Short communication

Synthesis of ZSM-23/ZSM-22 intergrowth zeolite with a novel dual-template strategy

Bingchun Wang a,b,*, Zhijian Tian a,c,*, Peng Li a, Lei Wang a, Yunpeng Xu a, Wei Qu a, Huaijun Ma a, Zhusheng Xu a, Liwu Lin c

a National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
b Graduate University of Chinese Academy of Sciences, Beijing 100049, China
c State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

1. Introduction

Zeolites have been extensively used as adsorbents, ion-exchangers and catalysts due to their internal pore structure and geometry [1,2]. Commonly, the phase-pure zeolite is obtained only when the synthesis parameters are finely tuned. Zeolites can form different families due to common structure building units for the frameworks. Therefore they have a tendency to form intergrowths between different structures within the same family. Nowadays, more and more studies have focused on the intergrowth zeolites for their special chemical and physical properties deviating from the individual structures. Zeolite beta, for example, is actually an intergrowth of two end-members, polymorph A and B [3–5], MFI/MEL [6–8], FAU/EMT [9,10], ERI/OFF [11,12], EUO/NES/NON [13], and the ABC six-membered ring structures [14] have also been widely studied. An overview of different types of intergrowth zeolites has been presented by Rao and Thomas [15].

ZSM-22 (TON topology) and ZSM-23 (MTT topology) are two high-silica zeolites with non-interconnected one-dimensional channels surrounded by ten-membered rings with a diameter of 0.57 nm × 0.46 nm and 0.52 nm × 0.45 nm, respectively [16]. As the members of the pentasil zeolite family, their framework structures are closely related to each other due to their identical subunits [17]. Thomas et al. [18] have provided direct evidence with HRTEM and proposed that ZSM-23 is a recurrently twinned variant of Theta-1, which is a type of TON zeolite. But there are few reports on their intergrowth zeolite. Rollmann et al. [19] obtain the sample of “ZSM-22/-23” but no further study. Zones and Burton [20] present a new zeolite SSZ-54, which is actually an intergrowing type zeolite with a fixed proportion of 70%ZSM-23/30%ZSM-22.

Herein, we present a novel dual-template strategy for the synthesis of ZSM-23/ZSM-22 intergrowth zeolite (named as DLZ-02). The dual-template system consisting of dimethylamine (DMA) and diethylamine (DEA) was used as structure-directing agent (SDA) in the synthesis process. Its prominent feature was that the ratio of DEA:DMA was the key factor for synthesis of intergrowth zeolites. We also found that fluoride anion could be involved in the process as a crystallization promoter.

2. Experimental

In brief, silicon source, aluminum source, and alkali were mixed with SDA to form a synthesis gel, and H2SO4 and HF were used to adjust pH value of synthesis gel. The gel further crystallized to form DLZ-02 intergrowth zeolite. A typical synthesis procedure was as
follows: 1.45 g NaOH, 18.2 g silica sol (30 wt% SiO₂) and 52 g H₂O were mixed. Then 0.6 g aluminum sulfate, 2.51 g DMA, and 0.19 g DEA were mixed and added into the above mixture. Finally pH value was adjusted to 13.5 with H₂SO₄. Molar ratio of the gel was: SiO₂:Al₂O₃:DMA:DEA:H₂O = 100:1:67:3:4500. Crystallization was carried out at 170 °C for 50 h under dynamic conditions. The obtained solids were washed and dried. In contrast, ZSM-22 and ZSM-23 were synthesized with DMA and DEA, respectively [21].

X-ray diffraction (XRD) spectra were collected by a Phillips X’Pert Pro X-ray diffractometer using nickel-filtered Cu Kα radiation (λ = 1.54 Å) at 40 kV and 40 mA. Scanning electron microscope (SEM) images were recorded on a JEOL JSN-6460LV.

Fig. 1. XRD patterns of the as-synthesized products: (a) DLZ-02 synthesized with aluminum sulfate as aluminum source, (b) DLZ-02 synthesized with sodium metaaluminate as aluminum source, (c) ZSM-23, and (d) ZSM-22.

Fig. 2. SEM images of the as-synthesized products: (a) DLZ-02 synthesized with aluminum sulfate as aluminum source, (b) DLZ-02 synthesized with sodium metaaluminate as aluminum source, (c) ZSM-23, and (d) ZSM-22.

Fig. 3. XRD patterns of DLZ-02 zeolites synthesized under fluoride-based conditions: (a) SiO₂/Al₂O₃ = 100, static synthesis, (b) SiO₂/Al₂O₃ = 100, dynamic synthesis, (c) SiO₂/Al₂O₃ = 40, dynamic synthesis, and (d) SiO₂/Al₂O₃ = 200, dynamic synthesis.
3. Results and discussion

Table 1 listed the chemical compositions of starting gels and XRD results of the as-synthesized samples under different synthesis conditions. When aluminum sulfate was used as aluminum source, and H$_2$SO$_4$ was used to adjust pH value, only amorphous materials were obtained with DMA or DEA as a single SDA. DLZ-02 zeolite was obtained when DMA and DEA were used as a dual-template system only with DEA:DMA molar ratio of 1:24 at the same synthesis conditions. With decreasing the amount of the two amines simultaneously but keeping DEA:DMA ratio, DLZ-02 zeolite could still be obtained. No DLZ-02 zeolite was obtained if we changed DEA:DMA ratio. These results revealed that DEA:DMA ratio was the key factor for synthesis of DLZ-02 zeolites.

When sodium metaaluminum was used instead of aluminum sulfate, and DEA:DMA ratio was 1:24, no DLZ-02 zeolite was obtained. However, DLZ-02 zeolite was synthesized successfully with a DEA:DMA ratio of 1:12. The results showed that the type of aluminum source could also influence the crystallization of DLZ-02. Different aluminum source formed different aluminum species in synthesis gel, which might make the synthesis process undergo different crystalline mechanism.

Fig. 1 gave the XRD patterns of DLZ-02 samples synthesized with different aluminum sources. The XRD patterns of ZSM-23 and ZSM-22 synthesized with the sole DMA and DEA were also shown as comparison. It could be seen that the patterns of different DLZ-02 samples were identical and obviously different from ZSM-23 and ZSM-22. According to the simulated XRD patterns of the intergrowth of ZSM-23 and ZSM-22 with different proportion [20], DLZ-02 was with the fixed proportion of 60%ZSM-23/40%ZSM-22, which was different from SSZ-54. SEM images (Fig. 2) also showed different morphology of DLZ-02 from ZSM-23 and ZSM-22.

![Fig. 4. SEM images of DLZ-02 zeolites synthesized under fluoride-based conditions, (a) SiO$_2$/Al$_2$O$_3$ = 100, static synthesis, (b) SiO$_2$/Al$_2$O$_3$ = 100, dynamic synthesis, (c) SiO$_2$/Al$_2$O$_3$ = 40, dynamic synthesis, and (d) SiO$_2$/Al$_2$O$_3$ = 200, dynamic synthesis.](image)

### Table 1

<table>
<thead>
<tr>
<th>Aluminum source$^a$</th>
<th>Synthesis conditions$^b$</th>
<th>Phase of product</th>
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<td>100 0.67 – –</td>
<td>Amorphous</td>
</tr>
<tr>
<td>AS</td>
<td>100 – 0.67 0.028 1:24</td>
<td>DLZ-02</td>
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<tr>
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</table>

$^a$ AS: aluminum sulfate, SN: sodium metaaluminate.
$^b$ Dynamic synthesis.
$^c$ H$_2$SO$_4$/SiO$_2$ = 0.16, HF/SiO$_2$ = 0.32.
$^d$ Static synthesis.
samples possessed uniform morphology of fluffy spheres agglomerated by rod-like crystals. Additionally, different aluminum source also resulted in differences of crystal size and morphology between the two DLZ-02 zeolites.

Fluoride anion was usually used as a crystallization promoter in zeolite synthesis [22,23]. XRD patterns and SEM images of the samples obtained under fluoride media were shown in Fig. 3 and Fig. 4, respectively. When HF was used instead of H$_2$SO$_4$ as shown in Table 1, DLZ-02 was produced by static synthesis under relative mild conditions of 170 °C and 50 h. The morphology of the sample was fascicular clusters aggregated by rod-like crystals. These results showed that fluoride anion could promote the crystallization process of DLZ-02 zeolite. DLZ-02 samples obtained by dynamic synthesis displayed higher crystallinity and uniform morphology. Additionally, DLZ-02 could be synthesized in a broad range with a SiO$_2$/Al$_2$O$_3$ ratio from 40 to 200. This might be due to the synergistic effects of the fluoride anion and the dual-template system consisting of DMA and DEA. These two samples also showed high crystallinity and perfect morphology.

Generally, zeolites with a single structure are directly applied in the special catalytic processes. However, in some cases mixed zeolites, composite zeolites and especially intergrowth zeolites are preferred for the exhibition of special performance due to the synergistic effect of zeolite systems. From crystallographical point of view, the presence of the intergrowth makes the unit cell dimension different from those of two mother zeolites. Moreover, intergrowth causes the change in pore shape, and ultimately affects the catalytic shape-selective properties. Recently, the catalytic hydroisomerization of long-chain paraffins of ZSM-22 and ZSM-23 zeolite catalysts has extensively been investigated owing to the importance in the industrial manufacture process of lube oil [24–26]. Therefore it is rational to expect that DLZ-02 zeolite possess peculiar catalytic performance for the hydro-isomerization of paraffins. Further work is now underway.

4. Conclusions

Well-crystallized ZSM-23/ZSM-22 intergrowth zeolite could be synthesized with a dual-template system consisting of dimethylamine and diethylamine. The molar ratio of diethylamine to dimethylamine was the key factor for the synthesis of intergrowth zeolites. Moreover, the ratio was changed with the type of aluminum source. The as-synthesized intergrowth zeolite possessed a fixed proportion of 60%ZSM-23/40%ZSM-22. Fluoride anion, which was involved in the synthesis process as a crystallization promoter, could facilitate the formation of intergrowth zeolite in a broad range of SiO$_2$/Al$_2$O$_3$ molar ratio from 40 to 200.

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References