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Yujiro Watanabe[a][b]; Hirohisa Yamada[b]; Junzo Tanaka[b]; Yu Komatsu[c]; Yusuke Moriyoshi[a]
[a] Faculty of Engineering, Hosei University, Tokyo, Japan [b] National Institute for Materials Science, Tsukuba, Ibaraki, Japan [c] Faculty of Engineering, Kanazawa Institute of Technology, Nonoichi, Ishikawa, Japan

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Ammonium Ion Exchange of Synthetic Zeolites: The Effect of Their Open-Window Sizes, Pore Structures, and Cation Exchange Capacities

Yujiro Watanabe,[1,2,*] Hirohisa Yamada,[2] Junzo Tanaka,[2] Yu Komatsu,[3] and Yusuke Moriyoshi[1]

[1]Faculty of Engineering, Hosei University, Koganei, Tokyo, Japan
[2]National Institute for Materials Science, Tsukuba, Ibaraki, Japan
[3]Faculty of Engineering, Kanazawa Institute of Technology, Nonoichi, Ishikawa, Japan

ABSTRACT

Ammonium ion exchange behavior of synthetic zeolites, i.e., sodalite (SOD), rho zeolite (RHO), Linde type A zeolite (LTA), and faujasite zeolite (FAU), was investigated by changing the initial concentration of ammonium ions and reaction time. Ammonium ion exchange behavior was dependent on the open-window sizes, the pore structures, and the cation exchange capacities of these zeolites. Regarding sodalite with Na^+ ions (Na-SOD), ammonium ion exchange did not completely

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*Correspondence: Yujiro Watanabe, Faculty of Engineering, Hosei University, 3-7-2 Kajinocho, Koganei, Tokyo 184-8584, Japan; E-mail: WATANABE@yujiro.nims.go.jp.

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occur at the equilibrium state because the open-window size is smaller than the diameter of ammonium ions. Regarding RHO with Na^+ and Cs^+ ions (NaCs-RHO), the larger cations, Cs^+ ion, in the cages obstructed the ion exchange at the initial stage. However, the amount of exchanged ammonium ions gradually increased with increasing reaction time, finally achieving equilibrium. Regarding LTA with Na^+ ions (Na-LTA), the amount of exchanged ammonium ions decreased with increasing reaction time, and then reached plateau. It indicated that both the ion exchange on the α-cages and physical adsorption on the β-cages occurred at the initial stage, which was followed by the equilibrium state of ion exchange on the α-cages. Regarding FAU with Na^+ ions (Na-FAU), no dependence on reaction time was observed, because the size of the open-windows is large enough for ion exchange of ammonium ions. The Na-FAU, which has the biggest open-windows among these zeolites, showed the highest exchange capacity for ammonium ions, 3.20 mmol/g.

Key Words: Ammonium; Ion exchange; Open-window size; Pore structure; Synthetic zeolite.

INTRODUCTION

Municipal wastewater often contains a considerable amount of ammonium ions, which causes an environmental problem. The ions are discharged after the primary process of flocculation and sedimentation, and the secondary process of biological treatment. The increase in an ammonium level causes increases in biochemical oxygen demand and chemical oxygen demand in rivers and lakes. Therefore, the establishment of a process to reduce the quantity of ammonium ions is needed. The use of activated carbon has been proposed for this purpose,[1] but this is comparatively expensive.

Zeolites are crystallites composed of hydrated aluminosilicates with exchangeable cations. The aluminosilicate portion of the structure is a 3-dimensional open framework consisting of a network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing of all the oxygen atoms. Zeolites have periodic- and molecular-sized pores and channels in their unique structure. Therefore, they have high cation exchange capacity, high ion adsorption capacity, and high ammonium ion selectivity.[2] The high affinity of zeolites for ammonium ions and the slow release of ammonium ions from them are of special interest for minimizing environmental pollution in municipal and industrial wastewater.

Natural zeolites, such as clinoptilolite and mordenite, are found in abundance in many locations. These are widely used as a low-cost ion exchanger.

The use of zeolites for the removal of ammonium ions from wastewater has been reviewed by a number of researchers.[3–8] Furthermore, zeolites have been proposed as an alternative to activated carbon and also can be used as a pretreatment material prior to biological processing to ensure a constant concentration feed to a biological treatment plant. In our previous studies, the ammonium ion exchange behavior of natural clinoptilolite and mordenite that have similar pore sizes and cation exchange capacities (CEC) was investigated with ammonium chloride solution. Natural zeolites are rich in clinoptilolite having the highest ammonium ion exchange capacity of 1.32 mmol/g.[3,8]

More than 100 different species of synthetic zeolites have been identified.[9] Among them, Linde type A (LTA) zeolite with α-cages and β-cages, and faujasite (FAU) zeolite with β-cages and super cages are the two most important zeolites that have been extensively used in industries for ion exchange, adsorption, catalysis, and other aspects. Studies of ammonium ion exchange with a sodium form of synthetic LTA and FAU have been carried out by various researchers till now.[2,10–14] Sodalite (SOD) and rho zeolite (RHO) are known as a zeolite with only β-cages[14,15] and a zeolite with α-cages,[16] respectively. These have been studied for applications ranging from catalysis to adsorption and ion exchange.[14–19]

In the present study, the behavior of ammonium ions in ion exchange on synthetic zeolites such as SOD with Na^+ ions (Na-SOD), RHO with Na^+ ions and Cs^+ ions (NaCs-RHO), LTA with Na^+ ions (Na-LTA), and FAU with Na^+ ions (Na-FAU) was investigated. In particular, the effects of the cage sizes, open-window sizes, pore structures, and CEC of the zeolites on ammonium ion exchange were examined to find the best candidate for ammonium adsorption from wastewater.

EXPERIMENTAL METHODS

Preparation of Zeolites

The synthesis of Na-SOD was performed under hydrothermal conditions by a modified procedure derived from the pioneering work of Barrer and coworkers.[14,15] A mixture of 1.802 g of SiO_2 (High Pure Chemical Co., Ltd., Japan), 1.529 g of Al_2O_3 (High Pure Chemical Co., Ltd., Japan), and 24.0 g of NaOH (Wako Pure Chemical Industries, Ltd., Japan) (the molar ratio, $SiO_2 : Al_2O_3 : NaOH = 2 : 1 : 40$) was dissolved in 50 mL of distilled water contained in a 100 mL Teflon cup fitted into a stainless steel pressure vessel (San-ai Scientific Co., Ltd., Japan), and heated at 150°C under autogenous pressure for 7 days.

NaCs-RHO was prepared by using a method similar to that of Robson et al.[16] Twelve grams of NaOH (Wako Pure Chemical Industries, Ltd., Japan) were dissolved in 19.4 mL of distilled water, and 9.33 g of aluminum hydroxide hydrate ($Al(OH)_3 \cdot xH_2O$(Aldrich Chemical Co., Inc.) was added to this solution with warming at 80°C. The solution then was cooled down and mixed with 12 mL of 50 wt% CsOH (purity 99.9%; Aldrich Chemical Co., Inc., USA) solution. Finally, the resulting solution was blended with 100 g of 30 wt% colloidal silica (Ludox HS-30: Aldrich Chemical Co., Inc., USA) by vigorous mixing to make the colloid homogeneous solution. During incubation of the solution at room temperature for 7 days, it turned to gel, and the gel, in a sealed Teflon container, then was heated at 85°C for 7 days. The molar ratio of the compositions of the gel was $Na_2O : Cs_2O : Al_2O_3 : SiO_2 : H_2O = 3 : 0.4 : 1 : 10 : 110$.

The Na-LTA and Na-FAU were supplied in a powder form by Wako Pure Chemical Industries, Ltd., Japan.

The zeolites described above were characterized by a powder x-ray diffraction (XRD) method with Cu Kα radiation (RIGAKU: RINT2200) and by scanning electron microscopy (SEM) (HITACHI: S-5500). Their chemical compositions were determined by inductively coupled plasma spectroscopy (ICP) (SEIKO: HVR1700). The solutions for ICP were prepared as follows: on Si and Al, 50.0 mg of the synthetic zeolites were melted with Na_2CO_3 and H_3BO_3 at 1000°C. The mixtures were dissolved in a HCl solution after cooling, and distilled water was added to the solutions to obtain the final volume of 100.0 mL. On Na^+, K^+, Ca^{2+}, and Mg^{2+}, 50.0 mg of the synthetic zeolites were dissolved in HF and H_2SO_4 solutions. After the solutions were evaporated, the dried residues were dissolved in a HCl solution at 60°C, and distilled water was added to the solutions to obtain a final volume of 100.0 mL. A photomultiplier tube was used as detector for ICP. The detection limits of ICP were 2×10^{-3} ppm of Na^+ and Si^{4+}, 4×10^{-3} ppm of Al^{3+}, 4×10^{-5} ppm of Ca^{2+} and Mg^{2+}, and 3×10^{-2} ppm of K^+.

Ammonium Ion Exchange

The experiments of ammonium ion exchange were carried out in two stages. Firstly, the effect of reaction time on ammonium ion exchange was examined. Thirty milliliters of a 10^{-2} M ammonium chloride solution were added to 0.1 g of synthetic zeolites in polyethylene tubes. The tubes then were shaken at 30 rpm by an end-over-end shaker (Towa Labo RKVSD 10101) at 25°C for 1 min to 7 days. The resultant suspensions were filtered with 0.45-μm membrane filters (Millipore, HA-type) at various reaction times. The ammonium concentrations of the filtered solutions were determined by using an ammonium ion-specific electrode (Toa Denpa Kogyo IM-20B, Ammonia Electrode Ae-235). The amounts of exchanged ammonium ions were calculated from differences between the concentrations of ammonium ions in the filtered solutions and that in the initial solution.

Secondly, the effect of the initial concentration of ammonium ions on ion exchange was examined. Thirty milliliters of ammonium chloride solutions whose ammonium concentrations ranged from 10^{-4} to 3×10^{-2} M were added to 0.1 g of synthetic zeolites in polyethylene tubes. The tubes were shaken at 30 rpm by an end-over-end shaker (Towa Labo RKVSD 10101) at 25°C for 7 days. The suspensions were filtered with 0.45-μm membrane filters (Millipore, HA-type). The ammonium concentrations of the filtered solutions were determined by using an ammonium ion-specific electrode (Toa Denpa Kogyo IM-20B, Ammonia Electrode Ae-235). The amounts of exchanged ammonium ions were calculated from differences between the concentrations of ammonium ions in the filtered solutions and those in the initial solutions.

RESULTS AND DISCUSSION

Structures and Compositions of Synthetic Zeolites

The powder XRD patterns and SEM images of the zeolites obtained are shown in Figs. 1 and 2, respectively.

The powder XRD pattern in Fig. 1(a) demonstrates Na-SOD as having no impurity and high crystallinity, as previously reported.[14] The grain size of Na-SOD was about a few hundred nanometers [Fig. 2(a)]. The chemical formula determined by ICP was the same as that of reported sodalite with Na^+ ions, $Na_8(AlSiO_4)_6(OH)_2 \cdot nH_2O$.[9,14]

The XRD pattern of NaCs-RHO in Fig. 1(b) agreed well with that of NaCs-RHO shown in a previous study.[16] The NaCs-RHO obtained in the present study had high crystallinity with no impurity. Morphologically, NaCs-RHO zeolite formed 0.5-1-μm rhombododecahedral crystals [Fig. 2(b)]. The chemical formula determined by ICP was $Na_7Cs_4(AlO_2)_{11}(SiO_2)_{37} \cdot nH_2O$ per unit cell. This result is slightly silica rich compared with the chemical formula reported by previous studies.[9,16]

The powder XRD patterns of Na-LTA [Fig. 1(c)] and Na-FAU [Fig. 1(d)] were the same as those of LTA and FAU with Na^+ ions, respectively, reported previously.[2] The chemical compositions of Na-LTA and Na-FAU determined by ICP were $(Na_{12})(Si_{12}Al_{12}O_{48}) \cdot nH_2O$ and $Na_{84}(Al_{84}Si_{108}O_{384}) \cdot nH_2O$, respectively, which were the same as those expected for LTA with Na^+ ions[9] and FAU with Na^+ ions ($Na_xAl_xSi_{192\text{-}x}O_{384} \cdot nH_2O$ $x = 77$–

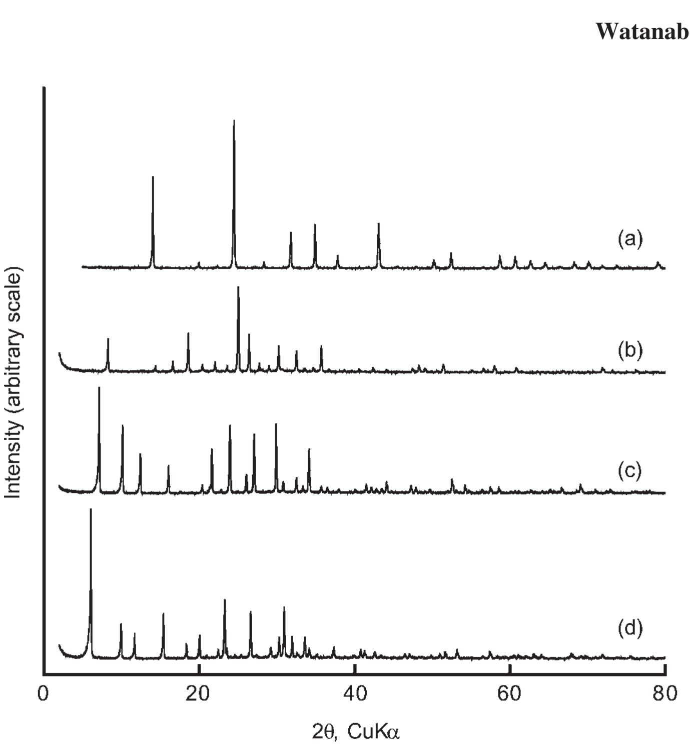


Figure 1. XRD patterns of the synthetic zeolites. (a) Na-SOD, (b) NaCs-RHO, (c) Na-LTA, and (d) Na-FAU.

96).[2] The Na-LTA was found to be the intergrowth of typical cubic crystallites of micrometer size [Fig. 2(c)] and Na-FAU was found to be the aggregate or intergrowth of fine octahedral crystallites of submicrometer size [Fig. 2(d)].

Ammonium Ion Exchange on Synthetic Zeolites

The relationship between the amounts of ammonium ions exchanged on the zeolite and the reaction times is shown in Fig. 3. Initial ammonium concentration was 10^{-2} M. The amounts of synthetic zeolites were 0.1 g. The amounts of ammonium ions exchanged on the samples were calculated from differences between the concentrations of ammonium ions in the filtered solutions and that in the initial solution.

Regarding Na-SOD, a small amount of ammonium ions, 0.60 mmol/g (about 20% of the original amount) was exchanged at the initial stage, but the amount of exchanged ammonium ions decreased with reaction time.

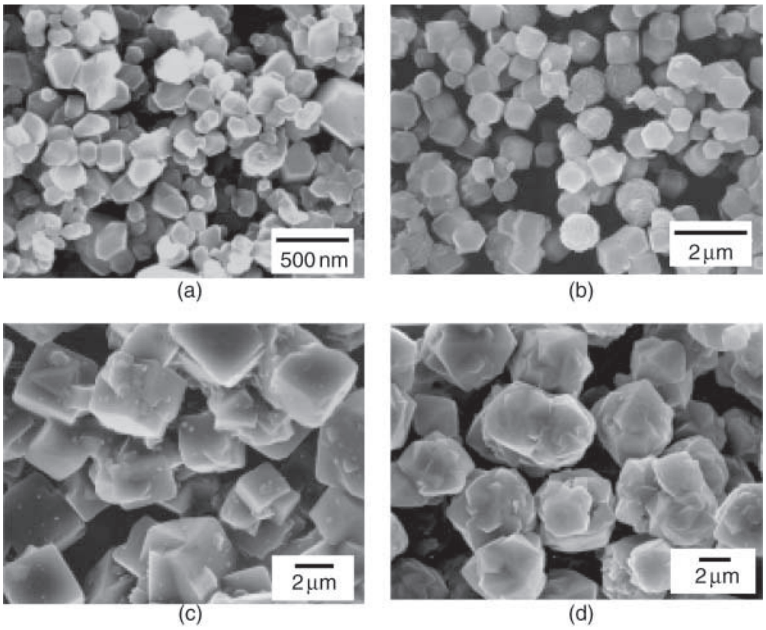


Figure 2. SEM photographs of the synthetic zeolites. (a) Na-SOD, (b) NaCs-RHO, (c) Na-LTA, and (d) Na-FAU.

After 7 days, about 10,000 min, no ion exchange was observed. Regarding NaCs-RHO, the amount of exchanged ammonium ions, 1.37 mmol/g (about 46% of the original amount) increased at 1–10 min, but after that, the amount of the ions became changeless. Regarding Na-LTA, the amount of exchanged ammonium ions increased at the initial stage and decreased at 1–10 min, and after that the amount of the ions became changeless. The value of the equilibrium state was 1.77 mmol/g (about 52% of the original amount). There was no such dependence on reaction time in Na-FAU. The value of the equilibrium state was 2.00 mmol/g (about 60% of the original amount). After the ammonium ion exchange, the crystal structure of these zeolites was confirmed as unchanged by the XRD patterns.

The framework structures of zeolites are schematically shown in Fig. 4. The structure of SOD is formed by placing β-cages (sodalite cages) on the body-centered cubic lattice [Fig. 4(a)]. There are relatively small windows of 2.2 Å in free diameter, which are smaller than the diameter of ammonium ions (2.9 Å). The framework of RHO consists of α-cages joined together by double eight-membered rings [Fig. 4(b)], and the size of the open-window is 3.6 Å which is slightly larger than that of ammonium ions. In LTA, large

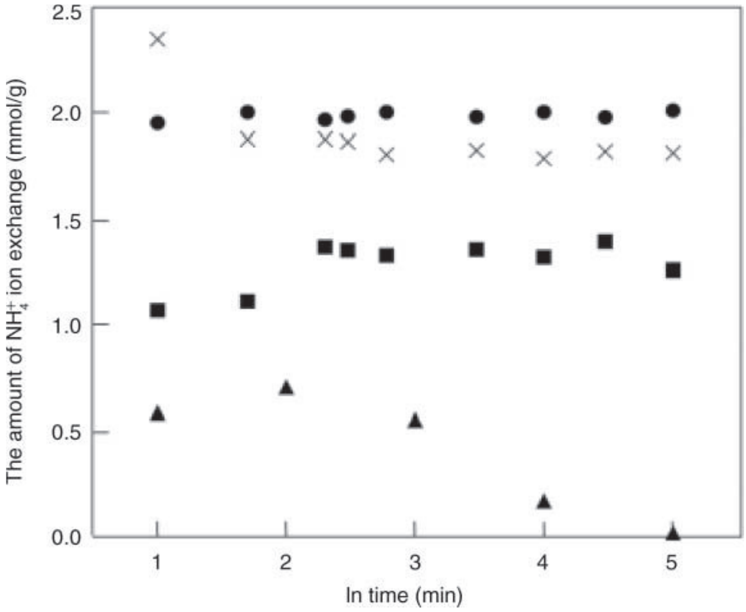
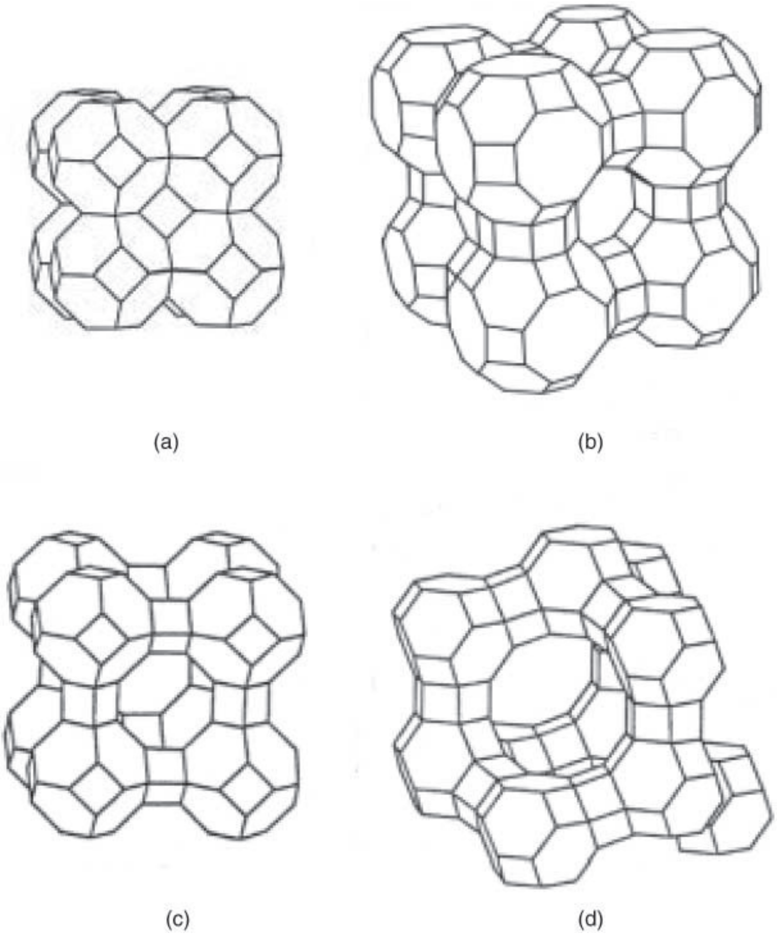


Figure 3. The relationship between the ion exchange amount of ammonium ion and the reaction time. Initial ammonium concentration: 10^{-2} M, amount of zeolite: 0.1 g ▲: Na-SOD, ■: NaCs-RHO, ×: Na-LTA, ●: Na-FAU.

cages (α-cages) with an inner diameter of about 11 Å are surrounded by eight β-cages linked by double four-membered rings [Fig. 4(c)]. The α-cages are arrayed in a simple cubic structure and are connected by shared windows with an inner diameter of about 5 Å. The size of the open-window is dependent on the type of exchangeable cations in the cages. The open-window size of Na-LTA is about 4 Å. The framework of FAU consists of β-cages linked by double six-membered rings [Fig. 4(d)]. In the FAU structure, the β-cages stack in the same way, the same as carbon atoms in diamond. The pore opening of Na-FAU is about 7.4 Å, which is largest among the presently studied zeolites.

Regarding the β-cages of Na-SOD, physical adsorption probably occurred at the initial stage but no ion exchange was observed at the equilibrium state. This conclusion is supported by the open-windows size of the β-cages of Na-SOD, which is smaller than that of ammonium ions.

The open-windows of the other three zeolites are larger than ammonium ions, which make ammonium ion exchange possible. Regarding RHO, the size of the open-windows in the α-cages is barely larger than ammonium ions.



(a) (b)

(c) (d)

Figure 4. The schematic representation of the framework structure of zeolites. (a) SOD, (b) RHO, (c) LTA, and (d) FAU.

Furthermore, large cations, Cs^+ ions, in the α-cages make the actual size of the open windows smaller. Therefore, the ion exchange of ammonium ions was more or less blocked in RHO in the present study. A similar behavior has been observed in previous studies of the ion exchange of Ag^+ ions.[19] Because of these reasons the amount of exchanged ammonium ions probably increased with increasing of the reaction time at the initial stage, and then the equilibrium state was reached in RHO. Regarding LTA, the amount of exchanged ammonium ions decreased with increasing of the reaction time, and then reached a plateau. It indicates that both the ion exchange on the α-cages and the physical adsorption on the β-cages occurred at the initial stage, which was followed by the equilibrium state of ion exchange on the α-cages. Regarding Na-FAU, no dependence on reaction time was observed, because the size of the open-windows is largest among the zeolites and large enough for ion exchange of ammonium ions. The result of Na-FAU also is supported by a case for ammonium ions to move inward. Therefore, instantaneous equilibrium was not achieved in ion exchange of Na-FAU.

Figure 5 shows the relationship between the exchanged amounts of ammonium ions and the concentrations of ammonium ions. The exchange capacities of Na-SOD, NaCs-RHO, Na-LTA, and Na-FAU calculated from their chemical formulas in this study as well as published data of other zeolites are shown in Table 1. Regarding Na-SOD, ammonium ion exchange was expected to happen in the various concentrations of ammonium ions at the equilibrium state, because the CEC of Na-SOD calculated from the chemical formula was 6.4 mmol/g, which is higher than those of clinoptilolite and mordenite (Table 1). But ammonium ion exchange did not completely occur at the equilibrium state (Fig. 5), because the open-window size is smaller than the diameter of ammonium ions.

Ammonium ion exchange occurred in other three synthetic zeolites because their open-window sizes are lager than the diameter of ammonium ions. The type of isotherm curves corresponded with the Langmuir type.

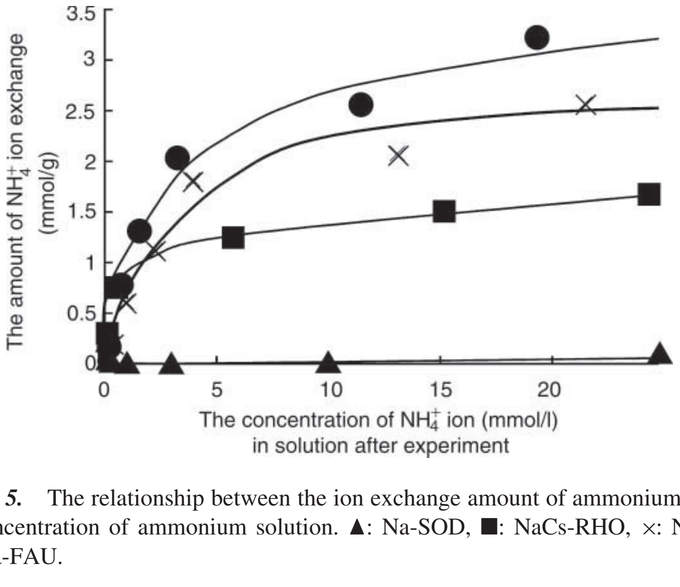


Figure 5. The relationship between the ion exchange amount of ammonium ion and the concentration of ammonium solution. ▲: Na-SOD, ■: NaCs-RHO, ×: Na-LTA, ●: Na-FAU.

Table 1. Exchange capacities of various zeolites.

Zeolite	CEC (mmol/g) anhydrous	Maximum ammonium exchange capacity (mmol/g)	Reference
Na-SOD	6.4	0	
NaCs-RHO	3.1	1.65	
Na-LTA	7.0	2.56	
Na-FAU(X)	6.4	3.20	
Clinoptilolite	2.6	1.35	[3]
Mordenite	2.6	1.05	[3]
Na-FAU(Y)	4.3	3.04	[10]

The curve occurs in probably a majority of cases of adsorption from dilute solution. The initial curvature shows that as more sites in the zeolites are filled, it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available.[20,21] Regarding NaCs-RHO, the ammonium ion exchange was higher than that of Na-LTA and Na-FAU at low ammonium concentrations. These results are not easy to explain precisely for a complex reaction, but the effect of Cs^+ ions on RHO is one probable factor. The maximum capacity was 1.65 mmol/g of ammonium. The value was lower than those of Na-LTA (2.56 mmol/g) and Na-FAU (3.20 mmol/g). The ammonium ion exchange mechanism is probably explained by Na^+ (Cs^+) exchange on zeolites occurring by the following ion exchange reaction [Eq. (1)].

$$\mathrm{Na(Cs)\text{-}Ze} + \mathrm{NH_4^+} - \mathrm{NH_4\text{-}Ze} + \mathrm{Na^+(Cs^+)(Ze : zeolite)} \qquad (1)$$

It is apparent that Na^+ ions bind very weakly to the structure of zeolites because the hydrogen energy of Na^+ ions is lower than other cations.[2]

Based on this reaction, the main factor that influenced the results is explained that the CEC of NaCs-RHO (3.1 mmol/g) calculated from the chemical formula is smaller than those of Na-LTA (7.0 mmol/g) and Na-FAU (6.4 mmol/g) (Table 1). But this explanation is not applied when the CEC of Na-LTA is compared with that of Na-FAU. The latter is better explained by ammonium ion selectivity of these zeolites. The selectivity is Na-FAU > Na-LTA when the percentages of ammonium ion exchange on these zeolites is higher than 10%.[2] Also added to the explanation is that the size of the open-windows of Na-FAU (7.4 Å) is not only larger than that of Na-LTA but also considerably larger than the diameter of ammonium ions (2.9 Å), therefore, physical ammonium adsorption was maintained at the equilibrium state. The Na-FAU showed the highest exchange capacity for ammonium ions among the synthetic zeolites tested in the present study as well as other zeolites reported previously[3,11] (Table 1). The maximum amount of ammonium ion exchange was 3.20 mmol/g. From these results and discussion, we conclude that the factors influencing ammonium ion exchange are ammonium ion concentration, reaction time of zeolite with ammonium ions, the open-window size, the pore structure of zeolite, and the cation exchange capacity of zeolite.

CONCLUSION

The behavior of synthetic zeolites, i.e., Na-SOD, NaCs-RHO, Na-LTA, and Na-FAU, in ammonium ion exchange was investigated at 25°C. The ammonium ion exchange activity of these zeolites was dependent on their open-window sizes, pore structures, and cation exchange capacities. The Na-FAU, which has the largest open-windows among these zeolites, showed the highest exchange capacity of ammonium ions, and, therefore, we conclude that this zeolite is an ideal candidate for the removal of ammonium ions from municipal wastewater.

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