



Vapor-enhanced CO₂ adsorption mechanism of composite PEI@ZIF-8 modified by polyethyleneimine for CO₂/N₂ separation

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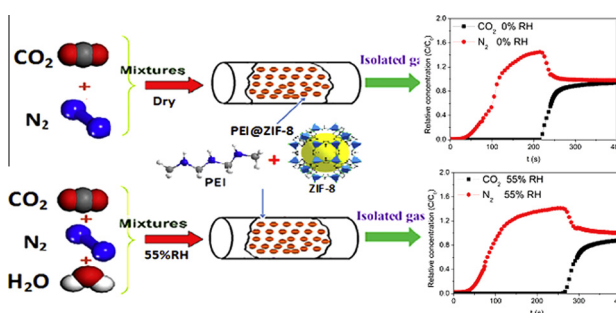
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HIGHLIGHTS

- Novel composite PEI@ZIF-8 with moisture resistance is prepared for CO₂ capture.
- Its CO₂ working capacity at 338 K is 6.2 times of that of ZIF-8 at 303 K.
- Its CO₂/N₂ selectivity at 338 K is 27 times of that of ZIF-8 at 303 K.
- Presence of water vapor further enhance its CO₂ capacity and CO₂/N₂ selectivity.
- Synergy action mechanism of water steam and PEI is proposed to enhance CO₂ capture.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel PEI impregnated ZIF-8 (PEI@ZIF-8) composites, with characteristic of water vapor enhanced adsorption property, were synthesized for CO₂/N₂ separation, and then characterized by N₂ adsorption, PXRD, IR and TG. CO₂ and N₂ isotherms were measured by static adsorption, and the breakthrough curves of CO₂/N₂ mixture ($v_{\text{CO}_2}/v_{\text{N}_2}$ of 1/1) through the fixed bed of the composites were determined in presence of water vapor. Results showed that CO₂ working capacity and CO₂/N₂ selectivity of as-synthesized PEI@ZIF-8 at 338 K were up to 1.61 mmol/g and 62, being 6.2 and 27 times of those of ZIF-8 at 303 K, respectively. PEI@ZIF-8 is thermally stable until 450 K. More importantly, it was found that the presence of water vapor in feed stream further enhanced the CO₂ capacity and CO₂/N₂ selectivity of PEI@ZIF-8, which separately reached 1.99 mmol/g and 89.3 at RH of 55% and 338 K, having increases of 23.6% and 44% in comparison with those under dry condition. The enhancement could be attributed to the synergy action mechanism of water steam and PEI. Calculation by density functional theory revealed that the presence of water vapor resulted in the formation of bicarbonate, and thus promoted more CO₂ molecules to be adsorbed on PEI@ZIF-8. This water vapor enhanced action mechanism can be applied to design rationally more efficient adsorbents for CO₂ capture under realistic situation where water vapor is always present.

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1. Introduction

With the rapid increase of the global population and industrialization, the consumption of fossil fuels in the past two centuries has led to drastic increases in CO₂ concentration in Earth's

atmosphere. The disruption in the carbon balance results in the greenhouse effect [1], which will lead to dramatic detrimental consequences for the biological ecosystems in the land and upper ocean [2] and has drawn unprecedented public attention to the issue of CO₂ emission. Therefore, effective separation of CO₂/N₂ has become a more important research subject in both academic and industrial communities worldwide.

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Adsorption of CO₂ using highly porous solids has been of increasing interest for carbon dioxide capture applications. Conventional adsorbents for CO₂ capture mainly include zeolites [3] and activated carbons [4,5]. However, their low CO₂ adsorption capacities and selectivity have limited their practical application. Thus, considerable efforts have been made to improve CO₂ adsorption of conventional adsorbents by surface modification. The application of some alkaline chemicals to modify the surfaces of conventional adsorbents was an effective approach since CO₂ is acidic molecule [6]. For example, polyethylenimine (PEI) was reported to be grafted or impregnated on conventional porous materials such as activated carbon [7], mesoporous silicas [8], MCM-41 [9], mesoporous alumina [10], clays [11] and chitosan [12]. As a result, CO₂ adsorption capacities of these modified adsorbents had obviously been improved.

Recent years, a new class of microporous materials known as metal organic frameworks (MOFs) have been rapidly emerging as potential adsorbents for effective separation and purification of gas mixtures [13–16]. Porous MOFs have been positioned at the forefront due to their high surface areas together with functionalizable pore walls. MOFs are considered as ideal and potential candidates for applications such as air purification, hydrogen storage, catalysis, and CO₂ capture. Yaghi's group reported that MOF-210 had a super high saturated CO₂ uptake of 2400 mg/g at room temperature at 50 bar [17]. Pirngruber et al. [18] reported that CO₂/N₂ selectivity of Cu-BTC was up to 8. Yaghi et al. [19] reported that MOF-177 had a high CO₂ capacity of 60.0 wt.% at 35 bar. Britt et al. [20] reported that Mg-MOF-74 had a high CO₂ storage capacity of 35.2 wt.% at 298 K and 1 bar. Unfortunately, although these MOFs had very high CO₂ adsorption capacity, their low physico-chemical stabilities (especially moisture stability) would limit their industrial applications since water vapor is ubiquitous in realistic situation [20,21]. It was reported that majority of MOFs do not possess thermodynamically stable property [22], and thus their crystal structures would be partly or completely destroyed after exposed to ambient air containing water vapor or oxygen. On the other hand, although a few of MOFs such as MIL-101(Cr) with thermodynamically stable property has not only high moisture stability but also high CO₂ capacity [16,23], its high hydrophilicity resulted in sharp decrease in its CO₂ uptake in humid atmosphere [24]. The reason may be that the unsaturated metal centers (UMCs) of these MOFs like MIL-101(Cr) have strong selectivity for CO₂ in presence of other gases, and meanwhile, these UMCs are very hydrophilic [25–27], which would promote competitive adsorption of water vapor [24,28]. Therefore, developing novel adsorbents with high CO₂ capacity and moisture resistance performance or vapor-enhanced CO₂ adsorption function is crucial.

Lin and Chen et al. [29] tried to prepare a PEI incorporated MIL-101, and reported that the resulting composites exhibited obviously enhanced CO₂ adsorption capacity at low pressures, and the adsorption isotherms of CO₂ on dry and humid PEI-MIL-101(Gr) samples were nearly the same, indicating no negative effect of water adsorption on the CO₂ adsorption, which is interesting. However, to the best of our knowledge, the work about functionalization of MOFs with PEI has been rarely reported. This was probably due to the low alkali stability of many MOFs, and thus their part structures would possibly be collapsed if strong alkali PEI was loaded.

In this work, we are going to study novel composites PEI@ZIF-8 for CO₂ separation and a novel synergy action enhancement mechanism of water steam and PEI loaded on ZIF-8, which not only restrains negative impact of water vapor, but also promote CO₂ adsorption by water vapor. A series of polyethylenimine (PEI) modified ZIF-8 were synthesized by wetness impregnation and then characterized. The breakthrough curves of CO₂/N₂ binary mixture were measured at different relative humidities by fixed bed

experiments for the first time. Effects of PEI loading, temperature and humidity on CO₂/N₂ separation performance of PEI@ZIF-8 were discussed. The mechanisms that the existence of water vapor in feed steam can distinctly enhance CO₂ capacity and CO₂/N₂ selectivity over PEI@ZIF-8 were clarified and reported here.

2. Experimental section

2.1. Synthesis of ZIF-8 and PEI@ZIF-8

ZIF-8 was synthesized by a hydrothermal method [30] which described in Supporting information (see S1).

PEI@ZIF-8 was prepared using a wet impregnation method. The preparation procedures were as follows: first, the ZIF-8 powders were heated at 423 K under vacuum for 12 h, removing the adsorbed water and coordinated water. Second, the desired amount (15%, 30% and 45%) of PEI was dissolved in 2 mL anhydrous methanol under ultrasonic for 5 min, and then added into 0.1 g of ZIF-8 powder under ultrasonic drop by drop. After that, the obtained gels were dried overnight at 313 K in nitrogen atmosphere, and further heated at 373 K for 12 h under vacuum. Finally, the obtained sample was denoted as 15PEI@ZIF-8, 30PEI@ZIF-8 or 45PEI@ZIF-8.

2.2. Characterization of PEI@ZIF-8

(a) Textural properties of PEI@ZIF-8 were characterized by nitrogen adsorption test using micromeritics ASAP 2020 adsorption porosimeter at 77 K. (b) The XRD features of ZIF-8 and PEI@ZIF-8 were identified by X-ray diffraction on a Bruker D8 Advance X-ray diffractometer at 40 kV, 40 mA, with a scan speed of 2°/min and a step size of 0.02° in 2–25°, using Cu K α radiation. (c) The surface functional groups on PEI@ZIF-8 were characterized using a Bruker 550 IR instrument equipped with a diffuse reflectance accessory. The sample chamber was kept purging with nitrogen during IR analyses. The spectrometer collected 64 spectra in the range of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹. (d) The thermal stability of the PEI@ZIF-8 samples were evaluated by thermo-gravimetry analyzer (TG), STA449, NETZSCH, Germany by heating the sample from 298 to 800 K at 5 K/min under N₂ at the flow rate of 30 cm³/min.

2.3. CO₂/N₂ adsorption experiments

2.3.1. CO₂/N₂ adsorption isotherms

The isotherms of CO₂ and N₂ were measured using micromeritics ASAP 2020. About 50 mg samples were degassed at 383 K for 10 h before measurement. The temperature was controlled by circulating water.

2.3.2. Fixed-bed breakthrough experiments of CO₂/N₂ binary mixture

The CO₂/N₂ breakthrough experiments were performed on a self-assembly experimental setup, which was shown in Fig. S1. Details of fixed bed experiment procedure were described in Supporting information S2. The calculation method of CO₂ working capacity and CO₂/N₂ dynamic selectivity on the basis of breakthrough curves were described in Supporting information S3 and S4.

2.4. Computational methodology

The optimization of adsorption complexes and the calculation of corresponding binding energies (BEs) were performed by density functional theory (DFT) using the Dmol³ code [31]. The PW91 functional combined with DNP basis set [32,33] was applied

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