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Novel improvement of CO_2 adsorption capacity and selectivity by ethylenediamine-modified nano zeolite

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ABSTRACT

In this study, nano zeolite (NZ) was modified with ethylenediamine (EDA) to improve the CO_2 adsorption–desorption properties. The CO_2 adsorption capacity of NZ-EDA increased as the temperature was increased from 20 °C to 70 °C, but then decreased as the temperature was further increased from 70 °C to 100 °C. The CO_2 adsorption capacity of NZ-EDA was 7.48 mmol/g, which is 2.6-fold more than that by NZ. The mechanism of CO_2 adsorption onto NZ is entirely physical interaction. With NZ-EDA, however, chemical interaction between CO_2 and NZ-EDA becomes the key adsorption mechanism. The adsorption selectivity of CO_2 over N_2 by NZ-EDA was influenced by temperature and peaked at 56.01 at 50 °C. The cyclic adsorption and desorption of CO_2 showed that the adsorbed CO_2 could be desorbed from the surface of NZ at 60 °C and NZ-EDA at 85 °C. The adsorption–desorption percentages of NZ and NZ-EDA remained above 80% even after 15 cycles. This stability of CO_2 adsorption–desorption characteristics after repeated cycling indicates that NZ-EDA can be a cost-effective sorbent for CO_2 capture.

1. Introduction

Global warming arising mainly from the greenhouse effect is affecting animal life worldwide through serious global climate change. CO_2 is the main contributor to global climate change and accounts for two thirds of the greenhouse gases produced by human activities such as combustion of fossil fuels and biomass [1–5]. The concentration of CO_2 in the earth atmosphere is increasing at an accelerating rate since the 1900s and reached 399 ppm in July 2014 [6]. To reduce CO_2 emissions from human activities, carbon capture and storage are considered important post-combustion capture activities or alternative measures to reduce the CO_2 concentration in the atmosphere and alleviate global warming [7–12]. Many researchers have tried to find ideal CO_2 sorbents with high capacity, high selectivity, fast adsorption/desorption kinetics, good mechanical properties, high hydrothermal and chemical stability, and low synthesis cost [13–17]. Adsorption appears to be a more promising technology due to its easy operation and low energy requirements. Chemical adsorption is particularly popular because of its associated high selectivity. Some adsorbents can also be prepared by functionalizing solid carriers with amines [18–19]. There have been some applications of amine-modified materials in CO_2 separation [20–22]. Solid sorbents have shown many potential advantages, including fast adsorption kinetics and low regeneration energy compared to amine-based CO_2 capture [19–21]. Among the solid sorbent studies, zeolite and metal–organic frameworks have been found to be excellent and inexpensive, solid CO_2 sorbents. However, the CO_2 adsorption capacity of these materials decreases drastically with increasing temperature. Zeolites with polar functionality, cationic frameworks, high surface area and large pore volume present a potential option for CO_2 capture. Amine-treated zeolites have been successfully used for CO_2 adsorption at moderate temperatures. In general, CO_2 adsorption increases with an increasing number of amine groups on the amine-treated adsorbents. In particular, nano zeolites (NZs) have recently received considerable attention for use as selective adsorbents for pollutants capture [23–27]. The reduction in the NZ particle size from the micrometer scale to the nanometer scale leads to substantial changes in its properties, which greatly affect the performance of zeolites in traditional application areas, particularly for adsorption processes. The aim of this study to analyze the impacts on the CO_2 adsorption capacity of NZ modified with ethylenediamine (EDA). This study also compared the physicochemical properties, adsorption capacity, selectivity and adsorption/desorption behaviors between NZ and the EDA-modified NZ (NZ-EDA) for CO_2 capture.

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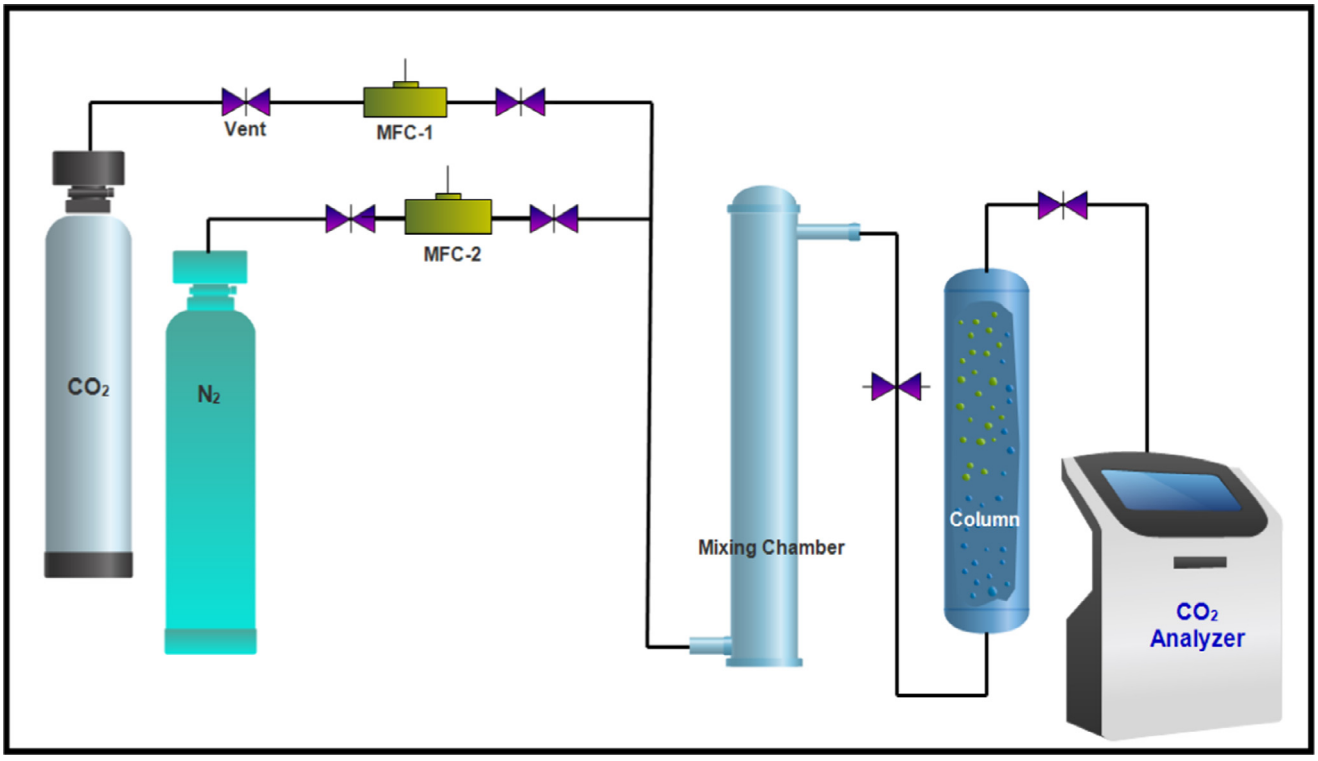

Fig. 1. CO_2 adsorption experiment system.

2. Materials and methods

2.1. Preparation of adsorbents

2.1.1. Modification of nano zeolite (NZ) by ethylenediamine (EDA)

The NZ was prepared in our lab and recent studies have shown the method used to synthesis of nano zeolite [43–45]. After a mixture of 0.35 g NaOH and 0.147 g sodium aluminate salt in H_2O was aged for 5 h at 20 °C, 6.6 g silica sol was added dropwise and the resulting mixture was stirred at room temperature for 24 h. The resulting homogenous mixture was heated for 24 h at 180 °C under autogenous pressure. The solid product was centrifuged and washed with deionized water until its pH reached 5.0. After drying the synthesized nano crystalline zeolite, it was used to prepare EDA-NZ.

Two grams of synthesized NZ was added to 50 ml ethylenediamine (EDA) solution concentration (30% of weight in methanol) and the resulting mixture was shaken for 60 min by rotating at 150 rpm. After the solution was filtered and dried at 100 °C for 3 h, the physico-chemical properties of the dried EDA-modified NZ (NZ-EDA) were analyzed and the CO_2 adsorption capacity of NZ-EDA was investigated.

2.2. Characterization of adsorbents

NZ-EDA was characterized by a series of analytical techniques. The NZ and NZ-EDA samples for analysis of IR spectra were prepared in the form of pellets with KBr at ambient conditions. Infrared spectra (Perkin-Elmer infrared spectrophotometer) were obtained using a Nicolet Nexus 470 FTIR spectrometer in the 4000–500 cm^{-1} region in transmission mode. The thermal degradation characteristics of NZ and NZ-EDA also were investigated by thermogravimetric analysis (TGA) in the Setaram Labsys Evo in N_2 flow with a temperature range of 50–600 °C and at a heating rate of 10 °C/min.

The specific Brunauer–Emmett–Teller (BET) surface area and pore size measurements of the NZ and NZ-EDA were conducted with Micromeritics ASAP 2020 apparatus under nitrogen air.

2.3. Adsorption experiments

Fig. 1 shows the CO_2 adsorption experimental setup. The system consisted of three parts: an adiabatic sorption column, a gaseous mixture system for controlling the composition and temperature of gaseous mixture, and a CO_2 analyzer. The temperature of the adsorption column could be adjusted and maintained at a constant value with an accuracy of ± 0.05 °C. In the adsorption experiments, 0.5 g of adsorbent was packed in the adsorption column (inner diameter (*I.D*) 2 cm ∗ length (*L*) 25 cm). The composition of the gaseous mixture was adjusted and controlled by a mass flow controller (MFC) which simultaneously controlled the flowrates of the two gases in the mixing chamber: CO_2 and N_2.

The adsorbent was first dried at 100 °C in pure N_2 for 60 min to remove moisture and/or other gases and then cooled down to the room temperature (20 ± 1 °C). After the temperature was stabilized, a mixture of CO_2 and N_2 was introduced into the sample chamber by using the MFC and the sample weight was recorded in order to calculate the CO_2 uptake. After CO_2 adsorption, the gas atmosphere was switched to N_2 and the temperature was increased in the range 20–100 °C to desorb the CO_2. Up to 15 adsorption–desorption cycles were performed to evaluate the stability of the adsorbents. The effects of reaction time and reaction temperature on the CO_2 adsorption capacity of NZ and NZ-EDA were determined by using a thermo-cloth under conditions similar to those used in the adsorption tests using a mixture of CO_2 and N_2. The CO_2 concentrations before and after passing the adsorption bed were monitored by an on-line CO_2 analyzer (Alpha Omega Instrument series 9610).

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