

Remarkable effect of moisture on the CO₂ adsorption of nano-silica supported linear and branched polyethylenimine



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ABSTRACT

Linear and branched polyethylenimines (PEIs) impregnated on hydrophilic and hydrophobic silica were prepared and evaluated for the effect of moisture on CO₂ adsorption. The adsorbents were exposed to exhaustive conditions such as varying temperature, CO₂ concentration, and specific humidity (SH) levels. Remarkable adsorption enhancements were observed when the adsorbents were exposed to a SH of 3.8–11.5 mg H₂O/g at 25 °C. Further increase of the SH above 11.5 mg H₂O/g either decreased the CO₂ uptake for branched PEI or had no additional benefit for linear PEI. Increasing the loading of PEI in the adsorbent resulted in an increase in water adsorption. However, branched PEI was more hydrophilic than its linear counterpart. Replacing the hydrophilic fumed silica support with a hydrophobic silica support decreased the overall water uptake while maintaining similar CO₂ capture capacity. Considering that these types of adsorbents are designed to be recycled preferably for thousands of adsorption/desorption cycles, this could translate into significant energy savings in the regeneration step where any water present on the adsorbent would also have to be heated and desorbed.

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1. Introduction

Since the dawn of the industrial revolution, the production of energy through the combustion of fossil fuels has allowed humankind to rapidly reach unprecedented levels of development and standard of living. The burning of fossil fuels is, however, accompanied by the release of carbon dioxide. This unwanted byproduct is increasingly raising concerns as its emissions are outpacing nature's recycling ability through photosynthesis. Increasing CO₂ concentration from anthropogenic sources in the atmosphere is now widely acknowledged as one of the main reasons for the observed global climate changes as well as other environmental effects such as ocean acidification and sea level rise. To continue using fossil fuels, which still provide 85% of global energy needs, while at the same time mitigating their environmental consequences, various ways to tackle our carbon conundrum have been suggested. Besides energy conservation and reduction in carbon intensity, carbon dioxide capture and

sequestration (CCS) and recycling (CCR) are among the most discussed, studied, and promoted [1–6].

To capture CO₂, a number of methods including physisorption, chemisorption and cryogenic separation have been proposed. Their applicability depends on numerous factors including CO₂ concentration in the source gas, temperature and pressure of the gas, flow rate and volume of gas to be treated, presence of impurities, etc. Solid CO₂ adsorbents based on amines supported on inorganic oxides have attracted particular interest in recent years owing to several characteristics, such as excellent selectivity for CO₂, relatively high capacities, and good stability. Due to their ease of preparation, the ones produced by simple impregnation of the amine on a solid support are potentially the most applicable for large scale CO₂ separation. For the preparation of these “hybrid” (organic/inorganic) adsorbents, various supports have been described and tested with a variety of amines [7–10]. Polymeric amines with low volatility are generally preferred because they do not suffer from leaching problems encountered with most of the lower molecular weight amines such as diethanolamine, tetraethylenepentamine, or pentaethylenhexamine [11–17]. Polyethylenimines (PEIs), due to their widespread availability, relatively low cost, and potential for high CO₂ adsorption capacity, have been some of the most studied polyamines for the preparation of hybrid solid CO₂ adsorbents [10,18–20].

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In our previous studies, we reported our results on amines and polyethylenimines impregnated on fumed silica and precipitated silica (nano-silica) for the capture of CO₂ from various sources including ambient air [11,19,21–23]. Compared to branched polyethylenimines (BPEIs), the use of linear polyethylenimines (LPEIs), containing only secondary amines, was found to offer some advantages due to its faster CO₂ desorption kinetics and lower heat of adsorption/desorption [21]. This could reduce the amount of energy needed for the endothermic desorption step. In the present work, we have investigated the effect of moisture on the CO₂ adsorption behavior of adsorbents based on LPEI impregnated on fumed silica. Several aspects such as moisture concentration, LPEI loading and adsorption temperature are discussed. Compared to dry conditions, the presence of moisture greatly enhanced the CO₂ adsorption capacity, especially at room temperature. A comparison under the same conditions with a similar adsorbent based on BPEI is also presented, as well as the effect of the fumed silica's hydrophilicity on the adsorption characteristics.

2. Experimental

2.1. Preparation of the adsorbents

Polyethylenimines were coated on the silica supports by a wet impregnation method. In a typical preparation, desired amounts of linear polyethylenimine (LPEI, number-average molecular weight = 25,000, Alfa Aesar) or branched polyethylenimine (BPEI, molecular weight = 25,000, Sigma-Aldrich) and hydrophilic fumed silica (Aerosil[®] 380, Evonik) or hydrophobic silica (HDK[®] H18, Wacker Chemie AG) were mixed together in methanol (Macron Chemicals). After stirring the slurry at room temperature for 24 h, methanol was evaporated using a rotary evaporator. The adsorbents were dried under high vacuum overnight, and stored in glass vials until further analysis. Adsorbents with various PEI loadings were prepared. The PEI loading in the adsorbent was determined by thermogravimetric analysis (TGA), which is described in detail in the SI. The adsorbents were named FS-LPEI-x or FS-BPEI-x, wherein x represented the % of PEI weight content in the adsorbent.

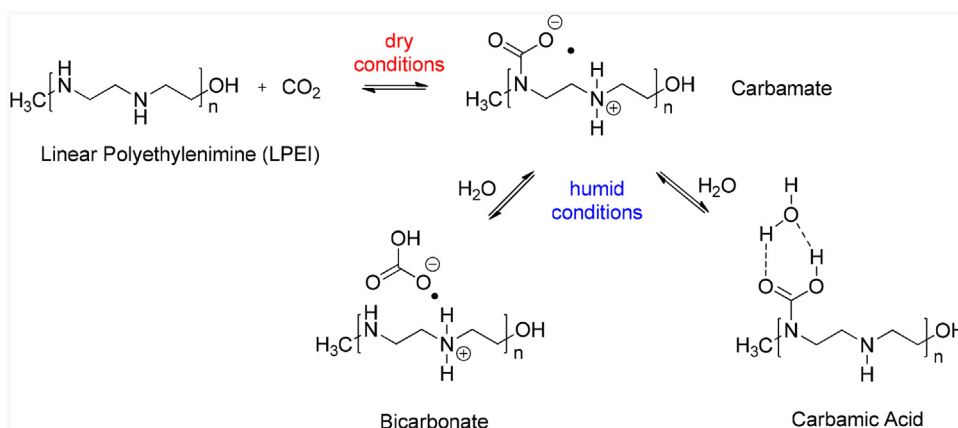
2.2. CO₂ adsorption and desorption under humid conditions (10% and 1% CO₂, 1 h adsorption experiment)

CO₂ adsorption and desorption under humid condition were performed by thermogravimetric analysis on a Shimadzu TGA-50 instrument. Typically, about 3 mg of adsorbent was tested for CO₂ adsorption capacity at 25, 40, 55, 70, 85, and 100 °C using 10% CO₂/

90% N₂. A detailed procedure for humidified gas stream generation and calculation of the specific humidity is presented in the SI. The sample was first heated to 110 °C under N₂ atmosphere to desorb water and CO₂. After 30 min, the temperature was lowered to 25 °C, and the adsorbent was pre-equilibrated in the target humidity level in N₂ atmosphere for 1 h. Afterwards, the sample was exposed to humidified 10% CO₂/90% N₂ to measure the adsorption capacity for 1 h. Upon completion, the gas flow was switched back to humid N₂ and heated to 85 °C to desorb for 30 min. The temperature was then lowered to 40 °C and the adsorbent equilibrated for 1 h in a flow of humidified N₂ until the weight of the sample stabilized. This was followed by the next 1 h adsorption step under humidified 10% CO₂/90% N₂ at 40 °C. Additional adsorption/desorption cycles were carried out for the remaining temperatures under similar conditions. Typically, 0, 3.8, 7.7, 11.5, 15.3, 17.2 mg H₂O/g specific humidity (SH) were tested for each sample. Adsorption experiments with 1% CO₂/99% N₂ were conducted in a similar way. The weight differences between the beginning and end of the CO₂ adsorption step recorded by TGA were taken to calculate the CO₂ adsorption capacity. The weight differences between the end and prior to start of the pre-equilibration time under N₂ were measured to calculate the water adsorption capacity.

3. Results and discussion

In both exhaust gases and the air, moisture is a ubiquitous component. Coal and natural gas burning power plants are reported to have between 6% and 15% moisture in their flue gases [24]. The relative humidity in major U.S. cities ranges from 20% to over 95% depending on the location and the time of the year [25]. For any large-scale real-world CO₂ capture application, the effect of moisture on adsorbents must therefore be considered. Various types of supported amine adsorbents were extensively studied under different combinations of temperatures and CO₂ concentrations. Significantly fewer studies have covered the effect of moisture. In reported cases, moisture generally increased the CO₂ adsorption capacities. For example, Song et al. found that with 15% moisture, the CO₂ adsorption capacity increased from 45 mLg⁻¹ (2 mmol g⁻¹) under dry conditions to 67 mLg⁻¹ (3 mmol g⁻¹) under humid conditions with an adsorbent containing 50% PEI on MCM-41 [24]. Sayari et al. reported, with aminopropyl-grafted pore-expanded MCM-41 silica, an amine efficiency (AE, number of mol CO₂ adsorbed per mol of amine present in the adsorbent) close to 0.5 under dry condition at 25 °C. The AE increased to 0.57 and further to 0.88 under 27% and 74% relative humidity in the gas stream, respectively [26]. The results obtained in other recent



Scheme 1. Proposed adsorption mechanisms between CO₂ and linear polyethylenimine (LPEI) under dry and humid conditions.

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