

Headline Articles

Synthesis of [Al]-SSZ-31 Molecular Sieves Using [Al]-Beta Zeolite ([Al]-BEA) as Precursors

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The aluminosilicate version of SSZ-31 ([Al]-SSZ-31) zeolite was synthesized by a new route including phase-transformation, wherein an aluminosilicate analog of beta zeolite ([Al]-BEA) was used as a precursor and 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide was used as a structure-directing agent (SDA). [Al]-BEA precursors synthesized by two routes, viz. the hydrothermal (HTS) and dry-gel conversion (DGC) method, were employed for the synthesis. [Al]-SSZ-31 with a low output SiO_2/Al_2O_3 ratio crystallized only when the precursor ($SiO_2/Al_2O_3 = 30$), prepared by DGC method, was employed. Precursors synthesized by the HTS method produced highly crystalline samples, however, only in the high silica region. In general, [Al]-SSZ-31 samples over a wide range of SiO_2/Al_2O_3 ratios could be synthesized using a precursor route. During crystallization, a phase transformation from [Al]-BEA to [Al]-SSZ-31 was observed, indicating dissolution of the beta phase, followed by its redirection towards the SSZ-31 phase in the presence of SDA. An increase in gel water helped to produce pure [Al]-SSZ-31. [Al]-SSZ-31 was found to crystallize in $NaOH/SiO_2$ window of 0.040–0.056. Scanning electron microscopy (SEM) showed plate-like crystals of about 5 μm in size. ^{13}C CP MAS NMR indicated that the SDA was intact inside the pores during crystallization. Furthermore, the samples were also characterized by ^{29}Si and ^{27}Al MAS NMR in addition to X-ray diffraction (XRD), temperature-programmed desorption of ammonia (NH_3-TPD), SEM, etc.

Zeolites are technologically important materials, and have found applications in variety of chemical processes, more specifically in petrochemical and refining industries,[1,2] and more recently in the synthesis of fine chemicals.[3] The zeolite pore structure and chemical compositions are important in determining selectivity and catalytic activity. Among the zeolites, high-silica zeolites with large (12-ring) and extra-large (14-ring) pores are in demand due to their potential application in the catalysis of relatively bulky molecules. A major part of the research is focused on the synthesis of novel zeolites, synthesis by new routes, such as crystallization in dense medium, or with the aid of gas phase.[4–6] A number of new large-pore and extra-large pore zeolites viz., NU-87 (NES),[7] SSZ-33,[8] SSZ-26,[9] CIT-1 (CON),[10] UTD-1 (DON),[11] CIT-5 (CFI),[12] GUS-1 (GON),[13] have been synthesized by a hydrothermal route using a particular structure-directing agent (SDA). The synthesis of some zeolites such as CIT-1, SSZ-33, SSZ-24 (AFI),[14] SSZ-31,[15] etc. was successful only in their borosilicate or all-silica version by the hydrothermal route. Aluminosilicate versions for these zeolites could be obtained by isomorphous substitution with an aluminum nitrate solution.

Among the relatively new large-pore zeolites, SSZ-31 is one of the interesting materials having a one-dimensional, elliptical pore (0.86 × 0.57 nm). This material was first synthesized in its siliceous form by Zones et al.[15] Later Lobo et al.[16] have proposed a framework model for this material as a highly faulted structure with an intergrowth of mainly four different polymorphs and closely related to NCL-1[17] and OU-1.[18,19] The framework of SSZ-31 also has some similarity to that of ZSM-12 (MTW), BEA and SSZ-24. The synthesis of borosilicate versions of SSZ-31 and a post-synthesis modification to its aluminosilicate version, using a number of starting materials and SDA, is well documented.[15,20–22] Recently, we reported a direct synthesis of [Al]-SSZ-31 on both large and small scales by a dry-gel conversion (DGC) method using 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide (**1**) as SDA (Chart 1).[23,24] By this method, however, [Al]-SSZ-31 with a SiO_2/Al_2O_3 ratio below 100 was not formed.

During an investigation of this synthesis, we observed a phase transformation from beta to SSZ-31, which later changed to MFI. Matsukata et al. observed a similar phase transformation from BEA to OU-1[18] during the synthesis of OU-1 by the DGC method using tetraethylammonium hydroxide (TEAOH) as SDA. Barrer has reported zeolite transformations

Chart 1. Structure of 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide (**1**).

in hydrothermal systems in the past.[25] Zones and Nordstrand reported a template-mediated phase change from cubic P to SSZ-13.[26,27] Recently, the synthesis of CIT-5 using highly dealuminated Y zeolite as a silica source has been reported.[28,29] Furthermore, Dwyer and Chu also observed the transformation of an amorphous phase to faujasite, that later being transformed to ZSM-4 in the presence of the tetramethylammonium (TMA) cation.[30] Later, it was found that zeolites could act as effective sources for alumina and silica. When zeolite P was used as an alumina source, rapid crystallization of organo-zeolite was observed;[31] the crystallization rates were enhanced when Y zeolite was used as an alumina source, leading to a search of active zeolite sources for synthesis. Zones et al. demonstrated the use of boron beta ([B]-BEA) as a precursor for the synthesis of borosilicate versions of SSZ-24, SSZ-31 and SSZ-33.[20,21] As another example of using the ''defined'' structure as silica and metal oxide sources, Takewaki et al. synthesized all-silica or metal-substituted BEA from corresponding MCM-41.[32]

Very recently, we demonstrated the synthesis of [Al]-SSZ-31 zeolite using [Al]-BEA as alumina and silica sources and **1** as SDA. By this technique, a sample with SiO_2/Al_2O_3 as low as 48 has been successfully crystallized, and the preliminary results were published in our previous communication.[33] We describe herein the synthetic behavior of SSZ-31 via ''the BEA precursor route'' in detail as well as the characterization of the product by various physicochemical techniques.

Experimental

Synthesis of the Structure-Directing Agent. Triethylamine (37.2 g, 368 mmol) was added to a solution of 1,6-dibromohexane (24.4 g, 96 mmol) in acetone (170 mL), and the whole mixture was refluxed for about 50–60 h. After the reaction, the mixture was filtered and washed with acetone (200 mL) and the solvent was removed in vacuo to give a white solid (38.9 g), which was dissolved in methanol (25 mL) by heating at 60 °C. After cooling to room temperature, crystals separated out slowly. Diethyl ether (200 mL) was added slowly to encourage the crystals to develop. The crystals were collected by filteration and washed with benzene (80 mL), and finally dried in vacuo. 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dibromide was obtained as colorless plates (37.8 g, 87%).

Diaion® SA10A(OH) (Mitsubishi Chemical Co.) anion exchange resin (185.5 g, corresponding to a 275 mmol exchange capacity) was added to a solution of the dibromide salt (15.3 g, 34.3 mmol) in distilled water (200 mL), and the whole mixture was gently stirred at room temperature for 24 h. After filtration, the aqueous solution was concentrated to give 0.257 mmol g^{-1} of 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide (R^{2+}-$(OH^-)_2$; **1**) based on titration of the resulting solution with a 0.05 N standard HCl solution.

Synthesis of [Al]-BEA Precursors. [Al]-BEA with a varied SiO_2/Al_2O_3 ratio was synthesized according to reported procedures by two methods: hydrothermal synthesis (HTS)[34] and dry-gel conversion (DGC).[6,19]

HTS Method: Sample 1 in Table 1 was synthesized by the following procedure: 2.1037 g (5 mmol) of TEAOH (Aldrich, 35 wt% aqueous solution) and 0.375 g (3 mmol) of NaOH (32 wt% aqueous solution) were taken in a Teflon jar, and stirred for about 60 min. 0.0786 g (0.33 mmol of Al_2O_3) $NaAlO_2$ (42.8 wt% Al_2O_3, 33.7 wt% Na_2O) dissolved in 1.61 g of distilled water (by heating at 80 °C) was added to the above solution and stirred for about 30 min. Finally, 1.502 g (10 mmol of SiO_2) of Ludox HS 40 (40 wt% of colloidal SiO_2) was added and the gel was stirred for about 1 h. This gel was then transferred into a 23 mL Teflon-lined autoclave, which was heated at 150 °C for 168 h. After crystallization, the product was filtered, washed with distilled water and dried overnight. The as-synthesized sample was calcined in an air flow (100 mL/min) at 550 °C for 7 h.

The typical procedure for synthesizing [Al]-BEA by a hydrothermal route in a high SiO_2/Al_2O_3 region (Table 1, sample 2) was as follows: 18.93 g (45 mmol) of TEAOH (Aldrich, 35 wt% aqueous solution), 18.91 g (90 mmol) of tetraethylammonium bromide (TEABr; Aldrich) followed by 0.276 g of $NaAlO_2$ (42.8 wt% Al_2O_3, 33.7 wt% Na_2O) were taken in a Teflon jar and stirred for about 10 min. To the above alkaline solution, 22.53 g (150 mmol) of Ludox HS 40 was added; this solution was stirred for another 10 min. Finally, 5.024 g (33 mmol) of triethanolamine was added and the gel was stirred for 3 h. This gel was then transferred into a 125 mL Teflon-lined autoclave and 0.045 g (0.5 wt%

Table 1. Gel Compositions for the Preparation of [Al]-BEA Precursors Used for Synthesis of [Al]-SSZ-31

No.	Gel composition	Method	Temp /°C	Time /h	SiO_2/Al_2O_3 Gel	SiO_2/Al_2O_3 Product[d)]
1	$1SiO_2$–0.5 TEAOH–0.3 NaOH–0.033 Al_2O_3–20 H_2O	HTS[b)]	150	168	33	19
2	$1SiO_2$–0.3 TEAOH–0.6 TEABr–0.02 NaOH–0.0077 Al_2O_3–15 H_2O–0.22 $(HOCH_2CH_2)_3N$	HTS[b)]	150	180	119	94
3	$1SiO_2$–0.5 TEAOH–0.3 NaOH–0.033 Al_2O_3–20 H_2O	DGC[c)]	175	72	33	29
4	$1SiO_2$–0.37 TEAOH–0.3 NaOH–0.01 Al_2O_3–17 H_2O	DGC[c)]	175	24	100	97
5	$1SiO_2$–0.37 TEAOH–0.3 NaOH–0.005 Al_2O_3–17 H_2O	DGC[c)]	175	12	200	175
6	$1SiO_2$–0.2 $R^{2+}(OH^-)_2$–0.0084 NaOH–0.0026 Al_2O_3–61 H_2O[a)]	DGC[c)]	150	78	384	158

a) $R^{2+}(OH^-)_2$ = 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide (**1**). b) HTS = Hydrothermal synthesis. c) DGC = Dry gel conversion. d) Determined by ICP analysis of as-synthesized sample.

Table 2. Synthesis of [Al]-SSZ-31 from Calcined [Al]-BEA Precursors

Sample No.	Gel composition					Phase	SiO_2/Al_2O_3		
	SiO_2[a)]	$R^{2+}(OH^-)_2$[e)]	NaOH	Al_2O_3[f)]	H_2O		Precursor[h)]	Gel	Product[j)]
1	1.0	0.13	0.056	0.0184	70	SSZ-31	29	54	48
2	1.0	0.13	0.056	0.0056	70	SSZ-31	97	179	171
3	1.0	0.13	0.055	0.0034	70	SSZ-31	158	292	362
4	1.0	0.13	0.055	0.0031	70	SSZ-31	175	323	221
5	1.0[b)]	0.10	0.042	0.0137	52	SSZ-31	29	73	65
6	1.0	0.13	0.056	0.0057	70	SSZ-31	94[i)]	175	197
7	1.0[c)]	0.13	0.057	0.0289	70	Beta	19[i)]	35	62
8	0.5[d)]	0.13	0.053	0.0173	66	Beta	29	29	40
9	1.0	0.13	0.056	0.0184	54	SSZ-31[g)]	29	54	48
10	1.0	0.13	0.056	0.0056	54	SSZ-31[g)]	94[i)]	179	111
11	1.0	0.13	0.040	0.0184	70	SSZ-31	29	54	52
12	1.0	0.13	0.068	0.0184	70	SSZ-31[g)]	29	54	50
13	1.0	0.13	0.101	0.0184	70	SSZ-31[g)]	29	54	65
14	1.0	0.13	0.007	0.0184	70	SSZ-31[g)]	29	54	57

a) 54 wt% SiO_2 came from [Al]-BEA and 46 wt% came from fumed silica, unless otherwise noted. b) 35 wt% SiO_2 came from [Al]-BEA and 65 wt% came from fumed silica. c) 49 wt% SiO_2 came from [Al]-BEA and 51 wt% came from fumed silica. d) All SiO_2 came from [Al]-BEA and same result was obtained when SiO_2 was 1.0. e) R^{2+} is 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane. f) All Al_2O_3 came from [Al]-BEA. g) Incomplete transformation form beta to SSZ-31. h) [Al]-BEA precursor was synthesized by DGC method unless otherwise noted; see Table 1. i) [Al]-BEA precursor was synthesized by HTS method. j) Determined by ICP analysis of as-synthesized sample.

of SiO_2) of beta zeolite as seed was added. The autoclave was heated at 150 °C for 180 h. The solid obtained was filtered, washed with distilled water and dried overnight. The sample was calcined in air (100 mL/min) at 550 °C for 10 h.

DGC Method: Sample 3 (Table 1) was synthesized as follows: after 1.125 g (9 mmol) of NaOH (32 wt% aqueous solution) was taken in a Teflon cup, to the above, 6.311 g (15 mmol) of TEAOH (Aldrich, 35% aqueous solution) was added. The solution was stirred for about 15 min. To the above solution, 4.506 g (30 mmol) of Ludox HS40 (40 wt% SiO_2) was added and the whole mixture was stirred for 30 min. Finally, 0.3388 g (0.99 mmol) $Al_2(SO_4)_3$ (anhydrous, Kanto Chemicals Co.) dissolved in 3.24 g (600 mmol) water at 80 °C was added and the gel was stirred for 2 h. The gel was then heated at 80–90 °C in an oil bath to complete dryness. This dried gel was ground to a fine powder, which was then poured into a small Teflon cup (20 mm × 20 mm). This cup was placed in a Teflon-lined autoclave (23 mL) with water at the bottom (1.06 g; 0.2 g per g of dried gel) in such a manner that the dry gel never came into the direct contact with water. The crystallization was carried out at 175 °C for 72 h at an autogenous pressure. The molar composition of the gel was SiO_2:0.3 NaOH:0.5 TEAOH:0.033 Al_2O_3:20 H_2O. After crystallization the autoclave was quenched in cold water, and the sample was filtered and washed thoroughly with distilled water for 12 h at room temperature. Similarly, [Al]-BEA with other SiO_2/Al_2O_3 ratios were prepared; their gel compositions are given in the Table 1.

Synthesis of [Al]-SSZ-31. The typical procedure for the synthesis of [Al]-SSZ-31 was as follows: 7.79 g (2.0 mmol) of an aqueous solution of **1** (0.257 mmol g^{-1}) was added to 0.105 g (0.84 mmol, 32 wt% aqueous) of NaOH. The resulting alkaline solution was stirred for about 10–15 min, and then 0.416 g of fumed silica (Cab-O-Sil M5, Cabot), followed by 11.4 g (1033.5 mmol; including water from SDA and NaOH) of de-ionized water, was added. The mixture was stirred for 30 min. Finally, 0.50 g of calcined [Al]-BEA was added and the mixture was stirred for 4 h (totally 14.8 mmol of silica; from precursor and fumed silica). The crystallization was carried out statically at 175 °C under autogeneous pressure for 6 d. The gel composition was: 1 SiO_2:0.13 $R^{2+}(OH^-)_2$:0.056 NaOH:0.0184 Al_2O_3:70 H_2O, where $R^{2+}(OH^-)_2$ is **1**. [Al]-SSZ-31 with varied SiO_2/Al_2O_3 ratios was synthesized using the above method; the gel compositions are listed in Table 2. After crystallization, the sample was filtered, washed with distilled water and dried for about 12 h at room temperature.

Calcination and Post-Synthesis Treatment of [Al]-SSZ-31. To remove the SDA occluded inside the zeolite pore, the as-synthesized zeolite was placed in a muffle furnace and heated stepwise in a flow of air (100 mL/min). The temperature was raised from room temperature to 540 °C over a period of 7 h, and maintained at this temperature for 4 h. The temperature was then raised to 600 °C over a period of 4 h and kept at this temperature for another 4 h. Finally, the sample was cooled to room temperature under ambient conditions to obtain a calcined (Na-form) sample.

The calcined sample was refluxed with an ammonium nitrate solution for 12 h with stirring. The mass of ammonium nitrate was the same as that of the zeolite, and the H_2O:zeolite ratio was 50:1 (w/w). The zeolite was filtered, and this process was repeated twice more, after which it was washed thoroughly with water and dried overnight at room temperature. Finally the NH_4-form of the zeolite was calcined in a flow of air for 8 h at 550 °C to obtain the H-form.

Physicochemical Characterization. The phase purity and the crystallinity of the samples was determined by powder X-ray diffraction (XRD-6000, Shimadzu) with Cu Kα radiation ($\lambda = 1.5418$ Å). Elemental analysis was performed using an inductively coupled plasma (JICP-PS-1000UV, Leeman Labs. Inc.). The crystal size and morphology of the samples were examined by scanning electron microscopy (SEM) using a Philips XL30 microscope. A thermal analysis of the as-synthesized samples was performed on a Shimadzu DTG-50 analyzer. Nitrogen adsorption measurements were carried out using a BELSORP

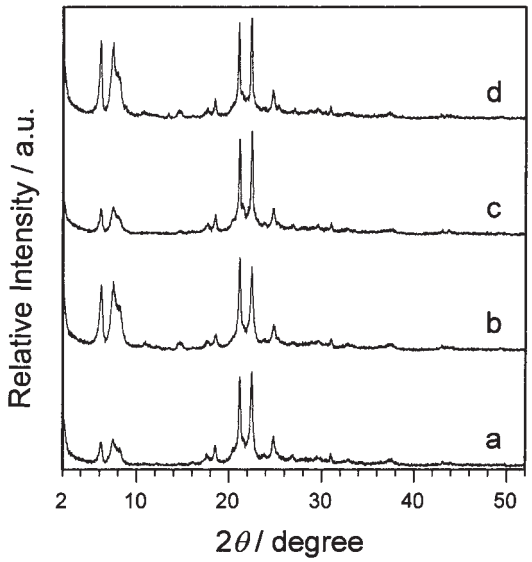

Fig. 1. Representative XRD patterns for [Al]-SSZ-31 from calcined [Al]-BEA precursors synthesized by DGC [(a) as-synthesized and (b) calcined] and HTS [(c) as-synthesized and (d) calcined].

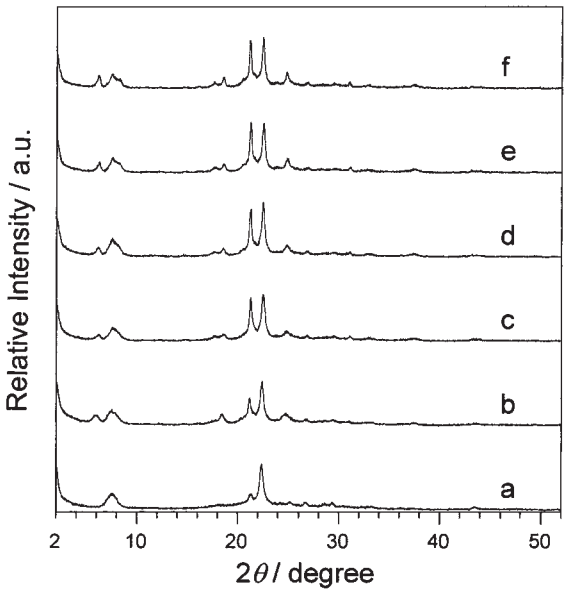

Fig. 2. Phase-transformation from [Al]-BEA (calcined) to [Al]-SSZ-31 as a function of time under standard synthesis conditions; (a–f) corresponding to 1–6 days of crystallization, respectively.

28SA (Bel Japan). Acidity measurements were performed by the temperature-programmed desorption of ammonia (NH_3-TPD) on a BEL TPD-66 apparatus (Bel Japan). ^{13}C CP MAS NMR, ^{29}Si and ^{27}Al MAS NMR spectra of the samples were recorded on a Varian Inova 400 FT-NMR spectrometer.

Results and Discussion

Table 1 displays the gel composition of the various [Al]-BEA samples used as precursors for the synthesis of [Al]-SSZ-31. As mentioned in the experimental section, [Al]-BEA synthesized by both the HTS and DGC methods was used as a precursor source. [Al]-SSZ-31 over a wide range of SiO_2/Al_2O_3 ratios could be synthesized using [Al]-BEA prepared by a variety of routes, as indicated in Table 2. Figures 1a and 1b display representative XRD patterns of as-synthesized and calcined [Al]-SSZ-31 samples synthesized from [Al]-BEA precursors prepared by the DGC method; Figs. 1c and 1d display the pattern of as-synthesized and calcined [Al]-SSZ-31 sample synthesized from [Al]-BEA precursors prepared by the HTS method. As is evident from the figure, the synthesized samples were crystalline and the pattern was in good agreement with reports in the literature.[14–16] Table 2 gives the synthesis conditions for the synthesis of [Al]-SSZ-31 from the precursor route. The method by which the precursor was synthesized had an effect on the final product. When [Al]-BEA synthesized by DGC method was used as a precursor, [Al]-SSZ-31 was produced with good reproducibility over a wide range of SiO_2/Al_2O_3 ratios (Table 2, samples 1–5). However, this was not the case when we used precursors made by the HTS method. When the precursor SiO_2/Al_2O_3 ratio was above 90 (high silica region), [Al]-SSZ-31 with good crystallinity was obtained (Table 2, sample 6). When a precursor synthesized by HTS method with SiO_2/Al_2O_3 ratio of about 20 was used, [Al]-SSZ-31 was not obtained (Table 2, sample 7). This observation suggested that more aluminum can be incorporated in the structure when a beta precursor synthesized by the DGC method was used, which may be attributed to slight differences in the particle size, consistent with some reports.[6] Actually, the particle sizes of [Al]-BEA samples synthesized by DGC and HTS were estimated to be 0.05 μm and 0.25 μm, respectively. Pure [Al]-SSZ-31 with SiO_2/Al_2O_3 over the range 48–500 could be successfully synthesized by employing the precursor route. In our previous studies, we found that the direct synthesis of [Al]-SSZ-31 below an input $SiO_2/Al_2O_3 = 100$ was difficult by the DGC method.[23,24] While synthesizing [Al]-SSZ-31 by the DGC method on a large-scale as well as a small-scale, the beta phase was observed initially, which then transformed into [Al]-SSZ-31. A similar transformation of beta to OU-1 (SSZ-31-like phase) under dry gel conditions was also observed by Rao et al.[18] using TEAOH as SDA at very high silica regions. From our observation, however, the transformation in a lower silica region was achieved only when beta zeolite was used as a precursor *and* in the hydrothermal system.

The synthesis of [Al]-SSZ-31 was sensitive to the amount of added fumed silica as the silica source. When the silica came entirely from the [Al]-BEA precursor, no transformation from beta to [Al]-SSZ-31 was observed, and the product was beta zeolite, even in presence of the SDA (Table 2, sample 8). The use of external fumed silica in addition to [Al]-BEA had a large effect, and the [Al]-SSZ-31 phase was obtained when [Al]-BEA/fumed silica added = 54/46 (w/w), (Table 2, sample 1). When the fraction of fumed silica added was increased to 65 wt%, [Al]-SSZ-31 was obtained (Table 2, sample 5). However, when the fraction of fumed silica added was above 65 wt%, we always observed an incomplete transformation from [Al]-BEA to [Al]-SSZ-31. Based on the fact that additional fumed silica is essential for the successful synthesis of the SSZ-31, there is a possibility that the added

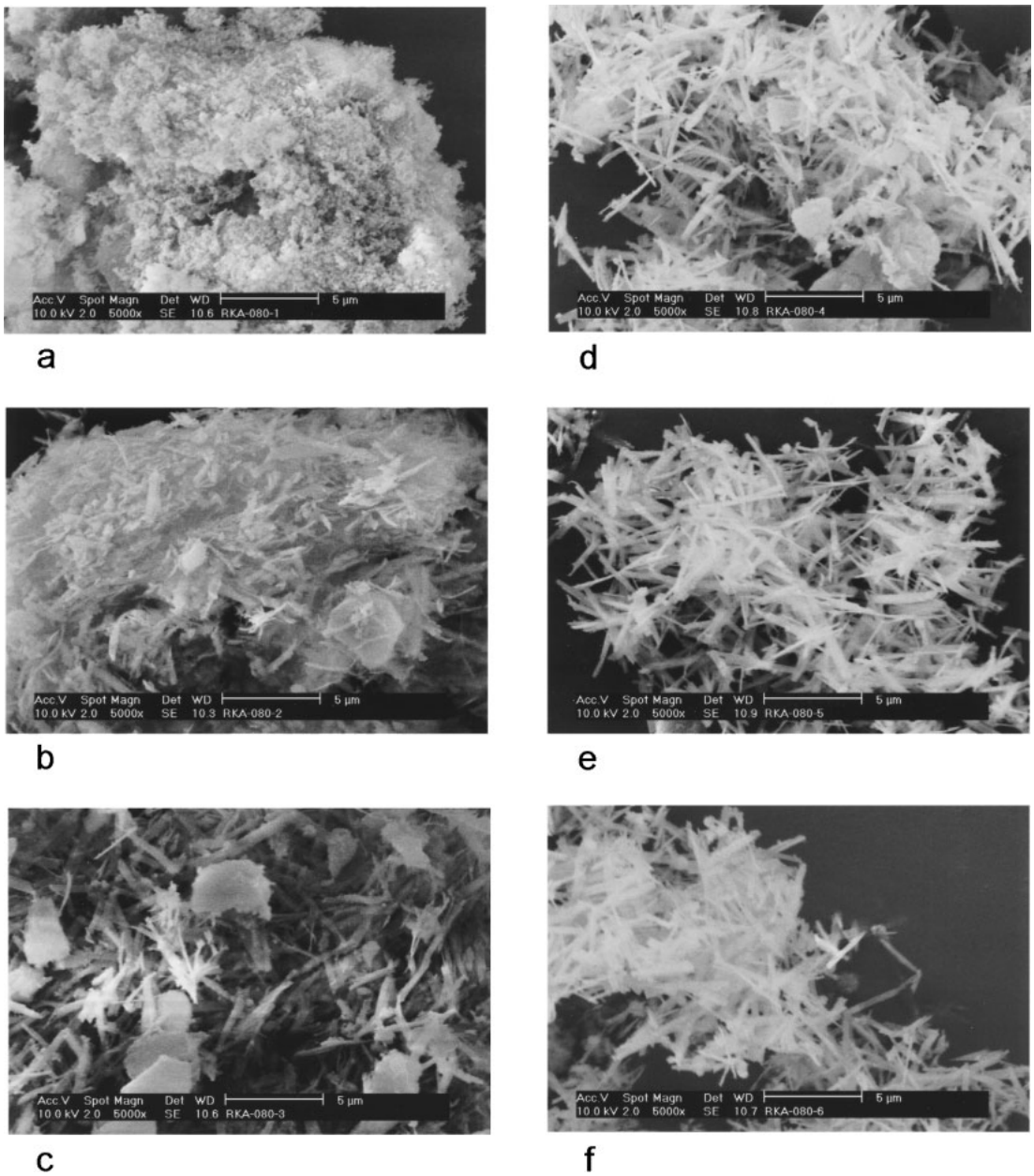

Fig. 3. SEM photographs of samples taken after (a) 1 d, (b) 2 d, (c) 3 d, (d) 4 d, (e) 5 d and (f) 6 d of crystallization time.

silica is used for the initial nucleation of SSZ-31 on the BEA surface. The nucleation of SSZ-31 on BEA is not unusual because the intergrowth of BEA and SSZ-31 really exists.[35]

The synthesis of the borosilicate analog of SSZ-31 using seeds of [B]-BEA zeolite has already been documented.[22] When we attempted to synthesize [Al]-SSZ-31 using [Al]-BEA or [Al]-SSZ-31 (synthesized by DGC method) as seeds, the synthesis was unsuccessful.

The amount of water played an important role in the synthesis of [Al]-SSZ-31 by the precursor route. In the case of precursors synthesized by both routes, an incomplete transformation of [Al]-BEA to [Al]-SSZ-31 was observed when less water was used in the gel (Table 2, samples 9 and 10). However, when the H_2O/SiO_2 ratio was increased from 54 to 70, pure [Al]-SSZ-31 crystallized (Table 2, samples 1 and 6). We speculate that the precursors dissolved partially in the solution, while leaving some secondary building units intact, which are later reconstructed towards SSZ-31 structure. A larger amount of water may have assisted in this dissolution process. In terms of the dissolution of precursors, it is interesting to note that as-synthesized [Al]-BEA prepared by DGC was also an effective precursor for [Al]-SSZ-31 (not shown in Table).

[Al]-SSZ-31 was obtained in a narrow $NaOH/SiO_2$ window. A $NaOH/SiO_2$ ratio of about 0.056 was found to be optimum for the synthesis. [Al]-SSZ-31 could be successfully crystallized with $NaOH/SiO_2$ in the range of 0.040–0.056. However, for a $NaOH/SiO_2$ ratio below 0.040 and above 0.056 a mixed phase of beta and SSZ-31 was observed (Table 2, samples 12–14). This behavior suggests that the NaOH concentration affects the dissolution process, to which the nucleation of SSZ-31 may be very sensitive. Unlike the DGC method, in

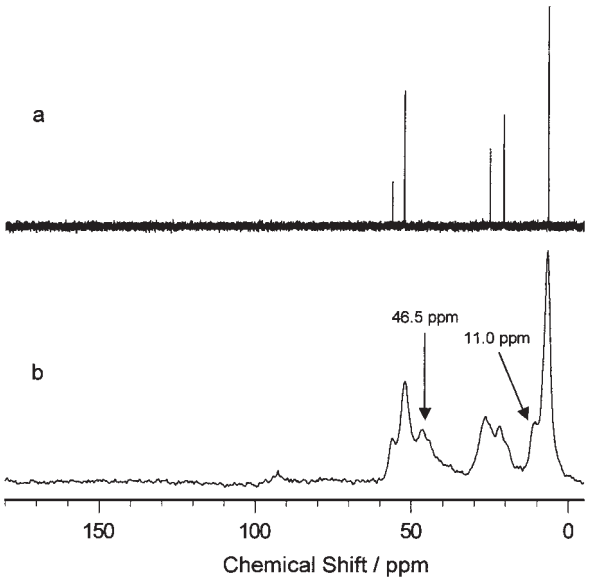

Fig. 4. ^{13}C NMR spectrum of **1** in D_2O (a) and ^{13}C CP MAS NMR spectrum of as-synthesized [Al]-SSZ-31 obtained by precursor route (sample 1, Table 2) (b).

which the phase transformation was faster (< 48 h) and further transformation to MFI was prominent when the NaOH concentration was too high or too low, such a further transformation was not observed in this precursor method.

Figure 2(a–f) shows the time-course of powder XRD patterns during the synthesis of [Al]-SSZ-31 from a calcined [Al]-BEA precursor. The gel composition was: 1 SiO_2:0.13 $R^{2+}(OH^-)_2$:0.056 NaOH:0.0184 Al_2O_3:70 H_2O and the samples were taken out every one day up to a total of 6 d and scanned by XRD. From the figure we can see that after almost one day, beta zeolite started dissolving and the SSZ-31 phase appeared to grow. After about 5 days, the crystallization was complete and a pure SSZ-31 phase was obtained (Fig. 2e).

The phase transformation was also examined by scanning electron microscopy (SEM). Figure 3(a–f) displays SEM photographs for the sample after 1, 2, 3,. . .6 d (corresponding to the XRD patterns in Fig. 2). A phase transformation to elongated plate-like crystals can be seen. Two phases were observed during the second, third and fourth day of the synthesis. After 5 days, crystallization was complete (also indicated by XRD) and a single phase consisting of elongated crystals was observed with a particle size of about 5 μm.

Figure 4a shows the ^{13}C solution NMR spectrum of the SDA **1** and Fig. 4b shows the ^{13}C CP MAS NMR spectrum of an as-synthesized sample (Table 1, sample 1). The spectra in Figs. 4a and 4b resemble each other, except for two additional new peaks observed at around 11.0 and 46.5 ppm. Molecule **1** inside a pore of SSZ-31 is known to give these two peaks, and we believe that these extra peaks could have come from the structural and environmental factors of SSZ-31 rather than the partial degradation of **1**.[24] In light of a discussion in Ref. 24, the SDA **1** should also be intact inside the pores of the sample 1.

The ^{27}Al MAS NMR spectrum of an as-synthesized [Al]-SSZ-31 sample (Table 2, sample 1) is displayed in Fig. 5a. A single peak at around 49.5 ppm was observed, suggesting

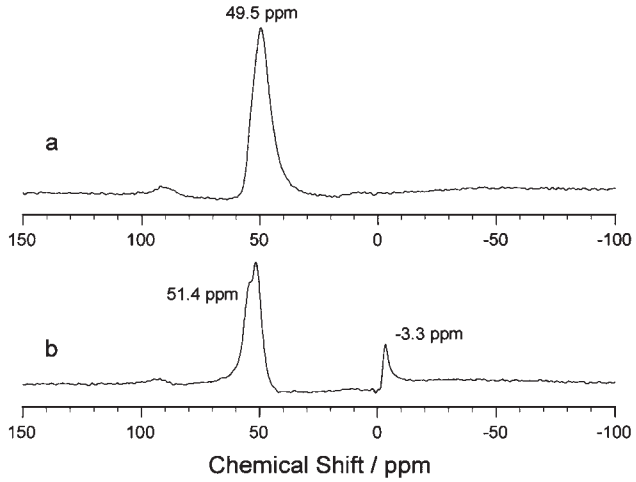

Fig. 5. ^{27}Al MAS NMR spectrum of (a) as-synthesized [Al]-SSZ-31 obtained by precursor route (sample 1, Table 2) and (b) H-[Al]-SSZ-31 derived from the same sample.

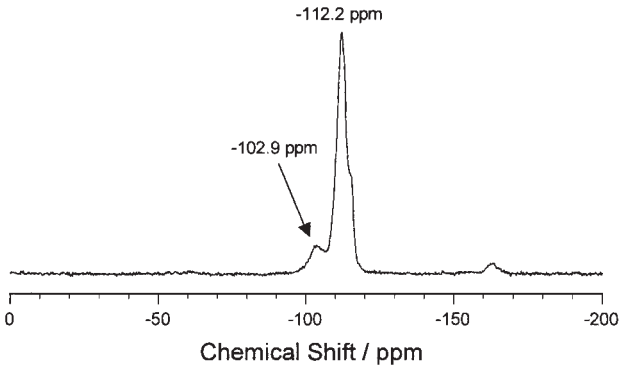

Fig. 6. ^{29}Si MAS NMR spectrum of H-[Al]-SSZ-31 derived from sample 1 in Table 2.

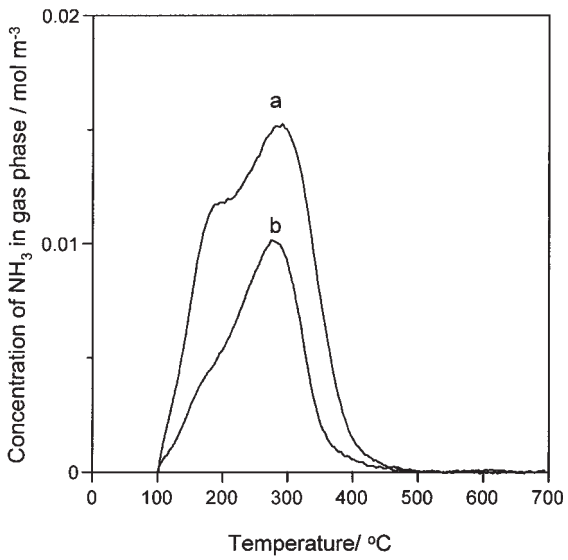

Fig. 7. NH_3-TPD profiles for (a) sample synthesized from DGC precursors (sample 1, Table 2) and (b) sample synthesized from HTS precursors (sample 6, Table 2).

a tetrahedral environment of Al and an absence of the octahedral Al species. As shown in Fig. 5b, however, a minor signal of the octahedral Al species appeared at −3.3 ppm after ion-exchange into the H-form by treating with NH_4NO_3, followed by calcination. This suggests that a slight dealumination from the framework occurred during the ion-exchange, although the sample still retained the high-aluminum feature in the acid catalysis.[36]

The ^{29}Si MAS NMR spectrum of the H-[Al]-SSZ-31 sample (derived from sample 1 in Table 2) is shown in Fig. 6. A signal of Si(4-OSi), i.e. Q^4, at around −110 to −113 ppm (peak 1) and a signal at around −101 to −103 ppm (peak 2) are observed. Peak 2 can be assigned to be the resonance corresponding to Si(3-OSi, 1-OH), i.e. Q^3, and/or Si(3-OSi, 1-Al). Upon deconvolution, the peak 1 to peak 2 ratio was approximately 87:13, indicating that peak 2 mainly consists of Q^3.

Figures 7a and 7b show the NH_3-TPD profiles for samples with SiO_2/Al_2O_3 ratios of 48 (Table 2, sample 1) and 197 (Table 2, sample 6), respectively. In the case of both samples, deconvolution indicated that there were two stages of ammonia desorption with peak maxima at around 180 °C and 288 °C. The first peak (180 °C; so-called *l*-peak[37]) resulted due to the desorption of strongly physisorbed ammonia, mainly on the external surface of the zeolite sample. The second peak (288 °C) may be attributed to the desorption of ammonia from Brønsted and Lewis sites. Such desorption of ammonia from different sites has been well documented in the literature.[37–40] The acid concentration calculated from the second peak was 0.197 and 0.104 mmol g^{-1} for sample 1 and 6 in Table 2, respectively. The acid concentration based on the second peak of the sample 1 was not as high as expected. Instead, the *l*-peak of the same sample was relatively large. This observation is consistent with the dealumination as suggested by ^{27}Al MAS NMR.

Nitrogen-adsorption measurements of [Al]-SSZ-31 (samples 1 and 6, Table 2) gave Type I isotherms, indicating that each sample had micropores. Sample 1 and sample 6 had micropore volumes of 0.112 $cm^3\,g^{-1}$ and 0.111 $cm^3\,g^{-1}$, respectively, which are typical values for one-dimensional 12-ring molecular sieves. A comparison of the catalytic performances of these samples will be described elsewhere.[36]

Conclusions

[Al]-SSZ-31 was successfully synthesized by a precursor route using 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide as SDA. [Al]-BEA synthesized by both the DGC and HTS methods produced [Al]-SSZ-31 with good reproducibility. [Al]-BEA prepared by the DGC method was found to be an effective precursor in the synthesis of an [Al]-SSZ-31 sample with a low SiO_2/Al_2O_3 ratio. A phase transformation from [Al]-BEA to [Al]-SSZ-31 was observed during crystallization. External silica in the form of fumed silica was found to be mandatory for crystallization, and [Al]-SSZ-31 was not obtained when [Al]-BEA was used as the sole source of silica and alumina. The synthesis of [Al]-SSZ-31 was unsuccessful when seeds of [Al]-BEA or [Al]-SSZ-31 were used for the synthesis. Crystallization was dependent on water amount in the gel, and the pure phase crystallized only when water was increased. [Al]-SSZ-31 by the precursor route crystallized in a $NaOH/SiO_2$ window of 0.040–0.056. SEM showed elongated plate-like crystals of about 5 μm in size. ^{13}C CP MAS NMR and ^{27}Al MAS NMR of an as-synthesized sample showed that the SDA was intact inside the pores and Al was in a tetrahedral environment. The precursor method may find an application in the synthesis of other zeolites which are difficult to synthesize by traditional methods.

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