Synthesis of Large Single Crystals of Mordenite from Clear Homogeneous Solutions

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In the absence of any templates, large single crystals of mordenite have been hydrothermally synthesized from clear homogeneous solutions, by using both Aerosil and sodium silicate as silicon source.

Large single crystals of zeolites are useful in many research studies and industrial applications.[1,2] However, zeolites are normally crystallized from a gel in an alkaline medium. Under such conditions, large crystals are often difficult to obtain. A new synthetic method of direct crystallization from homogeneous solution has been developed by Ueda *et al.*[3,4] and Pang *et al.*[5] with very high $OH^-:Al_2O_3$ and $H_2O:Al_2O_3$ ratios. In this way, some zeolites including mordenite have been synthesized. So far only a few patents report the synthesis of single crystals of mordenite, the crystals obtained have sizes of less than 50 μm, by using piperazine ethanol[6] and polyglycol[7] as templates, respectively. There are no reports in

Table 1 Synthesis conditions and products

Sample	Composition (mol ratio) $Al_2O_3:SiO_2:Na_2O:M^c:H_2O$	T/°C	t/d	Starting mixture[d]	Crystal size/μm	Product
A	1 : (60[a] + 15[b]) : 15 : 4NaCl : 550	150	15	c	185 × 125	MOR
B	1 : (60[a] + 15[b]) : 15 : 4NaAc : 550	150	15	c	27 × 30	MOR
C	1 : (60[a] + 15[b]) : 15 : 4KCl : 550	150	15	c	85 × 50	MOR
D	1 : (75[a] + 0[b]) : 15 : 4NaCl : 550	150	5	c	8 × 3	MOR
E	1 : (0[a] + 75[b]) : 15 : 4NaCl : 550	150	5	c	2 × 1	MOR
F	1 : (60[a] + 50[b]) : 15 : 4NaCl : 550	145	25	g	110 × 55	MOR

[a] Silica from Aerosil. [b] Silica from sodium silicate. [c] Amount of salt used. [d] c = clear solution; g = gel.

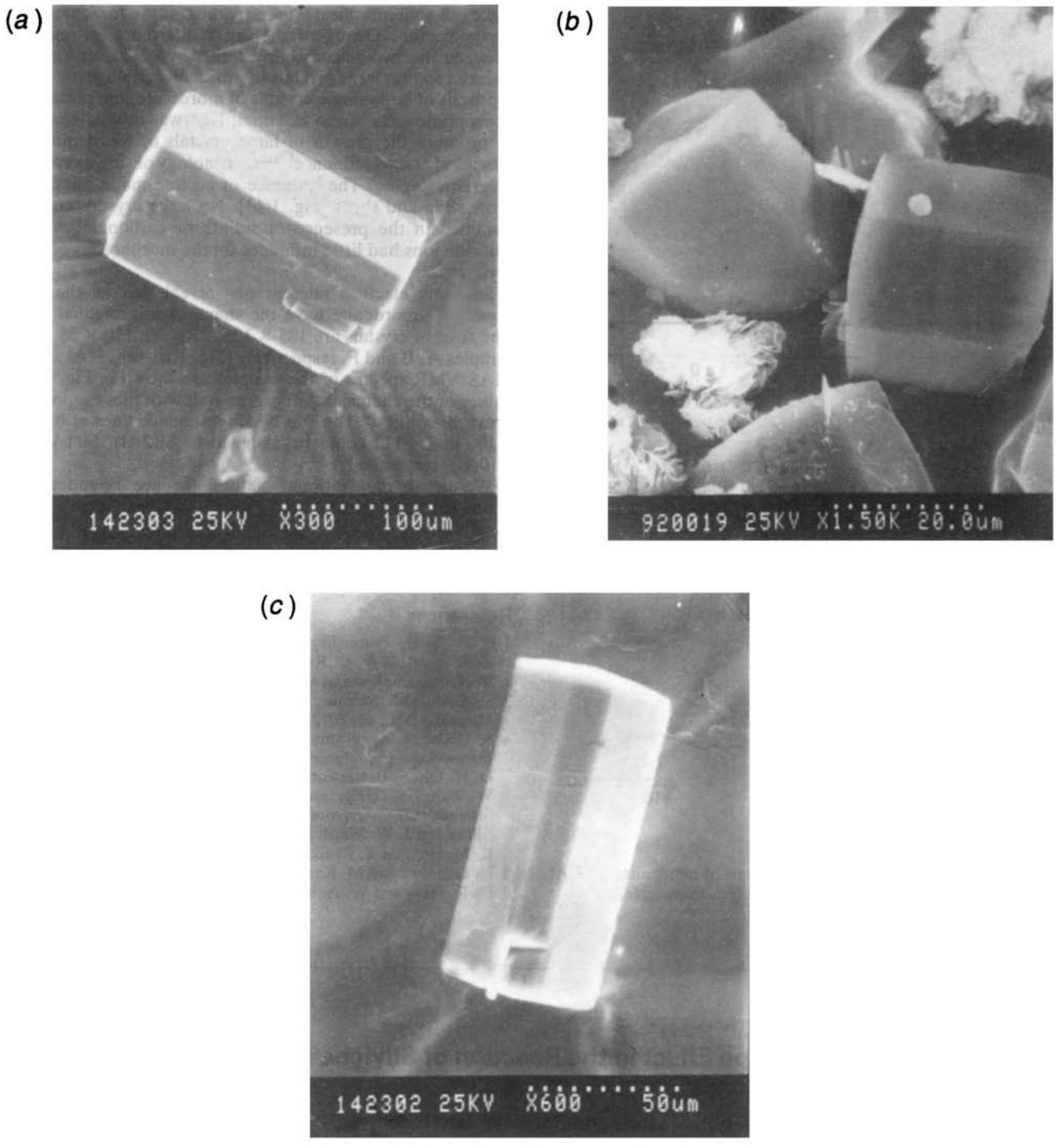

Fig. 1 Scanning electron micrographs of single crystals of mordenite: (*a*) sample A, (*b*) sample B and (*c*) sample F

the literature on the synthesis of large single crystals of zeolites from homogeneous solutions. Here we report the synthesis of large single crystals of mordenite from clear homogeneous solutions in the absence of any templates.

A typical synthesis began with the combination of water and sodium silicate solution (SiO_2 31%, Na_2O 10%), to which NaOH and Aerosil (99%) were added with stirring. The precursor mixture was aged for a short time under ambient conditions with agitation until a clear homogeneous solution was obtained. The crystallization of the reaction mixture was carried out in a Teflon-lined autoclave under autogenous pressure at 150 °C for 7–30 days. After crystallization, the products were filtered, washed, and dried at ambient temperature. The typical reactant compositions and synthesis conditions are listed in Table 1.

While the starting materials were mixed together, a small amount of gel was formed but this dissolved completely within 60 min to give a homogeneous solution. The silicon source consisting of sodium silicate solution and Aerosil is necessary for the synthesis of large crystals. Otherwise, mordenite may be completely crystallized in a short time and large crystals cannot be obtained. This might result from the difference in reactivity between the two silicon sources. Under suitable synthetic conditions, silica from sodium silicate should be present in the reaction prior to the inert Aerosil. When the silica from sodium silicate is exhausted, Aerosil would take the

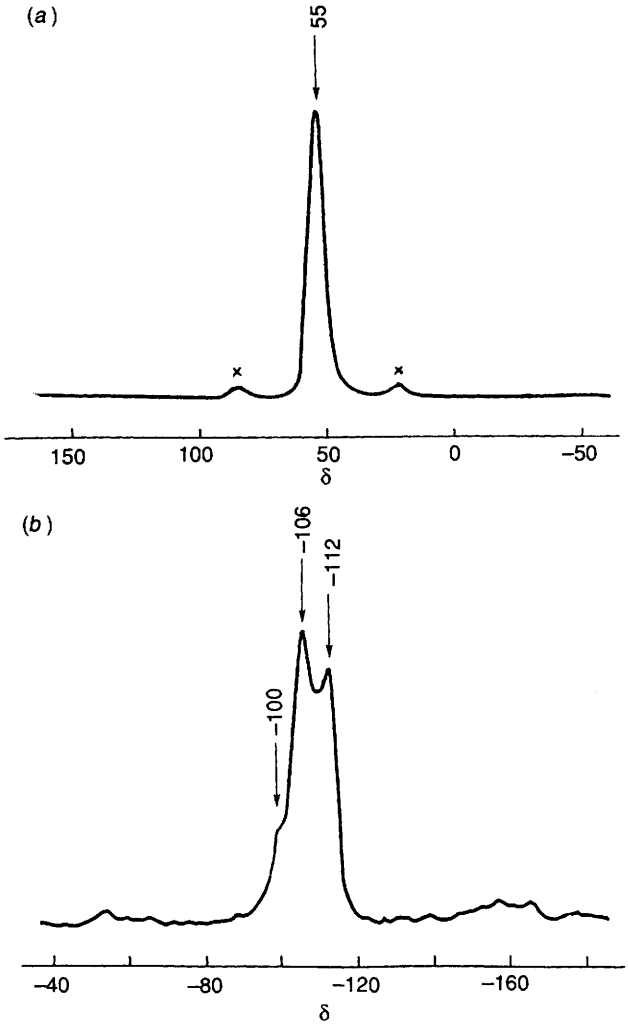

Fig. 2 MAS NMR spectra for single crystals of mordenite: (*a*) ^{27}Al NMR [rel. from $Al(NO_3)_3$]; (*b*) ^{29}Si NMR (rel. from $SiMe_4$)

place of sodium silicate in providing silica for continuous crystallization. Owing to the great difference in reactivity between the two silicon sources, the crystallization rate was reduced so that large crystals of mordenite could grow. In the synthesis of large single crystals of mordenite, the presence of appropriate salts is also essential; Na^+ was usually employed to promote the growth of large crystals of mordenite. The species of anions influence the morphology of single crystals to a certain degree. The presence of acetate made the crystals grow wide and short [Fig. 1(*b*)]. No large crystals could be obtained in the presence of sulfate or carbonate, whereas chloride ions had little influence on the morphology of single crystals.

Scanning electron micrographs reveal that all the single crystals of mordenite have the shape of a hexagonal prism. The sizes of crystals are 185 × 125, 27 × 30, 110 × 55 μm for samples A, B and F, respectively [Fig. 1(*a*)–(*c*)]. ^{27}Al and ^{29}Si MAS NMR spectra of the samples are shown in Fig. 2. The values of the chemical shifts agree well with those reported in previous studies.[8] The ^{29}Si NMR resonance lines at δ −100, −106 and −112 could be assigned to Si(2Al), Si(1Al) and Si(0Al), respectively.

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