Electron Micrographs (TEM) and N2 adsorption isotherms were obtained as described previously [14]. The 29Si MAS NMR spectra were acquired on Bruker spectrometers (MSL 300 and MSL 500) with different measurement times (>20 h) in order to achieve acceptable signal-to-noise ratios. The 27Al MAS NMR spectra were acquired on a Bruker Avance 400 spectrometer under identical conditions. Chemical analyses of the samples were accomplished using Inductively Coupled Plasma Emission analysis (ICP, Perkin-Elmer 400).

2.4. N2O decomposition

The catalytic testing of N2O decomposition was carried out at 450-525 °C under atmospheric pressure in a continuous flow fixed-bed reactor (10.3 mm ID) using 0.2 g (14-18
(mesh size) of the catalyst. Helium was used as the carrier gas. In the present study, a modified residence time of 36 g min mol\(^{-1}\) was used. The catalyst was activated prior to the reaction in Helium atmosphere at 550 °C for 2 h. Both the inlet and outlet concentrations of \(\text{N}_2\text{O}\) were monitored using a nondispersive infrared analyzer (Hartmann & Braun, Uras 10 E). The percentage conversion of \(\text{N}_2\text{O}\) was calculated as follows:

\[
\text{Conversion} = \frac{[\text{Inlet } \text{N}_2\text{O concentration (ppm)}] - [\text{Outlet } \text{N}_2\text{O concentration (ppm)}]}{[\text{Inlet } \text{N}_2\text{O concentration (ppm)}]} \times 100
\]

3. RESULTS AND DISCUSSIONS

First, we studied the influence of Al source on the synthesis of Al-FSM-16 materials. The physico-chemical properties of the Al-rich FSM-16 materials prepared using different Al sources are given in Table 1. Among the Al sources used, Na-aluminate is found to be the best source for the preparation of Al-rich FSM-16 material with a Si/Al ratio of 5. The XRD patterns of the Al-FSM-16 materials showed a single peak at around 1.81-2.06° (2θ) (not shown). All the XRD patterns were similar although there were differences in the relative intensity of the main reflection. As shown in Table 1, the Al-FSM-16 material (sample 1) prepared using Na-aluminate as Al source exhibits lower surface area and pore volume than the other two Al-FSM-16 materials. It seems that the extent of the decrease in surface area and pore volume is due to the extent of Al incorporation into the Al-FSM-16 material. Additionally, it could be due to the thicker pore walls (25.8 Å, sample 1). Therefore, Na-aluminate was chosen as the Al source for further studies.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>d-spacing (Å)</th>
<th>BJH pore diameter (Å)</th>
<th>BET surface area (m(^2)g(^{-1}))</th>
<th>Pore volume (cm(^3)g(^{-1}))</th>
<th>Wall thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Input</td>
<td>Product</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1(^b)</td>
<td>10</td>
<td>5</td>
<td>42.8</td>
<td>17</td>
<td>579</td>
<td>0.26</td>
</tr>
<tr>
<td>2(^c)</td>
<td>10</td>
<td>9</td>
<td>48.7</td>
<td>23</td>
<td>594</td>
<td>0.33</td>
</tr>
<tr>
<td>3(^d)</td>
<td>10</td>
<td>16</td>
<td>43.4</td>
<td>23</td>
<td>722</td>
<td>0.40</td>
</tr>
</tbody>
</table>

\(^a\)Synthesis gel composition: 0.30 Na\(_2\)O : SiO\(_2\) : 0.05 Al\(_2\)O\(_3\) : 0.10 CTMABr : 100 H\(_2\)O, \(^b\)Na-aluminate, \(^c\)Aluminum sulphate, \(^d\)Aluminum nitrate, \(^e\)Wall thickness = (d-spacing)-(BJH pore diameter).

To obtain better mechanistic insight into the formation of Al-FSM-16 materials, samples withdrawn at different stages during the preparation of the synthesis mixture were analyzed by XRD. The XRD pattern of kanemite (curve ‘a’ in Fig. 1A) matched well with the XRD pattern reported in the literature [15]. All the reflections are typical of kanemite with high crystallinity. The XRD pattern of the CTMA-kanemite mixture (curve ‘b’ in Fig. 1A) shows that most of the peaks due to kanemite have virtually disappeared. This means that the intercalation of kanemite with CTMA ions did affect drastically the structural integrity of the kanemite. However, the peaks due to kanemite reappeared after the addition of Na-aluminate into the CTMA-kanemite mixture. In spite of the reappearance of the peaks due to
kanemite, a new peak at around 1.98° (20) with very low intensity can be seen (curve ‘c’ in Fig. 1A), which indicates the formation of mesoporous Al-FSM-16 material even at room temperature. This result suggests that the single sheet structure of kanemite initially breaks up during the intercalation process and regains its structure upon the addition of Na-aluminate, and then condensation occurs between the adjacent silicate layers, leading to the formation of mesoporous Al-FSM-16 materials. This result is consistent with the observations made by Chen et al. [9]. Fig. 1A also includes the XRD patterns of the as-synthesized and calcined Al-FSM-16 (curves ‘d’ and ‘e’) samples. Both the XRD patterns of the samples are identical but the peak appears somewhat more intense and sharper for the calcined Al-FSM-16 sample than for the as-synthesized Al-FSM-16 sample. In general, three or four well-defined peaks are observed for FSM-16 samples with very low Al content (high Si/Al ratio) [3-4]. The absence of higher order diffraction peaks indicates a slightly disordered hexagonal packing of channels in the Al-FSM-16 samples.

The samples of Fig. 1A were further characterized by solid state $^{29}$Si- and $^{27}$Al MAS NMR measurements. The results are shown in Fig. 1B and 1C, respectively. The spectrum of kanemite clearly shows a sharp peak at around −97.6 ppm (curve ‘a’ in Fig. 1B), which is assigned to Q$^3$ silicon environments and is in good agreement with previous data of Kimura et al. [12] and Kato et al. [16]. The $^{29}$Si MAS NMR spectrum of CTMA-kanemite reveals a change in chemical shift from −97.6 ppm to −94.9 ppm (curve ‘b’ in Fig. 1B). Such a change in the chemical shift reflects a structural change in the silicate framework of kanemite upon intercalation. Moreover, the original spectrum reappears (curve ‘c’ in Fig. 1B) after the addition of Na-aluminate into CTMA-kanemite and further corroborates our XRD results. The spectra for both as-synthesized and calcined Al-FSM-16 (curves ‘d’ and ‘e’ in Fig. 1B) materials exhibit a broad and overlapped resonance (between −85 to −120 ppm) from which the quantification of Q$^3$ and Q$^4$ species is difficult. Broad Q$^3$ and Q$^4$ resonances indicate the disordered nature of the as-synthesized and calcined Al-FSM-16 samples.

The $^{27}$Al MAS NMR spectra of both kanemite and CTMA-kanemite (curves ‘a’ and ‘b’ in Fig. 1C), did not exhibit any characteristic signal between 100 to −50 ppm, indicating that the aluminium is absent within the detectable limit of NMR instrument. Interestingly, the sample collected after the addition of Na-aluminate into CTMA-kanemite shows a single peak at around 56 ppm assigned to the tetrahedral Al species (curve ‘c’ in Fig. 1C). This result suggests that the Al species present in solution phase are rapidly incorporated into the framework of kanemite. The spectrum of the as-synthesized Al-FSM-16 (curve ‘d’ in Fig. 1C) sample shows a relatively sharper peak, indicating an increase in structural ordering. However, the calcined Al-FSM-16 (curve ‘e’ in Fig. 1C) sample shows a much broader signal than that of the as-synthesized Al-FSM-16. Calcination of the Al-FSM-16 sample at 550 °C did not result in any change in the chemical shift, indicating that Al remains unchanged.

Fig. 2 shows the TEM images of the mesoporous Al-FSM-16 materials (Si/Al = 5 and 16) obtained from kanemite. It can be seen that the Al-FSM-16 materials display a hexagonal array of channels. It appears that the hexagonal channels are slightly disordered in agreement with the XRD measurements. The structures of these Al-FSM-16 materials are different from those of mesoporous materials obtained from kanemite by Inagaki et al. (hexagonal; pH = 8.5) [4] and Kimura et al. (lamellar; pH = 10.9 and square channels; pH = 4.0-6.0) [11-12]. This could be due to the different self-assembly pathways of CTMA ions that occur at different pH conditions.
Fig. 1. (A) X-ray powder diffraction patterns of: (a) kanemite and the samples withdrawn at different stages of transformation of kanemite into mesoporous Al-FSM-16 materials, (b) after the intercalation of CTMA ions into kanemite (CTMA-kanemite) at 25 °C for an intercalation period of 1 h, (c) addition of Na-aluminate into CTMA-kanemite at 25 °C for an intercalation period of another 1 h, (d) as-synthesized Al-FSM-16 at 100 °C (0.30 Na2O : SiO2 : 0.05 Al2O3 : 0.10 CTMABr : 100 H2O) and (e) calcined Al-FSM-16 at 550 °C for 12 h; (B) 29Si MAS NMR spectra of the samples of (A); and (C) 27Al MAS NMR spectra of the samples of (A).
Fe-containing FSM-16 materials are also known to be effective catalysts for reactions such as isomerization of 1-butene [17] and hydroxylation of phenol using aqueous solution of \( \text{H}_2\text{O}_2 \) as the oxidant [18]. In our group, the direct hydroxylation of toluene and benzene with \( \text{N}_2\text{O} \) using Fe-containing ZSM-5 type catalysts has been studied intensively [19-20]. In continuation of our previous studies, we have investigated the decomposition of \( \text{N}_2\text{O} \) over Fe-exchanged Al-FSM-16 samples. For comparison, the decomposition of \( \text{N}_2\text{O} \) was carried out over a H-Al-FSM-16 sample under similar reaction conditions. The chemical compositions of the samples used for this study are given in Table 2. It appears that more Al was lost (after the ion-exchange treatment) as a consequence of dealumination. The contents of iron in the Fe/Al-FSM-16 (0.025 M) and Fe/Al-FSM-16 (0.1 M) samples are 0.15 and 0.28 wt.\%, respectively.

Table 2
Chemical composition of the catalysts used for \( \text{N}_2\text{O} \) decomposition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
<th>Fe (wt. %)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Al-FSM-16 (0.1M)\textsuperscript{b}</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Fe/Al-FSM-16 (0.025 M)\textsuperscript{c}</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>Fe/Al-FSM-16 (0.1 M)\textsuperscript{c}</td>
<td>12</td>
<td>38</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Determined by ICP analysis, \textsuperscript{b}NH\textsubscript{4}NO\textsubscript{3} and \textsuperscript{c}Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O solutions were used.

Fig. 3 shows the conversions of \( \text{N}_2\text{O} \) over H-Al-FSM-16, (Fe(0.15 wt.\%)/Al-FSM-16) and (Fe(0.28 wt.\%)/Al-FSM-16) catalysts as a function of temperature (450-525 °C). As the reaction temperature increases from 450 to 525 °C, the conversion of \( \text{N}_2\text{O} \) increases significantly from 2.6% to 21.2%, and from 2.2% to 17.6% for the (Fe(0.15 wt.\%)/Al-FSM-16) and the (Fe(0.28 wt.\%)/Al-FSM-16) samples, respectively, while the H-Al-FSM-16 sample is found to be inactive in the temperature regime investigated.
Fig. 3. N₂O decomposition over H-Al-FSM-16 (■), (Fe(0.15 wt.%)/Al-FSM-16) (▲) and (Fe(0.28 wt.%)/Al-FSM-16) (●) catalysts. Reaction conditions: catalyst = 0.2 g, pressure = 1 atm and modified residence time = 36 g min mol⁻¹.

4. CONCLUSIONS

Al-rich mesoporous FSM-16 materials (Si/Al = 5-16) have been synthesized by intercalating kanemite with CTMA ions and sodium aluminate at room temperature followed by hydrothermal treatment at 100 °C. XRD and ²⁹Si MAS NMR results provide additional mechanistic insight into the formation of Al-FSM-16 materials. In addition, XRD and TEM reveals that the Al-FSM-16 materials obtained from kanemite possess a slightly disordered hexagonal structure. The catalytic tests reveal that Fe-exchanged Al-FSM-16 materials are active for N₂O decomposition. Further studies on the characterization of Fe/Al-FSM-16 materials and their catalytic performance in the hydroxylation of toluene using N₂O as oxidant are ongoing.

REFERENCES


