Development of a new clay supported polyethylenimine composite for CO_2 capture

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HIGHLIGHTS

- We develop a new low cost clay-supported polyethyleneamine sorbent for CO_2 capture.
- Effects of acid- and alkaline-treatments on the porosity-enhancement of clays.
- Effects of the PEI loading, sorption temperature, and H_2O addition on CO_2 sorption.
- The PEI/HCl-modifed montmorillonite sorbent is regenerable and thermally stable.

ARTICLE INFO

ABSTRACT

A new inexpensive inorganic–organic composite sorbent for CO_2 capture was prepared by the immobilization of a branched polyethyleneimine (PEI) onto porosity-enhanced clays using the wet impregnation method. In the composite, a low cost and naturally abundant clays (e.g. kaolinite and montmorillonite) was used as the supporting material, which was pre-modified by acid- or alkaline-treatment to improve its textural properties, i.e. pore volume and surface area, for accommodating the CO_2-philic PEI. Among the modified clays, the montmorillonite modified by 6 M HCl (Mon_HCl_6M) showed the highest porosity with the pore volume of 0.71 cm^3/g from 0.16 cm^3/g, and BET surface area of 253 m^2/g from 72 m^2/g. The cost of the Mon_HCl_6M was estimated as \$0.14/kg, which was significantly lower than reported supporting materials for the amine-based sorbents for CO_2 capture. At the optimal PEI loading of 50 wt% on the Mon_HCl_6M support, the CO_2 sorption capacity reached 112 mg CO_2/g-sorbent at 75 °C under dry condition, which can be further enhanced to 142 mg CO_2/g-sorbent with the moisture addition (ca. 3 vol%) due to the change in the interaction mechanism between CO_2 and amine in the presence of moisture. Moreover, the PEI/Mon_HCl_6M sorbent showed a good regenerability for 10 sorption–desorption cycles tested and a good thermal stability in the temperature range of CO_2 sorption (75 °C) and desorption (100 °C).

1. Introduction

The rapidly increasing concentration of CO_2 in the atmosphere has drawn great attention as it can be one of the main anthropogenic contributors to the global warming [1–3]. Mitigating CO_2 emission, while meeting the increasing energy demand by using the fossil-fuel based energy for a sustainable development involving energy, catalysis, adsorption and chemical processing has become a major global challenge [4,5]. Therefore, CO_2 capture and storage (CCS) has become an important research topic in the government, industry and research community worldwide.

A traditional and commercially-available CO_2 capture technology widely used in the industry is liquid amine scrubbing, which selectively absorbs CO_2 from the gas stream over monoethanolamine (MEA)-type of liquid amines via chemisorptions. However, the application was limited due to its drawbacks of serve corrosion to the equipment, foaming problems, solvent loss during regeneration, oxidative degradation, and high energy consumption for regeneration [6]. Therefore, it is desirable to design more energy-efficient and environment-friendly approaches for CO_2 capture from flue gas.

Adsorption, on the basis of the ability of a solid sorbent to adsorb certain compounds selectively under mild conditions, has been widely applied in the clean energy and environment research, such as desulfurization and denitrogenation for ultra-clean transportation fuels [7,8], water purification [9], etc. On the basis

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of natural physical, biological, and/or chemical properties of the targeted contaminants, namely adsorbates, functional sorbents can be designed for the selective removal or separation of adsorbates. A new class of sorbents, named "molecular-basket sorbent (MBS)" [4,6,10–13] has been proposed in our lab for CO_2 capture, where polymers with functional amine groups, e.g. polyethylenimine (PEI), tetraethylenepentamine (TEPA), etc. (In comparison, PEI-based sorbents demonstrated higher regenerability and stability than TEPA due to the mitigated degradation of sorbents caused by leaching during regeneration, which has a negative economic and environmental impact [14]), have been immobilized on porous substrates, and achieved high sorption capacity and selectivity for CO_2 [15–18]. The sorbent preparation can be considered green since it can be readily prepared by one step immobilization under ambient conditions. In the previous studies, progresses have also been made on immobilizing amine-based polymers onto various supporting materials, including SBA-15 [19–20], MCM-41 [21], MCM-48 [22] SBA-16 [23], silica form [24], etc. for carbon dioxide and/or hydrogen sulfide separations, and high adsorption capacity and selectivity were achieved. However, most of these supporting materials are not commercially available and costly in a scaled-up industrial preparation. Moreover, these mesoporous molecular sieves can be unstable under hydrothermal conditions, which impedes their applications for CO_2 capture from real flue gas (~100 °C, 8–20 vol% moisture content [25]). Hence, developing a supporting material with low cost, abundant supply, and good hydrothermal stability is important for the industrial application of composite sorbents for CO_2 capture from the fossil fuel-fired power plants. However, limited work has been carried out on this aspect. Until now, the reported supporting substrates include only activated carbon [26] and silica gel [27], silica foam [28], silica monolith [29].

Clay, the main components of the mineral fraction of soils [30], is one of the most abundant natural materials at a low cost (~$50/ton). Generally, clay is composed of aluminum phyllosilicates, as well as variable amounts of other cations, i.e. iron, potassium, sodium, calcium, magnesium, zinc, etc. The molecular structures of clays can be built of tetrahedral silicate sheets and octahedral hydroxide sheets. Two typical clays, kaolinite and montmorillonite, consist of tetrahedral silicate sheets and octahedral hydroxide sheets at a ratio of 1:1 and 2:1, respectively. Clay can be a class of potential sorbent supporting materials due to its low cost, rich natural abundance, and high mechanical and chemical stability, yet the applications are limited by its poor textural properties (e.g. low pore volume, <0.2 cm^3/g). The drawback may be overcome by the acid- or alkaline-modification, as clay can react dramatically with acid and alkaline [31] due to its high cation exchange capacity, resulting in the improved textural properties, in particular, the pore volume and surface area. Consequently, the application of clays in the field of adsorption and separation can be greatly extended, yet limited work has been performed for immobilizing CO_2-philic polymer on the acid- or alkaline-treated clays for CO_2 capture.

In this work, commercially available and inexpensive clays, kaolinite and montmorillonite, were selected as the base supporting materials, which were further modified by acid or alkaline to improve the textural properties, i.e. pore volume and surface area, for immobilization of a CO_2-philic polymer PEI to develop a new type of inexpensive inorganic–organic composite sorbents for CO_2 capture. The developed composite sorbents were compared and further discussed for CO_2 capture, which was measured by thermogravimetric analyzer (TGA) and a flow sorption system using a simulated flue gas. The textural properties and morphological structures of the composite sorbents were characterized using N$_2$ adsorption test, scanning electron microscope (SEM), and Fourier transformation infrared spectroscope (FT-IR). The effects of the PEI loading amount, sorption temperature, and moisture presence on the CO_2 sorption performance, as well as the regenerability and thermal stability of the composite sorbents were investigated and further discussed herein.

2. Experimental

2.1. Materials

Two clay raw materials, kaolinite (commercial name as KC2000, termed as Kao2), and montmorillonite (termed as Mon) were provided by Kamin Company, US, and R & L Chemical Inner Mongolia Co., China, respectively. Polyethylenimine (PEI) with an average molecular weight (Mn) of 600 g/mol, methanol solvent (99.8%) for impregnation, hydrochloric acid (37%) and sodium hydroxide ($\geqslant$98.0%) for acid- and alkaline-treatments were purchased from Sigma–Aldrich and used as received.

2.2. Modification of clays by acid- or alkaline-treatments

In order to improve the textural properties, particularly pore volume and surface area of the clay samples, different clays were modified by acid- or alkaline-treatments with different concentrations of hydrochloric acid or sodium hydroxide solution. Typically, a desired amount of clays were added into the acid or alkaline solution with a fixed ratio of 10 ml-acid/g-clay or 8 ml-alkaline/g-clay, respectively. Then, the mixtures were heated in an oil bath at 110 °C for alkaline-treatment or 95 °C for acid-treatment, stirring at 600 rpm for 4 h. After that, the suspension was filtered and washed with large amount of distilled water and dried in an oven at 100 °C overnight. Finally, the powder was further dried in vacuum for 24 h before use. The desirable concentrations of HCl or NaOH solutions were determined as 6 M and 5 M, respectively, under which the highest pore volume and surface area after modification was obtained (The textural properties of montmorillonite treated by HCl or NaOH solutions at different concentrations are listed in the Supporting Information Tables 1 and 2)

2.3. Preparation of the PEI/clay composite sorbents

The PEI/clay composite sorbents were prepared by wet impregnation method. About 3 g of polyethylenimine (branched PEI with Mn of ~600 from Aldrich) was dissolved in 30 g of methanol under stirring for 30 min. Then, the modified clay was added into the above methanol solution and further stirred for 3 h under ambient conditions. After that, the slurry was dried in a vacuum oven at 75 °C for 12 h. To optimize the PEI loading onto the modified montmorillonite, the PEI/Montmorillonite (PEI/Mon) samples with different PEI loadings at 30, 40, 50, 55 and 65 wt% referring to the weight of the PEI/Mon sorbents, or 43, 67, 100, 122, 186 wt% referring to the weight of the modified montmorillonite, were prepared and further studied.

2.4. Textural structure characterization

(1) *N$_2$ adsorption test*: The characterization of the textural properties of the adsorbents was carried out by the physical adsorption of N$_2$ at 77 K by a Micromeritics ASAP 2020 analyzer. The modified clays were degassed at 200 °C under vacuum for 24 h, before measurements. The surface area was obtained from N$_2$ adsorption isotherm using Brunauer–Emmett–Teller (BET) equation. The total pore volume (V_t) was calculated on the amount of the absorbed N$_2$ after finishing pore condensation at a relative pressure of $P/P_o = 0.995$. The pore size was determined according to the BJH pore size distribution curve; (2) *Scanning electron microscope*