

Synthesis of clinoptilolite

YOSHIAKI GOTO

Department of Chemistry, Faculty of Technology
Gunma University, Kiryu, Gunma 376, Japan

Abstract

Clinoptilolite was synthesized at 200°C from reagent-grade starting materials of $(\text{Na,K})_2\text{Al}_2\text{Si}_7\text{O}_{18}$ composition in a weakly basic solution of pH 7.9.

It was identified by X-ray diffraction, scanning electron microscopy, and heating experiments. The experimental results indicate that the presence of K as well as Na in the starting materials, and a weakly basic residual liquid are important requirements for the crystallization of clinoptilolite. It seems likely that clinoptilolite is transformed to mordenite as the reaction proceeds.

Although clinoptilolite occurs in abundance in sedimentary rocks, the mineral has only recently been synthesized in the laboratory.¹

A clinoptilolite-like zeolite was synthesized by Ames (1963) in the course of an investigation on the crystallization of gels prepared from LiOH, Al(OH)₃, and silica-gel mixtures. The experiments were conducted under hydrothermal conditions at temperatures ranging from 250° to 300°C at *P*(total) of 625–1350 psi for 2–5 days with final pH of 7.1–8.7. The zeolite obtained was of reasonably high purity, and its X-ray powder data indicated a close structural relation to clinoptilolite. Typically clinoptilolite is (Na+K)-rich and contains no Li. Ca-, Sr- and Ba-clinoptilolites were synthesized by Hawkins (1967) using seeds of natural clinoptilolite. However, the author stated that it was not clear whether the mineral synthesized corresponds to clinoptilolite or heulandite.

In my research, one set of starting materials had compositions of $\text{Na}_{(2-x)}\text{Al}_{(2-x)}\text{Si}_{(7+x)}\text{O}_{18}$, where $x = 0.0, 0.5, \text{ and } 1.0$, while another set consisted of Na:K = 1:1 in place of Na. Reagents used were chemically pure silica gel, sodium aluminate, and potassium aluminate. Calculated amounts of the reagents were mixed and ground thoroughly with alcohol in an agate mortar and then dried at 50°C. The starting materials were found to be amorphous by X-ray diffraction. 500 mg of starting material and 1 ml of an aqueous solution were placed in a pyrex glass tube of

8 mm diameter and 150 mm length with one end closed. The aqueous solution added was, respectively, 0.1N and 0.001N NaOH, distilled water, and 0.1N and 0.001N HCl, for purposes of controlling pH in the fluid. After the tube was sealed, it was heated in an oven, under the following conditions: temperature, 200°C; run duration, 7, 25, and 65 days; *P*(total), ~15 atm. Temperature was controlled within ±5°C. After the run, the tubes were quenched in air. The reaction products were examined by X-ray powder diffraction.

In the series of compositions $\text{Na}_{(2-x)}\text{Al}_{(2-x)}\text{Si}_{(7+x)}\text{O}_{18}$ with $x = 0.0$ and 0.5, only mordenite was formed in all solutions run at 200°C for 7 days. The starting material with $x = 1.0$ did not crystallize under the same conditions.

For the compositions of $(\text{Na,K})_{(2-x)}\text{Al}_{(2-x)}\text{Si}_{(7+x)}\text{O}_{18}$, the experiments were carried out at 200°C for 25 days. In the case of $x = 1.0$, no crystalline phase appeared, except minor amounts of mordenite in the 0.1N NaOH solution. From the starting materials with $x = 0.5$, mordenite was formed in all solutions. In 0.1N HCl solution, the phase was associated with cristobalite. Mordenite was also formed in alkaline solutions, where $x = 0.0$. From this composition, clinoptilolite was synthesized both in distilled water and 0.1N HCl solution in the runs of 25 days, although in distilled water it was associated with mordenite. After a duration of 65 days, mixtures of clinoptilolite and mordenite were formed in both solutions. Final pH of residual fluids was 7.9. In the 0.001N HCl solution, however, mordenite and an

¹ See Appendix.

undetermined phase, but not clinoptilolite, were obtained. After the run duration of 65 days, the undetermined phase disappeared.

The X-ray powder data for synthetic clinoptilolite are tabulated in Table 1, together with the data for natural clinoptilolites (Wise *et al.*, 1969; Minato and Takano, 1964). The d spacings and the intensities of the synthetic clinoptilolite are in good agreement with those of the natural clinoptilolites (Mumpton, 1960; Mason and Sand, 1960) or synthetic Ca- and Sr-clinoptilolites (Hawkins, 1967). The discrepancy of the intensity of (002) or (112) in my synthetic clinoptilolite from that given by Wise *et al.* (1969) may result from the difference in the method of mounting, as well as the difference in crystallinity of the samples. The unit-cell parameters of the clinoptilolite are: $a = 17.665(11)$, $b = 17.901(13)$, $c = 7.357(7)$ Å, $\beta = 116.46(68)^\circ$, $V = 2083(2)$ Å³.

Scanning electron microscopy shows that the clinoptilolite forms platy crystals, about 5–10 μ m in diameter, and with variable thickness (Fig. 1). It was found that small amounts of amorphous material remained in the product.

Chemical analysis of clinoptilolite by electron-

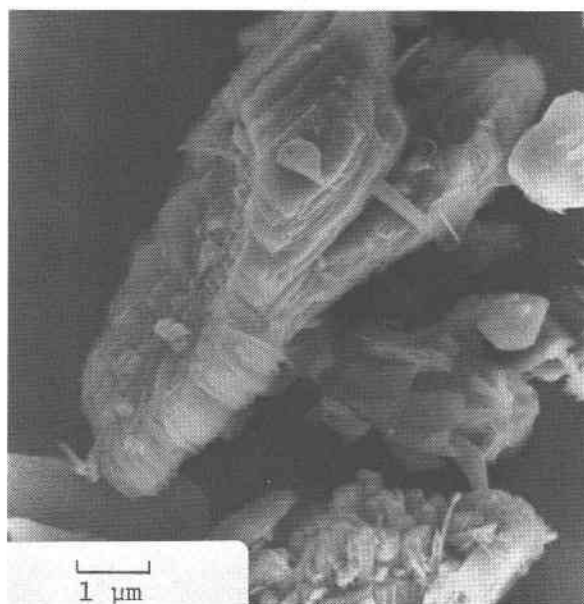


Fig. 1. Scanning electron micrograph of the product given in Table 1 (a).

Table 1. X-ray powder diffraction data for the synthetic (a) and natural (b, c) clinoptilolites

| (a) | | (b) | | (c) | | hk \bar{l} |
|---------|---------|---------|---------|---------|---------|--------------|
| d (Å) | I/I_0 | d (Å) | I/I_0 | d (Å) | I/I_0 | |
| 9.0 | 4 | 9.05 | 7 | 8.92 | 100 | 020 |
| 8.0 | 3 | 7.99 | 4 | 7.97 | 3 | 002 |
| | | 6.82 | 3 | 6.78 | 2 | 10 $\bar{1}$ |
| | | 6.60 | 3 | | | |
| | | 5.85 | 7 | 5.61 | 2 | 031 |
| | | 5.31 | 2 | | | |
| 5.15 | 4 | 5.13 | 3 | 5.15 | 7 | 112 |
| 4.69 | 3 | 4.67 | 2 | 4.65 | 14 | 130 |
| | | 4.53 | 2 | | | |
| | | 4.13 | 3 | 4.35 | 2 | 10 $\bar{3}$ |
| 3.98 | 10 | 3.983 | 10 | 3.964 | 55 | 132,004 |
| 3.91 | 6 | | | 3.897 | 57 | 042 |
| | | | | 3.74 | 7 | 14 $\bar{1}$ |
| | | | | 3.55 | 6 | 21 $\bar{1}$ |
| | | 3.476 | 5 | 3.48 | 3 | 051,114 |
| 3.42 | 4 | | | 3.419 | 16 | 220 |
| | | 3.347 | 4 | 3.324 | 4 | 202 |
| | | 3.221 | 3 | | | |
| 3.17 | 3 | 3.184 | 4 | 3.168 | 14 | 222 |
| | | | | 3.119 | 15 | 222 |
| | | | | 3.07 | 8 | 231 |
| 2.98 | 5 | 2.990 | 4 | 2.974 | 80 | 044 |
| | | 2.976 | 4 | | | |
| | | 2.894 | 1 | | | |
| 2.80 | 2 | 2.805 | 3 | 2.793 | 15 | 035,125 |
| | | 2.742 | 1 | 2.728 | 33 | 161 |

(a) Synthesized clinoptilolite from starting material having the initial composition $(Na,K)_2Al_2Si_7O_{18}$ in 1/10N HCl solution at 200°C, 15 atm and for 25 days.

(b) Natural clinoptilolite from Itaya, Japan (Minato and Takano, 1964).

(c) Single crystal of natural clinoptilolite from Agoura, California (Wise *et al.* 1969).

probe microanalysis was not possible, because of the minute size of the crystals. Therefore the identification of clinoptilolite was made by heating experiments (Mumpton, 1960; Alietti, 1972; Boles, 1972). Differential thermal analysis of the product showed a broad endothermic peak at 70–110°C, corresponding to that of clinoptilolite reported by Mumpton (1960).

Alietti (1972) has reported the results of heating experiment for distinguishing clinoptilolite and heulandite. Using a room-temperature diffractometer immediately after an overnight heating at 400°C, heulandite shows a transformation into phase B, a contracted phase with $d(020) \sim 8.25$ Å derived from natural phase with $d(020) \sim 8.95$ Å. Clinoptilolite is stable up to 750°C. Boles (1972) obtained similar results.

The products of the present experiments were quenched, after heating at various temperatures for 16 hours, and X-ray powder diffraction data were taken immediately at room temperature. The product was not transformed to phase B and had a high resistance to heating, this feature being characteristic to clinoptilolite. However, the clinoptilolite structure was destroyed completely at 700°C, a temperature much lower than 800°C for natural clinoptilolite (Goto *et al.*, 1968), presumably because of its poor crystallinity.

The experimental results indicate that the starting

material should contain K as well as Na and the residual fluid should be weakly basic for the crystallization of clinoptilolite. It seems likely that clinoptilolite is transformed to mordenite as the reaction proceeds.

Appendix

After this manuscript had been submitted, the study "Hydrothermal synthesis of clinoptilolite" was presented by D. B. Hawkins, R. A. Sheppard, and A. J. Gude, 3d at the International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites which was held June 6–11, 1976, in Tucson, Arizona. These authors reported that clinoptilolite as a single phase has been reproducibly synthesized from volcanic ash in 2.0 molar carbonate solution (1:1 K/Na) at temperatures of 130° to 150°C, 1 kbar pressure for 3 to 7 days. Mordenite was formed above 150°C. Clinoptilolite was identified by chemical analysis, X-ray diffraction, and heating experiments.

The present study differs from theirs in starting materials, solutions, pressures, and duration of runs. The results of their experiments, however, support the conclusion of the present study that the presence of K in starting material and a weakly basic fluid are necessary for the crystallization of clinoptilolite. Although the pH of residual fluids was not measured by Hawkins *et al.*, the basicity of carbonate solution will be lower than that of hydroxide solution. The transformation of clinoptilolite to mordenite below 200°C is also supported by their study.

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