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Carbon Dioxide Adsorption Properties in Ion-exchanged Zeolites Rho

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The carbon dioxide adsorption properties of zeolite Rho materials, containing various exchangeable cations have been investigated. All carbon dioxide adsorption properties were measured at a temperature of 25 °C over a pressure range of 0–100 kPa. The results show that the carbon adsorption properties are dependent on the cations present. The highest amount of CO_2 absorbed, measured at 4.0 mmol g^{-1}, was obtained for a proton-exchanged zeolite Rho (HRho), which was prepared by the calcination of NH_4^+-exchanged zeolite Rho at 350 °C.

Zeolites are crystalline microporous aluminosilicates that can be used as molecular sieves, catalysts, and ion-exchange agents.[1] In particular, a number of studies into the separation of CO_2 from gas mixtures using zeolites have been published. CO_2 emissions, derived from fossil fuels, have become a serious concern in relation to global warming.[2–4] Zeolites consist of an open three-dimensional structure made up of TO_4 tetrahedra (T = Si and Al).[5] Exchangeable cations are present in the cavities to balance the negative charges resulting from the aluminum atoms in the framework. Zeolites have attracted significant attention as the diameters of the cages and channels can be controlled to modify the ion-exchange properties, the valence states, and the sizes of the exchangeable cations.[6] Thus, the adsorption properties of zeolites will depend on the nature of cations, because the electric field gradients within the cages or channels, and acidic or basic characteristics, will vary according to the type of cation.[5]

Our previous studies have reported the CO_2 and N_2 adsorption properties for zeolite Rho, as prepared by hydrothermal synthesis using 18-crown-6 (18C6).[7] The NaCsRho zeolite has small pores (3.6 × 3.6 Å) and a low Si/Al ratio (2.5–3.0).[8] The ratio of CO_2 to N_2 adsorbed for zeolite Rho was higher than that for NaX and AlPO-34. The amount of CO_2 adsorbed with Rho zeolite is higher than that for AlPO-34 but lower than that for NaX. In this study, we investigate the carbon dioxide adsorption properties of zeolite Rho materials, containing Na^+, Cs^+, NH_4^+, H^+, and Ca^{2+}, to determine the role of the exchangeable cation.

The NaCsRho zeolite was prepared by hydrothermal synthesis as previously reported.[9] The initial mixture was prepared using colloidal silica, sodium aluminate, sodium hydroxide, cesium hydroxide, sodium hydroxide, and distilled water to provide SiO_2:Al_2O_3:Na_2O:CsO:18C6:H_2O with a molar ratio of 10:1:1.8:0.3:0.25:100. The mixture was aged at room temperature for 24 h under continuous stirring. The hydrothermal treatment was carried out at 110 °C for 96 h. Postreaction the solid was isolated by centrifugal separation (4000 rpm for 10 min) and washed with distilled water until the pH was neutral. The sample was dried overnight at room temperature. The NaCsRho was then calcined at 400 °C for 3 h. NH_4Rho and CaRho were prepared by ion exchange, using 0.01 M aqueous solutions of NH_4NO_3 and $CaCl_2$, respectively. For the Ca^{2+} ion exchange, the exchange procedure was repeated five times at 20 °C. HRho was prepared by the calcination of NH_4Rho at 350 °C for 3 h.

Powder XRD diffraction (XRD) patterns were obtained on RINT-TTR III (Rigaku, Japan) at 40 kV and 20 mA, with a 2θ range of 5–35°. Si, Al, Na, Ca, and Cs analyses were performed by EDX (GenesisXM2 EDAX). The concentrations of NH_4^+ in the supernatant were measured by ion chromatography (CTO-20AC, Shimazdu). FT-IR spectra were measured using an IR-Iffinity-1 (Shimazdu). CO_2 adsorption isotherms were measured at 25 °C on a Belsorp max (Bel Japan Inc.). All samples were treated at 150 °C for 3 h to deaerate.

The effects of ion-exchange operations on the XRD patterns are shown in Figure 1. All samples were confirmed to have signals derived from zeolite Rho and had no amorphous reflection at 2θ of about 25° or any other peaks. Thus, zeolite Rho was obtained with high crystallinity even after the ion-exchange procedure.

The relationship between the immersion time and the degree of substitution of Na^+ with NH_4^+ was confirmed. A concentration of 7 mmol g^{-1} NH_4^+ was exchanged after 1 min, which remained almost constant after 30 min. From the EDX measurements, the Na/Si ratio decreased from 0.20 to 0.04 after 30 min. Furthermore, the Cs/Si ratio decreased slightly from 0.079 to 0.073. It was confirmed that the Cs cations are difficult to exchange in comparison to Na cations. The NH_4Rho, which was used in the isotherm measurements, was prepared by immersion in 0.01 M aqueous NH_4NO_3 for 30 min. We then confirmed the calcination temperature required for the protonation of NH_4Rho. From FT-IR measurements, the sample calcined at 300 °C has peaks at 1402 and 1440 cm^{-1} that arise from the bound-bending

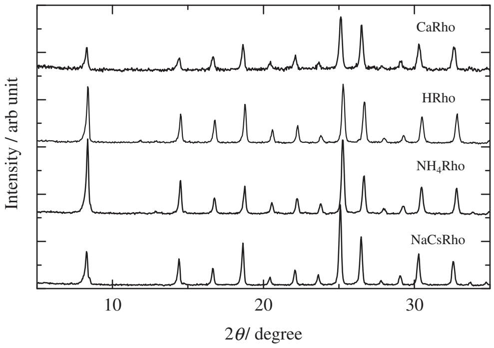

Figure 1. XRD pattern for zeolites Rho.

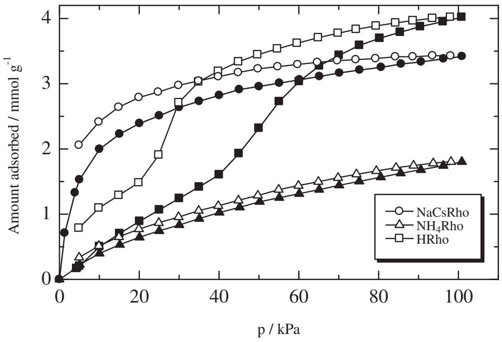

Figure 2. Adsorption (black) and desorption (white) isotherms for CO_2 at 25 °C.

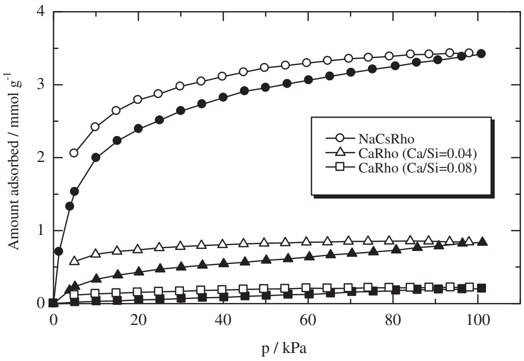

Figure 3. Adsorption (black) and desorption (white) isotherms for CO_2 at 25 °C.

frequencies of the ammonium ions. However, these peaks were not observed in the sample calcined at 350 °C. Therefore, protonation was accomplished upon calcination at 350 °C. Figure 2 shows the CO_2 adsorption and desorption isotherms for NaCsRho, NH_4Rho, and HRho. The amount of CO_2 adsorbed with NH_4Rho decreased to one-half of that for NaCsRho. The isotherms for NaCsRho and NH_4Rho were of a Langmuir type. The ionic radius of NH_4^+ is larger than that of the Na ion. Thus, this decrease is caused by the decrease in pore size and pore volume. On the other hand, the adsorption isotherm for the HRho rises at about 40 kPa, and hysteresis between the adsorption and desorption isotherms was observed. This implies that the increases in pore size or the changes in pore structure are caused by H^+ exchange, as the isotherm for HRho is a lot different from that of NaCsRho. The amount of CO_2 adsorption with HRho at 100 kPa increased from 3.4 to 4.0 mmol g^{-1}, which is an improvement of about 20% in comparison to NaCsRho. This improvement is also thought to be due to the increases in pore size or change in pore structure.

Based on the EDX results, the Na/Si ratio decreased from 0.20 to 0.11, and the Ca/Si ratio increased to 0.04, upon immersion in a 0.01 M aqueous $CaCl_2$ solution for 24 h. Moreover, the Na/Si ratio decreased to 0.02 and the Ca/Si ratio increased to 0.08 after the fifth immersion cycle. Conversely, the Cs/Si ratio remained at 0.08, regardless of the number of immersion cycles. The Cs cations were also difficult to exchange with Ca^{2+}. Figure 3 shows the CO_2 adsorption and desorption isotherms for CaRho, which has a Ca/Si ratio and isotherm different from NaCsRho. The CO_2 adsorption decreased with increasing Ca/Si ratio. CaRho with a Ca/Si ratio of 0.081 had a small CO_2 adsorption capacity of 0.2 mmol g^{-1}, which represents about 6% of that attainable with NaCsRho. With respect to zeolite A, the pore sizes for NaA and CaA are 0.3 and 0.48 nm, respectively. Thus, the pore size for CaA is larger than that of NaA. Montanari and Busca reported that the adsorption of CO_2 on KA is mostly limited to the external surface area, whereas the adsorptions for NaA and CaA occur mainly in the cavities.[10] Walton et al. reported that the CO_2 adsorption capacity for the X and Y zeolites increased with decreasing ionic radii.[5] Meanwhile, Yang et al. reported that CO_2 adsorption isotherm trends are not in direct agreement with the decreasing order of ionic radii.[11] They reported that the CO_2 adsorption capacity depends not only on the sizes and charges of the cations but also on their density and distribution throughout the framework. Furthermore, Langmi et al. proposed that the Ca^{2+} ions are large enough to occupy the eight-ring sites of zeolite Rho and adsorb hydrogen.[6] In this study, the partial blocking of pores with Ca^{2+} could partly explain the decrease in CO_2 adsorption.

In conclusion, the CO_2 adsorption efficiency of zeolite Rho was improved by approximately 20% upon the ion exchange of Na^+ for H^+. On the other hand, the amount of CO_2 adsorbed with CaRho and NH_4Rho decreased in comparison with NaCsRho. We propose that these results are caused by decreases in pore size and pore volume or the blocking pores. Cs^+ cations proved difficult to exchange with NH_4^+ or Ca^{2+}. Langmi et al. concluded that the hydrogen adsorption was inhibited by Cs^+ ions.[6] Similarly, there is a possibility that Cs^+ ions inhibit the CO_2 adsorption. The ion exchange of Cs^+ ions needs to be enhanced to improve the CO_2 adsorption properties.

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