Synthesis of [Al]-SSZ-31 by Dry-Gel Conversion (DGC) Method

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Synthesis of large-pore zeolite [Al]-SSZ-31 has been studied by dry-gel conversion method using 1,8-diazoniaoctane type of structure-directing agent. Pure SSZ-31 was obtained with NaOH/SiO_2 = 0.05-0.12, while the product was contaminated with MFI below or above this range. Snowtex-40 (colloidal), as the silica source yielded SSZ-31, while Cab-O-Sil M-5 and Ludox AS-40 yielded mostly MFI phase. A phase change: BEA→SSZ-31→MFI was observed with time course at optimum NaOH/SiO_2.

SSZ-31 is a one-dimensional, large-pore, high-silica zeolite, which is very promising material for shape-selective catalysis such as Friedel-Crafts alkylation of bulky aromatic compounds. The synthesis of all-silica SSZ-31 was reported by Zones et al.,[1] and the framework silicon was difficult to be substituted by other atoms. Synthesis of borosilicate version of SSZ-31, followed by conversion to its aluminosilicate version, has been studied using various structure-directing agents (SDAs) and different starting materials.[1-4] A model for the structure of SSZ-31 was proposed by Lobo et al.[5] Dry-gel conversion (DGC) technique is a comparatively new method for synthesizing zeolites which allows dry gel transformation to zeolites in high yield, and it involves nearly complete conversion of gel to zeolite. Earlier, synthesis and characterization of zeolites such as [Al]-BEA,[6,7] OU-1 (SSZ-31-like phase),[8] [B]-BEA, MFI and MTW,[9,10] and [Ti]-BEA[11,12] were studied by this method. Zeolites can be synthesized by this method by applying higher temperatures than those used in the hydrothermal method. Moreover, the DGC method enables us minimization of waste disposal and reduction in reactor volume. In the present study, the DGC method, more precisely steam-assisted conversion (SAC) method has been used to synthesize [Al]-SSZ-31. Effect of NaOH concentration in the starting gel, and phase change with the time course was investigated. From our previous experiences, making SSZ-31 phase with TEAOH[8] as SDA is slightly more difficult and slower, and we believe that our present method is more suitable to obtain [Al]-SSZ-31 directly, especially for the purpose of acid-catalyst preparation.

Typical procedure of synthesis of [Al]-SSZ-31 is as follows: first, 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dibromide was prepared by refluxing dibromohexane and excess triethylamine in acetone. The dibromide salt was converted to its dihydroxide form with ion-exchange resin, and the dihydroxide solution was used as SDA. Afterwards, an appropriate amount of the SDA was mixed with NaOH (32 wt% solution), followed by the addition of colloidal silica, and the mixture was stirred for 30 min. $Al_2(SO_4)_3$ was dissolved in distilled, de-ionized water and was added to the above mixture, and the resulting mixture was stirred for additional 2 h. The gel was then dried at 80-90 °C with continuous stirring. When the gel became viscous, it was stirred by a Teflon rod until it dried. The dry gel was ground into a fine powder and the powder was poured in a small Teflon cup. This cup was placed in a Teflon-lined autoclave (23 ml) with water (which was the source of steam) in its bottom (ca. 0.2 g) in such a manner that the dry gel never came into the direct contact with water. The crystallization of the dry gel was carried out at 175 °C for 24 h at autogenous pressure. The final gel composition was: SiO_2-$0.2R^{2+}(OH^-)_2$-{0.03-0.15}NaOH-$0.003Al_2O_3$, where R^{2+} is 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane cation. Afterwards, the autoclave was quenched with cold water, and the zeolite powder was taken out from the cup, and washed thoroughly with water and dried at room temperature. The as-synthesized zeolite thus obtained was characterized by XRD, SEM, TG-DTA, ICP, CHN analysis, N_2 adsorption, ^{13}C CP and ^{27}Al MAS NMR.

The XRD patterns of the as-synthesized samples showed crystalline products without any impure phase. Alkali concen-

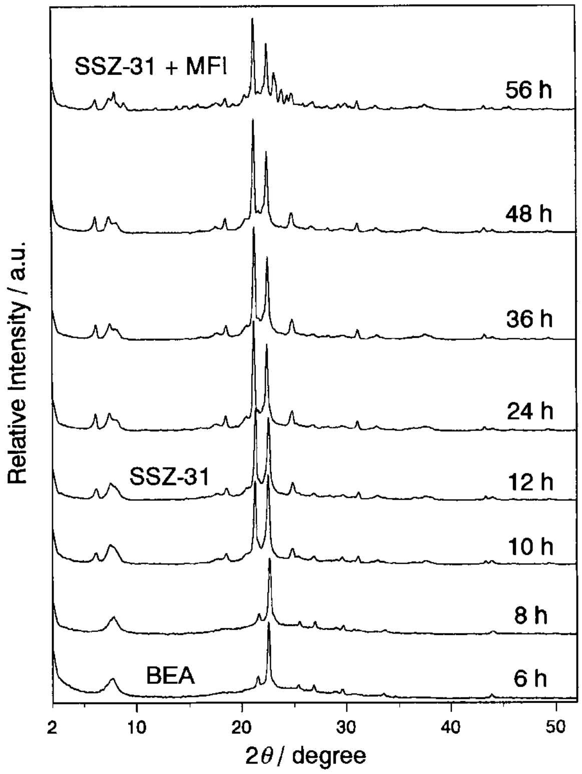

Figure 1. Phase change with time course as reflected in the powder XRD pattern of the as-synthesized samples; gel composition: SiO_2-$0.2R^{2+}(OH^-)_2$-0.08NaOH-$0.003Al_2O_3$.

tration in the starting gel played a major role during the synthesis. Pure SSZ-31 was obtained within the range of NaOH/SiO_2 = 0.05-0.12, while MFI phase was mainly formed below (ca. 0.03) or above (ca. 0.15) this range. The source of silica also affected the synthesis product. Snowtex-40 (colloidal silica, Nissan Chemical. Co.) showed the best results as the silica source to get SSZ-31, while Cab-O-Sil M-5 (fumed silica, Cabot) and Ludox AS-40 (colloidal silica, Du Pont) yielded mostly MFI phase. Presence of a small amount of NaOH of different concentrations in the colloidal silica source may have played some role. It was interestingly observed that a phase change occurred at optimum NaOH/SiO_2 ratio (ca. 0.08). A change of phase from BEA to SSZ-31, and finally to MFI was observed from shorter to longer time (Figure 1). At lower NaOH/SiO_2 (ca. 0.03), pure MFI phase was obtained after longer time course, whereas at higher NaOH/SiO_2 (ca. 0.15), pure BEA phase obtained at shorter time was converted to a mixture of SSZ-31 and MFI phase. Rao et al.[8] observed similar type of phase transformation of high-silica BEA to OU-1, however, the phase transformation from BEA to SSZ-31 in the present case is much faster than that from BEA to OU-1. From the above investigation the optimum condition for obtaining pure [Al]-SSZ-31 phase was found to be: NaOH/SiO_2 = 0.08; temp. = 175°C; time = 12-48 h. On the other hand, pure [Al]-MFI and pure [Al]-BEA phase could also be obtained using lower and higher NaOH contents in the starting gel, respectively.

From the ^{13}C CP MAS NMR of the as-synthesized [Al]-SSZ-31, the pattern resembled that of the NMR of SDA, indicating intactness of the SDA inside the zeolite pore. The ^{27}Al MAS NMR of the as-synthesized sample showed a single peak at around 53 ppm, indicating the tetrahedral framework nature of Al. In the elemental analysis of the samples by ICP showed that major portion of gel phase was converted to the zeolite phase; around 80% of the silica to alumina ratio of the starting gel being retained in the as-synthesized sample (Table 1). The yield of the [Al]-SSZ-31 samples was higher (about 75 to 90%) than that of [B]-SSZ-31 synthesized by the hydrothermal method (65%). The N_2 adsorption isotherm of calcined [Al]-SSZ-31 possessed a micrpore volume of 0.128 ml/g, and the BET surface area of 445 m^2/g. The CHN analysis of the as-synthesized sample showed N^+/Si = 0.054. Considering polymorph A of SSZ-31 having 28 T atoms per unit cell, it is observed that one unit cell contains 1.5 N^+, or in other words 0.75 SDA, which means the SDA is well packed inside the pore. Although the SiO_2/Al_2O_3 was kept constant at 333 in the present study, pure [Al]-SSZ-31 was also obtained at SiO_2/Al_2O_3 = 200. However, BEA and MFI phase was formed at lower (ca. 100) and higher (ca. 800) SiO_2/Al_2O_3 ratios, respectively. In conclusion, dry-gel conversion method was successfully applied to synthesize [Al]-SSZ-31 in high yield using 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide as SDA, and could be explored for further use as catalyst.

Table 1. Elemental analysis

SiO_2/Al_2O_3	
Starting gel	As-synthesized sample[a]
330	257
200	165

[a]Measured by ICP.

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