Synthesis of Borosilicate Zeolites by Dry Gel Conversion (DGC) Method

Rajib Bandyopadhyay,[†,††] Yoshihiro Kubota,[†] and Yoshihiro Sugi*[†]
[†]*Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193*
[††]*New Energy and Industrial Technology Development Organization (NEDO), Tokyo 170-6028*

(Received April 28, 1998; CL-980328)

Synthesis of borosilicate zeolites, namely [B]-BEA, [B]-MFI and [B]-MTW by dry gel conversion (DGC) method was described for the first time. Phase selection and thereby the outcome of the product was dependent upon the gel composition, mainly on the SiO_2/B_2O_3 ratio and the TEAOH content.

In recent decades, zeolites are finding widespread applications in various industries in the field of catalysis, ion-exchange, separation and adsorption. High silica zeolites are useful materials for catalysis and selective adsorption due to their hydrothermal stability, hydrophobicity and acid strength and stability.[1] Boron substituted zeolites are one class of high silica zeolites, and the syntheses of these zeolites have been studied by many researchers over the years.[2-8] The chemistry of boron is essentially different from that of aluminum, and substitution of boron in place of aluminum in conventional aluminosilicate zeolites might be expected to modify the acidic, and consequently the catalytic properties of the zeolite.[9,10] Another interesting aspect of borosilicate zeolites is that, during the postsynthesis treatment of boron-containing structures, boron can be extracted under extremely mild conditions leaving thermally stable silanol nests which can be reoccupied by other elements.[4] Thus, postsynthesis substitution of boron containing zeolites could be useful for synthesizing metallosilicate analogues, which are difficult to obtain by direct hydrothermal methods.

Recently new routes, or in other words, new crystallization methods of zeolites have been focused by some researchers. Vapor phase transport method of crystallization,[11-15] and more precisely, dry gel conversion techniques[16,17] have been adopted to study the synthesis of zeolites. Matsukata et al.[16] reported the synthesis of aluminosilicate BEAs (Beta zeolites) having wide range of silica to alumina ratio by dry gel conversion technique. However, synthesis of high silica boron zeolites by this method has not been reported so far. In the present study, we report the synthesis of borosilicate zeolites by dry gel conversion (DGC) technique. The effect of gel composition on the phase selection during the synthesis, and the characterization of the products were the main interests of the study.

For the synthesis of borosilicate zeolites, the general dry gel conversion technique reported by Matsukata et al.[16] was followed. In a typical procedure, appropriate amount of colloidal silica (Ludox AS40, DuPont) was mixed with TEAOH (35 wt% in water) solution, and the mixture was stirred for 10 min. NaOH was added to it and the stirring was continued for 30 min. Sodium borate ($Na_2B_4O_7.10H_2O$) was dissolved in distilled, deionized water and added to the above mixture, and the whole mixture was further stirred for 2 h. Afterwards, the gel was dried at 80 °C with continuous stirring. When the gel became thick and 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 (20 mm ID × 20 mm). 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 72 h in autogenous pressure. The molar composition of the gel was as follows: SiO_2 : 0.002-0.033 B_2O_3 : 0.056-0.1 NaOH : 0.36-1.2 TEAOH. After the crystallization was over, the autoclave was quenched with cold water, and the zeolite powder was taken out from the cup, filtered and washed thoroughly with water, and dried overnight at room temperature. The as-synthesized samples were analyzed by XRD, SEM, FTIR, TG-DTA, ICP and ^{13}C CP MAS NMR.

Table 1 shows the products obtained by DGC technique with different gel compositions. The results clearly indicate that the products obtained are dependent upon the gel composition, mainly on the SiO_2/B_2O_3 ratio and the $TEAOH/SiO_2$ ratio. Pure [B]-BEA was obtained at higher $TEAOH/SiO_2$ (0.8-1.2) and at comparatively lower SiO_2/B_2O_3 (30-50) (Table 1, Run 1,2,11,12). This is unlike the [Al]-BEA synthesized by Matsukata et al. where lesser $TEAOH/SiO_2$ was required.[16] Keeping SiO_2/B_2O_3 lower (30-50) when $TEAOH/SiO_2$ was lowered, MFI phase appeared with BEA (Run 3-5). Pure [B]-MFI phase was obtained with increasing SiO_2/B_2O_3 (100-200) (Run 6,7). At comparatively higher SiO_2/B_2O_3 (50-100) and higher $TEAOH/SiO_2$ (0.8-1.0) MTW phase started coming with BEA and MFI phase (Run 8-10, 13). $NaOH/SiO_2$ ratio also appeared to affect the product pattern. $NaOH/SiO_2$ ratio was shifted from 0.056 to 0.1 and pure MFI phase was obtained with SiO_2/B_2O_3 100 (Run 15,17). When SiO_2/B_2O_3 ratio was further increased

Table 1. Borosiloicate zeolites by dry gel conversion (DGC)[a]

Run	SiO_2	TEAOH	B_2O_3	NaOH	Product
1	1.0	1.0	0.033	0.056	BEA
2	1.0	0.8	0.033	0.056	BEA
3	1.0	0.6	0.033	0.056	BEA + MFI
4	1.0	0.36	0.033	0.056	BEA + MFI
5	1.0	0.36	0.02	0.056	BEA + MFI
6	1.0	0.36	0.01	0.056	MFI
7	1.0	0.36	0.005	0.056	MFI
8	1.0	1.0	0.01	0.056	BEA+MFI+MTW
9	1.0	0.8	0.02	0.056	BEA + MTW
10	1.0	1.0	0.02	0.056	BEA + MTW
11	1.0	1.2	0.02	0.056	BEA
12	1.0	1.0	0.02	0.1	BEA
13	1.0	0.8	0.02	0.1	BEA + MTW
14	1.0	0.6	0.033	0.1	BEA + MTW
15	1.0	1.0	0.01	0.1	MFI
16	1.0	1.0	0.005	0.1	MTW
17	1.0	1.2	0.01	0.1	MFI
18	1.0	1.0	0.002	0.1	MTW

[a]Synthesis was done at 175 °C for 72 h as described in the text.

(200-500), only pure MTW phase was observed (Run 16,18). It was important to notice that, we did not observe any phase change during the synthesis, even after the crystallization was continued for longer time (144 h), and it seems that the gel composition solely played as the major factor for the outcome of the product phase.

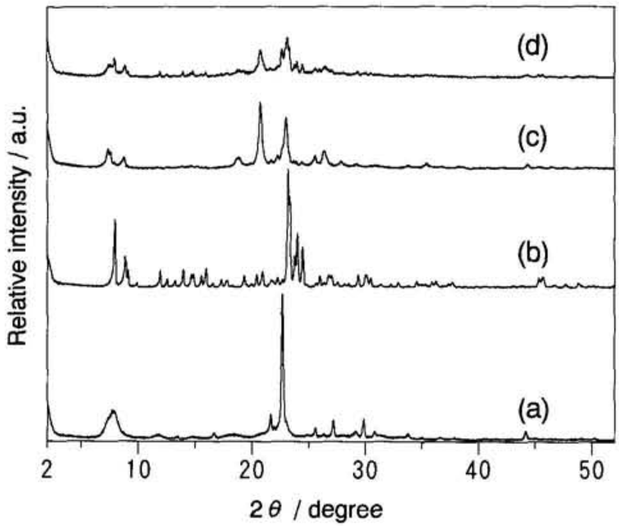

Figure 1. Powder XRD pattern of as-synthesized (a) [B]-BEA (Table 1, Run 1), (b) [B]-MFI (Run 6), (c) [B]-MTW (Run 16), and (d) mixture of 3 phases (Run 8) obtained from different gel compositions.

Figure 1(a,b,c) shows the XRD patterns of pure BEA, MFI and MTW phases obtained at different gel compositions. High intensity of the peaks and absence of any baseline drift indicated that the samples were highly crystalline. Figure 1d shows the XRD pattern consisting of all the three phases.

In the ^{13}C CP MAS NMR of the as-synthesized pure BEA, MFI and MTW phases, all the samples showed chemical shifts around 52-53 ppm and 6-7 ppm due to the presence of tetraethylammonium ion. This indicated that the template was intact in all the samples. However, apart from these signals, NMR of MFI sample showed obvious signals of olefin (123.60 ppm) and tertiary amine (47.07 ppm). NMR of MTW also showed very weak signals at 123.60 and 48.82 ppm, indicating partial decomposition[18] (mainly the Hofmann degradation) of the template in the MFI and MTW samples.

FTIR spectra of all of the as-synthesized samples (BEA, MFI, MTW) showed characteristic band around 900 cm^{-1}, due to the framework tetrahedral B(OSi)$_4^-$ entities and could be assigned to the stretching of the Si-O-B bond.[6] The intensity of the band was strongest in [B]-BEA and weakest in [B]-MTW which were well matched with the SiO$_2$/B$_2$O$_3$ ratio, or in other words, the amount of boron present in the starting gel as well as the as-synthesized samples analyzed by ICP.

Scanning electron micrographs of the as-synthesized samples indicated the absence of any amorphous material or any other crystalline phase impurities. The crystals of [B]-BEA were nearly cuboid in shape with average size of 3 μm. [B]-MFI crystals were mostly near-spheroid in shape (10-15 μm), though some cuboid crystals were also visible. [B]-MTW crystals were twinned, polycrystalline aggregates (2.5-4 μm).

From the thermal analysis (TG-DTA) of the as-synthesized samples, weight loss of 1.57%, 1.43% and 0.71% mainly due to the desorption of water up to 200 °C was observed for BEA, MTW and MFI, respectively. On the other hand, weight loss of 16.60%, 10.04% and 8.59% due to the decomposition of organic template up to ca. 700 °C was observed for BEA, MTW and MFI, respectively. Larger void volume of BEA was responsible for the higher water and template content.

In conclusion, borosilicate zeolites of various structures such as BEA, MFI and MTW, can be effectively synthesized by dry gel conversion (DGC) technique. The zeolite samples by this method could be obtained with high crystallinity and high purity. This method enables for the complete conversion of gel to zeolites. The phase selection, and thereby the outcome of the product depends upon the gel composition, mainly on the SiO$_2$/B$_2$O$_3$ ratio and the TEAOH content. This method of synthesis could be well applied for the synthesis of other borosilicate zeolites.

A part of this work was supported by the New Energy and Industrial Technology Development Organization of Japan.

References

1 J. Scherzer, ACS Symp. Ser., 248, Am. Chem. Soc., Washington, DC, 1984, p. 157.
2 G. Coudurier, A. Auroux, J .C. Vedrine, R. D. Farlee, L. Abrams, and R. D. Shannon, *J. Catal.*, **108**, 1 (1987).
3 A. Cichocki, J. P. Kaczmarska, M. Michalik, and M. Bus, *Zeolites*, **10**, 577 (1990).
4 R. de Ruiter, A. P. M. Kentgens, J. Grootendorst, J. C. Jansen, and H. van Bekkum, *Zeolites*, **13**, 128 (1993).
5 S. I. Zones and L. T. Yuen, U. S. Patent, 5187132 (1993).
6 R. de Ruiter, K. Pamin, A. P. M. Kentgens, J. C. Jansen, and H. van Bekkum, *Zeolites*, **13**, 611 (1993).
7 R. F. Lobo and M. E. Davis, *Microporous Mater.*, **3**, 61 (1994).
8 R. Bandyopadhyay, Y. Kubota, S. Tawada, and Y. Sugi, *Catal. Lett.*, **50**, 159 (1998).
9 K. G. Ione, L. A. Vostrikova, E. A. Paukshits, E. N. Yurchenko, and V. G. Stepanov, *Dokl. Akad. Nauk.*, **261**, 1160 (1981).
10 M. R. Klotz, U. S. Patent, 4268420, 4269813, 4285919 (1981).
11 W. Xu, J. Dong, J. Li, J. Li, and F. Wu, *J. Chem. Soc., Chem. Commun.*, **1990**, 755.
12 J. Dong, T. Dau, X. Zhao, and L. Gao, *J. Chem. Soc., Chem. Commun.*, **1992**, 1056.
13 M. H. Kim, H. X. Li, and M. E. Davis, *Microporous Mater.*, **1**, 191 (1993).
14 N. Nishiyama, K. Ueyama, and M. Matsukata, *J. Chem. Soc., Chem. Commun.*, **1995**, 1947.
15 N. Nishiyama, K. Ueyama, and M. Matsukata, *Microporous Mater.*, **7**, 299 (1996).
16 P. R. H. P. Rao and M. Matsukata, *Chem. Commun.*, **1996**, 1441.
17 T. Tatsumi, Q. Xia, and N. Jappar, *Chem. Lett.*, **1997**, 677.
18 A. Moini, K. D. Schmitt, and R. F. Polomski, *Zeolites*, **18**, 2 (1997).