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# Crystallization of mordenite from aqueous solutions

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## Abstract

Mordenite was formed directly at 100°C, 1 atm from clear aqueous Na–Al–Si solutions containing an extremely small quantity of Al. In seeded and unseeded systems, mordenite crystals up to 4μm × 2μm with acicular or prismatic habit were grown. They were elongated along the *c* axis of the orthorhombic cell with the prism zone formed predominantly by the (110) plane.

In the seeded systems, rapid crystallization of mordenite occurred because the seed surface provided nucleation sites. Mordenite grew on the seed surfaces, whether or not the morphology and the composition and structure of the seed differed widely from mordenite. Such growth phenomena were different from those observed with analcime grown in seed systems.

The chemical composition of mordenite was governed by the initial ratios of soda, alumina, and silica in the initial gels and was independent of the depletion of nutrient with reaction time.

These results probably can be explained by the crystallization mechanism for analcime proposed by Ueda and Koizumi (1979).

## Introduction

Most zeolites have been synthesized from active alkaline aluminosilicate gels consisting of heterogeneous phases in which amorphous solid and aqueous solutions coexist. The amorphous material decreases as the crystallization of zeolite proceeds, and consequently two solid phases, amorphous solid and crystalline material, coexist with solution until the reaction is completed. The crystallization mechanism in such heterogeneous phases is complicated and is not yet fully understood, but both the nature of the nutrient solid gel and the aqueous solution contribute directly to the zeolite formation.

Two hypotheses have been proposed for zeolite crystallization, namely, in the gel phase or from the solution phase. The former was postulated by Breck and Flanigen (1968), and later by McNicol *et al.* (1971, 1972), and Aiello *et al.* (1971a,b), and the latter was proposed by Kerr (1966, 1968), and later by Ciric (1968), Culfaz and Sand (1973), Cournoyer *et al.* (1975), and Ueda and Koizumi (1979).

In 1979 we reported that analcime, hydroxysodalite, and zeolite B crystallized from clear aqueous solutions. In the present study, the crystallization of mordenite from a low-Al solution phase in the $Na_2O$–$Al_2O_3$–$SiO_2$–$H_2O$ system was investigated at 1 atm.

Barrer (1948) first synthesized mordenite, and there are many studies of its mineralogy, geology and chemistry: Barrer and White (1952), Sand *et al.* (1957, 1971), Ames and Sand (1958), Coombs *et al.* (1959), Ellis (1960), Ames (1963), Domine and Quobex (1968), Sand (1968), Senderov (1968), Kranich *et al.* (1971), Senderov and Khitarov (1971), Whittemore (1972), Culfaz and Sand (1973), and Nakajima (1973). Mordenite syntheses were made under hydrothermal conditions in various types of high-pressure reaction vessels.

In our experiments, the following problems were examined: (1) the effect of added seed crystals on the crystallization and morphology of synthesized mordenite, (2) the selectivity of seed materials for morde-

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Table 1. Variation of $SiO_2/Al_2O_3$ ratios of synthetic mordenites in seeded systems

| Sp. nos. | Run (days) | Seed (g/l) | Wt. % of seed(*1) | Apparent ratios(*2) | Corrected ratios(*3) |
|---|---|---|---|---|---|
| 821 | 2 | 0.4 | 11.48 | 14.35 | 15.00 |
| 822 | 4 | 0.4 | 4.98 | 14.74 | 15.03 |
| 823 | 6 | 0.4 | 2.99 | 14.89 | 15.06 |
| 824 | 8 | 0.4 | 2.61 | 14.96 | 15.11 |
| 831 | 2 | 0.6 | 14.14 | 14.26 | 15.07 |
| 832 | 4 | 0.6 | 6.53 | 14.60 | 14.97 |
| 833 | 6 | 0.6 | 4.51 | 14.75 | 15.01 |
| 834 | 8 | 0.6 | 3.98 | 14.84 | 15.07 |
| 861 | 2 | 1.2 | 18.49 | 14.05 | 15.12 |
| 862 | 4 | 1.2 | 9.64 | 14.47 | 15.02 |
| 863 | 6 | 1.2 | 6.55 | 14.64 | 15.01 |
| 864 | 8 | 1.2 | 5.80 | 14.67 | 15.00 |

The $SiO_2/Al_2O_3$ ratio of natural mordenite used as seed was 9.32. Initial composition of gels corresponds to C2. (*1) weight % of seed in crystal aggregates, (*2) $SiO_2/Al_2O_3$ ratios of crystal aggregates, and (*3) the ratios calculated using the data of columns 4 and 5.

nite crystallization, and (3) the effect of reaction time and amount of added seed on the $SiO_2/Al_2O_3$ ratio of synthesized mordenite.

## Experimental

Gels with three fixed batch compositions (C1) $10Na_2O{\cdot}0.1Al_2O_3{\cdot}34SiO_2{\cdot}440H_2O$, (C2) $10Na_2O{\cdot}0.15Al_2O_3{\cdot}36SiO_2{\cdot}440H_2O$, and (C3) $10Na_2O{\cdot}0.15Al_2O_3{\cdot}32SiO_2{\cdot}440H_2O$ were prepared from a 10M solution of sodium hydroxide (90.0 volume percent $H_2O$), sodium aluminate (35.05 weight percent $Na_2O$ and 42.36 weight percent $Al_2O_3$), aqueous colloidal silica sol (0.3687g/ml $SiO_2$ and 83.5 volume percent $H_2O$), and distilled water. The total volume of each gel was adjusted to 250 ml in a 500 ml polypropylene bottle, which was used as a reaction vessel.

After the preparation of gels, milky turbidity was observed, which disappeared within 3 hrs by stirring and heating at 100°C in a water bath. Crystallization was observed in the clear solution systems after 30 hrs or longer at 100°C. Runs ranged in duration from 2 to 25 days.

In seeded systems, natural mordenite and quartz, synthesized mordenite, analcime, hydroxysodalite, and calcium carbonate were added to gels as seeds. The natural minerals were first ground to minus 200 mesh. After each run, the product was separated from the solution through a teflon microfilter, and washed thoroughly with hot water. The residue was dried at 110°C for 48 hrs, exposed to saturated water vapor at 25°C in a desiccator, weighed, and analyzed by X-ray powder diffraction (Cu$K\alpha$ radiation), optical microscopy, scanning electron microscopy (SEM), and DTA. Chemical analysis was made on several samples by gravimetric methods. The results are given in Table 1.

## Results and discussion

### *Crystallization of mordenite*

The crystallization of mordenite was characterized by a long induction period followed by a slow initial crystallization. In Figure 1, the amounts of mordenite synthesized from clear solutions of the batch compositions C1, C2, and C3 are plotted as a function of reaction time. The induction period was reduced as the initial $SiO_2/Al_2O_3$ ratio of gels increased.

Analcime, in addition to mordenite, appeared initially as a minor phase but increased with reaction time. The quantity of analcime was determined by an intensity ratio of X-ray diffraction peaks using a calibration curve.

The values on the longitudinal axis in Figure 1 indicate the absolute amounts of products per liter of gel. A relative indication such as weight percent was not used because accurate compositions of synthesized mordenite and analcime could not be determined.

As shown in Figure 2(a,b), acicular or prismatic crystals correspond to mordenite, and the spherical crystals are analcime. Electron diffraction analysis of the mordenite crystals showed that elongation of a crystal is parallel to the *c* axis of the orthorhombic cell, and the prism zone is formed by (100), (010), and (110) planes. As crystals grew, the (110) plane

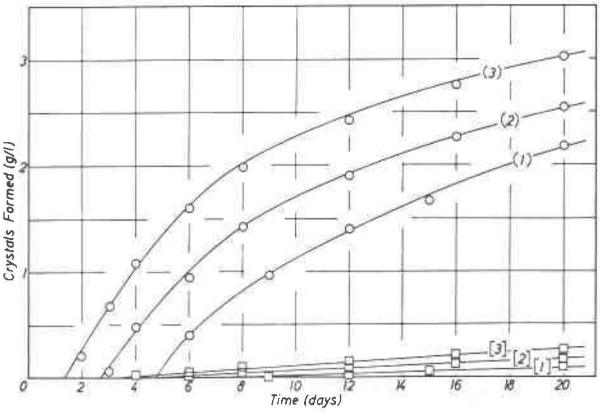

Fig. 1. Variation of the amounts of crystals formed from clear aqueous solutions as a function of time. Symbols for mordenite and analcime are circles and squares, respectively. Batch compositions of gels for curves 1, 2, and 3 correspond to C1, C2, and C3, respectively.

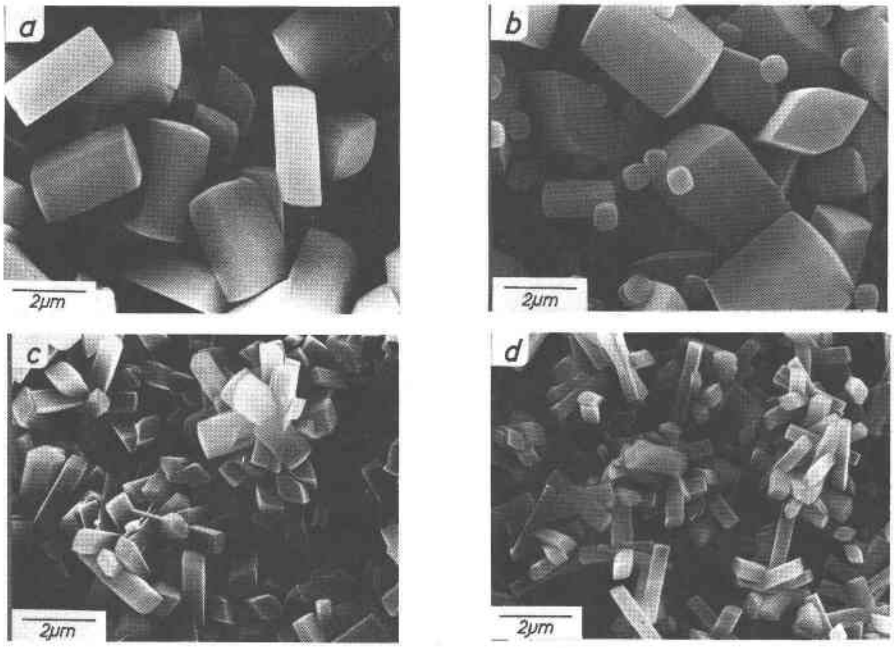

Fig. 2. SEM photographs of mordenite and analcime crystals: a and b: unseeded systems; c and d: seeded systems. Acicular or prismatic crystals are mordenite, and spherical ones are analcime. Batch compositions of gels are C2 for a, c, and d, and C3 for b. The weights of natural mordenite seed added to gels for c and d were 0.2g and 1.2g per liter of gel, respectively. Runs were 8 days for all cases.

became predominant, but the prism zone of the larger crystals increasingly deviated from the (110) plane. There was no regularity for such deviation even in the crystals produced from the same solution phase.

### *Effect of seeds*

Mordenite crystals from Shiroishi, Miyagi, Japan, were added to prepared gels with batch compositions C1, C2, and C3 (0.1 to 1.2g per liter of gel). In Figure 3, the weight of mordenite obtained in a constant time is plotted as a function of weight of seed crystals; the plotted values do not contain the weight of seed.

The suspension of seed crystals in solutions resulted in rapid crystallization, and the addition below 0.2g/liter was particularly effective. Mordenite crystallized and grew rapidly on seed surfaces. The crystals became smaller in size and larger in number with an increase of the quantity of seed, as represented in Figure 2(c,d). Analcime could no longer be observed in the products. Probably the mordenite crystallization was so fast that the nucleation of analcime was hindered.

Synthesized mordenite with a uniform size (1 to 3μm), previously prepared from gels of batch composition C2, was added to freshly prepared gels of batch composition C3. In Figure 4, the amount of mordenite formed with a constant weight of synthetic seed is plotted as a function of time. As can be seen in Figure 4, curves 1 and 2 shift upward beyond curve N for an unseeded system. However, the synthetic seed is less effective in promoting crystallization than the natural mordenite seed shown in Figure 3. This indicates that shape and size of seed have an effect on crystallization, because a larger euhedral crystal provides a smaller total surface area for nucleation.

These results agree with those of Culfaz and Sand (1973), who investigated extensively the nucleation and crystallization of mordenite from heterogeneous gels. They concluded that, in the unseeded system, the rate-determining step in the overall process is nucleation, and in the seeded system the diffusion of soluble species, which are readily available at the crystal–liquid interface, is the rate-limiting step.

### *Selectivity of seeds*

Synthesized analcime (12 to 14μm) and calcium carbonate (below 1μm) were used as seed for the growth experiment of mordenite. The results are represented in Figure 4, and show that these substances played a significant role in seeding for mordenite crystallization, because curves 3 to 6 in Figure 4 shift upward beyond curve N for the unseeded system.

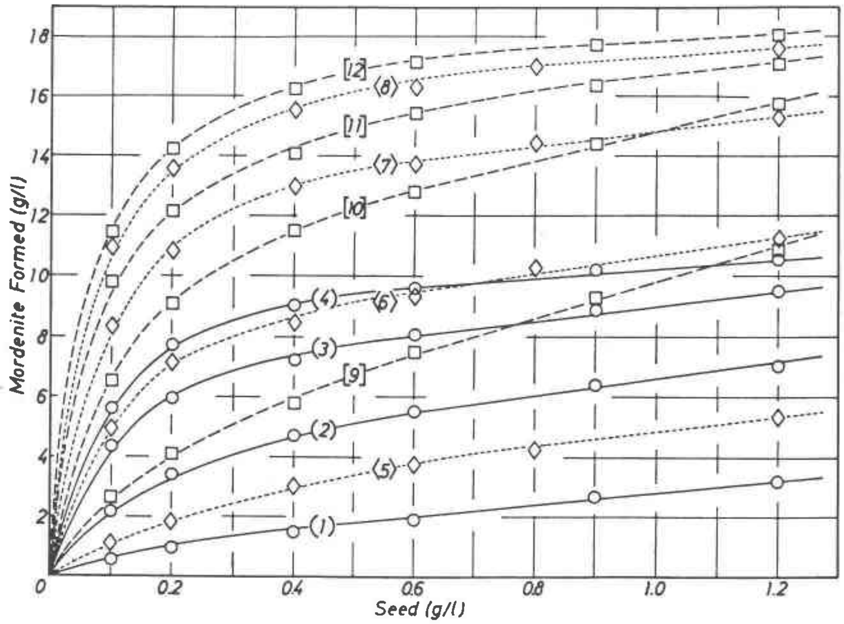

Fig. 3. Variation of the amounts of mordenite formed in natural mordenite seed system as a function of weight of seed. Batch compositions of gels are C1 for circles, C2 for diamonds, and C3 for squares. Runs were 2 days for curves 1, 5, and 9; 4 days for curves 2, 6, and 10; 6 days for curves 3, 7, and 11; and 8 days for curves 4, 8, and 12.

SEM photographs of the mordenite crystals grown on the surface of analcime crystals are shown in Figure 5(a,b), but no regularity of the growth habit which depends on the morphological features of analcime could be found. Although the crystal structure and composition of mordenite differ widely from the seeds, the latter surfaces are able to provide the nucleation sites for the mordenite crystallization.

On the other hand, whereas analcime also crystallized from the unseeded solution phase, in seeded systems its crystallization and growth were remarkably different from those of mordenite. With synthetic analcime (12 to 14$\mu$m), synthetic hydroxysodalite (3 to 4$\mu$m), and natural mordenite as seed, the growth experiment of analcime was carried out in clear solutions with the composition $10Na_2O{\cdot}0.075$

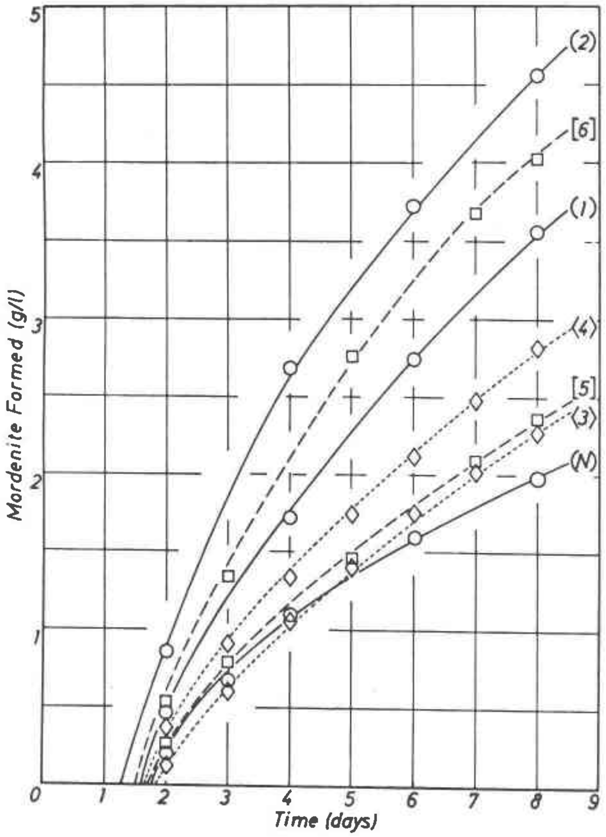

Fig. 4. Variation of the amounts of mordenite formed in three kinds of seeded systems as a function of time. (i) Synthetic mordenite seed for solid lines 1 and 2; (ii) synthetic analcime seed for dashed lines 3 and 4; and (iii) calcium carbonate seed for broken lines 5 and 6. However, curve N illustrates the results in unseeded systems, and corresponds to curve (3) in Fig. 1. The weight of seeds added were 0.2g per liter of gel for curves 1, 3, and 5, and 0.4g for curves 2, 4, and 6. In all cases, gels with batch composition C3 were used.

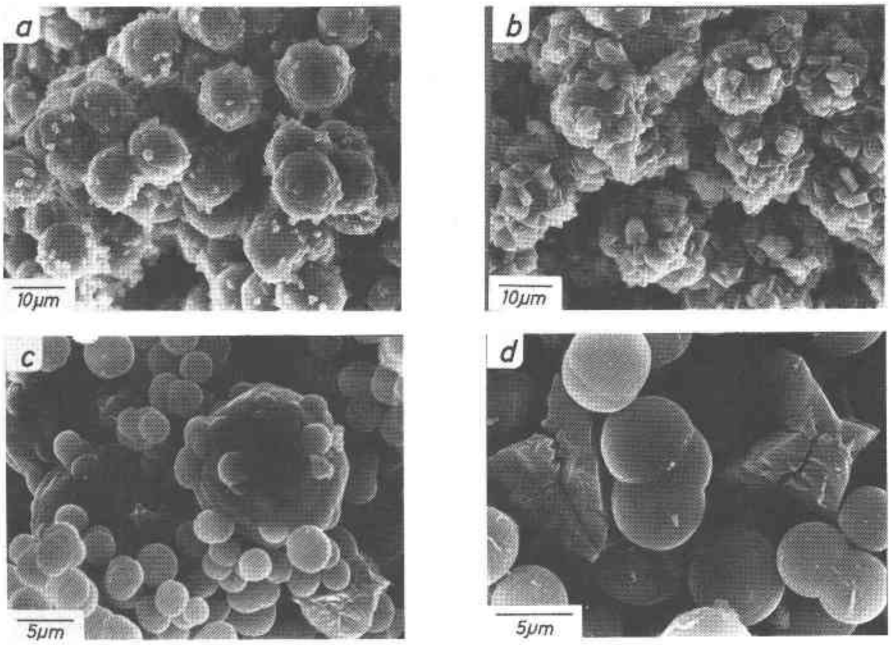

Fig. 5. SEM photographs of mordenite and analcime crystals formed in seeded systems: a and b illustrate prismatic mordenite crystals grown on the surface of analcime seed in the solution of batch composition C3; runs were 2 days for a and 4 days for b. c and d show spherical analcime crystals formed in synthetic analcime and natural mordenite seed systems, respectively. For c and d, the initial composition of gels used was $10Na_2O \cdot 0.075Al_2O_3 \cdot 10SiO_2 \cdot 370H_2O$; runs were 2 days for c and 4 days for d. In the case of c, the growth of seed (large particles) is observed. The weight of seeds added was 0.4g per liter of gel in all cases.

$Al_2O_3 \cdot 10SiO_2 \cdot 370H_2O$, which was an optimum composition for the synthesis of analcime.

In Figure 6, the amounts of analcime formed with a constant weight of seed are plotted as a function of time. Seeds other than analcime proved to be inert in the crystallization of analcime, because the observed values except for curves 1 and 2 in Figure 6 deviate downward from curve N for the unseeded system. From the fact that the deviation from curve N, especially in an early stage of reaction, increases with increasing weight of the inert seeds, we conclude that they interfered with the diffusion of soluble species of analcime in crystal–solution interface.

These results can be also explained using the SEM photographs shown in Figure 5. In analcime seeded systems (5c), large crystals are grown from seed, and small ones are newly-formed analcime. However, in the case of the natural mordenite seed system (5d), no definitive correlation between the formed crystals and the topology of seed surfaces is observed.

These results demonstrate the selectivity of seeds to crystallization and growth of analcime or mordenite, as follows. Analcime is spherical in shape at an early stage of crystal growth, and preserves a cubic trapezohedral crystal form. Accordingly, growth on the surface of seed crystals is difficult unless the seed is isostructural to analcime. On the contrary, mordenite is acicular or prismatic, and tends to elongate parallel to the *c* axis; in addition, the prism zone is not always formed by a definite plane such as the (110) plane. As the growth direction is more random, as represented in Figure 5(a,b), the topology of the seed surface is not a critical factor in the nucleation, crystallization, and growth of mordenite crystals.

### *Compositions of mordenites*

The composition of synthetic mordenite is characterized by the $SiO_2/Al_2O_3$ ratio, which varies over a relatively narrow range according to the conditions of synthesis. In most cases, the ratio varies between 9 and 10 for an ideal composition (Barrer and White, 1952; Nakajima, 1973). In some mordenites prepared by special methods, however, a ratio higher than 10 has been reported (Sand, 1968; Kranich *et al.,* 1971; Whittemore, 1972).

In our study, the accurate compositions of mordenites obtained in both seeded and unseeded systems were not determined directly, because the added seed in the seeded systems and the analcime phase in the unseeded systems were coexistent in the products.

However, in the natural mordenite seeded systems comparatively good results were obtained, as a large

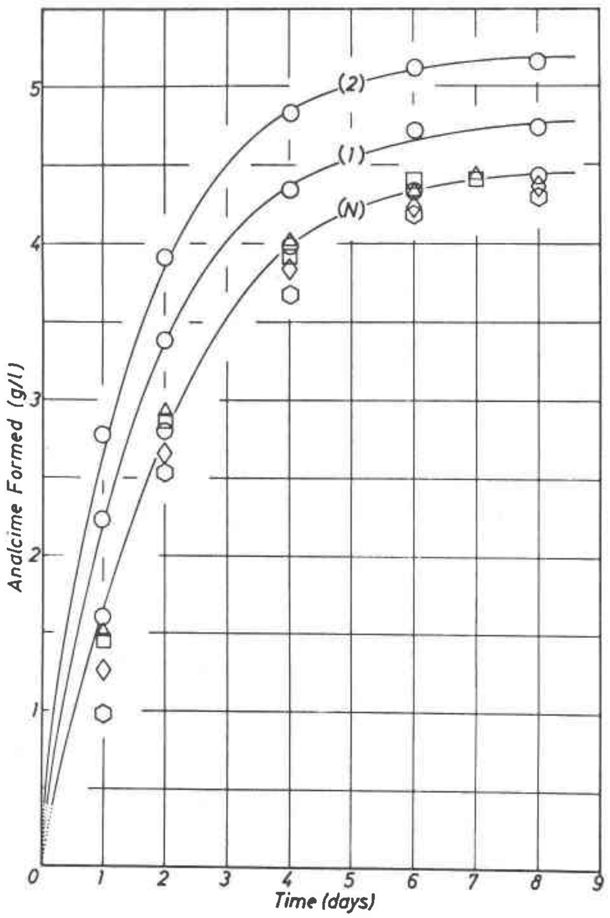

Fig. 6. Variation of the quantities of analcime formed in three kinds of seeded systems as a function of time. (i) Synthetic analcime seed for curves 1 (0.2g per liter of gel), 2 (0.4g), and N (unseeded), (ii) synthetic hydroxy-sodalite seed for triangles (0.2g) and squares (0.4g), and (iii) natural mordenite seed for diamonds (0.2g) and hexagons (0.4g). The initial gel composition was $10Na_2O \cdot 0.075Al_2O_3 \cdot 10SiO_2 \cdot 370H_2O$.

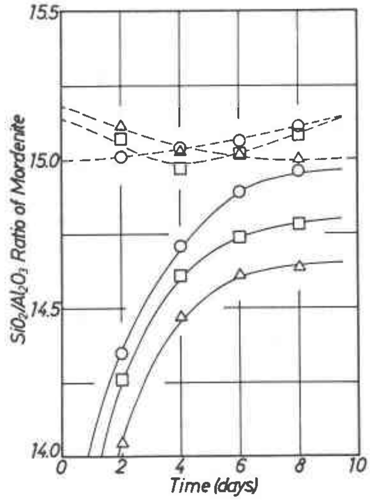

Fig. 7. Relationship between $SiO_2/Al_2O_3$ ratios of mordenite synthesized in natural mordenite seed systems and reaction time. The weights of seed added were 0.4g per liter of gel for circles, 0.6g for squares, and 1.2g for triangles. Solid lines illustrate the variation of $SiO_2/Al_2O_3$ ratio for crystal aggregates consisting of formed mordenite and seed. Dashed lines represent the corrected ratios which were calculated by considering the weight percent of seed in the crystal aggregates (see Fig. 8). In all cases, gels with batch composition C2 were used.

amount of mordenite was produced and the distribution of seed crystals was homogeneous in the crystal aggregates. In Figure 7, the apparent $SiO_2/Al_2O_3$ ratios of synthetic mordenites from solutions with the batch composition C2 are plotted as a function of time.

The solid lines in Figure 7 correspond to the variation of the ratios for the crystal aggregates. The ratio increases with reaction time and depends on the amount of seed. On the other hand, in Figure 8, the weight percent of seed in the crystal aggregates is plotted as a function of time. The $SiO_2/Al_2O_3$ ratio of the seed was 9.32. Accordingly, the values plotted on the solid lines in Figure 7 were corrected using the data represented in Figure 8, and the corrected values are plotted along broken lines in Figure 7. The average value thus obtained was 15.0, and similarly, in seeded systems, the average $SiO_2/Al_2O_3$ ratios of mordenites crystallized from clear solutions with batch compositions C1 and C3 were 13.7 and 13.1, respectively.

As can be seen from the three batch compositions,

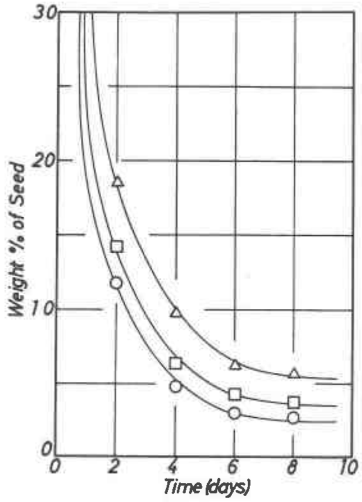

Fig. 8. Relationship between weight percent of seed contained in crystal aggregates and reaction time. Symbols of circles, squares, and triangles correspond to those in Fig. 7.

the alumina content was much lower than soda and silica contents, and consequently, owing to the formation of mordenite, the concentration of alumina in the solution phase decreased rapidly with reaction time as compared with those of other two components. Provided the $SiO_2/Al_2O_3$ ratio of the crystallizing mordenite varies with the change of the $SiO_2/Al_2O_3$ ratio of mother liquor, one might expect that the ratio in mordenite increases with reaction time. However, the corrected values along the broken lines in Figure 7 remain approximately constant regardless of the duration of reaction. Since the different batch compositions of starting materials led to different $SiO_2/Al_2O_3$ ratios of mordenites, it is obvious that the compositions of mordenites were governed by the initial ratio of soda, alumina, and silica in starting materials.

When mordenite crystallization occurs in clear aqueous solutions, its mechanism can probably be explained on the basis of the crystallization mechanism for analcime proposed by Ueda and Koizumi (1979).

## Conclusions

Mordenite crystallized directly from aqueous clear solutions containing no amorphous solid at 100°C at 1 atm. The addition of seed to the solutions resulted in the rapid crystallization and growth of mordenite, even on the surface of seeds whose compositions and structures differ widely from those of mordenite. The composition of growing mordenite was unchanged in the overall process and was independent of the depletion of soda, alumina, and silica contents of the solution phase during the formation of crystals. From these results, we conclude that the crystallization and growth probably can be explained by assuming a complex building block model in solution for the soluble chemical species. We suggest that such species possess fixed compositions and incipient ordered structures which are identical to those of mordenite and that they polymerize to form mordenite crystals. However, their physicochemical properties have not yet been determined directly, and remain a difficult subject to be investigated in future.

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