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Low-cost DETA impregnation of acid-activated sepiolite for CO_2 capture

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HIGHLIGHTS

- A cheap sepiolite-based adsorbent was synthesized by impregnation method.
- 80%-DETA loaded SH-18 demonstrates effective carbon capture characteristics.
- A cost estimation method was established to evaluate the impregnated adsorbents.

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ABSTRACT

In this paper, a low-cost sepiolite-based adsorbent for CO_2 capture was obtained by impregnating DETA into the acid-modified sepiolite. Thermogravimetric analysis, nitrogen adsorption-desorption isotherm, Fourier transform infrared spectroscopy and X-ray diffraction were used for the characterization of the sepiolite supports before and after DETA impregnation. Thermogravimetric analysis was also employed to evaluate the CO_2 adsorption performances of the adsorbents. The characterization methods revealed that DETA impregnated into the acid-modified sepiolite effectively. The CO_2 adsorption experimental results indicated that acid-activation and amine-loading simultaneously improved the CO_2 adsorption capacities of sorbents. For amine-loaded acid-modified sepiolite, low dosage of impregnated amine decreased the CO_2 adsorption capacities of sorbents at 35 °C due to the restrictions imposed in the transport and reaction of CO_2 due to pore blockage by amines. The highest CO_2 adsorption performance attained 1.65 mmol/g with the acid-modified sepiolite with 0.8 g-DETA loading. 95.2% of the adsorption capacity of 0.8-DETA/SH-18 maintains after 4 adsorption-desorption cycles, and the sorbent can be almost fully recovered at 75 °C, pure N_2. The kinetic studies showed that for low amine loadings the CO_2 adsorption is controlled by micropore blocking. For higher loadings a more complex diffusion and reaction process leads to a two-step adsorption kinetics. By contrast, it can be found that Avrami model is in good accordance with the adsorption kinetics of CO_2 on amine-functionalized sepiolite. A cost evaluation indicated that DETA-impregnated sepiolites are cheap adsorbents for CO_2 capture.

1. Introduction

Post-combustion CO_2 capture is considered as a promising way to capture and store CO_2 emitted from existing power plants and other industrial emitters [1,2]. CO_2 removal by chemical absorption with aqueous amine is a well-understood and robust post-combustion technology [3–7]. However, equipment corrosion, high-energy requirements for regeneration, low absorption efficiency, degradation, limit their applications [8]. Alternative post-combustion CO_2 capture processes by means of solid adsorption [9,10], membrane separation [11,12], ionic liquid sorption [13,14] have been intensively investigated, among which porous solid sorbents are favored for their fast adsorption kinetics, good mechanical properties, outstanding reusability and low equipment corrosion [15–17].

Xu et al. [18], the first researchers, introduced aqueous amines into MCM-41 and achieved high CO_2 adsorption capacities. This innovative combination of the advantages of porous solids with amines has been further investigated since then, and more efficient adsorbents have

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been synthesized. In general, there are two conventional ways of introducing amines into the solid supports. The first is to graft amine-containing alkoxysilanes on the support surface and the second is to load polyamines through impregnation [19]. Normally, the grafting method suffers low amine loadings due to the limited density of surface silanol groups on supports, which leads to a relatively low CO_2 adsorption capability [19]. Wet impregnation, however, is a promising technique to immobilize amines in porous solids. Monoamine, polyamine and hydramine all have been used to impregnate the solid adsorbents, such as MCM-41, MCM-48, SBA-15, KIT-6. These materials were tested at various CO_2 pressures and amine loadings under different temperatures, and exhibited CO_2 adsorption capacities between 1.26 and 7.92 mmol/g [8,18–30].

For commercialization and industrial applications, it is essential to produce low cost and efficient amino-adsorbents which reduce the capital and operational costs of CO_2 adsorption processes. There are some pioneering studies about amine-loaded cheap adsorbents, i.e. Martín et al. [8] and Elkhalifah et al. [37], who used commercial silica gel and bentonite as supporter. In this work, we are investigating the CO_2 capture properties of modified and non-modified sepiolite.

Sepiolite is a natural phyllosilicate fibrous clay mineral with abundant reserves and low prices (0.4–0.6 $/kg) in Hunan province, China [31]. It consists of discontinuous octahedrally coordinated magnesium layers and continuous tetragonally coordinated silicon layers which inverse their direction every several tetrahedral units, as showed in Fig. 1 [32,33]. Owing to its unique structure, sepiolite has uniform pore size, high porosity, surface area and abundant silanol groups [34]. All these properties make sepiolite a favourable solid adsorbent for amine loading. However, Chinese sepiolite usually has low purity and its porous channels are blocked by associated minerals. Generally, purification and other pretreatment are required to remove the residual carbonate in the sepiolite tunnel, increase the pore volume, adjust the pore structure and enlarge the surface area [34–36].

In this work, Chinese sepiolite was purified via sedimentation, acid activation and then impregnated with DETA. This type of amine is selected due to its small molecule size, low viscosity (easy to load on the porous solids), high CO_2 adsorption capacity, good cyclic capacity and lower desorption temperature [15]. The effect of DETA loading on CO_2 sorption capacity, adsorbent texture, thermal stability, the functional groups of the sorbents and the adsorption kinetics have been investigated and characterized.

2. Experimental

2.1. Materials

Raw sepiolite clay from Hunan, China was used as the starting material. The X-ray diffraction (XRD) analysis suggested that sepiolite is the predominant constituent with calcite, talc and quartz as the major impurities, and the raw sepiolite clay contains 30 wt% sepiolite. All chemical reagents used were of analytical grade without further purification and all solutions were prepared with deionized water.

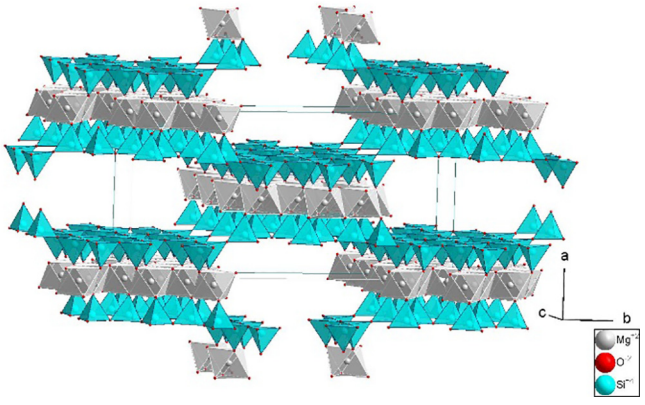

Fig. 1. Structure of sepiolite cell unit (without zeolite water).

2.2. Methods and equipment

2.2.1. Preparation of the sample

2.2.1.1. Sepiolite pretreatment. An adequate amount of sepiolite was purified by physical sedimentation to remove impurities [36], 20 g of raw sepiolite was mixed with 160 ml deionized water and the slurry was allowed to stand for around 28 h to adsorb water sufficiently. It was then added into a 0.2 wt% sodium hexametaphosphate solution (dispersant) and stirred at a rate of 400 rmp for 3 h to strip the impurities from the surface and the pores of the sepiolite. After 48 h sedimentation, the impurities sank while the sepiolites formed a stable slurry. The concentrated sepiolite was then collected after centrifugating the rich-sepiolite slurry at 9000 rpm for 5 min. It was then dehydrated by baking at 108 °C for 24 hr and it was further crushed into fine particles using a pestle and mortar. This purified sepiolite was kept in a sealed container and mechanically shaken to achieve uniform distribution.

After purification, acid activation was used to increase the pore volume, improve the pore structure and increase the specific surface area by extracting Mg ions from the sepiolite structure and connecting pores. For this, 15 g of purified sepiolite was treated with 150 ml of 20% HCl for 18 h in an open beaker under stirring. After treatment the slurry was filtered and washed with deionized water several times, dried at 108 °C and shaken. The so-obtained products were labelled as SH-18.

2.2.1.2. Preparation of DETA-impregnated sepiolite. For the wet impregnation procedure, the desired amount of Diethylenetriamine (DETA, Macklin, 99%) was dissolved in 20 g methanol (Hengxing, ≥99.8%) under stirring for about 30 min, after which 4 g of purified sepiolite or acid-modified sepiolite(SH-18) was added to the solution. The resultant slurry was stirred for 1 h, and then dried at 40 °C overnight at atmospheric pressure [18,37,38]. These sepiolites were labelled as X-DETA/SH-18 for acid modified sepiolites, where X represents the mass of DETA for per gram sepiolite sample. X was set as 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1. The weight ratios of amine to adsorbent can be easily calculated as 0, 4.76, 9.1, 16.7, 28.6, 37.5, 44.4, and 50%, respectively.

2.2.2. Techniques

The thermal stability, textural parameters(surface area, pore volume, pore size distribution), XRD patterns and surface functional groups of the sepiolite samples were tested by thermal gravimetric analysis (TGA, Mettler-toledo TGA/DSC 1), N_2 sorption analysis (Quantachrome SI analyzer), X-ray diffraction analysis(XRD, PANalytical X'Pert3 Powder XRD unit) and FT-IR analysis(Nicolet 380 FT-IR Spectrometer). The specific surface area was calculated by the Brunauer-Emmett-Teller(BET) method, and the total pore volume was determined from the total adsorbed amount of N_2 at $P/P_0 = 0.995$. The pore size distribution was calculated by applying the NLDFT model on the adsorption isotherm.

2.2.3. CO_2 adsorption measurements

The CO_2 adsorption capacity and kinetics was measured via TGA technique using same instrument connected to a GC-10 mass flow controller, allowing the control of the gas pressure entering the TGA apparatus. CO_2 (> 99.999%) is used of the adsorption measurements and N_2(> 99.999%) for purging/desorption. The experimental data are recorded by the STARe software on the computer linked to the TA apparatus. In a typical experimental route, 20 mg adsorbent was loaded into an alumina crucible. The sample was heated up to 100 °C at 10 °C/min under the flow of N_2 at 50 ml/min and left for 120 min for any