Crystallization of high silica BEA by dry gel conversion

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Abstract

Zeolite with BEA structure was prepared using a new crystallization method called 'Dry Gel Conversion Technique'. This dry gel conversion technique is a convenient method to prepare zeolites and enables one to synthesize zeolite BEA with SiO₂/Al₂O₃ ratios from 30 to infinity using tetraethylammonium hydroxide (TEAOH) as a structure directing agent. Zeolite BEA with SiO₂/Al₂O₃ ratios from 30 to 730 were rapidly crystallized in 3 and 12 h, respectively. The ²⁷Al NMR spectrum for BEA with SiO₂/Al₂O₃ ratio of 30 confirmed the absence of octahedrally coordinated aluminum. The crystallization rates were higher for BEA with low SiO₂/Al₂O₃ ratios than for those with high SiO₂/Al₂O₃ ratios. BEA crystallized by this method had uniform particles of about 60 nm. Higher Na⁺ ion concentrations in the gel promoted the formation of high silica BEA. Elimination of occluded TEA cations took place at lower temperatures (around 623 K) in high silica BEA than that in BEA with low SiO₂/Al₂O₃ ratios (around 900 K). This method also allowed to synthesize BEA in the form of self-bonded pellets. © 1998 Elsevier Science B.V.

Keywords: Zeolite BEA (beta); Dry gel conversion; High silica zeolite; Crystallization; Self-bonded zeolite pellet

1. Introduction

New crystallization methods for zeolite synthesis are interesting, as they may enable us to prepare zeolites with new structures, compositions and convenient forms such as membranes and films. One such vapor-phase transport method has been successfully employed for synthesis of powdery zeolites [1-3] and zeolitic membranes [4-6]. This method involves crystallization of dry aluminosilicate gel in the presence of volatile structure-directing agent(s) and steam. The amount of structure-directing agent required in this method is very small as compared to that used in the hydrothermal method. However, this method cannot be applied for the preparation of all types of zeolites, since many of them need non-volatile structure-directing agents for their crystallization. Recently, we have reported a new crystallization method Dry Gel Conversion Technique for crystallization of zeolite BEA [7].

Zeolite BEA, a three-dimensional wide-pore, a high silica zeolite, has potential technological applications in petrochemical processes and organic synthesis. Zeolite BEA synthesized by a hydrothermal method [8] always has a low product yield and could not be synthesized with SiO₂/Al₂O₃ ratios above 250 using...
TEAOH (tetraethylammonium hydroxide), TEAOH diethanolamine, TEABr-NH$_3$ or TEAOH-TEABr-triethanolamine [8,9]. van der Waal et al. [10] have reported an all silica BEA zeolite using dibenzyldimethyl ammonium cation, an expensive and not easily removable structure directing agent. Recently, Camblor et al. [11] have reported an all silica BEA using TEAOH and HF, however, its industrial production may not be possible since HF was used in the preparation.

In this study, we investigated the synthesis of zeolite BEA with various SiO$_2$/Al$_2$O$_3$ ratios using TEAOH as a structure-directing agent. We shall show that this method allows one to prepare zeolite BEA with higher SiO$_2$/Al$_2$O$_3$ ratios than those which have been obtained by the conventional hydrothermal synthesis method.

2. Experimental

2.1. Synthesis

Dry gels having compositions,

SiO$_2$ : aAl$_2$O$_3$ : bNa$_2$O : cTEAOH

where $a = 0 - 0.033$, $b = 0.014 - 0.092$ and $c = 0.16 - 0.50$ were prepared as follows.

Aluminum sulfate (Wako Pure Chem.) was dissolved in 10 g of distilled water at 353 K. A given amount of NaOH (4 M, Wako Pure Chem.) aqueous solution and TEAOH (20% in water, Wako Pure Chem.) were added to 10 g of colloidal silica (30.3% SiO$_2$, 0.42% Na$_2$O and 700 ppm of Al$_2$O$_3$, Nissan Chem.) at room temperature (298–303 K) while stirring. Fumed silica was used in the syntheses of all silica BEA. After 30 min, an appropriate amount of the aluminum sulfate solution and 5.5 g of water were added to the mixture and stirring was continued for 2 h. Then, the mixture was heated to 353 K and dried while stirring. When the gel became viscous, it was stirred using a teflon rod till it became a dry gel. The dry gel was crushed to powder and placed in a special autoclave (Fig. 1) where water as a source of steam was poured at the bottom. Crystallization of the dry gel was carried out in steam at 453 K and autogenous pressure for 3 to 12 h. All silica BEA was crystallized at 418 K for 120 h.

The product was washed thoroughly with deionized water and dried in air at 363 K for 12 h. The organic material was removed by calcination in air at 773 K. X-ray diffraction patterns were recorded on Philips X’s Pert-MRD instrument using CuK$_{α}$ radiation. Field Emission SEM (FE-SEM) images were taken by Hitachi S-5000L FE-SEM. Solid-state NMR measurements were carried out with GSX-400 (JEOL) spectrometer. $^{29}$Si-NMR spectra were recorded at 79.30 MHz with a pulse length of 5.2 μs, a pulse interval of 10 s and a spinning rate of about 6 kHz. $^{27}$Al-NMR spectra were recorded at 104.05 MHz with a pulse length of 5.1 μs, a pulse interval of 5 s and a spinning rate of about 6 kHz. TG-DTA experiments were performed with Shimadzu DTG-50/50H thermogravimetric analyzer.

3. Results and discussion

Fig. 2 shows the XRD patterns of the products obtained by crystallization of dry gels having different SiO$_2$/Al$_2$O$_3$ ratios and all silica BEA. Highly crystalline BEA samples with SiO$_2$/Al$_2$O$_3$ ratios from 30 to 730 were obtained directly in powdery form after crystallization was carried out for 3–12 h at 453 K. Zeolite BEA with SiO$_2$/Al$_2$O$_3$ ratios from 30 to 730 in which colloidal silica was used as a source of silica were fully crystalline without any impure phases (Fig. 2a–f). The crystallinity of all silica BEA (Fig. 2g) (fumed silica was used as the source of silica) was about 85% which has an additional reflec-
Fig. 2. X-ray diffraction patterns of as-synthesized BEA with different SiO$_2$/Al$_2$O$_3$ ratios. SiO$_2$/Al$_2$O$_3$ ratio: a, 30; b, 100; c, 200; d, 380; e, 480; f, 730; g, infinity.

Fig. 3. Rate of crystallization of BEA with different chemical compositions. SiO$_2$/Al$_2$O$_3$, SiO$_2$/Na$_2$O and SiO$_2$/SO$_4^{2-}$ ratios: a, 30, 23.8 and 20.9; b, 380, 23.8 and 528; c, 730, 10.9 and 10; d, 730, 23.8 and 0, respectively.

Fig. 4 shows the XRD patterns of calcined samples. As shown in Table 1, the products were calcined between 723–823 K in air for 12 h to remove the occluded organic material present within the pores of BEA. They were stable after calcination. In order to remove organic material from BEA with SiO$_2$/Al$_2$O$_3$ ratios of 30, a temperature as high as 823 K was required, whereas for the sample with SiO$_2$/Al$_2$O$_3$ ratios of 730 a calcination temperature of 723 K was sufficient. As shown in Table 1, BEA samples after calcination had BET surface areas in the range of 500–
Table 1

<table>
<thead>
<tr>
<th>SiO₂/Al₂O₃ ratio</th>
<th>Calcination temperature (K)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Langmuir surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel</td>
<td>Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>823</td>
<td>599</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>823</td>
<td>—</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>773</td>
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<td>723</td>
<td>529</td>
</tr>
<tr>
<td>480</td>
<td>480</td>
<td>723</td>
<td>505</td>
</tr>
<tr>
<td>730</td>
<td>730</td>
<td>723</td>
<td>580</td>
</tr>
</tbody>
</table>

*a Surface areas are at liquid nitrogen temperature by single point BET method.

NMR as well as chemical analysis matches with that of the initial gel, such results confirm the complete transformation of gel into the zeolite phase.

Fig. 5 shows the ²⁷Al and ²⁹Si NMR spectra for the sample with SiO₂/Al₂O₃ ratio of 30. The absence of a peak at 0 ppm in the ²⁷Al NMR spectrum indicates that no extra-framework aluminum was present in the sample. The SiO₂/Al₂O₃ ratio calculated from ²⁹Si NMR as well as chemical analysis matches with that of the initial gel, such results confirm the complete transformation of gel into the zeolite phase.

Fig. 6 shows the FE-SEM images for BEA with SiO₂/Al₂O₃ ratio of 30 (crystallized from the gel with SiO₂/Al₂O₃, SiO₂/Na₂O and SiO₂/SO₄²⁻ ratios of 30, 23.8 and 20.9, respectively). Uniform particles of about 60 nm in length were obtained. No amorphous phase seems to exist in the sample. Formation of uniform nano-crystals from dry gel powder is of particular interest to understand the mechanism of zeolite formation.

Table 2 compare the effect of Na⁺ ions on the product. BEA can be synthesized using wide ratios of SiO₂/Na₂O from 10 to 71. As shown in Table 2, when SiO₂/Na₂O ratio was 71 (which was originally present in the colloidal silica), the products from the
Fig. 6. FE-SEM images for BEA crystallized from the gel with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}/Na\textsubscript{2}O and SiO\textsubscript{2}/SO\textsubscript{2} ratios = 30, 23.8 and 20.9, respectively. Crystallization time: a - 3 h; b - 120 h.

Table 2

<table>
<thead>
<tr>
<th>SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</th>
<th>SiO\textsubscript{2}/Na\textsubscript{2}O</th>
<th>SiO\textsubscript{2}/SO\textsubscript{2}</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>13.5</td>
<td>20</td>
<td>BEA</td>
</tr>
<tr>
<td>60</td>
<td>23.8</td>
<td>29.4</td>
<td>BEA</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>71</td>
<td>BEA</td>
</tr>
</tbody>
</table>

Relative crystallinity of BEA is 100%.

Table 3

<table>
<thead>
<tr>
<th>SiO\textsubscript{2}/TEA\textsubscript{2}O</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>RFA</td>
</tr>
<tr>
<td>5.4</td>
<td>BEA</td>
</tr>
<tr>
<td>8.0</td>
<td>BEA</td>
</tr>
<tr>
<td>12.5</td>
<td>BEA+MTW</td>
</tr>
</tbody>
</table>

When water was not added in the autoclave, the product was always amorphous. A small amount of steam can still be formed by the dehydration of gel at gels with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios from 100 to 300 were BEA. On the other hand, the gel with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of 380 and 480 produced MTW and the gel with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of 30 gave amorphous material. In the gel with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of 380 and 480, when SiO\textsubscript{2}/Na\textsubscript{2}O ratio changed from 71 to 29.4 highly crystalline BEA with no MTW impurity was obtained. This shows that for the gels with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios of 380 and 480, higher sodium concentrations promoted the formation of BEA rather than MTW.

Table 3 lists the products formed by using different SiO\textsubscript{2}/TEA\textsubscript{2}O ratios. While several patents claim the formation of BEA with SiO\textsubscript{2}/TEA\textsubscript{2}O ratio from 4 to 20 [13], in most of the published papers BEA was synthesized using SiO\textsubscript{2}/TEA\textsubscript{2}O ratios around 4. Recently, Clearfield et al. [14] reported synthesis of BEA with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios from 14 to 32 using SiO\textsubscript{2}/TEA\textsubscript{2}O ratio of 12. Using our method, it is possible to synthesize BEA with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios 30–480 using SiO\textsubscript{2}/TEA\textsubscript{2}O ratio of 8.

When water was not added in the autoclave, the product was always amorphous. A small amount of steam can still be formed by the dehydration of gel at
The crystallization temperature of 453 K. Such a small amount of steam is, however, insufficient to transform the amorphous gel into a crystalline phase. A small amount of additional water to produce a sufficient amount of steam is essential for the crystallization of the dry gel.

Hydrothermal crystallization of BEA from the gel with a composition of SiO$_2$: 0.033 Al$_2$O$_3$: 0.05 Na$_2$O: 0.37 TEAOH: 20 H$_2$O (similar to the one used in the dry gel conversion method) at 453 K failed and the product was amorphous.

Fig. 7 shows the TG–DTG patterns of BEA samples with SiO$_2$/Al$_2$O$_3$ ratios 30 and 730 in the stream of air. The elimination of TEA ions from as-synthesized BEA with SiO$_2$/Al$_2$O$_3$ ratios of 30 and 730 was completed at around 723 and 950 K, respectively. The TG–DTG pattern for BEA with SiO$_2$/Al$_2$O$_3$ ratio of 730 has three steps. The first step appearing between 300–423 K was due to elimination of water.

Most of the organic material was removed in the second step between 423–623 K and the third step between 623–723 K was due to either partial or complete oxidation of a small amount of remaining organic material. The TG–DTG pattern for BEA with SiO$_2$/Al$_2$O$_3$ ratio of 30 has four steps that include elimination of water between 300–423 K, partial elimination of TEA ions between 423–623 K, oxidative decomposition of TEA ions between 623–773 K and complete elimination of remaining organic material between 773–923 K. The second step appearing between 423–623 K is minor as compared to that for BEA with SiO$_2$/Al$_2$O$_3$ ratio of 730, indicating that only a small amount of organic material is eliminated in this temperature range. TEA ions in BEA with SiO$_2$/Al$_2$O$_3$ ratio of 730 possibly have interactions.

Fig. 8. SEM images of surface (a) and inner (b) portions of a self-bonded BEA with SiO$_2$/Al$_2$O$_3$ = 150.
mostly with oxygens of Si-O-Si linkages as fewer Si-O-Al groups are present compared to BEA with SiO₂/Al₂O₃ ratio of 30. Since the interaction between TEA ions and oxygen of Si-O-Si linkages is believed to be weaker than that between TEA ion and oxygen of Si-O-Al linkage, TEA ions were eliminated at lower temperatures in BEA with SiO₂/Al₂O₃ ratio of 730. The TG-DTG pattern for BEA with SiO₂/Al₂O₃ ratio of 30 is in consistent with previous results on BEA synthesized by the hydrothermal method [15]. This shows that neither decomposition nor degradation of TEA ions occurred while preparing the dry gels.

Fig. 8 shows the SEM images of surface and inner portions of a self-bonded BEA pellet with SiO₂/Al₂O₃ ratio of 150. This method enables one to synthesize zeolite in convenient forms such as self-bonded pellets. Self-bonded pellets with 4 cm diameter (equivalent to the inner diameter of the gel container) were formed when the SiO₂/Al₂O₃ ratios > 100. Depending on the form of support used, we can synthesize convenient forms of self-bonded BEA. Crystallinity and particle sizes are uniform both at surface and inner portions with crystallinity as high as that for powder forms of BEA.

These experiments confirm that zeolites with a high crystallinity and a uniform particle size can be synthesized from amorphous dry gel powder in the presence of steam.

4. Conclusion

A new method was developed for the crystallization of zeolites, where BEA can be rapidly crystallized. BEA with SiO₂/Al₂O₃ ratios 30–730 were synthesized using TEAOH as a structure-directing agent. Complete conversion of gel to zeolite was obtained. Particle size of the products synthesized using this method was uniform even for high silica BEA zeolite. This method enables reduction in template concentration and synthesis of zeolite in convenient forms such as self-bonded pellets. This method may be useful for the synthesis of zeolitic membranes. Also this method might enable continuous production of zeolite, reduction in reactor volume and elimination of waste water treatment.

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References