Article

Air Classification of Korean Natural Zeolite to Improve Adsorption of Ammonium Ion

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Abstract

Korean natural zeolite with feldspar and illite as impurities was purified by air classification to improve the ammonium adsorption capacities. The treated zeolite was classified into 5 fractions with different amounts of zeolite minerals and impurities. Ammonium adsorptions on the air-classified samples in ammonium chloride solution were compared with that of unclassified zeolite. The highest capacity for ammonium adsorption was obtained for the air-classified sample operated at 12000 rpm with the largest amount of zeolite and the smallest amount of feldspar. The maximum adsorption capacity was 0.93 mmol/g, which was 1.2 times the unclassified sample.

Key words: air classification, ammonium adsorption, Korean natural zeolite

1 Introduction

Natural zeolites are used as low-cost ion exchangers in various industrial applications.[1-4] Clinoptilolite and mordenite are the main minerals of natural zeolites found in abundance in many locations.[5] These minerals have three-dimensional open-framework structures consisting of AlO_4 and SiO_4 tetrahedra linked together by oxygen sharing and contain channels and cavities in which cations and water molecules can diffuse as well as ion-exchange sites. The chemical behavior of natural zeolites in aqueous solutions has been investigated.[6-8] The use of natural zeolites for removal of ammonium ion in wastewater treatment has been reviewed by a number of researchers.[8-12] The adsorption behavior of processed zeolite obtained by chemical and physical treatment has also been investigated.[13] The efficiency of the use of natural zeolite for removal of ammonium ions in wastewater depends on the zeolite species, the form of exchangeable cations,[10] and the

amount of impurities.[8,14] As natural impurities such as feldspar reduces the capacity of ammonium adsorption, pretreatment is desired to remove them before use. In this study the ability of an air classification system to remove the impurities is presented. Air classification is an important process step to optimize product quality and classification of fine particles.[15] In an air classification system, particles are separated into fine and coarse fractions under the influence of airflow and inertial force such as gravity and centrifugal force. When the material consists of two or more constituents of different size, density, and hardness, purification is possible using air classification.

In the present study, air classification was applied to the natural zeolite from Pohang, southeast Korea to reduce the amount of impurities. Ammonium adsorption of the air-classified zeolites in ammonium chloride solution was compared with that of unclassified one. The results obtained were also compared with those published for other zeolites.

2 Experimental

2.1 Materials

Natural zeolite mined from Pohang, southeast Korea, was used in the present study. The zeolite consisted of clinoptilolite and mordenite, with feldspar and illite as impurities. The zeolite was powdered at first using a jaw crusher and a raymond mill, and then separated through a zigzag air classifier (HOSOKAWA-ALPINE Laboratory Classifier 100 MZR). The classifier consists of classifying wheel with 32 zigzag channels, wheel speed controller, classifying chamber and air blower. The classifier used in this investigation is a laboratory one for analytical or preparation separations which precisely separates powder particles with steplessly adjustable separating range of 2–80 μm . The powdered zeolite was separated into fine and coarse fraction with the desired wheel speed. The coarse fraction was then separated into the fine and the coarse fraction at a different rotational speed of classifier wheel. This procedure was repeated several times, and then the air-classified products operated at 4000, 6000, 8000, 10000 and 12000 rpm were obtained. The unclassified powdered zeolite, the air-classified products at 4000, 6000, 8000, 10000, and 12000 rpm were denoted to be K00, K04, K06, K08, K10, and K12, respectively.

2.2 Characterization

Mineral identification was carried out by the powder X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation (RIGAKU RINT 2200). For the identification of layered silicate in the samples, the ethylene glycol treatment was performed according to Yamada et al.[16] The intercalation of ethylene glycol occurred for smectite, but not for illite.[17] The particle size distribution of the untreated and air-classified samples was measured by laser diffraction (HELOS & RODOS Laser Diffraction Analyser, Sympatec GmbH, Clausthal-Zellerfeld). The chemical composition of the minerals was carried out grain by grain with energy dispersive X-ray (EDX) analysis (JEOL JED-2110 attached to scanning electron microscope (JEOL JSM-5800LV)) operated at 15 kV. The chemical compositions of the unclassified and air-classified products were determined by inductively coupled plasma spectroscopy (ICP, Nippon Jarrell-Ash IRIS Advantage). A photomultiplier tube was used as the detector for ICP. The solutions for ICP were prepared as follows: for Si, Al, Ca, and Mg, 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 2.0 mL of 11.6 mol/L HCl solution, and pure water was added to the solution to a final volume of 100 mL. For Na, K, and Fe, 30 mg of sample was dissolved in 2.0 mL of 26 mol/L HF and 1 mL of 9 mol/L H_2SO_4 solutions. After the solution was evaporated, the dried residue was dissolved in 1.0 mL of 11.6 mol/L HCl solution with heating, and pure water was added to the solution to a final volume of 100 mL.

2.3 Ammonium adsorption experiment

For ammonium adsorption experiments, 30.0 mL of each solution containing different proportions of NH_4Cl (10^{-3} - 2×10^{-2} mol/L) was added to 0.1 g of air-dried 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 15000 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) with the accuracy of more than 95%.

3 Results and Discussion

3.1 Characterization of untreated and air-classified zeolites

Fig. 1 shows the XRD patterns of the samples before and after the air classification. All samples consisted mainly of clinoptilolite and mordenite with feldspar and trace of illite. Since no expansion to 17 Å on glycol solvation was observed, the layered silicate in the sample was identified as illite. The relative peak intensities of clinoptilolite, mordenite, and feldspar except peaks overlapped with those of the minerals in each sample were normalized to those of K00 (Table 1). The relative peak intensities of clinoptilolite and mordenite became weaker in the order of $\text{K12} > \text{K10} > \text{K08} > \text{K00} > \text{K06} > \text{K04}$, whereas that of feldspar became stronger in the reverse order of $\text{K12} < \text{K10} < \text{K08} < \text{K00} < \text{K06} < \text{K04}$. These results indicate that the amount of clinoptilolite and mordenite increased and the amount of feldspar decreased as rotational speeds of classifier wheel increased. The particle size distributions of the samples were

Table 1. Relative XRD peak intensities of minerals.

	Clinoptilolite	Mordenite	Feldspar
K12	128	136	39
K10	126	140	42
K08	97	126	83
K06	84	103	155
K04	59	88	199
K00	100	100	100

Fig. 1. X-ray diffraction patterns of (a) K00, (b) K04, (c) K06, (d) K08, (e) K10 and (f) K12. ●: mordenite. ◆: clinoptilolite. ◇: feldspar. □: illite.

Fig. 2. Particle size distribution of K00 (●), K04 (×), K06 (○), K08 (◇), K10 (□), and K12 (Δ).

measured by laser diffraction, as shown in Fig. 2. The particle size distributions of the air-classified samples were sharp. But the distribution of unclassified one was very broad and showed small several peaks. The average particle size of the air classified samples decreased systematically as the rotational speeds of classifier wheel increased; 6.3 μm , 9.4 μm , 13.2 μm , 20.6 μm and 35.6 μm for the samples treated at 12000 rpm, 10000 rpm, 8000 rpm, 6000 rpm and 4000 rpm, respectively. The zigzag air classification effectively made a precise separation. Because the hardness and specific density of constituent minerals in the sample were different, the separation of zeolites and impurities also should be

performed. The speculation was consistent with those obtained by the above XRD results. The chemical compositions of minerals in untreated sample; clinoptilolite, mordenite, feldspar and illite are determined by EDX analysis (Table 2). These morphologies and chemical compositions corresponded with those of published studies.[7, 18,19] The Si/Al mole ratios of clinoptilolite and mordenite are higher than those of feldspar and illite. The illite contains significant Fe and Mg, and the feldspar richly contains significant Na as compared with clinoptilolite and mordenite. The chemical compositions of the samples before and after air classification determined by ICP are shown in Table 3. As the speeds of classifier wheel increased, the Si/Al mole ratio increased and the amounts of Na decreased systematically. These results indicate that the amounts of clinoptilolite and mordenite increased, and that of feldspar decreased after the air-classification. The amounts of Fe and Mg in their samples were almost constant before and after the air classification. XRD and chemical analyses of untreated and air-classified samples concluded that the present zigzag air classification was effective at reducing the amount of impurities, especially feldspar, of the Korean natural zeolite.

3.2 Ammonium adsorption behavior

The ammonium adsorption isotherms of the samples in ammonium chloride solution are shown in Fig. 3. The sample K12 showed the highest ammonium adsorption capacity among the samples, with a capacity of 0.93 mmol/g in 10 mmol/L NH_4Cl , which was 1.2 times as much as that of K00. Ammonium adsorption capacity decreased in the order of K12 > K10 > K8 > K00 > K06 > K04. This order was observed to correspond to both decreasing amount of zeolites (clinoptilolite and mordenite) and increase of impurity (feldspar) in the samples with the decrease of wheel speed of classifier in the previous section. So this phenomenon can be explained by the difference in component percentages of minerals among the samples. K12 was identified to be sample with the largest amount of clinoptilolite and mordenite and with smallest amount of feldspar among the samples. The

Table 2. Chemical compositions of minerals by EDX analysis (wt%).

	Clinoptilolite	Mordenite	Feldspar	Illite
Si	38.2	36.0	31.2	20.2
Al	6.5	6.9	12.1	7.2
Fe	N.D.	N.D.	N.D.	15.6
Mg	N.D.	N.D.	N.D.	8.7
Ca	2.5	1.8	2.8	N.D.
Na	1.3	1.3	4.7	N.D.
K	1.7	4.3	2.2	4.9
Si/Al	5.64	5.01	2.47	2.69

(mole ratio)

N.D. = not detected.

Table 3. Chemical compositions of unclassified and air-classified samples (wt%).

	K12	K10	K08	K06	K04	K00
Si	29.4	29.5	29.6	29.7	30.0	29.7
Al	6.47	6.57	6.80	7.33	7.74	6.94
Fe	0.95	0.96	1.00	1.01	0.87	0.98
Ca	1.66	1.71	1.78	1.95	2.13	1.77
Mg	0.50	0.52	0.55	0.54	0.39	0.49
Na	0.89	0.90	1.14	1.40	1.85	1.33
K	1.61	1.53	1.71	1.70	1.80	1.90
Si/Al	4.36	4.31	4.18	3.89	3.72	4.11

(mole ratio)

above order was also observed for the change of the particle size distribution of the air-classified samples (Fig. 2). Kang et al. compared the cation exchange capacities of Korean natural zeolite with different particle sizes by pulverizing and sieving.[20] They showed the magnitude of the measured cation exchange capacity was not significantly affected by the particle size. It is explained in most of the cation-exchange sites of zeolite exist in the pores and that the number of cation-exchange sites do not increase by pulverizing. The ammonium adsorption capacity of K12 is comparable to the high purity natural zeolite (clinoptilolite) from Shimane Prefecture, Japan.[8] K12 has similar but slightly higher exchange capacity than other previously reported zeolites.[1] The present results indicated that zigzag air classification was effective in improving ammonium adsorption of Korean natural zeolite as a direct result of the reduction of the amount of impurity, especially feldspar, from the natural zeolite. These results will be useful as a basic research for efficient removal of the ammonium ions from wastewater using natural zeolites.

Fig. 3. Ammonium adsorption isotherms of K00 (●), K04 (×), K06 (○), K08 (◇), K10 (□), and K12 (Δ).

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