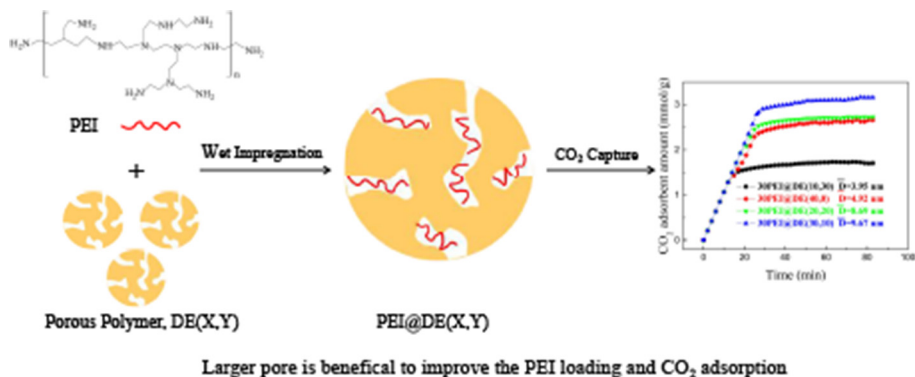


Regular Article

Synthesis of porous polymer based solid amine adsorbent: Effect of pore size and amine loading on CO₂ adsorptionFenglei Liu^a, Shuixia Chen^{a,b,*}, Yanting Gao^a^aPCFM Lab, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, PR China^bMaterials Science Institute, Sun Yat-Sen University, Guangzhou 510275, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

A series of porous polymers was synthesized by a suspension polymerization of divinylbenzene (DVB) and ethylene glycol dimethyl acrylate (EGDMA), which was further functionalized with polyethyleneimine (PEI) for CO₂ capture. The results showed that the synthesized DVB and EGDMA (DE) copolymers were an effective support for loading PEI because of its larger pore size and specific surfaces area. It was found that DE (30, 10) loaded with 30 wt% PEI exhibited a higher CO₂ adsorption amount of 3.28 mmol/g at 25 °C under dry condition. The CO₂ adsorption capacity would decline gradually as the temperature continuously raised, for the reaction between CO₂ and amine groups was an exothermic reaction. The kinetics study showed that Avrami kinetic model could accurately describe the whole CO₂ adsorption process, suggesting that both physical adsorption and chemical adsorption were involved with the CO₂ adsorption process. The intraparticle diffusion and Boyd's film diffusion models were applied to investigate the CO₂ diffusion mechanism, the intraparticle diffusion model could well distinguish the rate-limiting step during CO₂ adsorption process. This solid amine adsorbent could be regenerated with nitrogen stream at 75 °C, and it kept stable CO₂ adsorption capacity after eight adsorption-desorption cycles. All these features indicated that this porous polymer based adsorbent has a high potential for CO₂ capture and separation from flue gas.

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1. Introduction

CO₂ has been regarded as a major contributor to global warming and climate change, mostly produced from the burning of fossil fuels, such as coal, natural gas and oil [1,2]. How to capture and separate CO₂ effectively and economically is a critical environmental problem. To regulate the CO₂ emission, researchers have developed many methods, such as membrane separation [3], cryogenic fractionation [4] and amine scrubbing [5]. However, the approach to use aqueous amine does have some drawbacks, such as corrosion equipment, high regeneration energy and volatile amine loss, though it has been proven to be an effective method [6]. In an effort to address this challenge, feasible strategies are loading amine by impregnation or grafting onto solid support [7]. Benefits of anchoring amine on the solid support may include elimination of foaming and vapor entrainment, as well as the ability to maintain liquid and gas flow rates independently. Recently, various porous solid materials have been evaluated for CO₂ capture, like zeolites [8,9], porous carbon [10,11], SiO₂ [12,13] and MOF [14,15]. Although these adsorbents exhibit excellent CO₂ adsorption performance, they also have some weaknesses during the CO₂ capture processes, such as poor regeneration, intolerance to moisture and low selectivity. Therefore, searching for new materials for CO₂ capture is of great importance.

Porous polymer due to possess adjustable pore size, high surface areas and stable chemical structure, which is considered to be a highly promising solid adsorption material. In recent years, several porous polymers have been synthesized and examined for CO₂ adsorption. Han et al. developed a novel adsorbent for CO₂ capture by grafting PEI on porous polymer (PGMA), the CO₂ adsorption capacity for this material could reach as high as 4.85 mmol/g at 40 °C under moist condition [16]. Liu et al. synthesized the PEI modified hierarchically nanoporous poly(divinylbenzene) (PDVB) adsorbent by physical impregnation method, this composite material could adsorb 3.17 mmol of CO₂ at 25 °C [17]. Sung et al. found that the CO₂ capture ability for porous polymer (PAF-5) was far improved by impregnating with PEI, and this adsorbent could adsorb 2.52 mmol of CO₂ with PEI content 40 wt % [18]. Liu et al. prepared a novel moisture-resistant porous polymer adsorbent for CO₂ adsorption, they found that the maximum CO₂ adsorption amount (3.46 mmol/g) was obtained under a pressure of 100 kPa [19]. To our knowledge, although previous researchers have made great progress on porous organic polymer for CO₂ adsorption, it is still not enough. To illustrate, the porous polymer with suitable pore structure for PEI loading has not been evaluated in detail. Meanwhile, the relationship between porosity and the surface chemistry of the porous polymeric support and CO₂ adsorption performances of the adsorbent need to be explored to develop a high efficient adsorbent for CO₂ capture.

The aim of this work is to synthesize a series of porous polymer with different porosity by a suspension polymerization of DVB and EGDMA. Then, the obtained porous polymer was further functionalized with PEI for CO₂ capture. The effect of porosity of support, PEI content and adsorption temperature on the CO₂ adsorption performance was studied. Moreover, the CO₂ adsorption kinetics, adsorption mechanism and regeneration ability was also discussed.

2. Experimental

2.1. Materials

Divinylbenzene (DVB, purity 80%), ethylene glycol dimethyl acrylate (EGDMA), benzoyl peroxide (BPO), branched type polyethylenimine (PEI, MW = 600) and Polyvinyl alcohol (PVA)

were purchased from Shanghai Aladdin Chemical Company. Toluene, *n*-heptane, acetone and ethanol were obtained from Guangzhou Jinghong Chemical Company. Highly pure N₂ and CO₂ were supplied by Guangzhou Zhuorui Company. All the chemical reagents were analytical grades and used without further purification.

2.2. Synthesis of solid amine adsorbent

The synthesis process of solid amine adsorbent was shown in Fig. 1. In the first step, the porous polymer was prepared by suspension polymerization according to the method described in Ref. [20]. Briefly, 0.2 g of BPO was dissolved in 20 mL of organic phase (DVB 16 g, EGDMA 4 g, porogen 40 g). Then, the organic phase was slowly added to the aqueous phase (pure water 120 mL, PVA 1.2 g and NaCl 12 g). Toluene and *n*-heptane (total mass of 40 g) were used as porogen. To obtain the largest specific surface area and porosity, the proportion between toluene and *n*-heptane was changed in synthesis process. The copolymerization reaction was kept at 80 °C for 12 h. After completion of the reaction, the product was filtered, washed and extracted by acetone in Soxhlet apparatus for 24 h and dried at 60 °C for 6 h. Finally, the obtained white beads were denoted as DE (X, Y), X, Y represents the mass of toluene and *n*-heptane content in the porogen.

In the second step, the PEI modified DE samples were prepared by a physical impregnation method [21]. A desired amount of PEI was dissolved in 10 mL of ethanol under stirring for 20 min. Then, different mass of DE beads were added to PEI solution. After 6 h, the ethanol was removed by evaporation at 60 °C for 4 h. The obtained PEI modified adsorbents were denoted as Z@DE (X, Y), where Z represents the weight percentage of PEI in the composite.

2.3. Characterization of the adsorbents

Adsorption-desorption isotherms of N₂ was measured with an automatic gas adsorption instrument at 77.35 K (ASAP2020, Micromeritics, Norcross, GA, USA) to characterize the pore structure of the adsorbents. The total pore volume was calculated based on the nitrogen amount adsorbed at P/P₀ = 0.95. The Brunauer-Emmett-Teller (BET) and density functional theory (DFT) method were used to calculate the specific surface area and pore size distribution, respectively. Fourier Transform Infrared (FT-IR) Spectroscopy was applied to characterize the surface functional groups on the adsorbents with a Tensor-27 Spectrometer (Bruker, Optics, Mannheim, Germany) in the range of 4000–400 cm⁻¹. X-ray photoelectron spectroscopy (ESCALab 250, Thermo-VG Scientific, USA) was used to analysis the surface chemical composition of these samples. The thermal stability of all samples was determined by a thermogravimetric analyzer (TGA; Netzsch, TG-209C, Selb, Germany), in which all samples were placed in a platinum holder and heated from 25 °C to 700 °C at a rate of 10 °C min⁻¹ under a N₂ atmosphere.

2.4. CO₂ adsorption procedures

The dynamic CO₂ adsorption performance of the adsorbent was operated in a fixed-bed column. 1 g of adsorbent was placed in the middle of adsorption column ($\Phi = 1.3$ cm). Prior to CO₂ adsorption test, the fresh samples were treated with a pure N₂ for 20 min. After that, the CO₂/N₂ gas mixtures with a CO₂ concentration of 10% were introduced. The CO₂ concentration in the influent and effluent gas streams was analyzed by gas chromatography (Techcomp 7900, Shanghai, China) with a thermal conductivity detector (TCD).

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