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Synthesis of hierarchical beta zeolite by using a bifunctional cationic polymer and the improved catalytic performance

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Hierarchical beta zeolites have been hydrothermally synthesized by using commercial cationic polymer PDADMA as both microporogen and mesoporogen. The influence of various synthetic parameters on the products was systematically investigated. Products with narrow SiO/Al ratios were obtained under static crystallization conditions. By employing rotational condition and adding seeds in the initial gel, higher SiO/Al ratios over a wider range of 25 to 50 could be successfully achieved, which showed an obvious improvement. The 13C NMR, TG, XRF, N2 sorption as well as molecular mechanics simulation results indicated that PDADMA was incorporated in the final product without decomposition, acting as a SDA for the formation of beta zeolite and mesoporogen simultaneously. Further studies on the crystallization process revealed that hierarchical structures templated by PDADMA had been formed in the early solid. The amorphous Si-Al species around the micropore channels gradually evolved to the beta structure under the assistance of PDADMA, whereas the mesopores formed at the initial period remained less changed. A solid-mediated mechanism is thus proposed for the synthesis. Characterization results showed that the obtained products had sphere-like morphology composed of 10-20 nm crystalline domains, high mesopore volumes, and large external surface areas. More importantly, the hierarchical beta zeolites exhibited greatly enhanced catalytic activity and stability in the cracking reaction of triisopropylbenzene.

1. Introduction

Zeolites are a family of crystalline aluminosilicates, which have been widely used as catalysts in the refining, petrochemical and fine chemical industries due to their uniform channels, large surface area and tunable acidity.1,2 However, the relatively small micropore size of zeolites often brings diffusion limitation to the reaction involving bulky molecules, which can further cause negative effect on the activity, selectivity, and stability of the catalysts.3,4 Among the vast efforts made to enhance the mass transport in zeolites, creating mesopores in zeolite crystals has attracted great attention because it combines the advantages of mesoporous materials and zeolites.5-12 Hitherto, various strategies have been developed for the preparation of hierarchical zeolites, including desilication or dealumination by post treatment13,14 as well as through a hard-templates15,16 or soft-templating route.17-20

Direct hydrothermal synthesis of zeolites with mesoporosity is much interesting because it only involves a one-step procedure and can be easily scaled up. In addition, it may allow mesopore size adjustment while keeping the well integrity of the crystalline structure. Two general methodologies have been developed, including (i) dual templates strategy involving both micropore structure-directing agent (SDA) and mesoporogen (surfactants, polymers, etc.);17-27 (ii) bifunctional surfactant approach by using well-designed large molecule simultaneously containing micropore directing multi-ammonium heads and mesopore directing alkyl tails.28,29 As to the first method, phase separation sometimes is observed with a mixture of zeolite crystals and mesoporous materials as the product. This is possibly due to the weaker interactions between the surfactant and the silicate species, and the mismatched crystallization rates associated with two templates. Using bifunctional structure-directing surfactant may be an effective way to avoid this problem. With this method, many zeolites with nanosheet or mesoporous structures have been synthesized.

Zeolite beta, with a three-dimensional interconnected pore system composed of 12-membered rings,30 has exhibited excellent performance in hydroisomerization, hydrocracking, and alkylation.31-33 Commercial beta zeolite is generally synthesized with expensive tetraethylammonium hydroxide (TEAOH) as the SDA. The hydrothermal synthesis of hierarchical beta has been explored by a number of works according to the methods mentioned above.22-26 Novel di-/multi-quaternary ammonium surfactants or compounds have been creatively synthesized and used as SDA to construct mesoporous beta.34-37 Unfortunately, most of the reported novel SDAs are commercially unavailable.
and involve complex preparation process. It is highly desirable to develop a direct synthetic strategy by using a commercial and low cost template, which would benefit the industrial synthesis and application of hierarchical beta.

Herein, synthesis of hierarchical beta zeolite was realized by using a low-cost commercial cationic polymer polydiallyldimethylammonium chloride (PDADMA) as both microporogen and mesoporogen.\textsuperscript{38} Cationic polymers, with high charge density and distinct properties from surfactants, have been reported as mesoporegen or dual-function SDA to prepare hierarchical zeolites. Xiao et al. first reported the use of mesoscale cationic polymer to produce hierarchical beta and ZSM-5.\textsuperscript{22,27,39} Afterwards, nanobeta aggregates with tunable mesopore size were realized by using cationic polymer as a flocculating agent.\textsuperscript{20} Very recently, Xiao et al. synthesized hierarchical beta with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios of 18-24 as a dual-function template and fumed silica as the Si source with cationic polymer PDADMA as a dual-function template.\textsuperscript{40} In the present work, by using inexpensive silica sol as the Si source, mesoporous beta with tunable SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios (25-50), which is important for their catalytic applications, have been achieved with the help of PDADMA. The improved SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio should be due to the different Si sources (silica sol vs. fumed silica) and optimized synthetic conditions. The accelerated crystallization by a combination of seeds addition and rotational condition was believed to be the pivotal factor to obtain hierarchical beta with higher SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios. In addition, the influence of synthetic parameters on the products and the crystallization process were investigated in detail. 1,3,5-triisopropylbenzene (TIPB) cracking reaction was selected as a probe reaction to test the catalytic performance of the products.

2. Experimental

2.1 Typical synthesis procedure for hierarchical beta

The chemical reagents used in the experiments include: NaAlO\textsubscript{2} (54.55 % Al\textsubscript{2}O\textsubscript{3}, 40.95 % Na\textsubscript{2}O, Tianjin Guangfu Chemical Co.), colloidal silica (30.10 % SiO\textsubscript{2}, Qingdao Chengyu Chemical Co.), PDADMA (molecular weight: 600,000 g/mol, 40 % in water, Hangzhou Yinhu Chemical Co., Ltd.), NaOH (≥97 %, Tianjin Kemiou Chemical Reagent Co.), NH\textsubscript{3}·H\textsubscript{2}O, Tianjin Guangfu Chemical Co.), 1,3,5-triisopropylbenzene (≥95 %), and dicyandiamide ammonium chloride (60 % in water) bought from Aladdin Industrial Corporation. All the above reagents were used without further purification.

Typical synthesis of hierarchical beta zeolites under static condition: 2.08 g NaOH, 0.37 g NaAlO\textsubscript{2}, and 58.00 g distilled water were mixed at room temperature, followed by the addition of 20.00 g colloidal silica under vigorous stirring. After 1 h of stirring, 6.00 g PDADMA was added to the gel, and then the resulting mixture was stirred vigorously for an additional 3 h to obtain a homogenous gel. The final mixture with a molar composition of 0.02Al\textsubscript{2}O\textsubscript{3}:1.00SiO\textsubscript{2}:0.28Na\textsubscript{2}O:40H\textsubscript{2}O:0.14PDADMA (0.14 stands for the molar ratio of repeating unit in PDADMA) was transferred into a Teflon-lined stainless steel autoclave. The crystallization was carried out at 170 °C under static condition. The product was filtered, washed with distilled water, and dried at 100 °C for 12 h. The organic template in the product was removed by calcination at 550 °C for 5 h. The proton forms of the samples were obtained by ion exchange with 1 M NH\textsubscript{4}NO\textsubscript{3} aqueous solution (1 g calcined sample in 10 ml solution) at 80 °C under stirring, and the solution was renewed every 2 h for three times. The solid was filtered, washed with deionized water, dried in air at 100 °C for 12 h, and calcined at 550 °C for 4 h.

Synthesis of hierarchical beta zeolite under rotational condition: the synthesis procedure was similar to the above experiment except for the addition of beta seeds (as-synthesized sample 3 as seed, 5 wt% relative to SiO\textsubscript{2}). The crystallization was carried out at 180 - 200 °C rotated at 60 rpm.

2.2 Characterization

The powder XRD pattern was recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu-Ka radiation (λ = 0.15418 nm), operating at 40 kV and 40 mA. The chemical composition of the solid samples was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by scanning electron microscopy (Hitachi SU8020). Transmission electron microscopy (TEM) images were performed on a Tecnai G2 F20 S-TWIN microscope at an acceleration voltage of 200 kV. The sample was slightly ground before the TEM test. N\textsubscript{2} adsorption-desorption isotherms at -196 °C were determined on a Micromeritics ASAP 2020 system. Prior to the measurement, samples were degassed at 350 °C under vacuum for 5 h. The total surface area was calculated based on the BET equation. The micropore volume and micropore surface area were evaluated using the t-plot method. The mesopore size distribution was determined by the BJH method based on the adsorption branches of the isotherms. The liquid \textsuperscript{13}C NMR experiments were performed on a Bruker DRX-400 spectroscopy with a 5 mm probe. The chemical shifts were referenced to TMS. Solid state NMR experiments were performed on a Varian Infinity plus 400 WB spectrometer with BBO MAS probe operating at magnetic field strength of 9.4 T. The resonance frequencies were 104.2 and 79.4 MHz for \textsuperscript{27}Al and \textsuperscript{29}Si respectively. Chemical shifts were referenced to 1.0 M Al(NO\textsubscript{3})\textsubscript{3} for \textsuperscript{27}Al and 2, 2-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) for \textsuperscript{29}Si. The spinning rates of the samples at the magic angle were 4 and 6 kHz for \textsuperscript{27}Al and \textsuperscript{29}Si respectively. The thermal analysis was performed on a TA Q-600 analyzer with a temperature-programmed rate of 10 °C/min under an air flow of 100 ml/min. Temperature-programmed desorption of ammonia (NH\textsubscript{3}-TPD) was measured on a chemical adsorption instrument of Micrometric 2920. Each sample (40-60 mesh, 0.15 g) was loaded into a stainless U-shaped micro reactor (i.d. = 5 mm) and pretreated at 600 °C for 1 h in flowing He. After the pretreatment, the sample was cooled down to 100 °C and saturated with NH\textsubscript{3} gas. Then, NH\textsubscript{3}-TPD was carried out in a constant flow of He (20 ml/min) from 100 to 700 °C at a heating rate of 20 °C/min.

2.3 Catalytic reaction

1,3,5-triisopropylbenzene (TIPB) cracking was performed in a fixed-bed reactor at atmospheric pressure. 300 mg of the sample (40-60 mesh) was loaded into the reactor, and dehydrated in N\textsubscript{2} (50 ml/min) at 500 °C for 1 h prior to the reaction. The temperature of the catalyst bed was reduced to 230 °C in N\textsubscript{2} and...
3. Results and discussion

3.1 Synthesis of hierarchical beta under static condition

The synthetic parameters for the hierarchical beta zeolites under static condition using PDADMA as a dual-functional porogen are summarized in Table 1. The X-ray diffraction (XRD) patterns of the products are presented in Fig. 1 and Fig. S1.

Table 1 Gel compositions and products of the synthesis under static condition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Na$_2$O/SiO$_2$</th>
<th>P/SiO$_2$</th>
<th>t (day)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.28</td>
<td>0</td>
<td>7</td>
<td>MOR + Quartz</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.28</td>
<td>0.110</td>
<td>7</td>
<td>Amorphous</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.28</td>
<td>0.140</td>
<td>9</td>
<td>Beta</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.28</td>
<td>0.210</td>
<td>9</td>
<td>Beta</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>0.28</td>
<td>0.280</td>
<td>9</td>
<td>Beta</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0.25</td>
<td>0.140</td>
<td>7</td>
<td>Amorphous + Beta</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>0.30</td>
<td>0.140</td>
<td>9</td>
<td>Beta</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>0.32</td>
<td>0.140</td>
<td>7</td>
<td>Beta + ANA</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>0.40</td>
<td>0.140</td>
<td>7</td>
<td>ANA</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>0.28</td>
<td>0.140</td>
<td>6.5</td>
<td>Beta + ANA</td>
</tr>
<tr>
<td>11</td>
<td>40</td>
<td>0.28</td>
<td>0.140</td>
<td>9</td>
<td>Beta + ANA</td>
</tr>
<tr>
<td>12</td>
<td>70</td>
<td>0.28</td>
<td>0.140</td>
<td>7</td>
<td>Beta + Kenyaite</td>
</tr>
</tbody>
</table>

The products were analyzed on line by gas chromatography on an Agilent 6890 with an FID detector using a HP-5 column.

In the absence of PDADMA in the gel, mordenite with small crystal sizes of the present sample. The effect of Na$_2$O/SiO$_2$ ratio in the gel up to 0.32 was investigated by fixing other synthetic conditions (samples 6-9). It turned out that the synthesis of beta zeolite was very sensitive to the alkaline amount in the initial gel. The ratio suitable for the formation of pure beta zeolite was limited in the range of $0.28 \leq$ Na$_2$O/SiO$_2 < 0.32$. Lower Na$_2$O/SiO$_2$ ratio (0.25) greatly reduced the crystallization rate, whereas increasing the Na$_2$O/SiO$_2$ ratio in the gel up to 0.32 would cause the appearance of ANA phase. It should be noted that all the syntheses under static condition undergo long crystallization time (7-9 days). Possibly, the strong interactions between cationic polymer and negatively charged silica species slowed down the nucleation and growth rate. A detailed research on the crystallization process of beta zeolite would be given in the section below.

Preparation of hierarchical zeolites with adjustable SiO$_2$/Al$_2$O$_3$ ratio is always important, because it is closely related to their acidic/catalytic properties. Few reports on the synthesis of hierarchical beta pay attention to this issue, but more to the novelty of surfactant/compound porogens. Here, a series of experiments with different initial SiO$_2$/Al$_2$O$_3$ ratios were conducted at 170 °C under static condition (samples 10-12). As can be seen, the SiO$_2$/Al$_2$O$_3$ ratio in the gel is almost unadjustable. Otherwise, ANA phase or kenyaite would appear as the impurity. This is in agreement with the report of Xiao et al. in which a narrow SiO$_2$/Al$_2$O$_3$ ratio has been found for PDADMA-templated beta zeolites.

3.2 Synthesis of hierarchical beta with higher SiO$_2$/Al$_2$O$_3$ ratio under rotational condition

During the exploration of synthesizing beta zeolite with higher SiO$_2$/Al$_2$O$_3$ ratio, we found that rotational crystallization assisted by the seeds could allow an obvious improvement. Detailed synthetic conditions are listed in Table 2. The XRD patterns of the as-synthesized products are shown in Fig. S2.

Table 2 Gel compositions and products of the synthesis under rotational condition with the addition of 5 % seed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Na$_2$O/SiO$_2$</th>
<th>P/SiO$_2$</th>
<th>T (°C)</th>
<th>t (day)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>50</td>
<td>0.28</td>
<td>0.14</td>
<td>180</td>
<td>3</td>
<td>Beta</td>
</tr>
<tr>
<td>14</td>
<td>75</td>
<td>0.28</td>
<td>0.14</td>
<td>180</td>
<td>3</td>
<td>Beta</td>
</tr>
<tr>
<td>15</td>
<td>100</td>
<td>0.28</td>
<td>0.14</td>
<td>180</td>
<td>3</td>
<td>Beta</td>
</tr>
<tr>
<td>16</td>
<td>50</td>
<td>0.28</td>
<td>0.14</td>
<td>190</td>
<td>1.5</td>
<td>Beta</td>
</tr>
<tr>
<td>17</td>
<td>50</td>
<td>0.28</td>
<td>0.14</td>
<td>200</td>
<td>2</td>
<td>Beta + FER+ Quartz</td>
</tr>
</tbody>
</table>

$^a$ SiO$_2$/Al$_2$O$_3$ in the gel, not containing the compositions of the seed.

$^b$ P/SiO$_2$ stands for the molar ratio of PDADMA repeating unit and SiO$_2$ in the gel.

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surface of the particles. Therefore, the small particle size results in the increase of the external surface area and nanocrystals together with their interconnection ensure the high mesopore volume,\textsuperscript{43} in good agreement with the results of N\textsubscript{2} sorption. The large proportion of acid sites on external surface would be beneficial for reactions involving bulky molecules. In addition, the smaller crystal size could greatly shorten the diffusion length compared with conventional zeolites.

Fig. 4a displays the \textsuperscript{27}Al and \textsuperscript{29}Si MAS NMR spectra of the as-synthesized beta product (sample 3). There only exists one peak centered at 54 ppm, arising from the tetrahedral aluminum species. The \textsuperscript{29}Si MAS NMR spectrum of the same sample is shown in Fig. 4b. One strong resonance at -110 ppm together with three shoulders at -115 ppm, -105 ppm and -98 ppm can be observed. According to the literatures, the peak at -115 and -110 ppm are ascribed to Si(0Al) species and the peak at -105 ppm corresponds to Si(1Al) species.\textsuperscript{44} The small shoulder centered at -98 ppm is assigned to Si (OH) species in the defect sites. The corresponding SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio calculated based on the \textsuperscript{29}Si NMR spectrum is 29.8, in accordance with the XRF result.

Thermal analysis (TG-DSC) was carried out to investigate the content of the organic template in the product (sample 3). The results are shown in Fig. S3. Two weight losses could be clearly observed in the TG curve (sample 3). The first weight loss about 7 % in the temperature range of 0-200 \degree C with an endothermic effect is due to the removal of water from the zeolites. The second weight loss of 33 % in the temperature range of 200-650 \degree C with exothermic effect is attributed to the combustion removal of PDADMA or using the cationic monomer (dimethyl diallyl ammonium chloride) as a SDA. Such a high weight loss is consistent with the large mesopore volume of the sample.

13C NMR spectra were employed to investigate the status of organic polymer in the as-synthesized hierarchical product (Fig. S4). The spectrum of the liquid obtained by dissolving as-synthesized sample 3 in HF solution is similar to that of PDADMA solution, suggesting the intactness of the polymer during crystallization. In order to further understand the templating role of PDADMA, control syntheses without the use of PDADMA or using the cationic monomer (dimethyl diallyl ammonium chloride) as a SDA were conducted, but failed with a mixture of mordenite and quartz as the final products. It seems that the 5-membered cyclic quaternary ammonium cation in the polymer chain is important for the formation of beta structure.

Using polymer containing ten repeating units as the model compound, the geometrical optimization by molecular mechanics simulation was performed (Fig. 5). The maximum dimension of a repeating unit is calculated to be 0.65 × 0.42 nm, which is close to the pore sizes of beta zeolites (0.66 × 0.67 nm and 0.56×0.56 nm in the [100] and [001] direction, respectively). It is thus speculated that the polymer chain locates within the 12-membered rings along the direction of the channels. However, not the entire polymer chain is expected to be occluded in the channel because of its extreme length (the calculated chain length would be 2.4 \mu m for PDADMA with a molecular weight of \textit{6}×\textit{10}\textsuperscript{5} g/mol). The rest part of the chain outside the micropore of beta zeolite would have strong interaction with the negatively charged crystal surface (resulting from the alkaline media) due to its highly positive charge density. This electrostatic interaction would prevent the further growth of the crystal and result in the hierarchical structure. To further verify the speculation, N\textsubscript{2} sorption on the as-synthesized sample (Fig. S5) was performed, which gives a type-IV isotherm. The absence of micropore volume and lower mesopore volume (0.30 cm\textsuperscript{3}/g) as compared with that of calcined one indicates the total occupation of the polymer in the micropores and partial occupation in the mesopores,\textsuperscript{45} confirming our speculation well. In addition, based on the XRF results that only small amount of sodium and chlorine existed in the as-synthesized sample 3 (Cl 0.036wt%, Na/Al=0.034 in mole, the sample had been carefully washed), it confirmed that the polymer acted as the main SDA for the formation of beta zeolite, though the Na\textsuperscript{+} was indisposable for the synthesis as shown in the above (Table 1 and 2). Na\textsuperscript{+} may serve as a co-SDA together with the cationic polymer during the synthesis, but it only occupies a very small proportion.

3.4 Investigation of the crystallization process

In order to understand the growth process of hierarchical beta, samples with different crystallization time were investigated (the initial gel has the same molar composition as that of sample 3). The XRD patterns (Fig. 6) reveal the evolution of long-range order of the samples. No apparent diffraction peak was observed in the XRD pattern of the 1 d sample, indicating the amorphous characteristic. After 3 days, very weak diffraction peaks at 7.6 \degree and 22.3 \degree began to appear, which suggests the formation of small amount of beta zeolite. Subsequently, the peak intensities gradually increased with time and well-defined diffraction pattern could be obtained after 9 days. The SEM images (Fig. 7) indicated that there only existed irregular agglomerates in the 1 d
Fig. 6 XRD patterns of the as-synthesized samples with different crystallization times (The initial gel has the same molar composition as that of sample 3).

Fig. 7 SEM images of the samples with different crystallization time: (a) 1 day, (b) 3 day, (c) 5 day, (d) 7 day, (e) 9 day.

After heating for 3 d, less change could be found in spite of the presence of weak peaks in the XRD pattern. With the hydrothermal treatment time prolonging to 5 days, small amount of sphere-like crystals could be distinguished at the surface of amorphous materials. Afterwards, more sphere particles with diameter of about 500 nm formed, which closely connected with the residue amorphous materials. Finally, only pure beta crystallites could be observed in the 9 d sample.

The N\textsubscript{2} sorption analyses of the samples were performed to monitor the evolution of the porosity during the crystallization process (Fig. S6 and Table 4). Interestingly, porous structures have already been generated in the 1 d sample with a micropore and mesopore volume of 0.06 and 0.68 cm\textsuperscript{3}/g, respectively. The presence of large mesopore volume is understandable, owing to the removal of entrapped polymer. But it is somewhat unexpected to see the creation of the microporosity in this early amorphous solid. Further analyzing the pore size distribution (Fig. S7) reveals that the micropore aperture of the 1 d sample is different from that of the final beta product. The former is obviously larger than the latter. Following the formation of hierarchical beta as evidenced by XRD and SEM, both the microporosity and mesoporosity of the samples showed an increasing trend with time and reached their maximum at 9 days. It should be mentioned that the mesopores centred around 14 nm in the solid samples remained almost unaltered during the whole synthesis course. These results demonstrate that PDADMA has strong micropore-directing ability in the present system, which plays the role of microporogen and mesoporogen since the initial period of the crystallization. The amorphous Si-Al species around the micropore channels of the initial solid could evolve to uniform beta structure under the assistance of PDADMA, whereas the mesopores formed by PDADMA at the initial period remained less changed. In addition, it was found that the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios of the samples and the solid yields kept close to each other during the crystallization (Table 4). We thus suggest that a solid-mediated mechanism may occur during the crystallization of hierarchical beta.

3.5 Surface acidity and catalytic performance of hierarchical beta zeolite

The NH\textsubscript{3}-TPD experiment was carried out to investigate the acid properties of the protonated hierarchical beta and commercial sample. As shown in Fig. 8, all profiles exhibit two peaks centered at 182 °C and 345 °C. The low-temperature peak is assigned to ammonia desorbed from the weak acid site and the high-temperature peak corresponds to desorption from the strong acid sites. In comparison with the commercial sample, both hierarchical beta zeolites (samples 3 and 13) showed a

Table 4. Chemical compositions and textural properties of the samples with different crystallization time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} \textsuperscript{b}</th>
<th>Yield (%)</th>
<th>S\textsubscript{BET} \textsuperscript{c} (m\textsuperscript{2}/g)</th>
<th>S\textsubscript{micro} \textsuperscript{d} (m\textsuperscript{2}/g)</th>
<th>S\textsubscript{external} \textsuperscript{d} (m\textsuperscript{2}/g)</th>
<th>V\textsubscript{micro} \textsuperscript{d} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{meso} \textsuperscript{e} (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>29.8</td>
<td>47%</td>
<td>448</td>
<td>151</td>
<td>297</td>
<td>0.06</td>
<td>0.68</td>
</tr>
<tr>
<td>3d</td>
<td>29.4</td>
<td>47%</td>
<td>492</td>
<td>160</td>
<td>322</td>
<td>0.07</td>
<td>0.78</td>
</tr>
<tr>
<td>5d</td>
<td>29.5</td>
<td>49%</td>
<td>485</td>
<td>161</td>
<td>325</td>
<td>0.07</td>
<td>0.73</td>
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<tr>
<td>7d</td>
<td>29.5</td>
<td>49%</td>
<td>688</td>
<td>250</td>
<td>437</td>
<td>0.11</td>
<td>0.93</td>
</tr>
<tr>
<td>9d</td>
<td>29.3</td>
<td>48%</td>
<td>789</td>
<td>316</td>
<td>473</td>
<td>0.14</td>
<td>0.94</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The initial gel has the same molar composition as that of sample 3. \textsuperscript{b} Obtained by XRF (molar ratio). \textsuperscript{c} BET surface area. \textsuperscript{d} Micropore area, external surface area and micropore volume by t-plot method. \textsuperscript{e} Mesopore volume by BJH method.
considerable improvement in the weak acid concentration and slight increase in the strong acid concentration. Since sample 3 and 13 possessed slightly higher SiO$_2$/Al$_2$O$_3$ ratios than the commercial sample, the improved acid concentration of hierarchical samples may reflect the distinct Al location/distribution associated with the use of polymer and would benefit their catalytic applications.\(^48\)

The catalytic performance of the hierarchical samples was investigated by the reaction involving bulky organic molecules. The abundant mesoporosity and large external surface area are believed to facilitate the diffusion and the improvement of the catalyst activity and stability. Herein, the cracking of 1, 3, 5-trisopropylbenzene was used as a probe reaction. Both Brønsted and Lewis acid sites are active for the TIPB cracking.\(^49, 50\) For zeolite catalysts, the cracking activity is generally related to the Brønsted acidity.\(^51\) Given that the kinetic molecular dimension of TIPB (about 0.95 nm) is larger than the micropore size of the beta, the effective catalytic sites for the cracking should be mainly from the external surface of the catalysts (the acid sites in the micropores may contribute to the deep cracking such as cumene to benzene).\(^52\)

As shown in Fig. 9, both hierarchical beta zeolites displayed not only higher activity, but also much better stability. Under the investigated conditions, a 99% conversion of TIPB was achieved with hierarchical catalysts at the initial reaction, whereas 85% conversion obtained over the commercial one. Subsequently, commercial sample suffered from fast deactivation and the conversion of TIPB decreases to 39.6% at TOS of 137 min. The hierarchical samples showed less deactivation and the conversion of TIPB maintains at 90% at this time. In combination with the above results of textural property and acidity characterization, the good catalytic activities and stabilities of hierarchical samples should be attributed to their abundant mesoporosity and small crystal size, which increases the accessibility of reactants to the acid sites and facilitate the product diffusion.\(^50\)

4 Conclusions

In the present work, we synthesized hierarchical beta zeolite with low-cost commercial polymer PDADMA as a bifunctional porogen. The fastened crystallization process assisted by the seeds addition under rotational condition was found to be crucial to acquire hierarchical beta over a wider range of SiO$_2$/Al$_2$O$_3$ ratios. The SiO$_2$/Al$_2$O$_3$ ratios in the products could be tuned from 25 to 50, which are higher than the ratio of 18-24 achieved with the same polymer reported recently. This is also important for their catalytic applications. Investigation on the crystallization process revealed a solid-mediated mechanism for the present synthesis. Characterization results indicated that PDADMA served as the main SDA for the formation of beta structure and the products assembled by small zeolite crystallites (10-20 nm) featured very high surface areas and large mesopore volumes. The hierarchical beta zeolites exhibited excellent activity and stability in the cracking reaction of TIPB as compared to conventional sample. It is expected that this facile approach, taking advantage of low cost and tunable SiO$_2$/Al$_2$O$_3$ ratios, could bring new possibilities for the scale-up synthesis and industrial applications of hierarchical beta zeolite. In the future, exploration on the micropore-directing ability of cationic polymers to other kinds of zeolites would also be necessary.

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Notes and references