ETHYLENEDIAMINE-MODIFIED SBA-15 AS REGENERABLE CO_2 SORBENTS

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Introduction

The linkage between anthropogenic CO_2 and global climate change has been well established. Significant reduction of CO_2 emission from large point sources such as fossil fuel power plants is necessary to stabilize atmospheric concentration of CO_2[1]. Compared to the commercial liquid alkanolamines currently used in the absorption of CO_2 from power plant flue gas, solid regenerable sorbents can offer the advantages of lower toxicity and corrosiveness and can potentially reduce equipment cost and energy consumption. Such solid regenerable sorbents are also useful for CO_2 removal from enclosed habitable environments such as submarines and spacecrafts due to their small footprints and reusability.

Mesoporous silica that is chemically modified with amine functionalities is an attractive candidate as high performance CO_2 sorbents because of the combination of their high surface areas in mesopores and the chemical specificity of amines. Alkylamine groups can be grafted on to silica by the condensation of appropriate aminoalkoxysilanes. For example, silica gels and mesoporous silica grafted with 3-aminopropyl groups were reported to be able to adsorb CO_2 reversibly [2-5]. Ethylenediamine (EDA)-modified silica gel and mesoporous silica were also reported to adsorb CO_2 but there are few data on their adsorption capacity [7-8]. In this report we present CO_2 adsorption isotherm as well as breakthrough capacity data on an EDA-modified SBA-15 mesoporous silica.

Experimental

EDA-modified mesoporous silica synthesis. The SBA-15 mesoporous silica substrates were synthesized following the established procedures [6]. The BET surface area of the SBA-15 substrate was 700m^2/g. A typical batch of 10 grams of SBA-15 silica was dispersed in 150ml toluene and 3.2ml water and stirred for one hour for surface hydration. 10ml of N-[3-(trimethoxysilyl)propyl] ethylenediamine (approximately one monolayer equivalent, assuming 4 silanes/nm^2) was subsequently added and the reaction mixture was heated to reflux. After 4 hours at reflux, the reflux condenser was removed and replaced with a short-path still-head and the methanol and water azeotrope were distilled off. After the distillation was complete, the reaction mixture was allowed to cool, and product was collected by filtration, washed twice with 100ml isopropyl alcohol, and air dried. The EDA loading was calculated to be 3.0mmol/g based on final product weight.

Characterization Methods. The as-synthesized and the EDA-modified SBA-15 mesoporous silica samples were characterized by nitrogen adsorption measurements for BET surface area using a Quantachrome Autosorb system. FTIR and NMR measurements were also done to verify surface bonding of the EDA functional groups. Thermal gravimetric analysis (TGA) measurements were performed using a Netzsche STD 409 coupled with a mass spectrometer. The thermal stability of the modified SBA-15 in helium and air was studied with a temperature ramp of 10°C /min to 650°C. CO_2 adsorption isotherms were also measured from 0 to 750 torr CO_2 partial pressure using the TGA system. Breakthrough measurements and temperature programmed desorption (TPD) were carried out using a flow system, where the CO_2 concentrations in the feed gas were varied from 1% to 70% by volume with balance N_2 and in some tests also 2% water vapor. During TPD the sorbent sample was heated to 110°C at 10°C/min. The gas phase was analyzed using a mass spectrometer.

Results and Discussion

The TGA data taken in air are shown in Figure 1 with weight loss peak assignments based on simultaneous mass spectrometer data. The TGA data reveal that the CO_2 adsorbed from ambient air by the EDA-modified SBA-15 was released at 110°C. The EDA sorbent was found to be stable up to 220°C in air and over 300°C in helium.

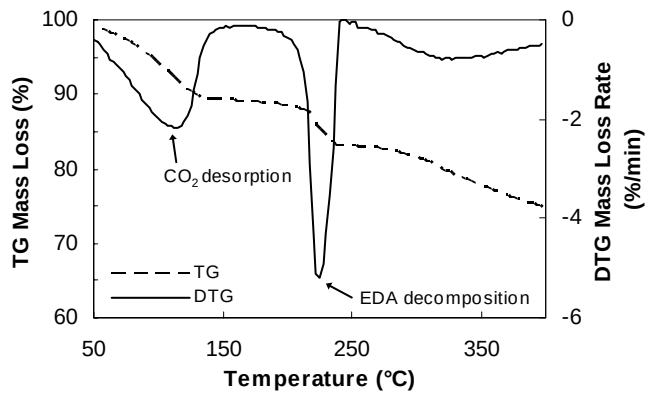

Figure 1. TGA data of the EDA-modified SBA-15 sorbent in air.

The CO_2 breakthrough time and adsorption capacity were measured using the flow system. In Figure 2, the gas phase CO_2 concentration, measured by a mass spectrometer during two consecutive breakthrough/TPD cycles, was shown. After breakthrough, the CO_2 concentration increased quickly to feed gas level, indicating fast adsorption kinetics. The sorbent can be regenerated by thermal swings to 110°C at 10°C/min, as evidenced by the same height of the two desorption peaks. When the EDA-SBA-15 sorbent was subjected to ten cycles of adsorption and desorption, it retained its CO_2 adsorption capacity and was fully regenerable.

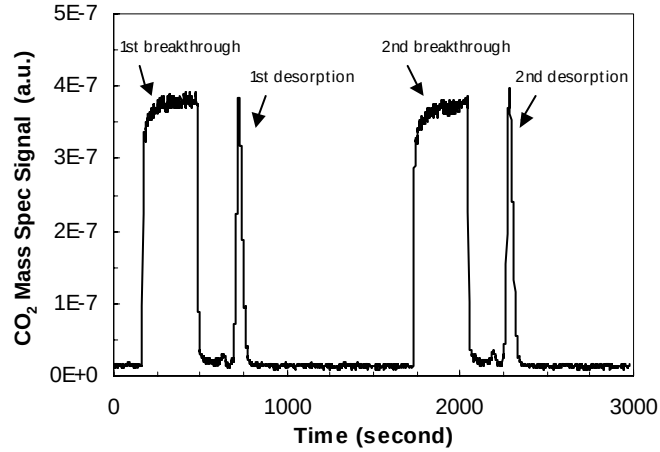

Figure 2. Gas phase CO_2 concentration during cyclic adsorption/desorption tests.

The isothermal adsorption capacity data on the EDA-SBA-15 sorbent are summarized in Figure 3. The EDA-SBA-15 silica adsorbs around 20mg/g of CO_2 at 25°C and 1 atm with 15% CO_2 (by volume) in N_2 in the flow system. At the same partial pressure of pure CO_2, the sorbent uptakes about 25 mg/g of CO_2 at 22°C based on the TGA data. At 1 atm CO_2 partial pressure, the adsorption capacity is 86 mg/g, which is lower than the stoichiometric chemisorption capacity of 132mg/g based on the initial estimate of 3.0mmol/g EDA loading, but compares favorably to the capacity of the aminopropyl-modified silica sorbents previously reported (20 to 90 mg/g at 1 atm CO_2 partial pressure at room temperature). It is believed that the actual available EDA loading on the EDA-SBA-15 sorbent is lower than 3.0mmol/g and can be increased by improvements in synthesis.

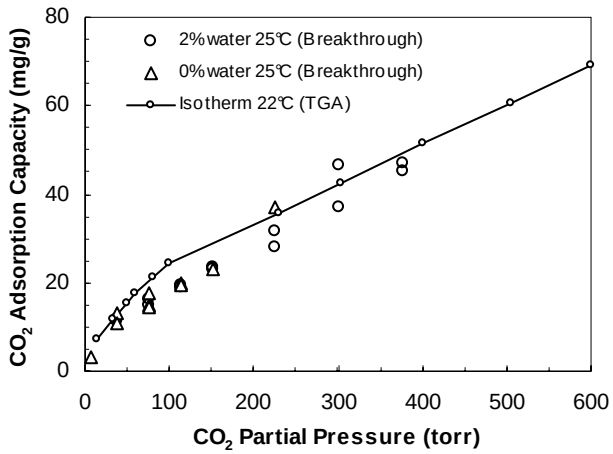

Figure 3. CO_2 adsorption isotherms of the EDA-SBA-15 sorbent.

The adsorption isotherm based on the TGA data agrees with the capacity data from breakthrough tests within experimental error. The presence of 2% water vapor in some of the breakthrough tests did not influence the CO_2 uptake. This behavior, although different from those of previously reported aminopropyl-modified silica, is expected as each EDA group contains two amine groups and can adsorb one CO_2 molecule. Two aminopropyl groups are necessary to bond one CO_2 molecule if no water is present. Carbamate formation on EDA-SBA-15 is of the intramolecular type that does not involve water molecules, and it should proceed faster than on aminopropyl-modified silica sorbents. It is believed that by tailoring the amine groups, CO_2 adsorption capacity and kinetics can be further improved.

Conclusions

We have synthesized an EDA-modified SBA-15 mesoporous silica and characterized its CO_2 adsorption properties. The CO_2 adsorption capacity of the EDA-SBA-15 sorbent is around 20mg/g at 25°C and 1 atm with 15% CO_2 (by volume) in N_2. This is comparable to the adsorption capacity of aminopropyl-modified mesoporous silica. However, while the adsorption of the latter decreases in the absence of water, the CO_2 adsorption capacity of the EDA-modified mesoporous silica is not influenced by humidity. Additionally, the EDA functional group allows CO_2 capture via intramolecular carbamate formation and therefore favorable kinetics. By tailoring the amine groups, it is expected that CO_2 adsorption capacity and kinetics can be further improved.

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