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CO_2 adsorption over ion-exchanged zeolite beta with alkali and alkaline earth metal ions

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Zeolite beta with high aluminum content (BEA, Si/Al = 7.4) was synthesized and evaluated as a CO_2 capturing agent after conducting ion-exchange with various alkali and alkaline earth metal ions (Li^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}). The extent of ion-exchange was confirmed by ICP-AES, and textural properties of the samples were measured by XRD, SEM, and BET surface area measurement. CO_2 adsorption isotherms of the ion-exchanged beta samples up to 101.3 kPa were obtained at 273 and 298 K, and the corresponding heats of adsorption were estimated by the Clausius–Clapeyron equation. CO_2 adsorption capacity increased in the sequence of $K^+ > Na^+ > Li^+ > Ba^{2+} > Ca^{2+} \fallingdotseq Cs^+ > Mg^{2+}$, and all of the evaluated metal ions showed high adsorption selectivity to CO_2 over N_2. The best performance of K^+-exchanged beta was also confirmed by a breakthrough curve analysis. Cyclic CO_2 adsorption–desorption performance of the sample was also studied by TGA in a flow system, exhibiting stable cyclic runs accompanied by complete CO_2 desorption at 473 K.

1. Introduction

Carbon dioxide is a greenhouse gas, and its effect on global warming is a world-wide concern. The need to reduce anthropogenic CO_2 emissions has been the driving force to consider new approaches and novel ideas for CO_2 management [1], and carbon capture and storage (CCS) are considered to potentially be the most effective means to alleviate the problem. The most common method for CO_2 capture is via gas absorption, with monoethanol amine (MEA) being the most widely used solvent. The current amine based systems for CO_2 removal, however, suffer from a high energy requirement for solvent regeneration and corrosion [2]. Thus, alternative CO_2 processes for CO_2 removal via selective adsorption on solid media such as zeolites [3], activated carbons [4], hydrotalcite-like compounds [5], metal oxides [6], and metal organic frameworks (MOFs) [7] have also been studied. Solid adsorbents typically employ cyclic and multi module processes of adsorption and desorption, with desorption induced by either a pressure or temperature swing [8].

Bonenfant et al. [9] summarized the influence of the structural characteristics of zeolites on the CO_2 adsorption as follows: first, the basic properties of zeolites generated by the different electron densities of the framework oxygen allow strong adsorption of acidic molecules. The basic strength of these sites, in general, decreases with the electronegativity of exchangeable cations, such that the basic strength of zeolites containing Group 1A elements increases in the following order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. This kind of adsorption usually involves high heat of adsorption and is not desirable for CO_2 capture due to the high energy demanded for the adsorbent regeneration by desorption, and is more relevant to catalysis by strong basic sites [10]. Second, the gas adsorption by the zeolites is also determined by the polarizing power of the exchangeable cations and their distribution, size, and number, which influence the local electric field and the polarization of the adsorbed molecules on zeolites. In general, the polarizing power of the cations is inversely proportional to their ionic radius. This cation-quadrupole interaction is the most important CO_2 adsorption mechanism in zeolitic adsorbents. Third, the Si/Al ratio in zeolites affects the adsorption capacity and selectivity in polar molecules, which increases with a decrease in the Si/Al ratio. This effect is also increasingly important when the quadrupole moment of molecules is high, such as in CO_2. Finally, the pore size of zeolites is another factor that influences the capacity and rate of CO_2 adsorption. Obviously, the pore size must fall in a range where adsorbate molecules can penetrate the interior of the zeolite framework. The relationship between the CO_2 adsorption capacity and the zeolite pore size is known to be dependent on the total CO_2 pressure [9].

Many papers dealing with CO_2 adsorption on zeolite have been published. Montanari and Busca [11] investigated the mechanism of adsorption and separation of CO_2 on zeolite A. The adsorption of CO_2 on 3A (K^+ form) was mostly limited to the external surface area, whereas the adsorption on 4A (Na^+ form) and 5A (Ca^{2+} form)

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mostly occurred in cavities. Palomino et al. [12] synthesized zeolite A with different Si/Al ratios and reported that the sample with a lower Si/Al ratio showed higher CO_2 adsorption capacity, higher heat of adsorption, and higher CO_2/CH_4 selectivity. According to Walton et al. [13], CO_2 adsorption capacity increased as follows: $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ in both zeolite X and Y. Shao et al. [14] measured the CO_2 adsorption isotherm of NaY at 303 to 473 K, and concluded that NaY zeolite is capable of CO_2 separation from flue gas at reasonably high temperature. Harlick and Tezel [15] meanwhile reported that 13X is a suitable adsorbent for effective adsorbent regeneration at a low pressure condition whilst NaY is more suitable at a high pressure regeneration condition. Dunne et al. [16] investigated the heat of adsorption over adsorption isotherms of various gases on NaX, H-ZSM-5, and Na-ZSM-5 zeolite. For CO_2, adsorption capacity increased in the following order: H-ZSM-5 < Na-ZSM-5 < NaX. Heats of adsorption of CO_2 on NaX, Na-ZSM-5, and H-ZSM-5 were 49.1, 50.0, and 38.0 kJ/mol, respectively, whereas heat of adsorption of CO_2 for H-ZSM (Si/Al = 20) and Na-ZSM (Si/Al = 20) was 21 and 27 kJ/mol, respectively [17]. Ridha and Webley [18] reported low pressure CO_2 adsorption capacities of chabazite as follows: Li-chabazite (6.3 molecule/cavity) > Na-chabazite (5.9 molecule/cavity) > K-chabazite (4.8 molecule/cavity). Pulido et al. [19] measured the adsorption of CO_2 on Na-exchanged ferrierite (Na-FER). Na-FER with a high content of Na^+ cations (Si/Al = 8.7) showed a very large isosteric heat of adsorption of CO_2 (up to 52 kJ/mol); this strong interaction was attributed to the formation of linearly bridged CO_2 complexes on the dual-cation sites. Park et al. [20] reported CO_2 retention ability on various alkali cation-exchanged ETS-10 samples at different temperatures. The CO_2 adsorption capacity was in agreement with the trend in ionic radii, and was in the order of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Pillai et al. [21] measured CO_2 adsorption isotherms on Na-ETS-4 at 288, 303, and 318 K. The CO_2 adsorption capacity of Na-ETS-4 was increased from 64 to 73 ml/g as the temperature decreased and the corresponding heat of adsorption was 67 kJ/mol. Pawlesa et al. [22] calculated Henry's constants for CO_2 on MCM-49. The Li-MCM-49 sample showed the highest Henry's constant (44.3 cm^3/g, STP). Ion-exchanged MCM-22 was also tested for CO_2 adsorption [23]. The CO_2 adsorption capacity deceased as follows: $K^+ > Li^+ > Na^+ > Cs^+$. Heat of adsorption for K-MCM-22 zeolite was ca. 41 kJ/mol, and the heat of adsorption decreased in the order of $K^+ > Cs^+ > Li^+ > Na^+$.

Zeolite beta consists of an intergrowth of two or more polymorphs comprising a three-dimensional system of 12-membered ring channels [24] having pore diameters of 0.76 × 0.64 nm and 0.55 × 0.55 nm. Owing to large pore size, surface area, and pore volume with controllable Si/Al ratios accompanied by ion-exchange capacity, zeolite beta is a good candidate for CO_2 adsorption. Li et al. [25] determined the adsorption equilibrium and diffusion properties of CO_2, CH_4, N_2, and O_2 gases on zeolite beta by pulse chromatography in a temperature range of 313 to 373 K. CO_2 had the highest adsorption Henry's law constants at all the temperatures studied, and good adsorption equilibrium separation factors of CO_2 from O_2, N_2, and of CH_4 were confirmed. Xu et al. [26] employed zeolite beta in H^+ and Na^+ forms for the adsorption of CO_2, CH_4, and N_2. At a temperature of 303 K and a pressure of 0–1 atm, the selectivity of CO_2 over N_2 in Na^+ form (50.3) was higher than that in H^+ form (25.6). CO_2 showed higher initial heat of adsorption CO_2 (27.4 kJ/mol) than CH_4 (16.2 kJ/mol) and N_2 (16.4 kJ/mol), and, after ion-exchange with Na^+, the initial heats of adsorption increased significantly for CO_2 (49.9 kJ/mol), whereas CH_4 (19.6 kJ/mol) and N_2 (22.8 kJ/mol) showed relatively small increases. Xu et al. [27] modified zeolite beta with MEA (40 wt.%). However, no systematic investigation of CO_2 adsorption over ion-exchanged beta except Na^+ and H^+ forms has been reported. Furthermore, investigations on breakthrough behavior in a flow system would provide useful supplementary data to compare the sorption capacity and adsorption selectivity in zeolite adsorbents. Elucidation of the desorption properties in zeolite beta for alkali or alkaline earth metal ions is also desirable to determine suitable regeneration conditions.

In this work, we investigated the effects of ion-exchanged alkali and alkaline cations on CO_2 adsorption in zeolite beta in a systematic manner. Consulting earlier studies, high aluminum content zeolite beta (BEA, Si/Al = 7.4) in Na^+ form was synthesized first and, after ion-exchanging with various alkali and alkaline earth metal cations (Li^+, K^+, Cs^+, Mg^{2+}, Ca^{2+} and Ba^{2+}), we measured the CO_2 adsorption capacities of the ion-exchanged material using both static and flow systems at 273 and 298 K up to 101.3 kPa. The heats of adsorption were calculated, and CO_2 adsorption selectivity over N_2 was measured by breakthrough experiments. The stability of the ion-exchanged beta was tested by recycle runs with adsorption at 298 K and desorption at 423 or 473 K.

2. Experimental

2.1. Synthesis

Zeolite beta in Na^+ form was synthesized following the protocol reported by Borade and Clearfield [28]. Initially, 19.20 g of tetraethylammonium hydroxide (35% TEAOH in water, Aldrich), 3.15 g of sodium aluminate (70%, Yakuri, Japan), and 17.52 g of de-ionized water were mixed under stirring. To this solution, 16.20 g fumed silica (Cab-Sil M5, Cabot) was added and the resultant mixture was mechanically stirred for 2 h. Hydrothermal reaction was then conducted at 443 K for 36 h. The obtained product was washed with a sufficient amount of de-ionized water and dried at 373 K for 12 h. The dried product was finally calcined at 813 K for 4 h to remove the organic template.

The calcined zeolite beta powders (Na-BEA) were converted into alkali and alkaline earth metal ion-exchanged forms by conducting ion-exchange using 1.0 M aqueous solutions of metal chlorides (Li^+, K^+, Cs^+, Mg^{2+}, Ca^{2+} and Ba^{2+}); 1 g of Na-BEA was dispersed and stirred at 353 K for 8 h in a solution of the respective salt. The procedure was repeated four times, and each exchange was conducted with fresh solution. After filtering with de-ionized water, ion-exchanged samples were dried overnight in air at 393 K.

2.2. Characterization

The crystallinity of the ion-exchanged samples was measured by X-ray diffraction using CuKα radiation (Phillips, PW-1700). Nitrogen adsorption–desorption isotherms were measured using a Micromeritics ASAP-2020 instrument at 77 K. The specific surface area of the M-BEA samples was calculated by the Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) was performed using a Hitachi S-4300 electron microscope. Elemental analysis of the M-BEA (where M represents the ions exchanged) was conducted by ICP-AES (Spectro, Modular EOP) to quantify the amounts of ion-exchanged cation species.

2.3. Adsorption–desorption measurements

Adsorption isotherm data for CO_2 and N_2 on each ion-exchanged beta sample (M-BEA) were measured using a BELSORP-mini (BEL, Japan). Prior to the measurements, each sample was heated at 453 K for 6 h under a vacuum condition. The sample was then maintained at 273 and 298 K, respectively, during adsorption measurements using a constant temperature water bath equipped with ethanol coolant. Adsorption isotherms were obtained for each material at pressures up to 101.3 kPa.