Phase Transformation of High Silica BEA to OU-1 and MTW

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(Received December 2, 1997; CL-970911)

Phase transformation of high silica BEA to OU-1 and MTW was demonstrated for the first time. Zeolite OU-1, an analogous material to SSZ-31 and NCL-1, was synthesized using tetraethylammonium hydroxide (TEAOH) as a structure directing agent. The influence of Na and Al ions on stabilization of BEA phase during crystallization is presented.

Zeolites are materials widely used in catalysis, adsorption and ion exchange. Zeolite pore structure and chemical compositions are very important since they determine shape selectivity and catalytic activity. A major part of recent research on zeolites is focused on synthesis of zeolites with new structures, synthesis using low cost organic materials as structure directing agents and new crystallization methods to perform crystallization in a dense media,[1] from or in a gas phase.[2-7]

Barrer described the transformation of zeolite structures during crystallization.[8] Transformation of LTA to hydroxy-sodalite and zeolite P was reported.[9] Norby pointed out such transformation as one of the possible routes for the synthesis of zeolites.[10] We recently reported the synthesis of highly crystalline BEA by dry gel conversion method. This method allowed to prepare BEA with SiO_2/Al_2O_3 = 30 to infinity using TEAOH as a structure directing agent in an alkaline medium.[4-6] In this study, we report the transformation of high silica BEA to zeolite OU-1 (an analogous material to SSZ-31[11] and NCL-1[12]) and MTW and the effect of gel compositions on the phase transformation.

Dry gels having compositions, SiO_2 : 0.0013 - 0.33 Al_2O_3 : 0.042-0.94 Na_2O : 0.37 - 0.38 TEAOH, were prepared as described elsewhere.[5,6] Crystallization of the dry gel was carried out in the presence of steam at 453 K and autogeneous pressure for 3 to 120 h. The products were characterized by XRD, SEM and N_2 adsorption.

Highly crystalline BEA was obtained by crystallization of dry gels with SiO_2/Al_2O_3 ratios = 30 - 730 for 3 - 12 h under autogenous pressure at 453 K. Crystallization was completed for the gels with SiO_2/Al_2O_3 = 30 within 3 h and produced highly crystalline BEA as previously reported.[5,6] No change in the crystallinity as well as particle sizes was observed in the products obtained from these gels (SiO_2/Al_2O_3 ratios = 30) even after 120 h of crystallization (Figure 1A). However, gels with SiO_2/Al_2O_3 ratios = 380 and 730, which produced pure BEA after crystallization for 12 h, transformed to other phases after prolonged crystallization. The products formed depended on the gel compositions as well as crystallization time. As shown in Figure 1B, a gel with SiO_2/Al_2O_3 = 380 produced BEA after crystallization time of 12 h. When the crystallization was carried out for 24 h, the product showed additional reflections in its XRD pattern typically at 2θ = 6.2, 7.4, 8.2, 21.2 and 24.9°, other than those for BEA. These reflections can be attributed to a new phase OU-1. Enrichment of these reflections and diminish of the reflections for BEA continued till 60 h of crystalllization, suggesting that BEA is transforming to another phase. Further prolonged crystallization led to the formation of cristoballite. The product crystallized for 60 h, after calcination at 723 K did not contain BEA, and a different phase OU-1 (an analogous material to SSZ-31 and NCL-1) was produced. XRD patterns of Figure 1B do not show any broad peak characteristic of amorphous material. Similarly, SEM images also show the absence of any amorphous phase. These results suggest the direct phase transformation from BEA to OU-1. SSZ-31 and NCL-1 were synthesized using N,N,N-trimethyltricyclo[5.2.1.0^{2,6}]

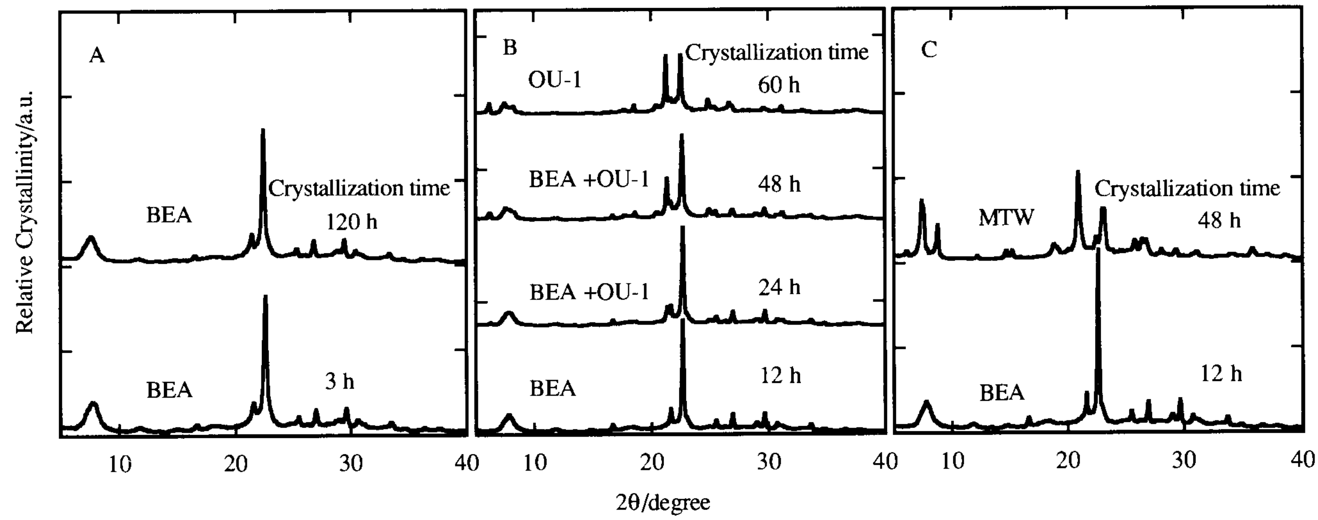

Figure 1. Effect of gel composition and crystallization time on zeolite product.
SiO_2/Al_2O_3 and Na_2O/SiO_2 ratios : A, 30 and 0.042; B, 380 and 0.042; C, 730 and 0.094, respectively.

decaneammonium and hexamethylene bis(triethylammonium bromide), respectively, as structure directing agents.[11,12] These structure directing agents are commercially not available. Lobo *et al.*[11] have shown that BEA, MTW and SSZ-31 have a similar (related) framework structure (projection). These zeolites have 12 membered pore opening with the difference in the connectivity of T-atoms and rearrangement of these T-atoms may lead to the formation of different structures. Our method enables to synthesize these three structurally related zeolites using TEAOH as a structure directing agent.

When the Na^+ ion concentration in the gel having SiO_2/Al_2O_3 ratio = 380 was Na_2O/SiO_2 ratio = 0.014, the product was transformed to MTW instead of OU-1. When the Na^+ ion concentration of the gel was raised to Na_2O/SiO_2 ratio = 0.094, stability of BEA phase was improved and product did not transform to other phases even after 60 h of crystallization. This suggests Na^+ ions play an important role in directing the structure of product. A lower Na^+ ion concentration (Na_2O/SiO_2 = 0.014) favors the formation of MTW and an increased Na^+ ion concentration (Na_2O/SiO_2 = 0.042) is required for the formation of OU-1. A further higher Na^+ ion concentration (Na_2O/SiO_2 = 0.094) improves the stability of BEA with SiO_2/Al_2O_3 ratio = 380 during crystallization. The gel having SiO_2/Al_2O_3 ratio = 730 and Na_2O/SiO_2 ratio = 0.014 did not crystallize and the product remained amorphous. When the Na_2O/SiO_2 ratio was raised to 0.042, the products after 12 and 48 h of crystallization were BEA (relative crystallinity = 75 %) and MTW, respectively. Gel with SiO_2/Al_2O_3 ratio = 730 and Na_2O/SiO_2 ratio = 0.094 formed highly crystalline BEA after 12 h of crystallization. However, when the crystallization was prolonged to 48 h, the product transformed from BEA to MTW (Figure 1C). This suggests that during crystallization, the stability of BEA phase decreases with increasing SiO_2/Al_2O_3 ratios, though their stability could be improved by increasing Na_2O/SiO_2 ratios to a certain extent. After crystallization, pure BEA samples with SiO_2/Al_2O_3 ratios = 380-730 were found to have high thermal stability and after transforming to H-form: They were stable even after calcination at 1373 K[6]. This suggests that a less stable phase during crystallization needs not be thermally a less stable phase.

Figure 2 shows FE-SEM images of BEA and OU-1. OU-1 crystals are rectangular in shape with 2 μm length and 1 μm width: Namely, the crystal shape of this phase is totally different from that of BEA. The BET surface areas of BEA, OU-1 and MTW were 529, 290 and 310 $m^2\ g^{-1}$, respectively. Sorption capacities for cyclohexane and m-xylene were measured at 303 K by TG. These two kinds of hydrocarbons saturated at 298 K in a stream of helium were supplied. The sorption capacities were about 4 and 2 wt% for cyclohexane and m-xylene, respectively. These adsorption properties strongly indicate that OU-1 is a high silica zeolite with 12-membered ring opening. Our preliminary studies on structural analysis by HRTEM and XRD confirmed that OU-1 is a large pore molecular sieve and has pore opening similar to that of SSZ-31.[13]

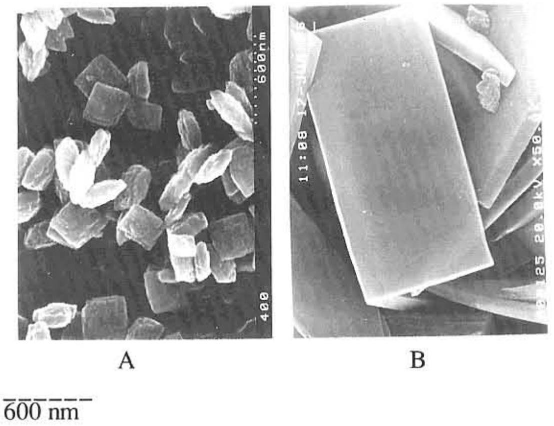

Figure 2. FE-SEM images of BEA (A) and OU-1 (B). SiO_2/Al_2O_3, Na_2O/Al_2O_3 and crystallization time: A, 400, 18.4 and 12 h; B, 380, 15.96, 60 h.

One of the authors (PRH) thanks Japan Society for the Promotion of Science for a research fellowship.

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