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Alkali-Hydrothermal Modification of Air-Classified Korean Natural Zeolite and Their Ammonium Adsorption Behaviors

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ABSTRACT

Korean natural zeolite in which clinoptilolite and mordenite coexisted with feldspar and illite as impurities, was treated with 1.0, 3.0, and 5.0 M NaOH solutions at 100, 150, and 200°C under autogeneous pressure for 17 hours either with or without an air classification as pretreatment. Phillipsite, analcime, and hydroxycancrinite were identified as reaction products depending on the reaction temperature and NaOH concentration. The air classification of the starting material prior to alkali-hydrothermal treatment effectively reduced the amount of feldspar, which hardly reacted to zeolite in the hydrothermal reaction. The ammonium adsorption behavior of the treated and untreated samples were investigated in solutions of between 10^{-3} M and 10^{-2} M NH_4Cl. The amount of adsorbed ammonium ions in alkalihydrothermally treated product from air-classified material was higher by about two times than was that of corresponding untreated zeolites. The air-classified zeolite treated in 3 M NaOH solution at 100°C showed the highest adsorption of ammonium ion among samples. It was explained by both the phase change of clinoptilolite and mordenite to phillipsite with higher cation exchange capacity and the reduction in the amount of feldspar that was less reactive under hydrothermal conditions for the formation of phillipsite. The results indicated that the combination of the air classification and alkali-hydrothermal treatment effectively improved the adsorption behavior for ammonium ions on natural zeolites with impurities.

Key Words: Korean natural zeolite; Air classification; Alkali-hydrothermal treatment; Clinoptilolite; Mordenite.

INTRODUCTION

Natural zeolites such as clinoptilolite and mordenite are often used for the removal of ammonium ion in wastewater because of their high selectivity for ammonium ions.[1–8] The adsorption behavior of natural zeolites can be improved by transformation to phillipsite under the alkali hydrothermal conditions.[9–11] Kang and Egashira (1997)[9] and Kang et al. (1998)[10] synthesized phillipsite with trace feldspar from natural clinoptilolite and mordenite by hydrothermal treatment with 2 M NaOH during 16 h at 103°C. They also found that natural clinoptilolite treated hydrothermally transformed into phillipsite, faujasite, and hydroxysodalite depending on the reaction conditions. The cation exchange capacity of the synthesized phillipsite was higher than that of faujasite, hydroxysodalite, and starting materials. Watanabe et al. (2001)[11] reported that the ammonium adsorption capacity of alkali-hydrothermal products containing mainly phillipsite was twofold higher than that of the starting materials. However, impurities in natural zeolite such as feldspar and quartz were not transformed into phillipsite to any large extent during alkali hydrothermal treatment resulting in the decrease of cation exchange capacity of the product containing these materials.[9–11] To reduce the amount of feldspar and quartz in the alkali hydrothermal product, fusion with NaOH powder has been proposed as the pretreatment.[10]

Air classification is a method to separate mixtures of minerals into two or more products on the basis that the particles fall through airflow.[12,13] Recently, many kinds of air classifier have been developed and commercially used in the manufacturing process of powdered materials because of the advantage in reducing energy consumption as compared to the conventional wet classification processing.[12–14] In an air classification system, particles are separated into fine and coarse fraction under the influence of airflow and inertial force such as gravity and centrifugal force. When the material consists of two or more constituents with different size, density, and hardness, purification is possible using air classification.

In the present study, Korean natural zeolite with impurities was treated at alkali-hydrothermal conditions to obtain high purity of phillipsite either with or without an air classification as pretreatment. Ammonium adsorption behavior of the products was investigated and compared with those of corresponding untreated zeolites.

EXPERIMENTAL

Materials

Natural zeolite consisting of clinoptilolite and mordenite, with feldspar and illite as impurities was mined in Yangbok located in Kyongju city, Kyongbok province, southeast Korea. The zeolite was powdered, first using a jaw crusher and a Raymond Mill, and then separated through a zigzag type air classifier (ALPINE Laboratory Classifier 100 MZR). The classifier used in the present study was designed for analytical or preparative separations that separate particles with a steplessly adjustable range of 2–80 μm. The classifier mainly consists of feeding, separating, and collecting parts. Efficiency of the classifier is generally affected by feeding rate, air volume, and speed of the classifying wheel, which has 32 zigzag channels. The most important adjustment for determining the particle size of the product lies in the wheel speed. In the present study, the powdered zeolite was separated into fine and coarse fraction at 12,000 rpm of wheel speed. The unclassified powdered zeolite and the overflow product recovered at 12,000 rpm of wheel speed were denoted to be K00 and K12, respectively.

Hydrothermal Treatment

For the hydrothermal treatment, the mixture of 2.0 g of the zeolite sample and 30 mL of 1.0, 3.0, and 5.0 M NaOH solution were placed in a Teflon cup fitted into a stainless steel pressure vessel and heated in an oven at 100, 150, and 200°C for 17 hours. After the hydrothermal treatment, the product was filtered through a membrane filter of 0.45 μm, washed several times with distilled water by centrifugation at 15,000 rpm for 15 minutes and decanted. Then it was freeze dried for 24 hours.

Characterization of Products

Mineral identification was carried out by powder X-ray diffraction (XRD) with CuKα radiation (RIGAKU RINT 2200). For the identification of layered silicate in the samples, the ethylene glycol treatment was performed according to Yamada et al., (1991).[15] The intercalation of ethylene glycol occurred for smectite, but not for illite.[16] Morphology and chemical compositions of the products were observed by scanning electron microscopy (SEM, JEOL JSM-5800LV) fitted with an energy dispersive X-ray (EDX) analysis (JEOL JED-2110).

The chemical compositions of K00 and K12 were determined by inductively coupled plasma (ICP) spectroscopy (ICP, Nippon Jarrell-Ash IRIS Advantage). A photomultiplier tube was used as the detector for ICP. The operating conditions for ICP are given in Table 1. The solutions for ICP were prepared as follows: for Si and Al, 50 mg of sample was mixed with 0.5 g of Na_2CO_3 and 0.2 g of H_3BO_3 powders. The mixture was dissolved by addition of 2 mL of 15.7 M HNO_3 solution, and pure water was added to the solution to a final volume of 100 mL. For Na, K, Ca, Mg, and Fe, 50 mg

Table 1. Operating conditions for ICP.

Frequency	27.12 MHz
RF power	1.15 kW
Plasma gas	14 Lmin^{-1}
Auxiliary gas	0.5 Lmin^{-1}
Carrier gas	26 psi
Analytical lines:	
Si: 288.158 nm	Al: 394.401 nm
Fe: 260.709 nm	Na: 588.995 nm
K: 766.490 nm	Ca: 393.366 nm
Mg: 280.270 nm	

of sample was dissolved in 2 mL of 26 M HF and 1 mL of 9 M H_2SO_4 solutions. After the solution was evaporated, the dried residue was dissolved in 1 mL of 11.6 M HCl solution with heating, pure water was added to the solution to a final volume of 100 mL. The detection limits of ICP analyses were 0.002 ppm for Na and Si, 0.004 ppm for Al, 0.00004 ppm for Ca and Mg, 0.030 ppm for K, and 0.001 ppm for Fe.

Ammonium Adsorption

For ammonium adsorption experiments, 30.0 mL of each solution containing different proportions of NH_4Cl (10^{-3} to 10^{-2} M) was added to 0.1 g of air-dried zeolite samples in stoppered polypropylene tubes. The tubes were shaken by an end-over-end shaker (TOWA LABO RKVSD10101) at room temperature for 17 hours. The mixture was separated by centrifugation at 15,000 rpm for 15 minutes and then filtered with a 0.2 μm membrane filter (FUJIFILM CASL-20). The ammonium concentration of the filtered solution was determined using an ammonium ion–specific electrode (TOA Electronics Ae-235). It has an analytical error of 10%.

RESULTS AND DISCUSSION

Characterization of Untreated, Air-Classified, and Hydrothermal Products

From XRD data of untreated and air-classified materials [Fig. 1 (a) and (b)], clinoptilolite and mordenite were detected as a major component. Feldspar was also detected in relatively large quantities, and illite was present in small quantities. The layered silicate in the sample was identified as illite, since no expansion to 17 Å on glycol solvation was observed. The characteristic XRD peaks of clinoptilolite and mordenite, the major zeolite species in the powdered materials, increased in their intensities after air classification. The peak intensity of feldspar in the material decreased after air classification. The relative peak intensities of clinoptilolite, mordenite, and feldspar were normalized to those of K00 (Table 2). It indicated that the amount of clinoptilolite and mordenite increased and the amount of feldspar decreased after air classification. The air classification was an effective method to reduce the impurities. As the result, the purity of the zeolite of the samples depended greatly on the amount of feldspar in them. K12 was considered to higher in purity than K00. Their chemical composition is given in Table 3. Contents of Na and K were significantly decreased after air classification due to the diminished amount of feldspars.

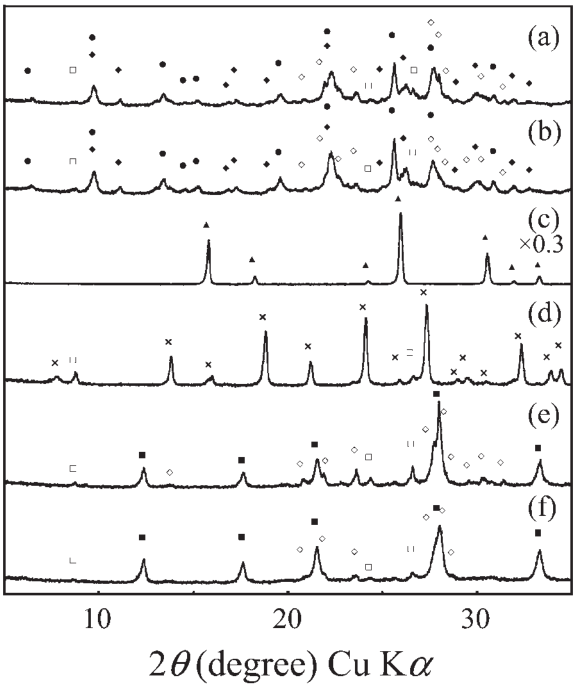

Figure 1. X-ray diffraction patterns of (a) unclassified zeolite (K00), (b) zeolite after air classification at 12,000 rpm (K12), (c) K12 treated by 1 M NaOH at 200 °C, (d) K12 treated by 3 M NaOH at 200 °C, (e) K00 treated by 3 M NaOH at 100 °C (P00), (f) K12 treated by 3 M NaOH at 100 °C (P12). ●: mordenite. ◆: clinoptilolite. ◇: feldspar. □: illite. ■: phillipsite. ▲: analcime. : × hydroxycancrinite.

Phase changes of K00 and K12 by the alkali-hydrothermal treatment are summarized in Table 4. Phillipsite, analcime, and hydroxycancrinite were identified as reaction product depending on the reaction temperature and NaOH concentration. The species of minerals appearing in the products were less dependent on the starting samples. Phillipsite was obtained as the main phase after the treatment in 3 M NaOH at 100°C [Figure 1 (e) and (f)], which was observed under SEM as rosettes like intergrowth of crystals with diameter of 2 ∼ 4 μm [Fig. 2 (a)]. Phillipsite also appeared with other phases and unreacted starting material after the treatment with 1 M NaOH solution at 100°C and 150°C. Analcime was obtained as a single phase with treatment of sample K12 at 200°C with 1 M NaOH solution [Fig. 1 (c)], it can be seen with the euhedral icositetrahedral shape under SEM [Fig. 2 (b)]. After treatment with 1 M NaOH solution at 150°C and

Table 2. Relative XRD peak intensities of minerals and adsorption amount of ammonium ion in 10 mmol/L NH_4Cl.

	Clinoptilolite	Mordenite	Phillipsite	Feldspar	NH_4^+ (mmol/g)
K00	100	100	—	100	0.78
K12	128	136	—	39	0.93
P00	—	—	100	142	1.35
P12	—	—	122	47	1.59

—: not detected.

200°C, and 3 M NaOH solution at 150°C, analcime appeared with other phases. Hydroxycancrinite was obtained at 3 M NaOH at 150 and 200°C [Fig. 1 (d)] and 5 M NaOH at 100, 150, 200°C with prismatic needles of a few μm in length [Fig. 2 (c)]. These results are consistent with previous studies.[9–11,17]

The products treated with 3 M NaOH solution at 100°C from samples K00 and K12 [Figure 1 (e) and (f)] contained a high purity of phillipsites with small amount of impurities. These products, which were obtained from K00 and K12, are referred to as P00 and P12, respectively. The relative peak intensity of the impurity (i.e., feldspar) was normalized to K00, while the intensity of phillipsite in P12 was normalized to P00 (Table 2). This indicates that pretreatment by air classification can effectively reduce the amount of impurities and resulted in a purer phillipsite phase in the hydrothermal products. The Si/Al ratios of phillipsite in P00 (1.65) and P12 (1.77) from the results of EDX analysis are almost similar. It indicated that the chemical compositions of the phillipsite were unaffected by the air classification.

Table 3. Chemical composition of unclassified and air-classified zeolites.

	K00	K12
Si	29.7	29.4
Al	6.94	6.47
Fe	0.98	0.95
Ca	1.77	1.66
Mg	0.49	0.50
Na	1.33	0.89
K	1.90	1.61

Table 4. Hydrothermal products of unclassified and air-classified zeolites.

Starting materials	C_{NaOH} (N)	T (°C)	Products
K00	1.0	100	Phi, Mor, Cli, Fs, Il
		150	Phi, Ana, Fs, Il
		200	Ana, Fs, Il
	3.0	100	Phi, Il, Fs
		150	Can, Ana, Il
		200	Can, Il
	5.0	100	Can, Il, Fs
		150	Can, Il
		200	Can, Il
K12	1.0	100	Phi, Mor, Cli, Fs, Il
		150	Phi, Ana, Fs, Il
		200	Ana
	3.0	100	Phi, Il, Fs
		150	Can, Ana, Il
		200	Can, Il
	5.0	100	Can, Il, Fs
		150	Can, Il
		200	Can, Il

C_{NaOH} (N): NaOH concentration in normality.
Ana: analcime; Can: hydroxycancrinite; Cli: clinoptilolite.
Fs: feldspar; Il: illite; Mor: mordenite; Phi; phillipsite.

Ammonium Adsorption Behavior

Watanabe et al. (2001)[18] pointed out that the adsorption capacities of ammonium ion were different for various synthetic zeolites and were dependent on pore structure, especially windowsize, of the cage. From this data, it is clear that the ammonium adsorption did not occur for analcime and hydroxycancrinite. Therefore, the ammonium adsorption experiments were carried out for the hydrothermal products containing phillipsite as a main phase, P00 and P12, and starting materials containing clinoptilolite and mordenite, K00 and K12.

Figure 3 shows the adsorption isotherm of ammonium ion on K00, K12, P00, and P12. The ammonium adsorption of alkali-hydrothermal zeolite from air-classified material was approximately two times higher than that of corresponding untreated air-classified materials. Sample P12 showed the highest ammonium capacity among the samples, with a capacity

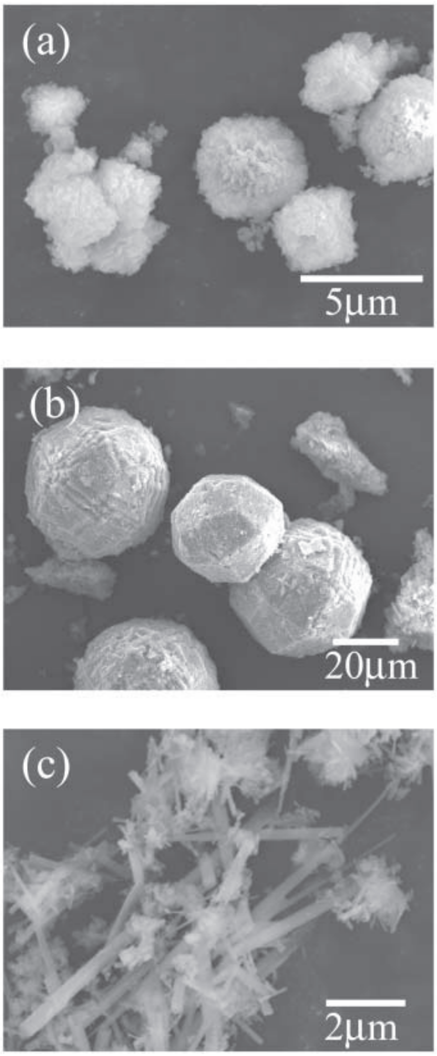

Figure 2. SEM photographs of samples. (a) K12 treated by 3 M NaOH at 100 °C, (b) K12 treated by 1 M NaOH at 200 °C, (c) K12 treated by 3 M NaOH at 200 °C.

of 1.59 mmol/g in 10 mM NH_4Cl, which was comparable to that of the previous study.[11] Ammonium adsorption capacity decreased in the order of P12 > P00 > K12 > K00. This phenomenon can be explained by the difference in the amount of zeolite, the species of zeolite, and the amount

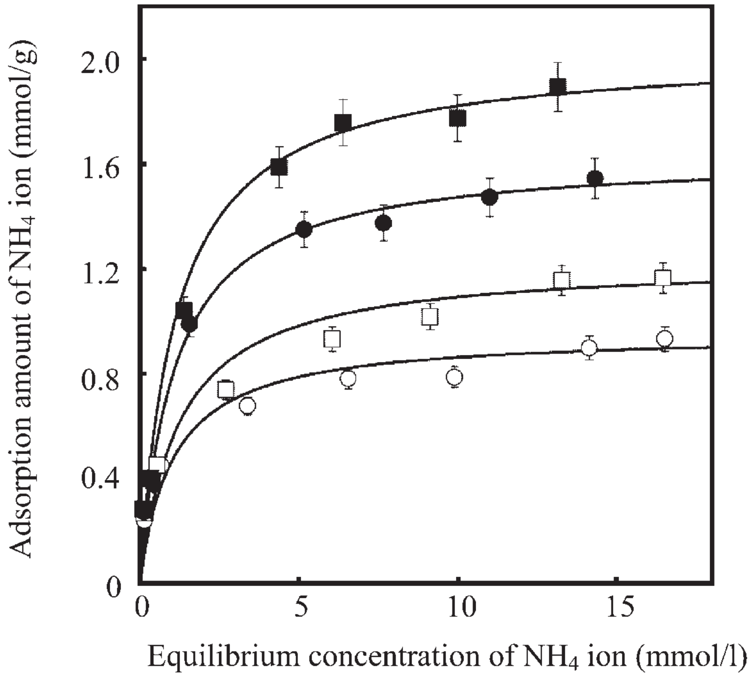

Figure 3. Adsorption isotherm of ammonium ion on the samples. ○: unclassified zeolite (K00). □: zeolite after air classification at 12,000 rpm (K12). ●: K00 treated by 3 M NaOH at 100 °C (P00). ■: K12 treated by 3 M NaOH at 100 °C (P12).

of impurity, which was feldspar (Table 4). The amount of ammonium adsorption showed a positive correlation on the amount of zeolites and negative on the amount of feldspar as impurity. The amount of clinoptilolite and mordenite in K12 was larger than that of K00, and the amount of feldspar as impurity in K12 was smaller than that of K00. So the ammonium adsorption capacity of K12 was higher than that of K00. Since the chemical compositions of phillipsite in P00 and P12 were almost similar, the difference in the amount of ammonium adsorption arises from the difference in the amount of feldspar as an impurity. The above order was explained, finally, by the difference of the cation exchange capacity among zeolites. The capacity of phillipsite (4.7 meq/g) is higher by about two times than that of clinoptilolite and mordenite (2.6 meq/g).[19] All samples contained small amount of illite as an impurity. However, cation exchange capacity of illite (0.1 and 0.4 meq/g)[20] is small and its contribution to the adsorption behaviors is negligible.

These results indicated that the present combination of air classification and hydrothermal treatment was effective in improving the ammonium adsorption behavior because of the reduction of the amount of impurity, especially feldspar, of the natural zeolite, and the conversion of low-capacity zeolite (clinoptilolite and mordenite) to high-capacity zeolite (phillipsite).

CONCLUSIONS

Korean natural zeolite with impurities was treated at alkali-hydrothermal conditions to improve the adsorption behavior for ammonium ions either with or without an air classification as pretreatment. Phillipsite, analcime, and hydroxycancrinite were obtained depending on the reaction temperature and NaOH concentration. The air-classified zeolite treated in 3 M NaOH solution at 100°C showed the highest adsorption of ammonium ion among samples. The combination of air classification for reducing the amount of impurity and hydrothermal treatment for obtaining high-quality zeolite effectively improved ammonium adsorption behavior.

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