Dry-gel conversion technique for synthesis of zeolite BEA

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A new method is developed to crystallize zeolites; for the first time, a zeolite with BEA structure is synthesized by a dry-gel conversion technique.

Recently, research has focused on the development of new methods for crystallization of zeolites, which allow the preparation of zeolites in convenient forms, especially as membranes. Vapour-phase transport is one such method, which involves crystallization of a dry aluminosilicate gel in the presence of volatile structure-directing agents and steam. This method requires a smaller amount of structure-directing agent than that used in hydrothermal methods and was used for the synthesis of powdery zeolites[1–3] and zeolitic membranes;[4–6] a defect-free mordenite membrane has also been prepared by this method.[6] However, the vapour-phase transport method cannot be applied for the preparation of all types of zeolites, since many of them need non-volatile structure-directing agents for their preparation. Sano *et al.*[7] have observed crystal growth of MFI zeolite under steam, indicating the possibility of preparing zeolites from their dry gels in the presence of steam. In this communication, we report the first synthesis of commercially important zeolite BEA by a dry-gel conversion technique. This synthetic method involves crystallization of the zeolite from dry gels that include a non-volatile structure-directing agent in the presence of steam. We shall show that this method allows the preparation of zeolite BEA with higher SiO_2/Al_2O_3 ratios than those obtained by the conventional hydrothermal synthesis method.

Dry gels having compositions $SiO_2:a\ Al_2O_3:b\ Na_2O:c\ K_2O:d$ TEAOH, where a = 0.0011–0.033, b = 0.014–0.074, c = 0–0.03, d = 0.16–0.50 (TEAOH = tetraethylammonium hydroxide), were prepared as follows. Aluminium sulfate (Wako Pure Chem. Ind. Ltd) was dissolved in 10 g distilled water at 353 K. An NaOH (4 mol dm^{-3}, Wako Pure Chem. Ind. Ltd) solution and TEAOH (20% in water, Wako Pure Chem. Ind. Ltd) was added to 10 g colloidal silica (30% SiO_2, Nissan Chem. Co. Ltd) at room temperature while stirring. After 30 min, the aluminium sulfate solution and 5.5 g water was added to the mixture and stirring continued for 2 h, then the mixture was heated to 353 K and dried while stirring. When the gel became viscous, it was stirred using a Teflon rod until it became a dry gel. This was powdered and placed in a special autoclave into which water as a source of steam was poured. Crystallization of the dry gel was carried out in steam at 453 K and autogenous pressure for 3–6 days.

Table 1 Effect of SiO_2/Al_2O_3 ratio on the crystallization of zeolite-β from dry gels (Cris. = cristobalite)[a]

Crystallization time/h	SiO_2/Al_2O_3					
	30	60	100	200	600	900[b]
72	BEA	BEA	BEA	BEA	BEA	BEA
120	BEA	BEA	BEA	MFI + BEA + Cris.	Cris. + BEA	
140	BEA	—	BEA + Cris.	—		—

[a] Na_2O/SiO_2 = 0.05, $TEAOH/SiO_2$ = 0.37. [b] Na_2O/SiO_2 = 0.046, $TEAOH/SiO_2$ = 0.37; gel was aged for 12 h.

Table 1 shows the phases of the products obtained by crystallization of dry gels with compositions of $SiO_2:a\ Al_2O_3:0.05\ Na_2O:0.37$ TEAOH (a = 0.00165–0.033) and $SiO_2:0.0011\ Al_2O_3:0.046\ Na_2O:0.37$ TEAOH. Zeolites with BEA structure were crystallized in powdery form from the gels with SiO_2/Al_2O_3 ratios of 30–900 after 72 h as typically shown in Fig. 1. X-Ray powder patterns showed that the products were highly crystalline. No phase transformation was observed in the products obtained from gels with SiO_2/Al_2O_3 ratios of 30–100 even after 120 h of crystallization. However, the gels with an

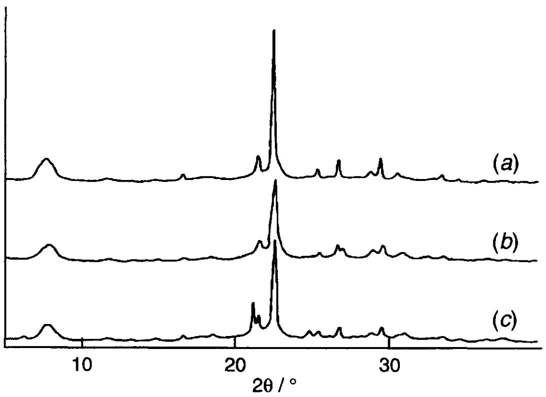

Fig. 1 X-Ray diffraction patterns of zeolite BEA after a crystallization time of 72 h. SiO_2/Al_2O_3 ratio; (*a*) 30, (*b*) 200 and (*c*) 900.

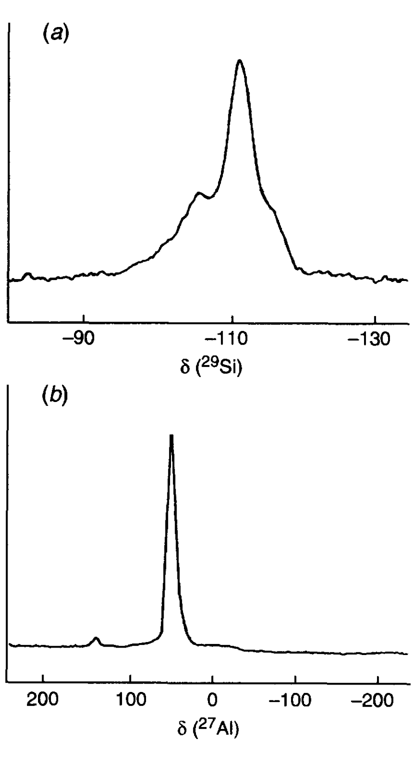

Fig. 2 (*a*) ^{29}Sl and (*b*) ^{27}Al NMR spectra of zeolite BEA (SiO_2/Al_2O_3 = 30) prepared by the dry-gel conversion technique

SiO_2/Al_2O_3 ratio of 200 yielded MFI + BEA + cristobalite and that with an SiO_2/Al_2O_3 ratio of 600 yielded cristobalite + BEA after 120 h of crystallization.

Pure zeolite BEA with an SiO_2/Al_2O_3 ratio of 60 was synthesized using wide ratio limits of TEAOH/SiO_2 = 0.25–0.50 and (Na_2O + K_2O)/SiO_2 = 0.014–0.104. When the TEAOH/SiO_2 ratio was 0.16, a mixture of zeolites, BEA and MTW was formed. Gels with compositions of SiO_2 : (0.033–0.0011) Al_2O_3 : 0.05 Na_2O : 0.37 TEAOH were modified to obtain gels with compositions of SiO_2 : (0.033–0.0011) Al_2O_3 : 0.44 TEAOH, by reducing sodium to the level present in colloidal silica (SiO_2/Na_2O = 0.014) and compensating with an equivalent number of moles of TEAOH. The product from the gel with an SiO_2/Al_2O_3 ratio of 30 was amorphous even after 120 h of crystallization. Zeolites with BEA structure were obtained from the gels with SiO_2/Al_2O_3 ratios of 100–400. An unidentified phase was formed from the gel with SiO_2/Al_2O_3 ratio of 600. This shows that higher sodium concentrations in the gels with SiO_2/Al_2O_3 ratios > 400 promote the formation of zeolite BEA rather than that of unidentified phases.

When water was not added in the autoclave, the product was always amorphous. A small amount of steam can still form by the dehydration of the gel at the crystallization temperature (453 K). However this small amount is insufficient to transform the amorphous gel into a crystalline phase. Hydrothermal crystallization of zeolite BEA from the gel with a composition of SiO_2 : 0.033 Al_2O_3 : 0.05 Na_2O : 0.37 TEAOH : 20 H_2O (similar to that used in the dry-gel conversion method) at 453 K failed and the product was amorphous. Perez-Pariente *et al.*[8] also were not successful in synthesizing zeolite BEA at a temperature as high as 423 K using the hydrothermal synthesis method.

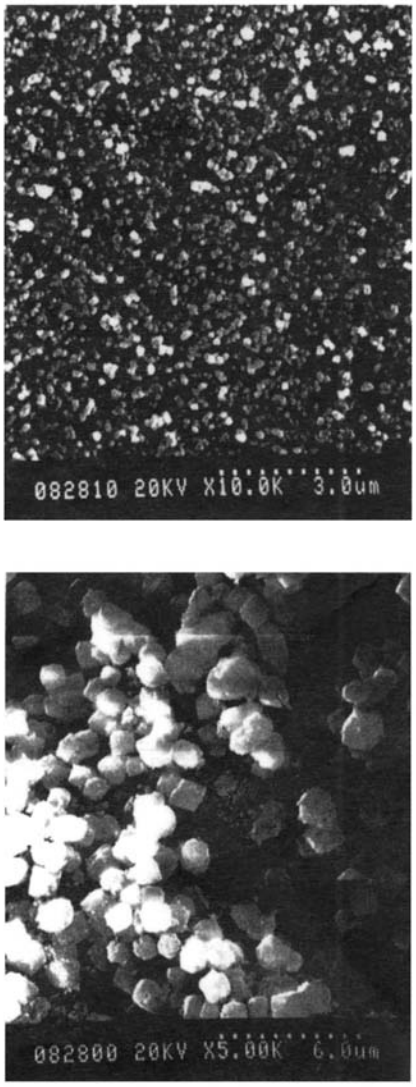

Fig. 3 SEM images of zeolite BEA having SiO_2/Al_2O_3 = 30. TEAOH/SiO_2 ratio; (*a*) 0.50 and (*b*) 0.37.

Fig. 2 shows the ^{27}Al and ^{29}Si NMR spectra of the sample with SiO_2/Al_2O_3 = 30. The absence of a peak at δ 0 in the ^{27}Al NMR spectrum indicates that no extraframework aluminium is present in the sample. The SiO_2/Al_2O_3 ratio calculated from 29Si NMR as well as chemical analysis matches with that of the initial gel, the result of which confirms the complete transformation of gel into the zeolite phase. The BET surface areas of the samples with SiO_2/Al_2O_3 = 30 and 600 measured at liquid-nitrogen temperatures are 480 m^2 g^{-1}, indicating that zeolite pores are not blocked by any non-removable occluded material.

Fig. 3 shows the SEM images of zeolite BEA with SiO_2/Al_2O_3 ratio of 30. The particle sizes of the products are uniform. No amorphous phase exists in the samples. Smaller particles in the order of submicrons (0.1–0.02 μm) were obtained from the gels with higher TEAOH concentrations, possibly indicating that the number of nuclei formed during crystallization depends on the alkalinity and the crystal size can be adjusted by controlling the alkalinity of the gel. BEA particles of *ca.* 1.5 μm were obtained from the gel with a composition of SiO_2 : 0.033 Al_2O_3 : 0.05 Na_2O : 0.37 TEAOH. Formation of uniform crystals from the dry gel powder is of particular interest to understand the mechanism of zeolite formation.

These experiments confirm that zeolites with a high crystallinity and a uniform particle size can be synthesized from amorphous dry gel powder in the presence of steam. The particular finding in the present study is the successful preparation of zeolite BEA with higher SiO_2/Al_2O_3 ratios than those prepared by the hydrothermal synthesis method. Higher temperatures can be applied for crystallization of zeolite BEA from dry gels than that used in the hydrothermal synthesis method.

In conclusion, a new method has been developed for the crystallization of zeolite BEA, where high SiO_2/Al_2O_3 ratios and complete conversion of gel to zeolite were obtained. This method might enable continuous production of zeolite, reduction in reactor volume and elimination of waste-water treatment and may be applied for the synthesis of other types of zeolites and zeolitic membranes.

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