Indication of Successful Crystallization of Dry Gel into *BEA-type Zeolite

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Tetraethylammonium (TEA^+)-containing silicate dry gels exhibiting a maximum in the reflection peak at $2\theta = 28^\circ$ in an XRD pattern using Cu Kα radiation are always transformed into *BEA-type zeolite with steam-assisted crystallization.

Zeolites, microporous aluminosilicate crystals, are generally crystallized under hydrothermal conditions. An alternative method of crystallizing zeolites, the dry gel conversion (DGC) method, was developed in the early 1990s.[1–3] In this method, dried aluminosilicate gel powder is crystallized to zeolites in the presence of steam. Since then, the DGC method has been extensively used to synthesize various kinds of microporous crystals[4] and has recently applied to prepare a commercial zeolite catalyst for diethanolamine synthesis.[5] Therefore, this method has been approved as one of the general methods for crystallizing zeolites. *BEA-type zeolite is a high-silica molecular sieve having three-dimensional pore systems consisting of 12-membered-rings and is one of the most commonly used catalysts in aromatic alkylation processes.[6] We have previously reported that *BEA-type zeolite can be produced by the steam-assisted crystallization (SAC) method,[7] one of DGC techniques. In the SAC method, dry aluminosilicate gel containing tetraethylammonium cation (TEA^+) as structure-directing agent, can be transformed to *BEA-type zeolite in the presence of steam. Moreover, this technique can produce *BEA-type zeolite with a wide range of SiO_2/Al_2O_3 molar ratios, from seven to infinity[7c] and has been applied to crystallize *BEA containing Ti,[8] B[9] or Ga[10] in tetrahedral sites.

Identification of whether a dry gel can be transformed into *BEA-type zeolite will drastically reduce the efforts required to seek crystallization conditions. We know through experimentation that in the SAC method, the product phase strongly depends on the contents of TEA^+ and Na^+ in the dry gel. In the crystallization of high silica Al-*BEA,[7b] the low content of TEA^+ or Na^+ in the dry gel leads to the formation of the MTW phase. Bandyopadhyay et al.[9] studied the SAC of various borosilicates and reported that dry gel with a low content of TEA^+ is transformed into the MFI or MTW phase instead of the *BEA phase. In this study, we extensively explored the XRD patterns of dry gels with various contents of TEA^+. Furthermore, a sort of precursor of *BEA-type zeolite formed in a dry gel with $TEA^+/SiO_2 \geq 0.37$ was found, and the XRD measurement of a dry gel with TEA^+ provided sufficient information to determine whether a dry gel can be transformed into *BEA-type zeolite.

Preparation of dry gels containing various amounts of TEA^+ and the SAC of dry gels was performed according to our previous reports.[7] Table 1 lists the chemical compositions of parent dry gels prepared and crystallization temperatures. The dry gels and resultant products were characterized by using XRD (Miniflex, Rigaku) with Cu Kα radiation. The high-energy X-ray diffraction (HEXRD) experiments were conducted at the bending magnet beamline, BL04B2, of SPring-8. The recorded data were normalized for flux, corrected for background, Compton scattering and absorption, and then converted to the total structure factor, $S(Q)$. Total correlation functions, $T(r)$, were calculated from the weighted interference functions, $Q[S(Q) - 1]$, by Fourier transformation up to $Q_{\max} = 25\,\text{Å}^{-1}$.

Table 1. Chemical compositions of dry gels and crystallization temperatures

Entry	Silica source	Chemical compositions of dry gels				Crystallization temperature/°C
		SiO_2	Al_2O_3	TEAOH	NaOH	
1	Colloidal silica	1.0	0.0014	0	0.06	175
2		1.0	0.0014	0.10	0.06	
3		1.0	0.0014	0.20	0.06	
4		1.0	0.0014	0.37	0.06	
5		1.0	0.033	0.37	0.06	
6		1.0	0.010	0.37	0.06	
7	TEOS[a]	1.0	0	0.45	0.06	150

[a] TEOS means tetraethylorthosilicate.

Figure 1 shows the XRD patterns of the dry gels with various contents of TEA^+ and the products obtained from the steam-assisted crystallization of each dry gel. Figure 1B (k)–(m) indicates that aluminosilicate dry gels **4**, **5** and **6** with $TEA^+/SiO_2 = 0.37$ gave *BEA-type zeolite after 24 h of crystallization at 175 °C. Pure silica dry gel **7** was also transformed to the *BEA phase after 5 days of crystallization at 150 °C, as shown in

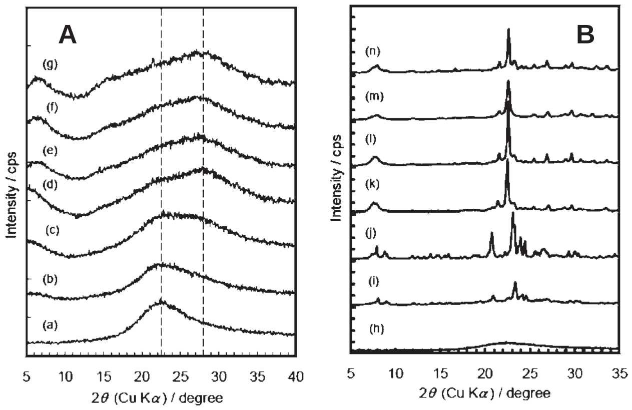

Figure 1. (A) XRD patterns for dry gels (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6** and (g) **7**. (B) XRD patterns for the products from dry gels (h) **1**, (i) **2**, (j) **3**, (k) **4**, (l) **5**, (m) **6** and (n) **7**.

Figure 1B (n). On the other hand, in dry gels **1**, **2** and **3**, the products that crystallized after 24 h were still amorphous. Figure 1B (i) and (j) shows that prolonged crystallization (over 7 days) of dry gels **2** and **3** gave a mixture of MFI and MTW phases. Moreover, Figure 1B (h) indicates that the product obtained after 7 days of crystallization from dry gel **1** was amorphous.

All the XRD patterns of the dry gels show a broad reflection peak at $2\theta = 15$–35°, as illustrated in Figure 1A. This broad peak suggests the existence of an amorphous structure in the dry gel. Figure 1A (a) shows that dried colloidal silica with an amorphous structure exhibited a maximum in the broad reflection peak at $2\theta = 22^\circ$ in the XRD pattern. A broad peak always appears at $2\theta = 28^\circ$ in the XRD patterns of the dry gel that gives *BEA-type zeolite after the SAC. Dry gels **4**, **5**, **6** and **7** with $\mathrm{TEA^+/SiO_2} \geq 0.37$ exhibited a maximum in the broad reflection peak at $2\theta = 28^\circ$, as shown in Figure 1A (d)–(g). Additionally, a broad peak at $2\theta = 28^\circ$ is observed in the XRD pattern of the dry gel, which can be transformed into B, Ti or Ga-containing *BEA-type zeolite (see Supporting Information 2).[11] On the other hand, Figure 1A (b) and (c) indicates that dry gels **2** and **3**, which do not form the *BEA phase, exhibited the broad reflection peak at around 22° in the XRD pattern. Thus, we observed that the dry gels exhibiting the broad peak at $2\theta = 28^\circ$ in the XRD pattern form *BEA-type zeolite by the SAC method.

Furthermore, we investigated the appearance of a broad reflection peak at around $2\theta = 28^\circ$ in the XRD patterns by using HEXRD. Figure 2A shows the S(Q) of dry gel **1** without $\mathrm{TEA^+}$ and dry gel **4** with $\mathrm{TEA^+/SiO_2} = 0.37$. The maximum of the first sharp diffraction peak (FSDP) of dry gel **4** appears at around 2.0 $\mathrm{Å^{-1}}$, which was larger than that of dry gel **1**, at 1.6 $\mathrm{Å^{-1}}$. The position of FSDP in dry gel **1** gave d spacing $= 3.9_3$ Å, which was almost equal to $d = 3.9_5$ Å estimated from the maximum of Cu Kα–XRD broad peak of dry gel **1**, resembling general amorphous silica. Similarly, $d = 3.1_8$ Å estimated from the position of FSDP in dry gel **4** is almost the same as $d = 3.1_4$ Å estimated from the maximum of Cu Kα–XRD broad peak of dry gel **4**. Figure 2B shows the $T(r)$ data of the two kinds of dry gels. Both dry gels exhibited three peaks at 1.6, 2.6 and 3.1 Å, corresponding to first-neighbour Si–O, first-neighbour Si–Si and first-neighbour O–O separations, respectively. The positions of these three peaks below 3.5 Å showed no significant differences in both the dry gels. On the other hand, only dry gel **4** exhibited a peak at 3.8 Å, which is in the range of 3.5–4.5 Å, corresponding to the second-neighbour Si–O separations. Based on a previous HEXRD work[12] reporting the peak appearing at 3.7–3.9 Å in $T(r)$ of LTA-type zeolite corresponds to the 4-membered rings (4MRs) in the crystal structure, the peak appearing at 3.8 Å suggests the existence of smaller silicate-rings like 4MRs in dry gel **4**. In a previous study, ^{29}Si NMR measurement revealed that a silicate solution with $\mathrm{TEA^+/SiO_2} = 1.0$ possesses only double-3-ring (D3R) anions.[13] Moreover, single crystal X-ray diffraction of a $\mathrm{TEA^+}$-silicate composite demonstrated the formation of $\mathrm{(TEA^+)_6Si_6O_{15}\cdot 40.8H_2O}$ single crystal consisting of D3R anions.[14] Based on these previous studies, we assume that the D3R anions that stabilized in the $\mathrm{TEA^+}$-silicate solution with $\mathrm{TEA^+/SiO_2} \geq 0.37$ are transformed into 4MRs during the process of drying to form a dry gel. These small silicate rings could be the precursors of the *BEA structure. Arrangement of these precursors during steam treatment will result in the formation of *BEA. Hence, we suggest that a dry gel with an abundant amount of precursors to crystallize in the *BEA phase exhibits a maximum in the broad reflection peak at $2\theta = 28^\circ$ in the XRD pattern of the dry gel.

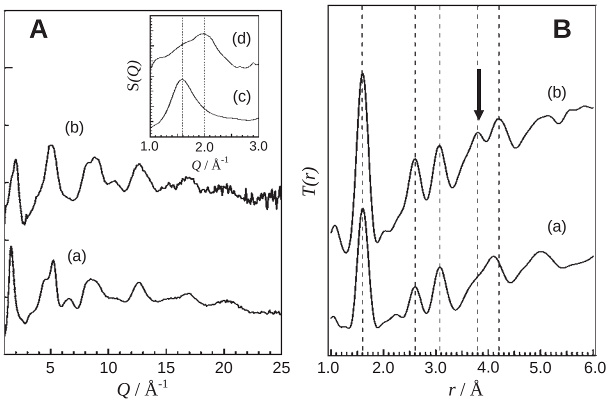

Figure 2. (A) Total structure factors, $S(Q)$, of dry gels (a, c) **1** and (b, d) **4**. (B) Total correlation functions, $T(r)$, of dry gels (a) **1** and (b) **4**.

In conclusion, we propose that XRD measurement of a dry gel with $\mathrm{TEA^+}$ gives sufficient information to determine whether the crystallization of *BEA-type zeolite from the dry gel will occur. When a dry gel with $\mathrm{TEA^+}$ exhibits a maximum in the reflection peak at $2\theta = 28^\circ$ in the XRD pattern, a *BEA-type zeolite from such a dry gel could be obtained by the SAC method.

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