Article

Modification of Natural Mordenite by Alkali Hydrothermal Treatments

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Abstract

Natural mordenite from Shimane Prefecture, southwest Japan, was treated at temperatures of 50 – 200 °C and autogeneous pressure for 7 days, changing the NaOH concentration from 1 to 10 M ($M = \text{mol dm}^{-3}$). The several types of zeolites, such as phillipsite, hydroxysodalite and analcime were obtained by the transformation from mordenite after alkali hydrothermal treatments. The formation of hydroxycancrinite was observed for the first time under the hydrothermal treatment of the natural mordenite and the conditions were determined for the transformation. These results indicated that the phases of the zeolite formation from mordenite were clearly dependent on both NaOH concentration and treated temperature. The present results may provide a technology for the improvements of low-grade natural zeolites into high-grade ion exchangers.

1 Introduction

Zeolites are known as aluminosilicates with three-dimensionally ordered nanopores, and have cation exchange and ion adsorption ability. Especially natural zeolites were widely used as low cost ion exchangers and environmental purification materials.[1-3] Unfortunately they usually contain a range in amounts and kinds of impurities, such as quartz and feldspars. There are several reports on the methods to improve the capabilities of natural zeolites with impurities, and to transform them into high-grade cation exchangers. The hydrothermal treatment with NaOH solution is one of the methods, in which zeolites can be easily dissolved and transformed into other phases of the zeolite.[4-6]

Kang and Egashira[4] synthesized zeolite Na-P from Korean low-grade natural zeolites by the hydrothermal treatment with 2 M NaOH for 16 h at 103 °C. They showed that a significant amount of quartz and feldspar contained in the natural zeolites as impurities reduced the transformation efficiency into high-grade zeolites even by the hydrothermal treatment with 2 M NaOH for the Korean zeolites. Kang et al.[5] modified low-grade natural zeolites to form high-power zeolites such as zeolite Na-P, zeolite Na-X and hydroxysodalite, without impurities by fusion with NaOH powder prior to the hydrothermal reaction. Watanabe et al.[6] reported that

Japanese natural zeolites were successfully transformed into high-grade zeolites of phillipsite, analcime and hydroxysodalite under alkali hydrothermal conditions for 7 days at 25 - 150 °C with 0.1 - 3.0 M NaOH solutions. These preceding studies[1-6] indicated that the transformed phases of the zeolites and the amount of impurities remained in the products depended on the concentration of NaOH solution, the reaction temperature, the reaction time and the chemical composition of starting zeolites.

In present study, the results of treatments for Japanese natural zeolite, mordenite, with trace amounts of impurities were reported on the treatment with the higher concentrations of NaOH solutions at temperatures up to 200 °C for 7 days. The modification of mordenite was confirmed after that alkali hydrothermal treatments to other types of the zeolites.

2 Experimental Method

Natural zeolite mined in Shimane Prefecture, southwest Japan was used as the starting material. The samples of the zeolite were sieved and the particles below 50 µm were only used for the starting materials. The chemical composition was determined by inductively coupled plasma spectroscopy (ICP) (SEIKO HVR 1700). The detection limits of the ICP were 0.002 ppm for Na and Si, 0.004 ppm for Al, 0.00004 ppm for Ca and Mg, and 0.030 ppm for K.

The solutions of the mixture of 2.0 g starting material and 30 ml of 1, 3, 5 and 10 M NaOH solutions were placed in Teflon cups fitted into a stainless steel pressure vessel and heated in an oven at 50, 100, 150 and 200 °C under autogeneous pressure for 7 days. After the hydrothermal treatment, the product was filtered through a membrane filter of 0.45 µm and washed several times with distilled water. Then the separated solids dried at room temperature.

Mineral identification of the dried residue was carried out by the powder X-ray diffraction (XRD) method with Cu K α radiation using RIGAKU RINT2200 diffractometer. Morphological changes of the products were observed by a scanning electron microscopy (SEM) using HITACHI S-5000 electron microscope.

3 Results and Discussion

The starting material was identified to be mordenite containing quartz and a trace of layered silicate as impurities (Fig. 1a). The characteristic peak of layered silicate was below the range shown in this figure so that it was not displayed. The composition determined by the ICP showed that the starting material was a homogeneous powder of Si 30.8 wt %, Al 6.4 wt %, Fe 0.5 wt %, Na 1.9 wt %, K 1.5 wt %, Ca 0.9 wt % and Mg 0.4 wt %. The Si/Al ratio was 4.85.

The original morphology of the starting material, mordenite, showed a minute prismatic

Fig. 1 X-ray powder diffraction patterns of a) starting material and the product after treatment b) in 3 M NaOH solution at 100 °C, c) in 1 M NaOH solution at 200 °C, d) in 3 M NaOH at 200 °C solution and e) in 10 M NaOH solution at 200 °C.

M: mordenite, P: phillipsite, A: analcime, C: hydroxycancrinite, S: hydroxysodalite, Q: quartz, F: feldspar

Fig. 2 SEM photographs of (a) natural mordenite and product after treatment of untreated sample (b) in 3 M NaOH solution at 100 °C, (c) in 1 M NaOH solution at 200 °C, (d) in 3 M NaOH solution at 200 °C and (e) in 10 M NaOH solution at 200 °C.

crystal with length of 1 to 5 μm and from 0.05 to 0.1 μm in diameter (Fig. 2a).

The phases obtained of the other forms of zeolites, such as phillipsite, the hydroxysodalite, etc., by the alkali hydrothermal treatments are summarized in Table 1 together with the previous results [6]. The transformation of the mordenite to hydroxycancrinite and analcime depends on the reaction conditions of the hydrothermal temperature and NaOH concentration as can be seen in Table 1.

The treatment at 100 °C with 3 M NaOH solution transforms mordenite to phillipsite, which was known as the aggregates or inter-grown phase of the fine rosettes crystallites with the size of sub μm (Figs. 1b and 2b). In Figs. 1c and 2c, one can see that the treatment with 1 M NaOH solution at 200 °C resulted in the transformation into analcime with characteristic icositetrahedral

Table 1 Product after hydrothermal treatment

$T(^{\circ}\text{C})$	$C_{\text{NaOH}}(\text{M})$	Product
50	1.0	Mor, Qz*
	3.0	Phi, Mor, Qz*
	5.0	Qz, Sod, Mor
	10.0	Qz, Sod, Mor
100	1.0	Phi, Qz, Fs*
	3.0	Phi
	5.0	Can
	10.0	Sod, Qz
150	1.0	Ana, Qz, Fs*
	3.0	Phi, Can
	5.0	Can
	10.0	Sod, Can
200	1.0	Ana
	3.0	Can
	5.0	Can
	10.0	Sod

Ana: analcime, Can: hydroxycancrinite, Sod: hydroxysodalite, Mor: mordenite, Phi: phillipsite, Qz: quartz, and Fs: feldspar, *: Watanabe et al. (2001) [6].

shape of 10-40 μm in diameter. The mordenite treated by 5 M NaOH solution at above 100 $^{\circ}\text{C}$ was transformed to single phase of hydroxycancrinite with hexagonal prism-like needles of a few μm in length (Figs. 1d and 2d). The treatment with 10 M NaOH solution at 50 - 150 $^{\circ}\text{C}$ led to the formation of hydroxysodalite together with quartz or cancrinite; however, the hydroxysodalite was only formed at 200 $^{\circ}\text{C}$ with euhedral shape of a few μm in diameter as shown in Figs. 1e and 2e. These results show that the phase transformations for the natural zeolites considerably depended on the hydrothermal treatment conditions of the concentration of NaOH solution and the treated temperatures.

The formation conditions of phillipsite agree well with those of the previous studies.[4-6] The formation of hydroxycancrinite is observed in this study at higher concentration of NaOH and higher treated temperature. As far as we know, this is the first report of the hydroxycancrinite formation from natural zeolite by hydrothermal treatment. Kang and Egashira[4] showed that the significant amounts of quartz and feldspar impurities in the natural zeolites reduced the transformation to the other phases of the zeolites by the hydrothermal reaction with lower concentrations of NaOH solution. Kang et al.[5] indicated that the pre-processing by NaOH powder is necessary for the fusion processing of the zeolite prior to the hydrothermal reaction for the transformation to high-power zeolites from the natural zeolites. The present study showed that the treatment with higher concentrations of NaOH solution and higher temperatures is effective for obtaining high-power zeolites such as phillipsite, analcime, hydroxysodalite and hydroxycancrinite. These results may provide one of the effective technologies for the improvements of the low-grade natural zeolites into high-grade ion exchangers.

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References

- 1) C. B. Murphy, O. Hrycyk, W. T. Gleason, "Natural Zeolites: Occurrence, Properties, Use" (Eds. L. B. Sand and F. A. Mumpton), Pergamon Press, New York (1976), pp. 471-478.
- 2) F. A. Mumpton, "Natural Zeolites: Occurrence, Properties, Use" (Eds. L. B. Sand and F. A. Mumpton), Pergamon Press, New York (1976), pp. 3-27.
- 3) K. Torii, "Natural Zeolites: Occurrence, Properties, Use" (Eds. L. B. Sand and F. A. Mumpton), Pergamon Press, New York (1976), pp. 441-450.
- 4) S. J. Kang and K. Egashira, *Appl. Clay Sci.*, **12**, 131-144 (1997).
- 5) S. J. Kang, K. Egashira and A. Yoshida, *Appl. Clay Sci.*, **13**, 117-135 (1998).
- 6) Y. Watanabe, H. Yamada, Y. Kokusen, J. Tanaka, Y. Moriyoshi, and Y. Komatsu, Proceedings of the 18th International Japan-Korea Seminar on Ceramics, (2001), pp. 548-551.