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Temperature-programmed desorption of CO_2 from polyethylenimine-loaded SBA-15 as molecular basket sorbents

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ABSTRACT

In this work, we conducted a study on temperature-programmed desorption (TPD) of CO_2 over molecular basket sorbent (MBS) consisting of polyethylenimine (PEI) immobilized in mesoporous silica SBA-15. A series of MBS sorbents with different PEI loadings in SBA-15 have been studied for CO_2-TPD to gain an insight into the fundamental characteristics of CO_2 sorption/desorption mechanism. Effects of sorption temperature, sorption time, and PEI molecular weight on the CO_2 sorption capacity and desorption behavior of 50 wt% PEI/SBA-15 sorbent were also examined. The results show that two PEI layers, i.e., the exposed PEI layer and the inner bulky PEI layer may exist in PEI/SBA-15 sorbents, and their proportions vary with PEI loading and sorption temperature. Consequently, a two-layer model for CO_2 sorption over PEI/SBA-15 sorbent is proposed, which rationalizes the sorption results with consideration of CO_2 sorption kinetics and thermodynamics. It was also found that CO_2 sorption capacity decreases with increasing PEI molecular weight, which may be mainly attributed to the decrease of primary amine content and the increase of tertiary amine content as well as increased interactions between polymeric chains in the PEI molecules.

1. Introduction

Capture of anthropogenic CO_2 from various gas streams, especially from large sources of emission such as fossil fuel fired power plants, is of critical importance in mitigating the effect of greenhouse gas on global climate change [1,2]. Although liquid amine scrubbing is a mature and commercially available technology for CO_2 separation, it is highly energy-intensive and costly for CO_2 capture from flue gas [3,4], with some other drawbacks such as equipment corrosion, foaming problem, solvent loss in regeneration and oxidative degradation [2,5–7]. As a result, it is highly desired to develop a more energy-efficient and environmentally benign method for CO_2 capture from flue gas.

In the past decade, various solid amine sorbents have been explored worldwide for CO_2 capture [8–20]. Via proper design, high CO_2 working capacity and selectivity, fast CO_2 sorption kinetics and low energy requirement for regeneration could be achieved using solid amine materials including the solid "molecular basket" sorbent (MBS). The detailed description on the MBS concept and the design strategy can be found in our early reports [21,22]. The MBS materials show promising applications in CO_2 capture [22–26], SO_2/NO_2 removal [27] from flue gas, and H_2S separation from fuel gases [28,29]. As for CO_2 capture, the previous study has revealed that the CO_2-MBS has several potential advantages, including a high CO_2 capacity (>2 mmol-CO_2/g-sorbent at a CO_2 partial pressure of 15 kPa) [22,23], high selectivity (CO_2/N_2 > 1000) [24], little or no corrosion, easy regeneration [22,25,29], promotion effect of moisture on the sorption capacity [25,28], and fast sorption/desorption rate [23,29]. Recently, we have improved the MBS formulation by using SBA-15 as the inorganic matrix instead of MCM-41 and a much higher CO_2 sorption capacity has been achieved at 15 kPa of CO_2 partial pressure and 75 °C, reaching ca. 3.18 mmol-CO_2/g-sorbent [21,30].

In order to further improve the sorption performance of the sorbents, a fundamental understanding of the sorption mechanism and the relationship between the sorbent structure and performance is highly desired. Therefore, we have conducted a detailed temperature programmed desorption (TPD) study on CO_2 sorption mechanism over the polyethylenimine (PEI)-SBA-15-based MBS. TPD is a very useful technique for characterizing chemically bonded surface or adsorbed species, and thus has been used extensively to characterize catalysts and zeolites, where the nature of the adsorbed species and decomposition of surface complexes can be studied [31–36]. Meanwhile, the adsorption energies and the amounts adsorbed can also be obtained via this technique. Some comprehensive reviews on TPD technique have been published by

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Falconer and Schwarz [31], Kreuzer [37], Bhatia et al. [38], Cerofolini [39] and Tovibin [40].

In the present study, a series of PEI loaded SBA-15 sorbents with different PEI contents were prepared and studied by the CO_2-TPD method to gain an insight into the CO_2 sorption/desorption mechanism over the nanoporous PEI/SBA-15 sorbents. Effects of sorption temperature, sorption time, and PEI molecular weight on the CO_2 sorption capacity and desorption behavior of 50 wt% PEI/SBA-15 sorbent have been examined. Based on the results, a CO_2 sorption model is proposed and discussed. To the best of our knowledge, it is the first model to interpret the CO_2 sorption process over solid amine sorbent with high amine loadings. Furthermore, the influence of PEI molecular weight on the sorption capacity of PEI/SBA-15 sorbent has also been discussed in this work.

2. Experimental

2.1. Sorbent

Mesoporous molecular sieve SBA-15 was synthesized by the hydrothermal method [41,42]. Typically, a homogeneous mixture composed of tri-block copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800, Aldrich) and tetraethyl orthosilicate (TEOS, 98%, Aldrich) in aqueous hydrochloric acid solution, was stirred at 40 °C for 20 h and further treated at 100 °C for 24 h. The solid was then recovered by filtration, washed by de-ionized water, dried in an oven at 100 °C overnight and finally calcined at 550 °C for 6 h.

The nano-porous "molecular basket" sorbent, PEI/SBA-15, was prepared by loading a desired amount of polyethylenimine (PEI, linear with average molecular weight, ~423, Aldrich) into SBA-15 via a wet impregnation method, which was dried at 75 °C under vacuum. To study the effect of PEI molecular weight, other PEIs (from Aldrich) with different molecular weight (Mn) including 600, 1800, 10,000, and 60,000 were also loaded on SBA-15 at a content of 50 wt% through the same procedure. The prepared SBA-15 and PEI/SBA-15 samples were characterized by various techniques including low-angle X-ray diffraction (XRD) for the meso-structure, N_2 adsorption–desorption for the porosity, SEM for the morphology and FTIR for the surface interactions between SBA-15 matrix and loaded PEI. The details in preparation and characterization of SBA-15 and PEI loaded SBA-15 sorbents can be found elsewhere [28–30,43]. The characterization results firmly support that the loaded PEI was completely located inside the meso-pore channels of SBA-15 when PEI loading was no more than 50 wt%.

2.2. TPD procedure

The carbon dioxide temperature-programmed desorption (CO_2-TPD) was conducted on a Micromeritics AutoChem 2910 instrument equipped with a TCD. Unless it is specified otherwise, the typical CO_2-TPD process was carried out as follows: about 100 mg of PEI/SBA-15 sample was placed into a U-shape quartz reactor and pretreated at 100 °C under helium flow (30 ml/min) for 20 min. When the temperature was reduced to 75 °C, CO_2 sorption was performed by flowing CO_2 (10 ml/min) for 30 min. Then the temperature was decreased to 40 °C under the same CO_2 flow. After that, the desorption experiment was executed by purging helium gas (50 ml/min) through the sorbent bed and ramping the temperature from 40 to 110 °C at a rate of 5 °C/min and holding at 110 °C for 20 min. The CO_2 uptake or sorption capacity in millimole of CO_2 per gram of sorbent (mmol/g-S) was calculated on the basis of the desorbed CO_2 amount from the desorption curve, which was calibrated by a certain amount of CO_2.

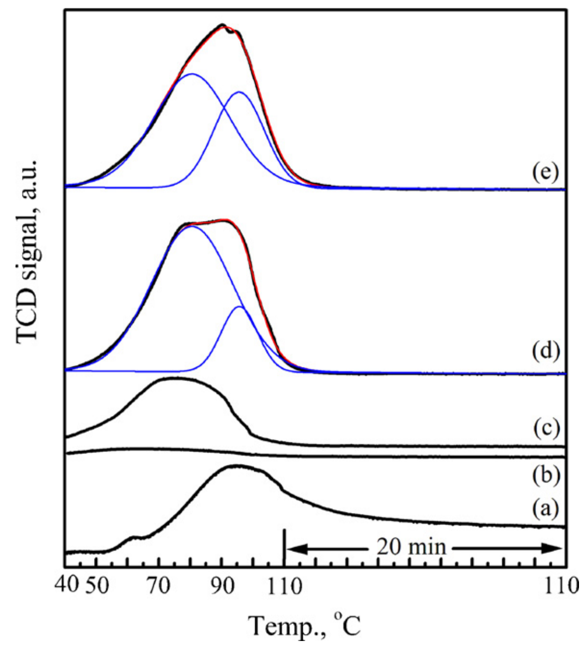

Fig. 1. CO_2-TPD profiles of (a) pure PEI, (b) 15 wt% PEI/SBA-15, (c) 30 wt% PEI/SBA-15, (d) 50 wt% PEI/SBA-15 and (e) 65 wt% PEI/SBA-15 with peak deconvolution (blue lines). Sorption conditions: gas, pure CO_2; Temp., 75 °C; sorption time, 30 min; flow rate, 10 ml/min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Results

3.1. Effect of PEI loading

Fig. 1 shows the TPD profiles for pure PEI and PEI/SBA-15 sorbents with different PEI loadings, on which CO_2 sorption was performed at 75 °C. The corresponding CO_2 sorption capacities based on these TPD curves are listed in Table 1. As seen, over the 15 wt% PEI/SBA-15 sample, a broad desorption peak centered at about 60 °C with a completion at about 100 °C is observed. But the intensity is quite low (Fig. 1b), corresponding to a CO_2 uptake of 0.31 mmol/g-S. When the PEI loading increases, both the CO_2 uptake and the desorption peak temperature increase (Table 1). Compared to the 15 wt% PEI/SBA-15 sample, the desorption signal obtained over 30 wt% PEI/SBA-15 shows much stronger and the peak position shifts to a higher temperature (about 75 °C). The CO_2 uptake increases to 1.98 mmol/g-S. Further increasing the PEI content to 50 and 65 wt%, the peak intensity becomes even stronger, and the peak temperature gets even higher. In addition, the peak shape turns from symmetric to distinctly asymmetric. The CO_2 uptake is 3.94 and 4.41 mmol/g-S for 50 and 65 wt% PEI/SBA-15, respectively. As for pure PEI, the CO_2 desorption profile exhibits a wide peak with the peak temperature at about 96 °C, and gives a CO_2 uptake of 2.39 mmol/g-S. It should be noticed that the TCD signal for pure PEI sample does not return to the baseline even after the desorption being performed at 110 °C for 20 min, while it is already completed at 110 °C over PEI/SBA-15 samples. It indicates that CO_2 desorption over pure PEI is slow and requires higher temperature and longer time to complete even at 110 °C, as also reported by Xu et al. [22].

Since SBA-15 alone has only a CO_2 uptake of 0.11 mmol/g-S, the CO_2 uptake of PEI/SBA-15 comes mainly from the loaded PEI. Considering the desorption behavior of 30 wt% PEI/SBA-15 and pure PEI, the asymmetric peak in the CO_2-TPD profiles of 50 and 65 wt% PEI/SBA-15 samples could be deduced and divided into two components: one with the desorption peak temperature similar to that