Hydrothermal modification of natural zeolites to improve uptake of ammonium ions

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Abstract: The modification of natural zeolites was carried out under hydrothermal conditions to improve the effectiveness of the uptake of ammonium ions. Natural zeolites originating in Japan, such as mordenite and clinoptilolite with quartz, feldspar and a trace of layered silicate, were treated with 0.1, 0.3, 1.0 and 3.0 M NaOH solutions at temperatures from 25 to 150 °C under autogenous pressure for 7 days. After the hydrothermal treatment, the transformation of the zeolites to phillipsite, hydroxyl-sodalite and analcime was observed, depending on the temperature and NaOH concentration. The amounts of ammonium ions taken up into the hydrothermally-treated zeolites were compared with those of the starting materials. The treated products, containing mainly phillipsite, took up twice the amount of ammonium ions as the starting materials. The maximum uptake of ammonium ions was 1.92 mmol g^{-1}. The number of ammonium ions taken up into phillipsite was equal to the number of Na$^+$ ions released from phillipsite. These results indicate that the uptake of ammonium ions proceeds by an ion-exchange mechanism with Na$^+$ ions.
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1 INTRODUCTION

Clinoptilolite and mordenite are the main natural zeolite minerals found in abundance in many locations.[1,2] They have high cation exchange capacity (CEC) and ion adsorption capacity with remarkably high selectivity for ammonium ions.[3] They are widely used as low cost ion-exchangers and are especially used for the removal of ammonium ions in wastewater treatment.[4–6]

Synthesis of high-quality zeolites by hydrothermal treatment of various materials, such as fly ash,[7–9] kaolinite,[10] smectite,[11,12] bentonite[13] and natural zeolite,[14,15] has been reported. Kang and Egashira *et al* have synthesized sodium phillipsite (Na-P) with a trace of feldspar from natural clinoptilolite and mordenite by hydrothermal treatment with 2 M NaOH for 16 h at 103 °C.[14] They have found that when the natural clinoptilolite is treated hydrothermally it changes to Na-P, sodium faujasite (Na-X) and hydroxy-sodalite depending on the reaction conditions.[15] The CEC of the synthesized Na-P is higher than those of Na-X, hydroxy-sodalite and the starting materials. The improvement in the CECs of natural homoionic zeolites by Na$^+$ exchange has also been reported by many researchers.[16–18]

In the present study, natural zeolites originating in Japan, such as mordenite and clinoptilolite with traces of quartz and feldspar, were treated hydrothermally with 0.1, 0.3, 1.0 and 3.0 M NaOH solutions at temperatures in the range of 25–150 °C for 7 days. The amounts of ammonium ions taken up by the hydrothermally-treated zeolites were compared with those of untreated zeolites. The uptake mechanism of ammonium ions was confirmed by investigation of the modified material with the highest CEC for ammonium ions.

2 EXPERIMENTAL PROCEDURE

Two natural zeolitic rocks mined in Shimane Prefecture, located in the south-west of Japan, were used as starting materials. The mineral composition and morphology of this zeolite have been reported by Watanabe *et al*[19] The first sample (CLI1) was clinoptilolite with traces of quartz, feldspar and layered silicate. The clinoptilolite in CLI1 was a submicron-sized coffin-shaped crystallite. The Si/Al molar ratio of CLI1 was 4.94, which is similar to that published for natural clinoptilolites,[18,20] the surface area was 91.8 m^2 g^{-1}, and the pore volume was 0.144 mm^3 g^{-1}. The second one (MOR3) consisted mainly of mordenite with quartz and a trace of layered silicate. The mordenite in MOR3 had a fibrous morphology with the fibres having lengths of 1–5 μm and diameters of 0.05–0.1 μm. The Si/Al molar ratio of MOR3 was 4.85, which is similar to the

published value of natural mordenite,[20] the surface area was $129.6\,m^2\,g^{-1}$, and the pore volume was $0.143\,mm^3\,g^{-1}$. They were sieved and only particles with sizes below $50\,\mu m$ were used as starting materials.

The mixtures consisting of 2.0 g of a starting material and $30\,cm^3$ of 0.1, 0.3, 1.0 and 3.0 M NaOH solutions were placed in Teflon cups fitted into stainless steal pressure vessels and heated in an oven at 25, 50, 100 and 150 °C under autogenous pressure for 7 days. The modification of natural zeolites was performed under alkaline conditions because this reaction is for recrystallization. The hydrothermal treatment was carried out for 7 days in order to remove as much of the impurities as possible. After the hydrothermal treatment, the resultant products were filtered through $0.45\,\mu m$ pore size membrane filters and washed several times with distilled water. Then they were freeze-dried for 24 h.

Identification of minerals was carried out by the powder X-ray diffraction (XRD) method with monochromatized $CuK\alpha$ radiation at 40 kV and 40 mA using an RIGAKU RINT2200 diffractometer. Morphological changes of the crystallites were observed by scanning electron microscopy (SEM) using a Hitachi S-5000 electron microscope. The chemical composition of the sample obtained was determined by inductively coupled plasma spectroscopy (ICP) (Seiko HVR 1700) with a photomultiplier tube as a detector. The test solutions were prepared as follows. For the measurement of Si and Al, 50 mg of a sample were fused with Na_2CO_3 (0.5g) and H_3BO_3 (0.2g) in a platinum crucible at 1000 °C for 10 min. The mixtures were dissolved in HCl solution after cooling, and distilled water was added to the solutions to give a final volume of $100\,cm^3$. For the measurement of Na, K, Ca and Mg, 50 mg of a sample were dissolved in $2\,cm^3$ of HF ($27\,mol\,dm^{-3}$) and $1\,cm^3$ of H_2SO_4 ($18\,mol\,dm^{-3}$) and evaporated. The dried residue was then dissolved in HCl solution with heating, and distilled water was added to the solutions to give a final volume of $100\,cm^3$. The specific surface areas were measured by the multipoint Brunauer–Emmet–Teller (BET) method using a Beckman Coulter SA3100 instrument with nitrogen gas as an adsorbent after degassing at 200 °C for 3 h in vacuum.

For experiments on the uptake of ammonium ions, $30.0\,cm^3$ of solutions containing different concentrations of NH_4Cl (10^{-3}–10^{-2} M, initial pH = 5.1–5.4) were added to 0.1 g of each product in stoppered polyethylene tubes. The tubes were shaken at 30 rpm by an end-over-end shaker (Towa Labo RKVSD 10 101) for 7 days at 25 °C, and then the solids phase was separated by centrifugation at 15 000 rpm for 30 min and filtration using membrane filters of $0.45\,\mu m$ pore size.

The concentrations of ammonium ions in the filtered solutions were determined with an ammonium specific ion electrode (Toa Dempa Kogyo IM-20B, Ammonia Electrode Ae-235). The amounts of ammonium ions taken up were calculated from differences between the concentrations of ammonium ions in the filtered solutions and those in the initial solutions. The values were the averages of three samples. The concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} in the filtered solutions were determined by ICP analysis (Seiko SPS4000). Before and after the experiments on uptake, the separated solids were examined for the confirmation of the changes in the zeolite structures by the powder XRD method. The CECs of the samples were determined by extracting ammonium ions with 1 M KCl solution (pH = 7) from the ammonium-saturated samples obtained by repeating centrifugal washing with 1 M CH_3COONH_4 solution (pH = 7).[14] The amounts of ammonium ions were determined with an ammonium specific ion electrode.

3 RESULTS AND DISCUSSION
3.1 Characterization of hydrothermally-modified products
Changes of the phases of the natural zeolites, CLI1 and MOR3, by hydrothermal treatment are shown in Table 1. The transformation of the natural zeolites to phillipsite, hydroxy-sodalite and analcime depended on the types of the zeolitic rocks, and the reaction conditions such as hydrothermal temperature and NaOH concentration.

The structure of CLI1 was not changed after treatment with 0.1 M NaOH solution at temperatures below 150 °C. The CLI1 samples treated with 0.3 M NaOH solution at 25, 50 and 100 °C also did not show any change in their XRD patterns. But after treatment at 150 °C, the amount of clinoptilolite, which is the major zeolite species in CLI1, decreased, and analcime was formed. CLI1 treated with 1 M NaOH solution at 25 °C did not show any phase change, but at 50 °C, the low intensity pattern of phillipsite was identified. Treatment at 100 °C transformed CLI1 mainly to phillipsite with a trace of feldspar, and at 150 °C, analcime with a cubo-octahedral shape of $10-30\,\mu m$ in diameter was formed. The CLI1 treated with 3 M NaOH solution at 25 °C did not show any phase change. At 50 °C, the phase consisted mainly of phillipsite with traces of clinoptilolite and feldspar. The treatment at 100 °C led to phillipsite and hydroxy-sodalite with a trace of feldspar, and that at 150 °C led to sodalite with layered silicate.

On the other hand, MOR3 treated with 0.1 M NaOH solution at temperatures below 150 °C and with 0.3 M NaOH or 1 M NaOH solution at below 50 °C did not show the structural changes. After treatment with 0.3 M NaOH solution at 100 and 150 °C, phillipsite started to appear. After treatment with 1 M NaOH solution at 100 °C, the main phase became phillipsite with traces of quartz and feldspar, whereas at 150 °C MOR3 was mainly transformed to analcime with traces of quartz and feldspar. The MOR3 in 3 M NaOH solution was transformed to

Table 1. The hydrothermal modifications of natural zeolites, CLI1 and MOR3

Starting material	T(°C)	C_{NaOH}(M)	Products
CLI1	25	0.1	Cli, Feld, Qtz, LS
		0.3	Cli, Feld, Qtz, LS
		1.0	Cli, Feld, Qtz, LS
		3.0	Cli, Feld, Qtz, LS
	50	0.1	Cli, Feld, Qtz, LS
		0.3	Cli, Feld, Qtz, LS
		1.0	Cli, Feld, Qtz, LS, Phi
		3.0	Phi, Cli, Feld, Qtz, LS
	100	0.1	Cli, Feld, Qtz, LS
		0.3	Cli, Feld, Qtz, LS
		1.0	Phi, Feld
		3.0	Phi, Sod, Feld
	150	0.1	Cli, Feld, Qtz, LS
		0.3	Cli, Ana, Feld, Qtz, LS
		1.0	Ana
		3.0	Sod, LS
MOR3	25	0.1	Mor, Qtz, LS
		0.3	Mor, Qtz, LS
		1.0	Mor, Qtz, LS
		3.0	Mor, Qtz, LS
	50	0.1	Mor, Qtz, LS
		0.3	Mor, Qtz, LS
		1.0	Mor, Qtz, LS
		3.0	Phi, Mor, Qtz, LS
	100	0.1	Mor, Qtz, LS
		0.3	Mor, Phi, Qtz, LS
		1.0	Phi, Qtz, LS
		3.0	Phi
	150	0.1	Mor, Qtz, LS
		0.3	Mor, Phi, Qtz, LS
		1.0	Ana, Qtz, Fed
		3.0	Phi, Sod

C_{NaOH}(M): NaOH concentration (M).
Cli: Clinoptilolite, Mor: mordenite, Phi: phillipsite, Ana: analcime, Sod: sodalite, Qtz: quartz, Feld: feldspar, LS: layered silicate.

Figure 1. The SEM image of phillipsite obtained after treatment of natural mordenite (MOR3) with 3 M NaOH solution at 100 °C.

The relationship between the amounts of ammonium ions taken up by the modified samples of CLI1 and MOR3, and the equilibrium concentrations of ammonium chloride are shown in Figs 2 and 3, respectively.

Phillipsite obtained from MOR3 treated at 100 °C in 3 M NaOH solution has a greater capacity for the uptake of ammonium ions than the untreated sample, as reported by Watanabe *et al*[19] In the present study, the amount of ammonium ions ion-exchanged by phillipsite (1.92 mmol g^{-1} in 10 mM NH$_4$Cl) was about two-fold greater than that obtained by MOR3. The surface area of phillipsite was 31.4 m^2 g^{-1}, which is lower than that obtained from MOR3 (129.6 m^2 g^{-1}), and the pore volume was 0.119 mm^3 g^{-1}. These results indicate that the surface area is not related to uptake of ammonium ions.

phillipsite or hydroxy-sodalite depending on treatment temperature.

The chemical composition of MOR3 obtained after treatment with 3 M NaOH solution at 100 °C as determined by ICP analysis showed that the Si/Al molar ratio was about 1.64, and the amount of Na$^+$ ions was 13.0 wt%, which is nearly equal to the Si/Al molar ratio and CEC of synthetic PHI.[3] K$^+$, Ca^{2+} and Mg^{2+} were not detected by ICP analysis.

The SEM image of the phillipsite showed aggregates or intergrown fine rosette crystallites, submicrons in size (Fig 1). These results indicate that the phase transformation of natural zeolites as the result of hydrothermal treatment depends on the compositions of starting zeolite materials, hydrothermal temperature and NaOH concentration.

3.2 Ammonium uptake

Experiments on the uptake of ammonium ions were carried out with the samples modified by hydrothermal treatment with 1 and 3 M NaOH solutions at 100 °C.

● , phillipsite with trace of feldspar (1 M NaOH, 100°C)
■ , phillipsite with traces of hydroxy-sodalite and feldspar (3M NaOH, 100°C)
…., starting material (CLI1)

Figure 2. The adsorption isotherms for modified clinoptilolite.[19]
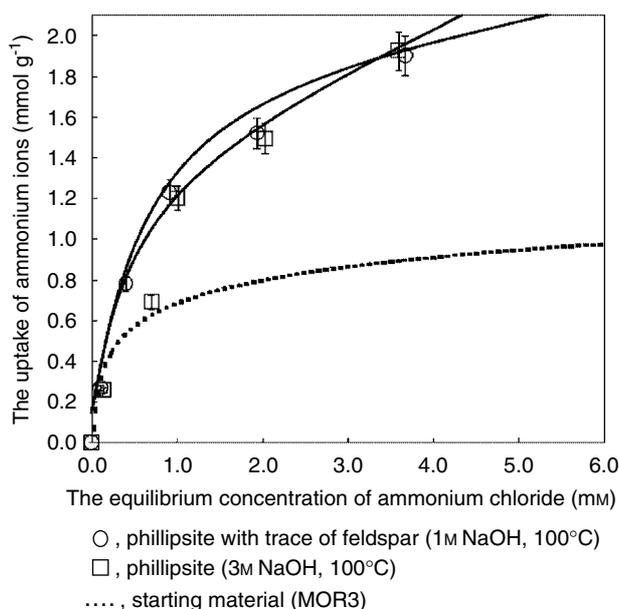
Figure 3. The adsorption isotherms for modified mordenite.[19]

Legend:
○ , phillipsite with trace of feldspar (1 M NaOH, 100°C)
□ , phillipsite (3 M NaOH, 100°C)
···· , starting material (MOR3)

Similar results were obtained from CLI1 treated with 1 M NaOH solution at 100 °C. When CLI1 was transformed to phillipsite, the uptake of ammonium ions increased. The increase in the uptake of ammonium ions by phillipsite is related to the larger number of ion-exchange sites in the phillipsite framework compared with those in mordenite and clinoptilolite lattices.[20] The real CECs of CLI1, MOR3 and the treated zeolites are shown in Table 2. The CECs of phillipsite obtained from CLI1 and MOR3 treated with 3 M NaOH at 100 °C were 2.88 and 3.13 meq g^{-1}, respectively, but the values were nearly two times larger than those of CLI1 (1.40 meq g^{-1}) and MOR3 (1.12 meq g^{-1}). From these results we conclude that the change of clinoptilolite and mordenite to phillipsite improves CEC and uptake of ammonium ions.

The CECs of the zeolites used in this study are compared with other published data on zeolites in Table 3. This comparison indicates that the treated zeolites composed of mainly phillipsite have similar but slightly higher exchange capacities than reported previously for other zeolites.[15,17,21,22]

Table 2. Cation exchange capacities of CLI1, MOR3 and treated zeolite

Starting material	T(°C)	C_{NaOH}(M)	CEC (meq g^{-1})
CLI1	–	–	1.40
	100	1.0	2.76
	100	3.0	2.88
MOR3	–	–	1.12
	100	1.0	2.30
	100	3.0	3.13

C_{NaOH}(M): NaOH concentration (M).

Table 3. Cation exchange capacities of various zeolites

Zeolite origin	Cation exchange capacity meq g^{-1}	Reference
CLI1	1.40	
MOR3	1.12	
CLI1 treated, 3 M, at 100 °C	2.88	
MOR3 treated, 3 M, at 100 °C	3.13	
Natural clinoptilolite	1.75	15
Na-P	4.18	15
Natural clinoptilolite (Na type)	0.44	17
Faujasite (Na type)	3.20	21
Natural clinoptilolite (Na type)	2.05	22

3.3 Ion-exchange mechanism of ammonium ions

Phillipsite modified from MOR3 at 100 °C in 3 M NaOH solution, with the highest ion-exchange capacity for ammonium ions, was used to investigate the uptake mechanism of ammonium ions. Figure 4 shows the relationship between the uptake of ammonium ions by phillipsite and the amounts of Na$^+$ released from phillipsite. The numbers of ammonium ions taken up by phillipsite were equal to those of Na$^+$ released from phillipsite. The amounts of K$^+$, Ca^{2+} and Mg^{2+} were not detected. These results indicate that the uptake of ammonium ions proceeds by an ion-exchange mechanism. X-ray diffraction patterns did not show any structural change of phillipsite after ion-exchange, which proves that the framework structure is stable under this condition.

4 CONCLUSION

Natural zeolitic rocks, such as mordenite and clinoptilolite with traces of quartz and feldspar, were treated hydrothermally with 0.1, 0.3, 1.0 and 3.0 M NaOH solutions at temperatures below 150 °C. The phase changes of these zeolites depended on
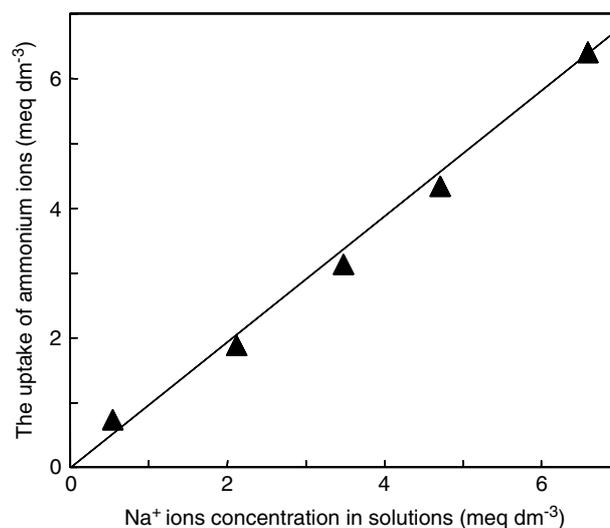
Figure 4. The relationship between the amounts of Na$^+$ ions released and the amounts of ammonium ions taken up by phillipsite (3 M NaOH, 100 °C).

reaction conditions such as hydrothermal temperature and NaOH concentration, as well as the chemical compositions of the starting materials.

The amount of ammonium ions taken up by the product modified from MOR3 at 100 °C in 3 M NaOH solution, which contained mainly phillipsite, was two-fold greater (1.92 mmol g^{-1}) than that taken up by the starting material. This result is explained by the higher CEC of the phillipsite framework in comparison to mordenite and clinoptilolite. The mechanism of ammonium uptake by phillipsite involved ion-exchange of Na$^+$ ions with ammonium ions. The framework structure of phillipsite was stable in ammonium ion solutions, and therefore we conclude that phillipsite is ideal for use as an industrial ion-exchanger to remove ammonium ions from wastewater.

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