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Hydrothermal synthesis of [Al]-SSZ-31 from [Al]-BEA precursors

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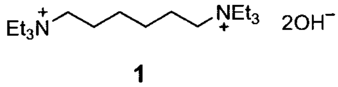
The direct synthesis of [Al]-SSZ-31, a one-dimensional, high-silica, large-pore zeolite, using [Al]-BEA as precursors *via* a hydrothermal route is described.

High silica zeolites with 12- and 14-ring pores are in demand due to their potential applications in catalysis of relatively bulky molecules. A number of new large-pore zeolites with intersecting channels *viz.* SSZ-26,[1] SSZ-33,[2] CIT-1[3] and unidimenional channels *viz.* UTD-1,[4] CIT-5,[5] have been synthesized by hydrothermal routes. CIT-1, SSZ-33, SSZ-24 and SSZ-31 were first synthesized in their borosilicate forms followed by their conversion to aluminosilicate forms by post-synthesis modification. Direct synthesis of aluminosilicate versions of the above *via* traditional hydrothermal routes was found to be difficult. Zones and Nakagawa[6] reported that borosilicate zeolites, typically boron beta ([B]-BEA) could be used as a source of boron and silicon (precursors) for the synthesis of other borosilicate zeolites such as [B]-SSZ-24, [B]-SSZ-33 and [B]-SSZ-31. Futhermore, Takewaki *et al.*[7] reported the synthesis of [B]-BEA, [Ti]-BEA, *etc.* using mesoporous materials (*e.g.* MCM-41) as precursors. Zones and Norstrand[8] and Dwyer and Chu[9] demonstrated that some aluminosilicate zeolites (zeolite P and faujasite) could be used as silica and alumina sources.

SSZ-31, a large-pore, high-silica, one-dimensional zeolite with pore dimensions 8.6 × 5.7 Å was first reported by Zones *et al.*[10] and later a model structure was proposed by Lobo *et al.*[11] Synthesis of the borosilicate analog of SSZ-31 ([B]-SSZ-31) using a number of structure-directing agents (SDAs) has also been documented.[10] We recently reported the direct synthesis of [Al]-SSZ-31 by a dry-gel conversion (DGC) method;[12] however, direct synthesis of [Al]-SSZ-31 from [Al]-BEA precursors by a hydrothermal route, to the best of our knowledge, is not yet known. In this communication we report the successful phase transformation from [Al]-BEA to [Al]-SSZ-31, with relatively high aluminium content, under hydrothermal conditions.

[Al]-BEA precursors for the synthesis of [Al]-SSZ-31 were synthesized by hydrothermal synthesis (HTS)[13] as well as the DGC method[14] following reported procedures,[13,14] with slight modifications in order to obtain samples with various SiO_2/Al_2O_3 ratios.



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The SDA, 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide (**1**), required for [Al]-SSZ-31 synthesis was prepared as follows: a mixture of 1,6-dibromohexane and an excess of triethylamine in acetone was refluxed for 48 h. The formed dibromide salt was converted into its hydroxide form (**1**) using an ion exchange resin, and the aqueous solution of **1** was used for synthesis of the zeolite.

A typical procedure for synthesis of [Al]-SSZ-31 was as follows: 7.79 g (1.60 mmol) of an aqueous solution of **1** (0.257 mmol g^{-1}) was added to 0.105 g (0.62 mmol) of 32% aqueous NaOH. The resulting alkaline solution was stirred for about 10–15 min, and then 0.416 g (10.0 mmol) of fumed silica (Cab-O-Sil M5, Cabot) followed by 11.4 g (750 mmol) of deionized water were added. The mixture was stirred for 30 min. Finally 0.50 g [Al]-BEA was added and the mixture was stirred for 4 h. The crystallization was carried out statically at 175 °C under autogeneous pressure for 6 days. The gel composition was: $1\ SiO_2 : 0.16\ R^{2+}(OH^-)_2 : 0.062\ NaOH : 0.0165\ Al_2O_3 : 75\ H_2O$, where $R^{2+}(OH^-)_2$ is **1**. All the samples were identified by powder X-ray diffraction (Cu-Kα radiation) for phase purity. The elemental analysis was performed by ICP analysis.

Table 1 shows the results of synthesis of [Al]-SSZ-31 from [Al]-BEA precursors. Calcined forms of [Al]-BEA with SiO_2/Al_2O_3 29, 97, 158 and 175 prepared by the DGC method and SiO_2/Al_2O_3 19 and 94 prepared by the HTS method were used as precursors. The method by which the precursor was synthesized had an effect on the final product. When [Al]-BEA synthesized by the DGC method (with any given SiO_2/Al_2O_3) was used as precursor, pure [Al]-SSZ-31 with varied SiO_2/Al_2O_3 ratio was produced with good reproducibility (Table 1, samples 1–5). Fig. 1(a) and (b) display the X-ray diffraction pattern of as-synthesized and calcined samples with $SiO_2/Al_2O_3 = 48$ (Table 1, sample 1), respectively. Although the diffraction peaks were slightly sharper when [Al]-BEA synthesized by hydrothermal method was used as the precursor (Table 1, sample 6; Fig. 1(c) and (d)), the precursor was only effective for higher silica contents. For [Al]-BEA with SiO_2/Al_2O_3 ratio of 19 synthesized hydrothermally no phase transformation was observed (Table 1, sample 7). However, pure [Al]-SSZ-31 crystallized when [Al]-BEA ($SiO_2/Al_2O_3 = 29$) synthesized by the DGC method was used as precursor (Table 1, sample 1), suggesting that more aluminium may be incorporated in the framework when a beta precursor synthesized by the DGC method was employed. This may be attributed to the slight differences in particle size of the precursors *via* the two synthesis methods, being consistent with some reports.[14] Pure [Al]-SSZ-31 with SiO_2/Al_2O_3 in the range 48–500 could be successfully synthesized employing the precursor route. In our previous studies, we found that direct synthesis of [Al]-SSZ-31 below input $SiO_2/Al_2O_3 = 100$ was difficult by the DGC method.[12] When synthesizing [Al]-SSZ-31 by the DGC method on either a large or a small scale, beta phase was observed initially which then transformed into [Al]-SSZ-31. Similar transformation of beta to OU-1 (SSZ-31-like phase) under dry gel conditions was also observed by Rao *et al.*[15] using TEAOH as the SDA at very high silica regions. From our observation, however, the transformation in low

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Table 1 Synthesis of [Al]-SSZ-31 from [Al]-BEA precursors

	Gel composition						SiO_2/Al_2O_3		
Sample	SiO_2[a]	$R^{2+}(OH^-)_2$[e]	NaOH	Al_2O_3[f]	H_2O	Phase	Precursor[h]	Gel	Product
1	1.0	0.16	0.062	0.0165	75	SSZ-31	29	60	48
2	1.0	0.16	0.062	0.0048	75	SSZ-31	97	208	171
3	1.0	0.16	0.062	0.0028	75	SSZ-31	158	357	488
4	1.0	0.16	0.062	0.0025	75	SSZ-31	175	400	201
5	1.0[b]	0.12	0.045	0.0121	58	SSZ-31	29	83	65
6	1.0	0.16	0.062	0.0049	75	SSZ-31	94[i]	204	197
7	1.0[c]	0.16	0.062	0.0165	75	Beta	19[i]	60	62
8	0.5[d]	0.16	0.062	0.0165	75	Beta	29	29	40
9	1.0	0.16	0.062	0.0165	45	SSZ-31[g]	29	60	48
10	1.0	0.16	0.062	0.0165	45	SSZ-31[g]	94[i]	204	111
11	1.0	0.16	0.043	0.0165	75	SSZ-31	29	60	52
12	1.0	0.16	0.073	0.0165	75	SSZ-31[g]	29	60	50
13	1.0	0.16	0.111	0.0165	75	SSZ-31[g]	29	60	65
14	1.0	0.16	0.007	0.0165	75	SSZ-31[g]	29	60	57

[a] 54 wt% SiO_2 from [Al]-BEA and 46 wt% from fumed silica, unless otherwise noted. [b] 35 wt% SiO_2 from [Al]-BEA and 65 wt% from fumed silica. [c] 49 wt% SiO_2 from [Al]-BEA and 51 wt% 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 from beta to SSZ-31. [h] [Al]-BEA precursor synthesized by the DGC method unless otherwise noted. [i] [Al]-BEA precursor synthesized by the HTS method.

silica regions was achieved only when beta zeolite was used as precursor and for the hydrothermal system. Synthesis of [Al]-SSZ-31 using [Al]-SSZ-31 seeds (synthesized by the DGC method) was unsuccessful. When only [Al]-BEA (prepared by the DGC method) was used as the silica source, no phase transformation was observed even after 6 days (Table 1, sample 8).

Interestingly, the amount of water played an important role in the synthesis of [Al]-SSZ-31 by the precursor route. For precursors synthesized by either route, incomplete transformation of [Al]-BEA to [Al]-SSZ-31 was observed when less water was used in the gel (Table 1, samples 9 and 10). However, when the H_2O/SiO_2 ratio was increased from 45 to 75, pure [Al]-SSZ-31 crystallized. We speculate that the precursors dissolve partially in the solution leaving some secondary building units intact, which are later reconstructed leading to the SSZ-31 structure; a larger amount of water may assist in this dissolution process. In terms of dissolution of precursors, it was interesting to note that as-synthesized [Al]-BEA prepared by DGC was also an effective precursor for [Al]-SSZ-31.

An $NaOH/SiO_2$ ratio of about 0.062 was found to be optimum for the synthesis. [Al]-SSZ-31 could be successfully crystallized with $NaOH/SiO_2$ in the range 0.043–0.062. However, for $NaOH/SiO_2$ ratios below 0.043 and above 0.062 a mixed phase of beta and SSZ-31 was observed (Table 1, samples 11–14).

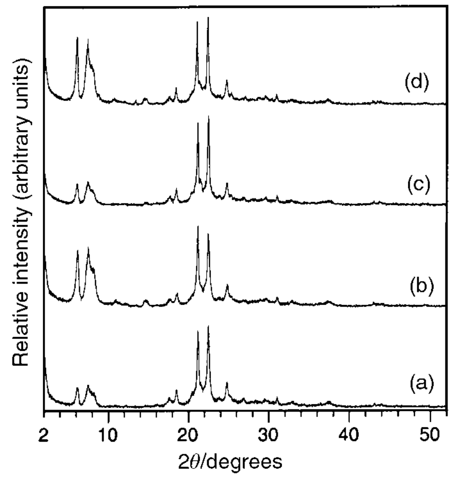

Fig. 1 X-Ray diffraction patterns for [Al]-SSZ-31 samples synthesized from precursors prepared by DGC or the hydrothermal method; (a) DGC method (as-synthesized); (b) DGC method (calcined) $SiO_2/Al_2O_3 = 48$; (c) hydrothermal method (as-synthesized) and (d) hydrothermal method (calcined) $SiO_2/Al_2O_3 = 197$.

The kinetics of crystallization over a period of 6 days with a starting gel composition 1 SiO_2 : 0.16 $R^{2+}(OH^-)_2$: 0.062 NaOH : 0.0165 Al_2O_3 : 75 H_2O, was investigated and Fig. 2 displays the results. Samples were removed after each day, up to 6 days. From Fig. 2, it can be seen that after almost one day, the BEA phase started transforming into the SSZ-31 phase while after two days, the crystallinity of SSZ-31 started increasing; and it is observed that pure SSZ-31 phase could be obtained within 6 days.

The kinetics of the phase transformation was also examined by scanning electron microscopy (SEM). Fig. 3(a), (b) and (c) display SEM photographs for samples after 1, 3 and 5 days, respectively. A morphology transformation to elongated plate-like crystals is clearly seen. Fig. 3(c) shows that the particles of the product are around 5 μm in length and no amorphous or impurity phase is present after complete crystallization (5 days).

^{27}Al MAS NMR of an as-synthesized sample (Table 1, sample 1) showed a single peak at around 49.5 ppm, indicating a tetrahedral environment of Al. The ^{13}C MAS NMR spectra of the same as-synthesized sample showed that the SDA was

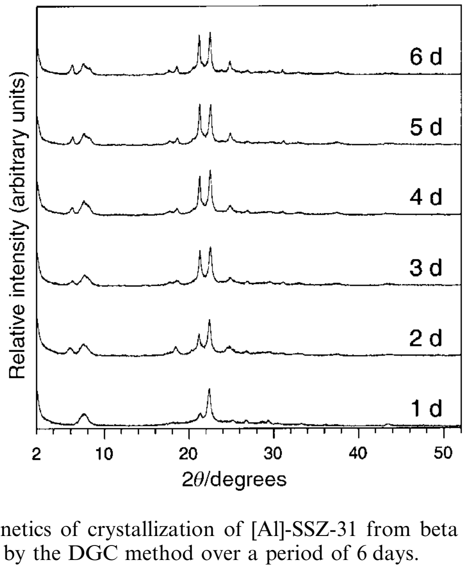

Fig. 2 Kinetics of crystallization of [Al]-SSZ-31 from beta precursor prepared by the DGC method over a period of 6 days.

intact inside the pores of [Al]-SSZ-31 throughout the crystallization process. The nitrogen absorption isotherm of calcined [Al]-SSZ-31 (Table 1, sample 1) showed a micropore volume of 0.11 $cm^3 g^{-1}$ and a BET surface area of 380 $m^2 g^{-1}$, which are typical values for one-dimensional 12-ring molecular sieves.

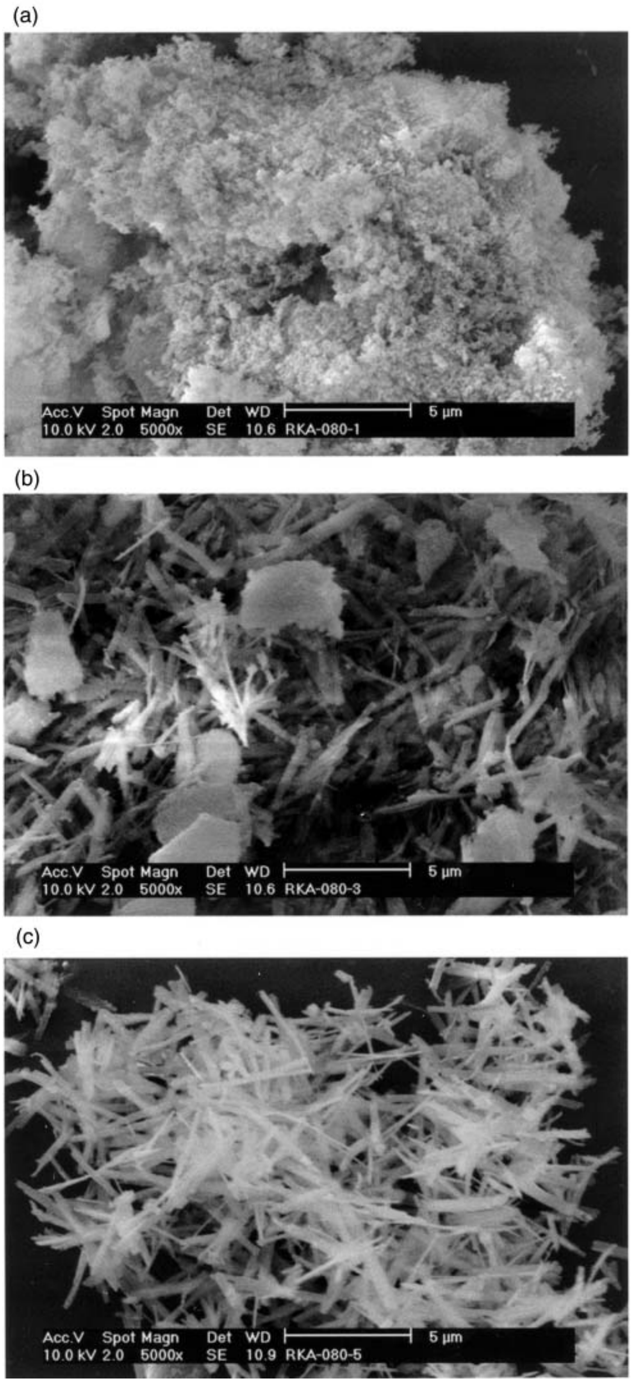

Fig. 3 SEM photographs of samples taken after (a) 1, (b) 3 and (c) 5 days crystallization.

In conclusion, [Al]-SSZ-31 with low silica to alumina ratios can be synthesized successfully using [Al]-BEA zeolite as precursor. We believe this result may provide a new optional route for zeolite synthesis especially where direct synthesis of aluminium versions is difficult.

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