

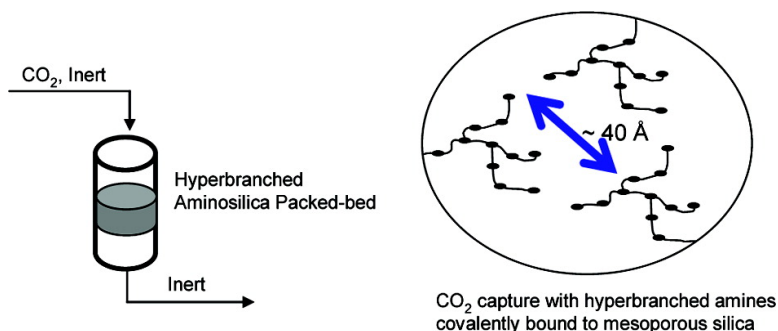
Communication

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Designing Adsorbents for CO₂ Capture from Flue Gas-Hyperbranched Aminosilicas Capable of Capturing CO₂ Reversibly

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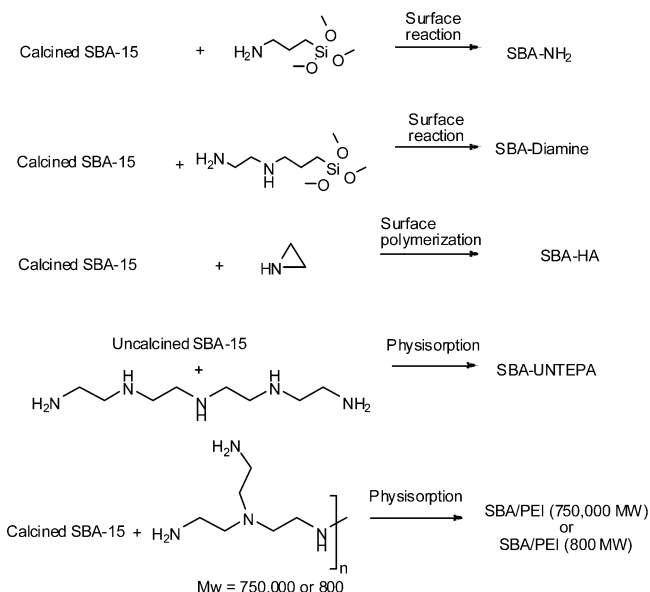
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Due to the increasing CO₂ concentration in the atmosphere, contemporary research has focused on ways to slow or stop this trend. CO₂ capture has attracted attention due to the potential to trap and sequester large amounts of CO₂ from concentrated sources such as power plants. Traditional technologies in capturing CO₂ include absorption by aqueous amines.¹ However, utilization of this process is energy intensive and expensive when used for large volumes of dilute gas, such as flue gas.² This is primarily due to the high heat capacity of water and use of temperature swings to induce CO₂ desorption. Many types of amine-modified silica materials have been reported (e.g., amine-tethered silica materials,³ amines impregnated into porous silicas,^{4,5} etc.) as possible solid adsorbents for CO₂ capture from flue gas streams. However, these materials generally suffer from low CO₂ capacities or lack stability over many cycles, especially when amines are physisorbed onto the support. Therefore, it is advantageous to synthesize an organic/inorganic hybrid amine-tethered silica material with high amine loadings (>6 mmol/g) capable of reversibly binding CO₂ rather than employing physisorbed, impregnated adsorbents that may be unstable after several cycles. Here we describe the synthesis of a covalently tethered hyperbranched aminosilica (HAS) material^{6–8} capable of binding CO₂ reversibly from simulated flue gas, and we compare its CO₂ capacity with those of other reported solid amine adsorbents (Scheme 1). We conceived of these HAS materials as practical CO₂ adsorbents due to their simple synthesis, covalent inorganic-organic linkage, and low cost. The HAS material has the highest fully regenerable CO₂ capacity for a covalently supported adsorbent under simulated flue gas conditions.

The synthesis of HAS was performed via a one-step reaction between aziridine and the silica surface.⁶ As previously reported on silica wafers, the surface silanols initiated aziridine polymerization off the surface.⁶ Due to low surface areas, hybrid aminosilica materials constructed on silica wafers are impractical adsorbents. However, the formation of hybrid aminosilicas on high surface area mesoporous silica materials^{7,8} can lead to materials capable of reversibly binding CO₂ with substantial capacities (>2 mmol CO₂/g). The aziridine monomer was added to SBA-15 dispersed in a toluene solution with catalytic amounts of acetic acid and stirred at room temperature in a glass pressure reaction vessel. The resulting HAS material (SBA-HA) was washed extensively to remove physisorbed aziridine or unbound oligomer from the surface. The organic loading of the grafted hybrid aminosilica used here was determined via elemental analysis as 7.0 mmol N/g material.

For these studies, the hybrid aminosilica was uniformly dispersed in sand and tested in a fixed bed flow system. The adsorbent/sand

Scheme 1. Solid CO₂ Adsorbents



mixture allowed for decreased heat effects and reproducible flow through the bed. The SBA-HA material was analyzed for CO₂ capture at 25 °C and 75 °C with 10% CO₂/Ar saturated with water flowing at a rate of 20 mL/min. The adsorption of CO₂ on the aminosilica was determined by monitoring the effluent gas with a mass spectrometer. After the adsorption experiment, the gas was switched to pure argon, and the CO₂ was desorbed from the surface at 130 °C for at least 3 h. As shown in Figure 1, the SBA-HA material captured CO₂ reversibly in all 11 experiments performed with an average capacity of 1.98 mmol CO₂/g adsorbent (6.6 mmol CO₂/g aziridine monomer or 0.28 mmol CO₂/mmol N).⁹ The CO₂ adsorption capacities were found to be relatively constant, ranging between 1.9 and 2.1 mmol CO₂/g. Hence, under simulated flue gas conditions, the SBA-HA material demonstrated promising CO₂ adsorption properties.

Additionally, the SBA-HA material reported in the literature was compared to a number of the best materials (Scheme 1). For instance, traditionally functionalized (SBA-NH₂)¹⁰ and diamine-functionalized (SBA-diamine) aminosilicas were synthesized with amine loadings of 1.9 mmol N/g and 2.5 mmol N/g, respectively. When analyzed in the fixed bed flow system, these materials captured CO₂ with capacities of approximately 10% (SBA-NH₂) and 20% (SBA-diamine) that of the SBA-HA material at 25 °C (Table 1). The high loading of amines on the hybrid aminosilica (SBA-HA) allowed for a CO₂ capacity of 3.1 mmol CO₂/g at 25 °C, which is the basis for the data in Table 1.

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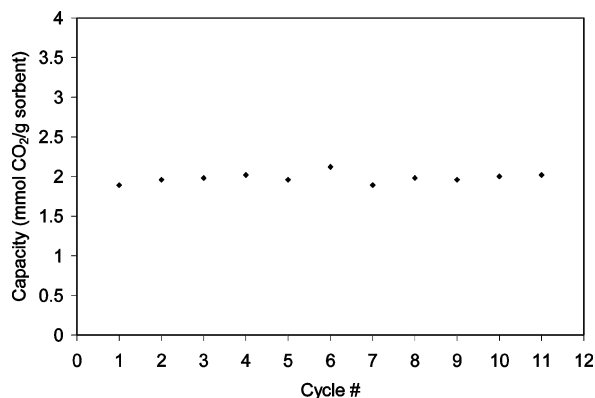


Figure 1. Multicycle CO₂ testing of SBA-HA at 75 °C.

Table 1. Comparison of Amine Adsorbents as Solid CO₂ Traps

material	analysis temp (°C)	mmol N/g ^a	capacity/capacity HA	mmol CO ₂ /mmol N
SBA-HA	25	7.0	1.00	0.44
SBA-HA	75	7.0	0.68	0.30
SBA/PEI _(750 000 MW)	25	7.4	0.64	0.27
SBA/PEI _(750 000 MW)	75	7.4	0.69	0.29
SBA/PEI _(800 MW)	25	10.9	nd ^b	nd ^b
SBA/PEI _(800 MW)	75	10.9	nd ^b	nd ^b
SBA-UNTEPA	25	10.5	0.88	0.26
SBA-UNTEPA	75	10.5	1.09	0.32
SBA-diamine	25	2.5	0.23	0.28
SBA-NH ₂	25	1.9	0.13	0.21

^a Values were determined from elemental analysis. ^b Capacities were not determined or reproducible due to the tacky nature of the material from the addition of PEI. The materials could not be dispersed in the packed-bed uniformly. All capacities are normalized to the capacity of SBA-HA at 25 °C (3.11 mmol CO₂/g sorbent).

Three additional materials were synthesized via impregnation of (i) a high molecular weight PEI⁴ into calcined SBA-15 (SBA/PEI_(750 000 MW)), (ii) a low molecular weight PEI into calcined SBA-15 (SBA/PEI_(800 MW)),⁴ or (iii) tetraethylenepentamine (TEPA) into uncalcined SBA-15⁵ (SBA-UCTEPA). The SBA/PEI_(750 000 MW) material captured approximately 70% as much CO₂ per gram adsorbent as the SBA-HA material. Similar to previous reports,⁴ the capacities of the SBA/PEI materials increased at a higher temperature, possibly due to swelling of the amine polymer within the porous support. However, when SBA/PEI_(800 MW) was studied, the capacities were not reproducible due to the texture of the material. When the PEI was impregnated in the SBA-15, the resulting material was very “sticky” due to the addition of the PEI polymer to the internal and external surface of the SBA-15. Furthermore, these materials typically clogged the adsorption column, creating a significant decrease in the volumetric flow rate and a large pressure drop. Thus, CO₂ adsorption capacities with these materials could not be determined in our system. The sample prepared by impregnation of TEPA into uncalcined SBA-15 (SBA-UCTEPA) captured CO₂ with high capacities at 75 °C. However, a decrease in CO₂ capacity was observed after subsequent runs (see the Supporting Information), likely due to leaching of the physisorbed TEPA from the support. Furthermore, at lower temperatures, the capacity decreased substantially (Table 1). Although high amine loadings can be obtained by physically adsorbing low molecular

weight amines onto the support material, the longevity of such a material appears limited due to leaching of the organics from the support.

The easy to synthesize, robust HAS material is capable of adsorbing CO₂ reversibly with very high capacities of 3.1 mmol CO₂/g material at 25 °C. The advantage of this adsorbent over previously reported adsorbents rests in its large CO₂ capacity and demonstrated multicycle stability. The material was recycled by thermally desorbing the CO₂ from the surface with essentially no changes in capacity. Furthermore, the organic groups on the surface were stable in the temperature range between 25 and 130 °C due to the covalent attachment between the support and the organic groups. We report the first use of hybrid aminosilicas of this type for CO₂ capture. Based on the high amine loading, the ability to recycle the materials, and the high CO₂ affinity, these materials are very promising new materials for acid gas capture from flue gas streams.

Acknowledgment. This work was fully supported by the U.S. Department of Energy, National Energy Technology Laboratory under contract no. 41817M3226.

Supporting Information Available: Control material adsorption testing, experimental methods, XRD, FT-Raman spectra, CPMAS ¹³C NMR spectra, porosity data, and polymer characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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