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Influence of Al³⁺ on polymorph A enrichment in the crystallization of beta zeolite

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ABSTRACT

Using tetraethylammonium hydroxide as the organic structure-directing agent and in the presence of fluoride, polymorph A-enriched silica beta zeolite was synthesized under concentrated hydrothermal conditions. The introduction of Al species into the same starting mixture resulted in a decrease in the degree of enrichment of polymorph A in beta zeolite and an Al-incorporated beta zeolite resulted. The crystallized polymorph A-enriched silica beta zeolite and the Al-incorporated beta zeolite and their crystallization processes were investigated by X-ray diffractometry, elemental analysis, thermogravimetric analysis-differential thermal analysis, nitrogen adsorption, scanning electron microscopy, and solid-state magic angle spinning nuclear magnetic resonance. The introduction of Al species accelerated crystallization and reduced the crystal size of Al-incorporated beta zeolite. The intermediate of five-coordinated Al species accounted for a decrease in the degree of enrichment of polymorph A in the crystallization of Al-incorporated beta zeolite.

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1. Introduction

Beta zeolite was first synthesized by Mobil using tetraethylammonium hydroxide (TEAOH) as an organic structure-directing agent (OSDA) from a basic aqueous aluminosilicate gel in 1967 [1]. The structure of beta zeolite was determined independently by Newsam *et al.* [2] and by Higgins *et al.* [3] in 1988. Structural analysis suggests that beta zeolite is a highly disordered structure formed by the random intergrowth of two polymorphs A and B [2], in a 44/56 ratio. Polymorph A belongs to space group *P*₄122 or *P*₄322 and polymorph B be-

longs to space group *C*2/c. Polymorph A has a chiral structure, with a helical pore running along the *c* axis, and is the only known real zeolite structure that exhibits chirality. However, synthesis of a pure form of chiral polymorph A remains a goal of zeolite synthesis and a difficult challenge. Many attempts have been made to synthesize pure polymorph materials. The first effort was reported by Davis and Lobo in 1992 [4]. The authors suggested a strategy for the synthesis of one enantiomorph of polymorph A, in which a chiral OSDA with appropriate size and sufficient thermal stability is necessary. By using an unspecified chiral OSDA, the authors synthesized a beta

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zeolite that was enriched in polymorph A, as determined from a comparison of the experimental X-ray diffraction (XRD) pattern of the resulting beta zeolite with the simulated pattern of the pure polymorph A. This sample of beta zeolite could perform enantioselective adsorption and catalysis and yield a low enantiomeric excess (5%). For the first time, Cambor *et al.* [5] presented the unseeded synthesis of silica beta zeolite in 1996 and showed that the resulting material is highly hydrophobic with a very high thermal stability. The XRD pattern of the silica beta zeolite shows a slightly higher amount of polymorph A (~50% A), but no detailed analysis was provided. Xia *et al.* [6] synthesized a series of metal-incorporated beta zeolite in fluoride medium for asymmetric hydrogenation in 2003. The majority of these materials showed similar XRD patterns to the silica beta zeolite prepared by Cambor *et al.*, and ~10% enantiomeric excess was obtained when applied in the hydrogenation of tiglic acid. In 2007, Takagi *et al.* [7] reported on the synthesis of polymorph A-enriched beta zeolite in the presence of chiral amine or rhodium complex. Later, Taborda *et al.* [8] reported on aging drying synthesis and the characterization of silica beta zeolite. They also found that the addition of organic solvents during thermal treatment tunes the crystal morphology but does not affect polymorphic enrichment. However, profiles of the experimental XRD patterns that they have reported are very similar to those of normal beta zeolite. Tong *et al.* [9] and Guo *et al.* [10] reported on the synthesis of polymorph A-enriched silica beta zeolite with a polymorph A percentage as high as 66%.

Silica beta zeolite is not usually used as a catalyst without modification. The incorporation of heteroatoms into the zeolite framework without affecting the framework structure could generate catalytically active sites and provide more applications. For example, titanium-incorporated beta zeolite performs well as a selective oxidative catalyst and could replace homogeneously catalyzed processes that generate waste and react under stringent conditions [11]. Stannum-incorporated beta zeolite could exhibit good catalytic activity in Baeyer Villiger oxidation reactions [12]. Mesoporous Sn-beta zeolite also exhibits superior performance in α -pinene isomerization and isomerization of glucose in water [13]. Co-beta zeolite is a good catalyst for converting ethane to acetonitrile with high rate and selectivity [14]. Iridium-containing beta zeolite is a high-performance ring-opening catalyst in the hydroconversion of decalin [15]. Al-free Zr-beta zeolite as a regioselective catalyst in the Meerwein Ponndorf Verley reaction is robust and yields good results even with 10% water content in the reaction mixture [16]. Thus, the incorporation of heteroatoms into the framework of polymorph A-enriched beta zeolite may generate active sites in enantioselective catalysis.

In this work, we investigated the synthesis of polymorph A-enriched silica beta zeolite and the influence of Al^{3+} on the enrichment of polymorph A in the crystallization of beta zeolite. The well-crystallized silica and Al-incorporated beta zeolite products were characterized by XRD, elemental analysis, thermogravimetric analysis (TGA)-differential thermal analysis (DTA), nitrogen adsorption, and scanning electron microscopy (SEM). Their crystallization was investigated by XRD and sol-

id-state magic angle spinning nuclear magnetic resonance (MAS NMR).

2. Experimental

2.1. Synthesis

For the synthesis of silica polymorph A-enriched beta zeolite, 16.0 g tetraethyl orthosilicate (TEOS, 99 wt%) was added to a solution of 15.7 g TEAOH (35 wt% in water). After the hydrolysis of TEOS for 5 h, the resulting mixture was stirred for a further 4 h under infrared radiation to evaporate ethanol and most of the water, and was then placed in an 80 °C oven for several days until the ratio of water to silicon dioxide was ~0.3. The solid was ground into a powder, and 1.5 g ammonium fluoride (99 wt%) was added under continuous grinding to form a uniform mixture. The mixture was divided into several parts and heated for different periods of time (0, 5, 37, and 168 h) in autoclaves at 150 °C and quenched in cold water. The solid product was dried under vacuum at ambient temperature without further water washing. The 168 h product was washed with water several times, dried at 100 °C overnight, and calcined at 550 °C in air for 6 h.

To obtain the Al-incorporated polymorph A-enriched beta zeolite, an aluminum source was used in the synthesis procedure described above. The synthesis was carried out by adding 0.6 g aluminisopropoxide (99 wt%) to a solution of 15.7 g TEAOH stirred by magnetic stirrer. The solution was stirred for 30 min until all aluminisopropoxide was fully dissolved into the TEAOH. TEOS (16.0 g) was added to the stirring mixture, and the remaining heating, drying, washing, and calcining procedure is as described above.

2.2. Characterization

Powder XRD patterns were recorded on a Rigaku D/MAX-2550 diffractometer equipped with a graphite monochromator using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) operated at 50 kV and 200 mA. The samples were scanned in the 2θ range from 4° to 40°, with a step size of 0.02°. The morphology was studied by SEM using a JEOL JSM-6700F microscope. TGA-DTA was performed at 10 °C/min in air using a NETZSCH STA 449C analyzer. Nitrogen adsorption desorption was carried out on a Micromeritics 2020 analyzer at -196 °C after the sample had been degassed at 350 °C under vacuum. Single-pulse ^{27}Al MAS NMR experiments were performed on a Varian Infinity-plus 300 spectrometer at 78.11 MHz using a 4 mm probe at a sample spinning rate of 10 kHz. Spectra were recorded by the small flip angle technique with a pulse length of 0.5 μs and a recycle delay of 1 s. ^{29}Si MAS NMR spectroscopy was carried out at 9.4 T on a Varian Infinity-plus 400 spectrometer, equipped with a 5 mm probe, with resonance frequencies of 399.52 and 79.36 MHz for ^1H and ^{29}Si , respectively. Single-pulse ^{29}Si MAS experiments with ^1H decoupling were performed using a $\pi/2$ pulse width of 7.2 μs and a repetition time of 30 s. The MAS rate was set at 8 kHz. ^{19}F MAS NMR experiments were carried out on a Bruker-Avance III-500 spectrometer with a ^{19}F resonance fre-

quency at 470.97 MHz. Spectra were acquired with a single-pulse sequence using a $\pi/2$ pulse of 2 μ s and a repetition time of 5 s. The MAS rate was set at 25 kHz.

3. Results and discussion

3.1. Polymorph A-enriched silica beta zeolite

Fig. 1(a) shows the experimental powder XRD pattern of silica beta zeolite. The XRD pattern profile is similar to that of highly crystallized normal beta zeolite except for some characteristic peaks corresponding to polymorph A. Peak broadening in the low-angle region occurs because of stacking faults in the intergrowth of polymorphs A and B. In the beta zeolite synthesized under normal conditions (denoted normal beta zeolite), the polymorph ratio of A/B was determined as 45/55. Treacy's group [2] developed a DIFFaX program to evaluate the XRD pattern profile of the structure with different A/B polymorph ratios. Using this program, the powder XRD patterns of beta zeolite with different A/B polymorph ratios can be obtained. Fig. 1(b) shows the experimental and simulated powder XRD patterns of silica beta zeolite with A/B polymorph ratios of 50/50, 60/40, and 70/30. The data in Fig. 1(b) suggest that the percentage of polymorph A in silica beta zeolite varies between 60% and 70%.

The SEM morphology images of silica beta zeolite at differ-

Fig. 1. (a) Powder XRD pattern of silica beta zeolite; (b) Comparison of experimental (1) and simulated powder XRD patterns with different A/B polymorph ratios: (2) 0/100 (pure polymorph B); (3) 50/50; (4) 60/40; (5) 70/30; (6) 100/0 (pure polymorph A).

Fig. 2. SEM images of silica beta zeolite with different magnifications.

ent magnifications are shown in Fig. 2. The bulk sample consists of well-defined and broken crystals. The well-defined crystals with characteristic truncated bipyramidal shape have a typical size of 25 μ m. In the cross section of the broken crystals (Fig. 2(b)), thin-layer steps are visible, which suggests that the crystals of silica beta zeolite may form from a layer-stacking growth mode.

Fig. 3 shows the TGA-DTA curves of the as-synthesized silica beta zeolite, which shows four mass loss steps between ambient temperature and 800 $^{\circ}$ C. The mass loss in the first step from ambient temperature to 200 $^{\circ}$ C is $\sim$ 1.5%, which can be attributed to the removal of physically adsorbed water, whereas the mass losses from 200 to 280 $^{\circ}$ C, 280 to 380 $^{\circ}$ C, and 380 to 550 $^{\circ}$ C are $\sim$ 6%, 11%, and 2.5%, respectively.

In a previous study on the thermal analysis of silica beta zeolite synthesized from fluoride-containing media under argon, three mass losses occurred from 20–170 $^{\circ}$ C (I), 170–280 $^{\circ}$ C (II), and 280–700 $^{\circ}$ C (III) [17]. The first mass loss was attributed to occluded water. In the second temperature range, the Hofmann

Fig. 3. TGA-DTA curves of as-synthesized silica beta zeolite.

elimination reaction occurred, which resulted in the release of ethylene and triethylamine. If fluoride can be burned out in this step, hydrogen fluoride will be released; if not, a positive charge in the form of a proton will be occluded in the framework to compensate for the negative fluoride charge. The third mass loss was attributed to the decomposition of triethylamine. After thermal analysis, the sample became dark, which is attributed to coke formed in the third step.

In 1992, Bourgeat-Lami *et al.* [18] investigated the mechanism of the thermal decomposition of tetraethylammonium in fluoride-free aluminosilicate beta zeolite with different Si/Al ratios and observed four mass loss steps: I, 25–150 °C; II, 150–350 °C; III, 350–500 °C; IV, 500–700 °C. The mass loss in each step varied with Si/Al ratios (13.8–27.5). In the first step, the mass loss (25–150 °C, 3.9%–1.8%) was attributed to the desorption of physically adsorbed water. The major products released in the second step (150–350 °C, 3.6%–10.2%) were carbon dioxide, water, ethylene, and triethylamine, which indicates the decomposition of TEA⁺ *via* a Hofmann elimination reaction. Minor amounts of mono- and diethylamine and hydrocarbons with more than three carbon atoms were detected in the second step. The authors attribute the presence of hydrocarbons heavier than ethylene to the oligomerization of ethylene followed by rearrangement and cracking of the resulting oligomer on acidic sites. The same products were also detected in the third step (350–500 °C, 6.6%–3.0%), which suggests that the complete decomposition of TEA⁺ crossed the second and third steps. The mass loss in the fourth step (500–700 °C, 6.8%–4.6%) was attributed to the burning of organics. The authors therefore concluded that (1) all TEA⁺ decomposed into triethylamine and ethylene in a single step from 200–350 °C, (2) the amine re-adsorbed on the acidic zeolite sites and, as the temperature was increased, it decomposed into lighter amines by sequential Hofmann elimination reactions, (3) part of the ethylene also reacted with the acid sites to yield aliphatic and aromatic hydrocarbons, and (4) complete desorption of the organic species from the framework required a temperature higher than 500 °C.

Camblor *et al.* [19] investigated the thermal analysis of aluminosilicate beta zeolite synthesized in the absence of alkali cations and fluoride and also observed four mass loss steps: I, 25–150 °C; II, 150–350 °C; III, 350–500 °C; IV, > 500 °C. They assigned the mass loss in the first step to the desorption of occluded water and that in the second step to the TEA⁺ cations, which balance the charge of the Si–O[−] groups in connectivity defects. Above 150 °C but below 300 °C (second step), Hofmann degradation occurred to yield triethylamine and ethylene, which are then desorbed to form a Si–OH group. As the temperature increases, TEA⁺ combustion and occluded triethylamine resulted. They attributed the mass losses in the third and fourth steps to TEA⁺ cations that balance framework Al(OSi)₄[−] species. In the third step, the combustion of TEA⁺ occurred and coke was formed because of the incomplete pyrolysis of a fraction of the TEA⁺, which is burnt off in the fourth step.

Therefore, in this study, the mass loss of 6% in the second step occurs from the release of ethylene and partial triethylamine, and the mass loss of 11% in the third step can be at-

Fig. 4. ¹⁹F MAS NMR spectra of silica beta zeolite calcined at (1) 400 °C and (2) 550 °C.

tributed to the combustion of TEA⁺ and occluded triethylamine. This behavior corresponds to the two exothermic peaks at 280 and 380 °C in Fig. 3, respectively. In the fourth step, the mass loss may occur as a result of the burn-off of coke. However, the fluoride content in silica beta zeolite synthesized from fluoride medium is ~1.8%–2.0% [20]. To clarify whether the mass loss of 2.5% is fluoride, the same silica beta zeolite calcined at 400 and 550 °C was analyzed with ¹⁹F MAS NMR and the spectra are shown in Fig. 4. The data in Fig. 4 show that fluoride was still occluded in the beta zeolite framework at 400 °C. However, part of the fluoride was burned out at 550 °C. Therefore, the mass loss of 2.5% in the fourth step contains fluoride. Powder XRD studies imply that the silica beta zeolite structure is stable even with the decomposition of tetraethylammonium upon calcination at 550 °C.

The textural properties of calcined silica beta zeolite were determined by nitrogen adsorption desorption and a type I isotherm was obtained. The Brunauer-Emmett-Teller (BET) surface area was found to be 633.4 m²/g with a 0.77 nm pore size, and the total pore volume was 0.21 cm³/g, which is consistent with values reported in the literature [21].

3.2. Al-incorporated beta zeolite

To convert the silica beta zeolite to an efficient catalyst, the incorporation of heteroatoms such as Al into its framework is necessary. The data described above show that the synthesized silica beta zeolite is polymorph A enriched. It would be of interest to combine Al-incorporated and polymorph A-enriched beta zeolite, i.e., to obtain the aluminosilicate form of polymorph A-enriched beta zeolite. Therefore, Al was introduced into the above synthetic system. Since the pH of the synthetic system is near neutral, this co-synthesis strategy may work in the incorporation of Al into the silica beta zeolite framework during crystallization. Fig. 5 shows the experimental XRD patterns of Al-incorporated beta zeolite and normal beta zeolite and the simulated beta zeolite of polymorph A. The profile of Al-incorporated beta zeolite is almost the same as that of normal beta zeolite, which suggests that the introduction of Al species disturbs the enrichment of polymorph A during crystallization and the specific local environment that promotes the enrichment of polymorph A no longer exists. Thus, an investigation of crystallization of both synthetic systems may provide an understanding of the enrichment phenomenon of poly-

Fig. 5. Experimental XRD patterns of (1) Al-incorporated beta zeolite (Si/Al = 27), (2) normal beta zeolite, and (3) simulated beta zeolite of polymorph A.

morph A in the polymorph A-enriched silica beta zeolite under these conditions.

Fig. 6 shows SEM images of silica beta zeolite and Al-incorporated beta zeolite with Si/Al ratios of 45, 27, and 10. The data in Fig. 6 indicate that the introduction of Al into the synthetic system reduces the crystal size. Without Al, the typical crystal size is $\sim 25 \mu\text{m}$. A Si/Al ratio of 45 decreases the crystal size to $\sim 10 \mu\text{m}$ and changes the crystal morphology to an amygdaloidal from a truncated bipyramidal shape. A decrease in Si/Al ratio to 27 and 10 results in a crystal size of ~ 6 and $1 \mu\text{m}$, respectively, which suggests that the introduced Al species promote the nucleation rate of the synthetic mixture.

TGA-DTA analysis of the Al-incorporated beta zeolite is shown in Fig. 7. Similar to polymorph A-enriched silica beta zeolite, Al-incorporated beta zeolite has a mass loss of $\sim 2\%$ from ambient temperature to 160°C , which can be attributed to physically adsorbed water. Three steps were followed, namely, $160\text{--}320^\circ\text{C}$, $320\text{--}460^\circ\text{C}$, and $460\text{--}700^\circ\text{C}$, which correspond to mass losses of 10%, 4%, and 3%, respectively. As shown in Fig. 3, the temperature ranges of the corresponding steps for the silica beta zeolite are $200\text{--}280^\circ\text{C}$ (6%), $280\text{--}380^\circ\text{C}$ (11%), and $380\text{--}550^\circ\text{C}$ (2.5%). As discussed above, the reaction that

Fig. 6. SEM images of (a) silica beta zeolite and Al-incorporated beta zeolite with different Si/Al ratios: (b) 45; (c) 27; (d) 10.

Fig. 7. TGA-DTA curves of Al-incorporated beta zeolite (Si/Al = 27).

occurs in the second step is TEA^+ decomposition into triethylamine and ethylene and an exothermic peak at 320°C is visible. A higher mass loss of 10% for the Al-incorporated beta zeolite than that of 6% for the silica beta zeolite suggests that more TEA^+ is decomposed catalytically by the Al-incorporated beta zeolite. Compared with the silica beta zeolite, Al-incorporated beta zeolite can re-adsorb the amines decomposed by the TEA^+ , which results in a higher final temperature in the third step (460°C) and an exothermic peak at 450°C . From the literature, at the fourth step, the mass loss of 3.0% is attributed to coke. A broad exothermic peak centered at 600°C is visible. To clarify whether the mass loss of 3.0% is fluoride, the same Al-incorporated beta zeolite calcined at 460 and 700°C was analyzed with ^{19}F MAS NMR and the spectra are shown in Fig. 8. Fluoride was still occluded in the beta zeolite framework at 460°C . However, almost all fluoride has been burned out at 700°C . Therefore, the mass loss of 3.0% in the fourth step contains all fluoride occluded in the framework of Al-incorporated beta zeolite. Because of the incorporation of Al, the fourth step of the TGA-DTA curve of Al-incorporated beta zeolite ended at a higher temperature (700°C) than that of silica beta zeolite. The total mass loss from the second to the fourth steps for the Al-incorporated beta zeolite (17%) is less than that of the silica beta zeolite (19.5%).

Nitrogen adsorption-desorption measurements on the Al-incorporated beta zeolite (Si/Al = 27) gave a type I isotherm. The BET surface area was $952.34 \text{ m}^2/\text{g}$ with a 0.74 nm pore size, and the total pore volume was $0.28 \text{ cm}^3/\text{g}$. These results suggest that the BET surface area increases because of the incorporation of Al into the framework.

Fig. 8. ^{19}F MAS NMR spectra of Al-incorporated beta zeolite calcined at (1) 460 and (2) 700°C .

3.3. Crystallization of polymorph A-enriched silica beta zeolite and Al-incorporated beta zeolite

The above discussion indicates that the percentage of polymorph A in the silica beta zeolite was between 60% and 70%. However, this number decreased to ~45% when Al was introduced into the synthetic mixture. Thus, an investigation of the crystallization of both synthetic systems may help us understand the reason for the enrichment of polymorph A in the crystallization of silica beta zeolite under these conditions and that of the loss of the enrichment of polymorph A in the crystallization of Al-incorporated beta zeolite. Fig. 9 shows the powder XRD patterns of samples isolated throughout the hydrothermal treatment. The data in Fig. 9 indicate that a long-range ordering structure was formed in both synthetic mixtures and existed throughout the crystallization process. This long-range ordering phase was also observed by Taborda *et al.* [8] in the starting mixture in their investigation into the synthesis of beta zeolite with an aging drying method, which disappeared after calcination. Thus, they attributed this well-crystallized structure to the SDA (TEA⁺ cation) formed during the aging drying process. In this investigation, the crystallinity of this phase was enhanced by crystallization. However, it can be removed either by calcination at 300 °C or by washing with water, which suggests that this phase has an organic nature. If no Al is present, well-crystallized polymorph A-enriched silica beta zeolite is visible after 37 h of heating. The characteristic low-angle peak of polymorph A is clearly visible. Prolonging the heating time to 168 h yields highly crystallized polymorph A-enriched silica zeolite (washed with water). If the Al species is introduced into

Fig. 9. Powder XRD patterns of samples isolated throughout the hydrothermal treatment period. (a) Silica beta zeolite; (b) Al-incorporated beta zeolite.

the synthetic mixture, the crystallization rate is accelerated significantly. When the heating time reached 7.5 h, well-crystallized Al-incorporated beta zeolite was obtained, which indicates that the presence of Al species accelerates the crystallization of beta zeolite. Prolonging the heating time to 168 h (7 d) yields highly crystallized Al-incorporated beta zeolite. However, the profile of the XRD pattern is almost identical to that of normal beta zeolite, which indicates that the percentage of polymorph A in the Al-incorporated beta zeolite is ~45%. The introduction of Al into the synthetic mixture therefore disturbed the enrichment of polymorph A that occurred in the synthesis of silica beta zeolite.

To investigate the evolution of the coordination state and local environment of Si and Al during crystallization, we characterized typical products obtained during the crystallization of polymorph A-enriched silica beta zeolite and Al-incorporated beta zeolite using ²⁹Si MAS NMR and ²⁷Al MAS NMR. Fig. 10 shows the ²⁹Si MAS NMR spectra and deconvolutions of two typical products of silica and Al-incorporated beta zeolite. The ²⁷Al MAS NMR spectra of the same typical products of Al-incorporated beta zeolite are shown in Fig. 11.

As shown in Fig. 10, the spectrum of the starting mixture (0 h) for the crystallization of silica beta zeolite gives a broad resonance centered at -99.4 ppm with shoulder peaks at -90.5, -107.3, -110.4, and -113.5 ppm (area ratio of -99.4:-90.5:-107.3:-110.4:-113.5 = 61.9:7.8:17.9:8.5:3.9) and a less intense signal centered at -188 ppm because of SiF₆²⁻ ions [22].

Fig. 10. ²⁹Si MAS NMR spectra and deconvolution of typical products obtained during crystallization of polymorph A-enriched silica beta zeolite (a) and Al-incorporated beta zeolite (b).

Fig. 11. ^{27}Al MAS NMR spectra of typical products obtained during crystallization of Al-incorporated beta zeolite.

The shoulder peak at -90.5 ppm can be assigned to the Si atoms that connect two Si atoms *via* bridging O atoms and two OH groups (Q2: 2Si, 2OH) [23], whereas the shoulder peaks at -107.3 , -110.4 , and -113.5 ppm can be attributed to the Si atoms that connect four Si atoms *via* bridging O atoms (Q4: 4Si, 0OH) [23]. The main resonance at -99.4 ppm is from the Si atoms that connect three Si atoms *via* bridging O atoms and one OH group (Q3: 3Si, 1OH) [23]. When the heating time reached 37 h, well-crystallized polymorph A-enriched silica beta zeolite was formed as shown in Fig. 9(a). A sharp and intense signal centered at -109 ppm with very weak shoulder peaks at -99.2 , -104.7 , and -115.4 ppm (area ratio of -109 :- 99.2 :- 104.7 :- 115.4 = 90.6 : 4.5 : 2.9 : 2) is visible. However, the shape and intensity of the signal at -188 ppm does not change much, which indicates that the formation rate of SiF_6^{2-} is very similar to its incorporation rate into the beta zeolite framework. At this stage, the signal of Q2 (-90.5 ppm) disappeared completely. The shoulder peaks at -99.2 and -104.7 ppm can be attributed to Q3, whereas those at -109 and -115.4 ppm are from Q4. The spectral deconvolution suggests that few connectivity defects exist in the product as evidenced by the absence of signals of < -109 ppm.

As shown in Fig. 10, the shape and position of the resonances of the starting mixture (0 h) change significantly when the Al species is introduced. A broad resonance centered at -100.3 ppm with shoulder peaks at -91.3 and -109 ppm (area ratio of -100.3 :- 91.3 :- 109 = 60.9 : 7.2 : 31.9) and a less intense signal centered at -188 ppm assigned to SiF_6^{2-} ions are visible. The main resonance centered at -100.3 ppm can be assigned to the Si atoms that connect three Si atoms and one OH group (Q3: 3Si, 1OH), whereas the signals at -91.3 and -109 ppm can be attributed to Q2 (2Si, 2OH) and Q4 (4Si, 0OH), respectively [19]. When the heating time reached 7.5 h, well-crystallized Al-incorporated beta zeolite was formed as shown in Fig. 9(b). A sharp and intense signal centered at -109 ppm with very weak shoulder peaks at -99.2 , -103.5 , and -115.3 ppm (area ratio of -109 :- 99.2 :- 103.5 :- 115.3 = 72.2 : 11.5 : 10.7 : 5.6) is visible. A signal centered at -188 ppm with unchanged shape and enhanced intensity is also visible. The main resonance at -109 ppm and the shoulder peak of -115.3 ppm can be attributed to Q4 (4Si), whereas the signals at -99.2 and -103.5 ppm can be assigned to Q3 (3Si, 1OH) and the Si atoms connecting three Si atoms and one Al atom (3Si, 1Al), respectively [19]. These re-

sults suggest that the introduction of Al species changes the evolution of the coordination state of Si during crystallization, which may destroy the enrichment of polymorph A that occurs in the crystallization of silica beta zeolite.

Fig. 11 shows the ^{27}Al MAS NMR spectra of the same typical products of Al-incorporated beta zeolite. In the starting mixture (0 h), tetrahedral Al species (52 ppm) co-existed with the aluminum source (0 ppm). When the heating time reached 7.5 h, five-coordinated Al species (21.4 ppm) formed. Well-crystallized Al-coordinated beta zeolite is formed at this stage. At the end of crystallization, five-coordinated Al species and an aluminum source will be converted to tetrahedral Al species. The existence of five-coordinated Al intermediate may account for the loss in enrichment of polymorph A during the crystallization of beta zeolite.

4. Conclusions

Under concentrated hydrothermal conditions, well-crystallized polymorph A-enriched silica beta zeolite was synthesized in the presence of TEOH and fluoride. When Al species are introduced into the starting mixture, the degree of enrichment of polymorph A decreases significantly. The crystal size of Al-incorporated beta zeolite decreases with the decrease in Si/Al ratio in the starting mixture and final products. The crystallization of beta zeolite is accelerated significantly because of the presence of Al species. The formation of five-coordinated Al species was observed during crystallization of Al-incorporated beta zeolite. The intermediate of five-coordinated Al species altered the enrichment of polymorph A during crystallization of Al-incorporated beta zeolite.

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Graphical Abstract

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Influence of Al^{3+} on polymorph A enrichment in the crystallization of beta zeolite

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Polymorph A-enriched silica beta zeolite was synthesized. The degree of enrichment of chiral polymorph A was decreased owing to five coordinated Al species.

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铝离子在beta沸石晶化过程中对多形体A富集的影响

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摘要: 以四乙基氢氧化铵为有机结构导向剂, 采用超浓水热方法, 从氟离子体系合成出手性多形体A(简称A形体)富集的全硅beta沸石. 在同样的初始混合物中引入铝源后, 所合成的beta沸石中A形体含量明显降低, 产物为普通的硅铝beta沸石. 用粉末X射线衍射、元素分析、热重-差热分析、氮气吸附、扫描电子显微镜和固体魔角自旋核磁共振等表征手段对全硅beta沸石和硅铝beta沸石进行了详细的表征, 并研究了其晶化过程. 结果表明, 铝源的引入可以加速beta沸石的晶化, 得到的硅铝beta沸石晶体粒径明显减小. 在硅铝beta沸石的晶化过程中生成了五配位铝物种, 五配位铝物种可能是导致产物中A形体含量降低的原因.

关键词: beta沸石; 手性; A形体; 富集

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