Electronic Supplementary Information

Pure Silica CHA Type Zeolite for CO₂ Separation Using Pressure

Swing Adsorption at High Pressure

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Experimental details

Materials 11

Tetraethylorthosilicate, Iodomethane, dehydrated chloroform, anhydrous potassium carbonate, and hydrofluoric acid were purchased from Wako Pure Chemical Industries, Ltd. 1-Adamantylamine, Ludox[®] AS-30 colloidal silica, Ludox[®] AS-40 colloidal silica, tetraethylammonium hydroxide solution, and Dowex[®] 1x4 chloride form were purchased from Sigma-Aldrich. Anhydrous ethylenediamine, phosphoric acid, and aluminum isopropoxide was purchased from Nacalai Tesque, Inc. All reagents were used without further purification.

Synthesis of SDA for Si-CHA synthesis

N,*N*,*N*-Trimethyl-1-adamant ammonium hydroxide, which is a structure directing agent for synthesis of Si-CHA, was produced as follows. 1-Adamantylamine (4.667 g) was added to 50 g of dehydrated chloroform and completely

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dissolved at room temperature. Potassium carbonate (11.35 g) was mixed with the solution. Then, N_2 was introduced to the vessel for gas displacement, and the solution was cooled in an ice bath. Iodomethane (19.7 g) was mixed with the solution, and the mixture was stirred for 11 days. After filtering the solution to remove potassium carbonate, chloroform was evaporated. The residue was dissolved in methanol, refluxed at 363 K, then recrystallized. The obtained white crystals were mixed with anion-exchange resin in deionized water for 1 day. N,N,N-Trimethyl-1-adamant ammonium hydroxide crystals were obtained by evaporating the water.

Synthesis of Si-CHA

Si-CHA was synthesized according to the method reported by Camblor *et al.*¹ For synthesis of Si-CHA, tetraethyl orthosilicate was dissolved in *N*,*N*,*N*-trimethyl-1-adamant ammonium hydroxide aqueous solution (1 mol/L), and the solution was stirred overnight. After evaporation of water with vigorous stirring, hydrofluoric acid was added to adjust the pH to 7. The final composition of the synthesis sol was 1.0 SiO₂:0.8 *N*,*N*,*N*-trimethyl-1-adamant ammonium hydroxide:5.7 H₂O. Then, the mixture was introduced to a Teflon[®]-lined stainless steel autoclave and the hydrothermal synthesis was performed at 423 K with rotation at 5 rpm for 72 h. The product was filtered, washed, and then calcined at 853 K for 12 h.

Synthesis of Si-DDR

Si-DDR was synthesized according to an established method.² 1-Adamanthylamine (2.13 g) was dissolved in 7.27 g of ethylenediamine. AS-30 colloidal silica solution (6.0 g) was mixed with 26.3 g of deionized water, and this mixture was added into the 1-adamanthylamine/ethylenediamine mixture and stirred for 3 h at room temperature. Then, hydrothermal synthesis was carried out at 473 K with rotation at 5 rpm for 96 h. Products were filtered, washed with deionized water, and then calcined at 973 K for 4 h.

Synthesis of SAPO-34

SAPO-34 was synthesized according an established method.³ Aluminum isopropoxide (30 g) was dissolved in 122 g of phosphoric acid aqueous solution. After stirring for 12 h, 50.4 g of tetraethylammonium hydroxide was added, and the mixture was stirred for another 30 min. Then, 9.0 g of AS-40 colloidal silica was added, followed by stirring for 24 h. Hydrothermal synthesis was carried out at 473 K for 24 h with rotation at 5 rpm. Products were filtered, washed with deionized water, and then calcined at 823 K for 30 h.

All products were characterized by a scanning electron microscopy (SEM) observation (Fig. S5) and powder X-ray diffraction (XRD) measurement, exhibiting a single crystalline phase of each framework (Fig. S6). It was confirmed that the organic structure directing agent was efficiently decomposed after calcinations by a thermogravimetry (TG) analysis (Fig. S7).

CO₂ adsorption measurements

The CO₂ adsorption capacity in a single and CO₂/N₂ binary system was measured at 313 K with a BELSORP-BG (Bel Japan, Inc.) Approximately 2.0 g of the adsorbent was used for each measurement, and the adsorption isotherm was measured from 0 to 3.0 MPa total pressure. For the CO₂/N₂ binary system, each gas was introduced at approximately equivalent pressure to the sample chamber simultaneously. The adsorption amounts of CO₂ and N₂ were individually measured by combining a volumetric and gravimetric method.⁴ The CO₂ adsorption isotherm in the presence of water was also measured using the same equipment. In this case, saturated water vapor was supplied and pre-adsorbed before each measurement. Then, the CO₂ adsorption measurement was performed.

Breakthrough curve measurements

The breakthrough curve measurement was performed using equipment constructed in our laboratory (Fig. S8). Approximately 3.0 g of the sample was placed in a stainless steel column, and Ar was supplied at 313 K for an adequate time for displacement of the remaining air in the column. In wet conditions, oversaturated water vapor was also supplied to the column before starting a measurement by a humidifier. The total pressure in the column was then increased to 1.6 MPa. A mixture of CO_2/N_2 with approximately equimolar composition was supplied to the column at 313 K and 1.6 MPa. For the $CO_2-N_2-H_2O$ system, saturated water vapor was also supplied to the column by a humidifier. The concentrations of CO_2 and N_2 in the outlet flow were analyzed by two online gas chromatograph systems equipped with a thermal conductivity detector. The adsorption capacities of CO_2 and N_2 were estimated by comparison to a breakthrough curve of quartz sand, which was measured under the same conditions.

Figures



Fig. S1 Water adsorption isotherms on zeolites at 313 K. 13X (circle), SAPO-34 (rhombus), Si-DDR (triangle), and Si-CHA (square).



Fig. S2. CO_2 and water vapor adsorption isotherms on zeolite 13X at 313 K with co-existing of water from pre-sorption of water vapor. CO_2 : blue, H_2O : red.



Fig. S3 CO_2 and water vapor adsorption isotherms on Si-DDR at 313 K with co-existing water from pre-sorption of water vapor. CO_2 : blue, H_2O : red.



Fig. S4 Breakthrough curves for CO₂ (red) and N₂ (blue) in Si-CHA in the CO₂/N₂ binary system at 313 K and 1.6 MPa total pressure with a composition of $CO_2/N_2 = 50.2/49.8$. GHSV: 796 h⁻¹.



Fig. S5 SEM images of Si-CHA and Si-DDR



Fig. S6 XRD patterns of Si-CHA and Si-DDR



Fig. S7 TGA profile of Si-CHA and Si-DDR



Fig. S8 Schematic diagram of the equipment constructed in our laboratory for breakthrough curve measurements. For dry conditions, humidifier was not equipped.

References

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