Hydrothermal Synthesis of [Al]-SSZ-24 from [Al]-Beta Zeolite ([Al]-BEA) as Precursors

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The direct synthesis of [Al]-SSZ-24, a one-dimensional (1-D), high-silica, large-pore zeolite, using [Al]-**BEA** as precursors by hydrothermal route is successful.

Synthesis of high-silica zeolites with large (12-ring) and extra-large (>12-ring) pores are of great interest because of their potential applications in shape-selective catalysis of relatively bulky molecules.[1] SSZ-24 is a high-silica, large-pore molecular sieve isostructural with $AlPO_4$-5 (**AFI** topology[2]) and was first synthesized by Zones et al. in its pure-silica form using 1-trimethylammonioadamantane as a structure-directing agent (SDA).[3] Later the synthesis of borosilicate version ([B]-SSZ-24) was achieved using a calcined form of boron-substituted zeolite beta ([B]-**BEA**) as the boron and silicon sources.[4] Lobo and Davis reported the synthesis of [B]-SSZ-24 using 16-methyl-16-azoniasparteine ($MeSPA^+$) as SDA and using sodium borate as the source of boron. In this case, unlike the case by Zones et al., calcined [B]-**BEA** did not work as precursors for [B]-SSZ-24 synthesis.[5]

On the other hand, direct crystallization of aluminosilicate version ([Al]-SSZ-24) by hydrothermal synthesis (HTS) method is reported to be unsuccessful[5] and, to our best knowledge, there is no report of the direct synthesis of [Al]-SSZ-24 from [Al]-**BEA**. The [Al]-SSZ-24 has only been obtained by isomorphous substitution of [B]-SSZ-24.[5] In this paper, we report the successful phase transformation from [Al]-**BEA** to [Al]-SSZ-24 using $MeSPA^+$. The idea is based on the successful transformation from [Al]-**BEA** to [Al]-SSZ-31 using 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane.[6]

Calcined [Al]-**BEA** with SiO_2/Al_2O_3 ratio = 111 prepared by a HTS method[7] and with SiO_2/Al_2O_3 ratio = 31 prepared by a dry-gel conversion (DGC) method[8] were used as precursors for the synthesis of [Al]-SSZ-24. Each procedure to synthesize [Al]-**BEA** is described in detail elsewhere.[9] The aqueous solution of $MeSPA^+OH^-$ was prepared by a known procedure.[10]

A typical procedure for the synthesis of [Al]-SSZ-24 was as follows: 2.48 g (1.50 mmol) of an aqueous solution of $MeSPA^+OH^-$ (0.606 mmol g^{-1}) was mixed with 0.157 g (0.1 mmol) of 6.30 mmol g^{-1} aq NaOH solution and 5.76 g of deionized water. The resulting alkaline solution was stirred for 10 min, and then 0.30 g of calcined [Al]-**BEA** (SiO_2/Al_2O_3 = 111) followed by 0.30 g (5.0 mmol) of fumed silica (Cab-O-Sil M5, Cabot) was added. The mixture was stirred for another 4 h. The gel composition was: $1.0SiO_2{\cdot}0.15MeSPA^+OH^-{\cdot}0.1NaOH{\cdot}0.005Al_2O_3{\cdot}44H_2O$. The crystallization was carried out statically at 175 °C under autogeneous pressure for 24 h. All samples were identified by powder X-ray diffraction (XRD; Cu Kα radiation) for phase purity. The elemental analysis was performed by ICP analysis.

Table 1 shows the representative results of the synthesis of [Al]-SSZ-24. Before attempting [Al]-SSZ-24 synthesis from [Al]-**BEA** precursors, we verified that the synthesis of [Al]-SSZ-24 without using precursors is difficult (Entry 1). When [Al]-**BEA** (SiO_2/Al_2O_3 = 111) was used as precursor in the absence of additional silica source, incomplete but considerable phase transformation took place and the SSZ-24 was observed as a major phase accompanied by cristobalite as an impurity (Entry 2). When fumed silica was used as a silica source in addition to the [Al]-**BEA**, pure [Al]-SSZ-24 crystallized after 24 h (Entry 3 and Figure 1). At this starting gel composition, the kinetics of crystallization over a period of 120 h was investigated and Figure 1 displays the results. XRD data were taken after 6, 12, 24, 48, 72, and 120 h. It can be seen in Figure 1 that the **BEA** phase started transforming into the SSZ-24 phase after 6–12 h, and pure SSZ-24 was obtained after 24 h as already mentioned above. After 48 h, peaks assignable to cristobalite appeared and the intensity increased upon prolonging the heating period. This means that the phase transformation occurs in the following order: **BEA**→SSZ-24→cristobalite. Thus the main issue is pro-

Table 1. Synthesis of [Al]-SSZ-24[a]

Entry	Starting gel composition					Time	Phase	SiO_2/Al_2O_3		
	SiO_2	$MeSPA^+OH^-$	M^+OH^{-g}	$Al_2O_3{}^j$	H_2O	/h		Precursor[k]	Gel	Product[k]
1	1.0[b]	0.15	0.1	0.005	44	120	Amorphous	—	200	—
2	1.0[c]	0.15	0.1	0.009	44	24	SSZ-24 + BEA + Cristobalite	111	111	—
3	1.0[d]	0.15	0.1	0.005	44	24	SSZ-24	111	222	202
4	1.0[e]	0.15	0.1	0.005	44	24	SSZ-24	31	207	224
5	1.0[f]	0.15	0.1	0.008	44	24	SSZ-24 + BEA + Cristobalite	31	124	—
6	1.0[f]	0.15	0.1	0.008	68	72	SSZ-24 + trace BEA	31	124	128
7	1.0[f]	0.15	0.1	0.008	68	96	SSZ-24	31	124	140
8	1.0[d]	0.15	0.1[h,i]	0.005	44	24	SSZ-24	111	222	227[h] (234[i])

[a]Hydrothermal synthesis was carried out at 175 °C. [b]All SiO_2 came from fumed silica. [c]All SiO_2 came from [Al]-**BEA**. [d]50 wt % SiO_2 from [Al]-**BEA** and 50 wt % from fumed silica. [e]15 wt % SiO_2 from [Al]-**BEA** and 85 wt % from fumed silica. [f]25 wt % SiO_2 from [Al]-**BEA** and 75 wt % from fumed silica. [g]M is Na unless otherwise noted. [h]M = Li. [i]M = K. [j]All Al_2O_3 came from [Al]-**BEA**. [k]Determined by ICP analysis.

moting the transformation from **BEA** to SSZ-24 while suppressing that from SSZ-24 to cristobalite. It is obvious that fumed silica partly added was effective for this purpose. The role of fumed silica may be just to adjust the SiO_2/Al_2O_3 ratio in the gel because the transformation is successful whenever the ratio is as high as 200 (Table 1, Entries 3 and 4). The gel with higher aluminum content led to the formation of cristobalite before complete conversion from **BEA** to SSZ-24 (Entry 5). Larger amount of water together with longer heating period made it possible to form [Al]-SSZ-24 with higher purity (Entry 6). Finally, the SSZ-24 with SiO_2/Al_2O_3 as low as 140 was obtained (Entry 7).

In the case of common HTS with an amorphous silica source and all-silica composition, CIT-5 (**CFI**) is obtained when the alkali cation (M^+) is Li^+ whereas SSZ-24 crystallizes when M = Na or K.[10] In this precursor method, however, there was almost no influence of the kind of alkali cations on the crystallization of SSZ-24, and pure [Al]-SSZ-24 was obtained when Li^+ or K^+ was used instead of Na^+ (Entry 8).

^{13}C CP MAS NMR spectra of as-synthesized samples revealed that the $MeSPA^+$ was intact inside the pores of [Al]-SSZ-24. ^{27}Al MAS NMR of the as-synthesized product from Table 1, Entry 3 showed a single peak at 52.3 ppm and no peak at around 0 ppm, indicating tetrahedral environment of Al. The nitrogen adsorption isotherm of the corresponding calcined sample showed micropore volume of $0.16\,cm^3\,g^{-1}$ and BET surface area of $414\,m^2\,g^{-1}$, which are typical values for 1-D 12-ring molecular sieves and well agree with those obtained from the typical [B]-SSZ-24 sample.

Figure 2 displays the scanning electron microscopy (SEM) photographs of [Al]-**BEA** precursor ($SiO_2/Al_2O_3 = 111$) used and the [Al]-SSZ-24 formed. A morphology transformation from small cuboid particles to hexagonal rod-shaped crystals is clearly seen.

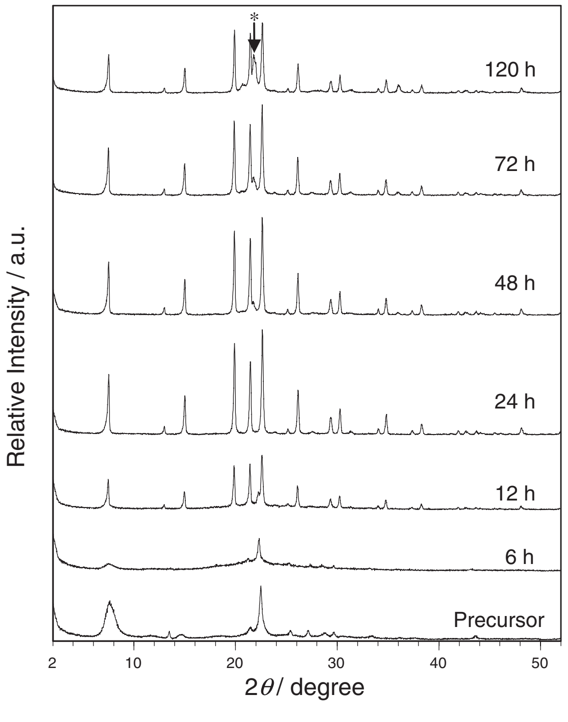

Figure 1. Phase change with time course as reflected in the powder XRD pattern of the as-synthesized samples; gel composition is shown in Table 1, Entry 3. The peak marked with an asterisk is assignable to a peak of cristobalite.

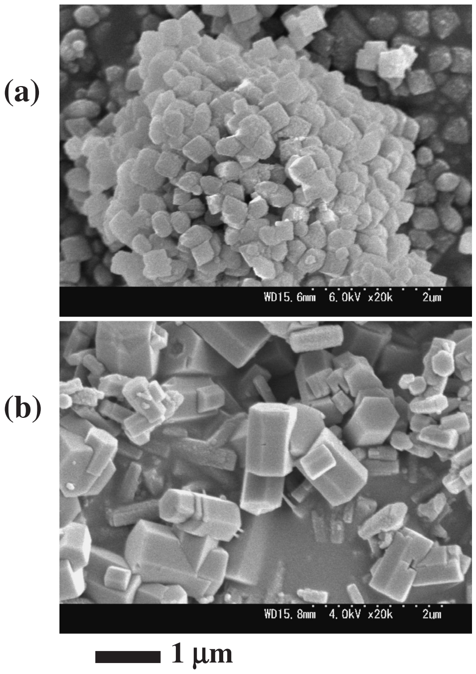

Figure 2. SEM photographs of (a) [Al]-**BEA** precursor with $SiO_2/Al_2O_3 = 111$ and (b) [Al]-SSZ-24 product in Table 1, Entry 3.

In conclusion, [Al]-SSZ-24 with SiO_2/Al_2O_3 ratio as low as 140 was synthesized successfully using [Al]-**BEA** zeolite as precursors and $MeSPA^+$ as a SDA. This result may provide a new optional route for zeolite synthesis especially where direct synthesis of aluminum versions is difficult. Catalytic performance of the samples obtained in this work is under investigation and will be reported elsewhere.

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