CARBON DIOXIDE CAPTURE USING AMINE-BASED MOLECULAR ANCHORS ON MULTI WALL CARBON NANOTUBES

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Introduction

Carbon dioxide emission from hydrocarbon power plants continues to increase. In fact, atmospheric carbon dioxide levels a century from now are anticipated to exceed twice those of a century ago[1]. Capture and storage/use of carbon dioxide is preferable to directly adding to the carbon dioxide content of the atmosphere.

Solid-state sorbents offer an attractive option for reversible capture of carbon dioxide due to their promise of high operating temperatures and long usage lifetime. Porous materials enabled with carbon dioxide-capturing functionality can provide a high capacity with their large gas-accessible surface areas.

Carbon nanotubes are an appealing option for a high surface area material with large values of thermal conductivity[2]. An option for adding carbon dioxide-capturing capability to carbon nanotubes surfaces without diminishing the desirable thermal properties of the tubes is the use of molecular anchors[3,4]. These bifunctional molecules have an anchor portion that adheres to nanotubes surfaces through hydrophobic and/or pi-stacking interactions and a functional portion to reversibly capture carbon dioxide. Such molecules with pyrene-based anchors have low volatility and high relative thermal stability. Amine-based functional portions of the molecules should enable the temperature-dependent chemical adsorption and desorption of gas-phase carbon dioxide molecules.

Experimental

Molecular Anchor Synthesis. Pyrene methylamine hydrochloride (Aldrich) is coupled with picolinic acid (Aldrich) to form the pyrene methyl picolinimide (PMP) anchor seen in **Figure 1**. Model anchors such as 1-bromoacetyl pyrene and 1-pyrene carboxaldehyde were used as purchased (Aldrich).

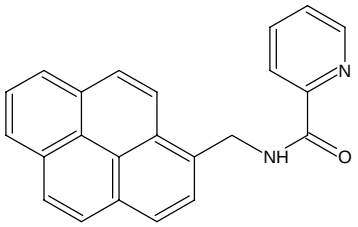

Figure 1. Schematic of bifunctional anchor consisting of pyrene anchor portion and amine carbon dioxide capture portion.

Materials and Deposition. Multi wall carbon nanotubes were used as received (Nanostructured and Amorphous Materials, #1230NMG). Molecular anchors were deposited onto the surfaces of powder-form carbon nanotubes using supercritical fluids. In a typical experiment carbon nanotubes and anchor molecules were mixed and added to a stainless steel vessel, which was placed in a reaction chamber and heated to 150C. The chamber was purged with the reaction gas (propane or carbon dioxide) and sealed. The pressure of the gas in the chamber was then raised to 7500psi using a syringe pump filled with the gas. Mixtures of nanotubes and anchors were held at these conditions for 10 minutes before the reaction fluid/gas was expelled from the system and the vessel was removed from the chamber to cool. Degree of loading of the nanotubes with the anchor molecules was controlled through choice of initial reaction mixture proportions.

Characterization. Presence of anchor molecules on the multi wall carbon nanotubes is confirmed using thermal gravimetric analysis (TGA). Initial attempts at characterizing carbon dioxide uptake of the material have been attempted using a residual gas analyzer (RGA) consisting of a temperature controlled gas flow cell and a mass spectrometer.

Results and Discussion

Carbon nanotubes are seen to be thermally stable when heated in a nitrogen atmosphere to 500C, while pyrene anchors are seen to volatilize and/or decompose resulting in a sample mass loss at around 250C. Degree of anchor loading on the nanotubes can be inferred from the total sample mass loss as seen in **Figure 2**.

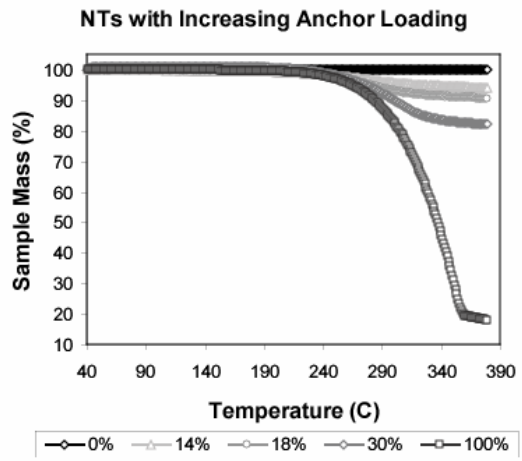

Figure 2. Anchor fraction of sample reaction mixture is seen to track well with TGA mass loss.

Carbon dioxide flowed through a cell containing nanotubes that have been modified with the PMP anchor is seen to adsorb to the material before reaching saturation as see in **Figure 3**.

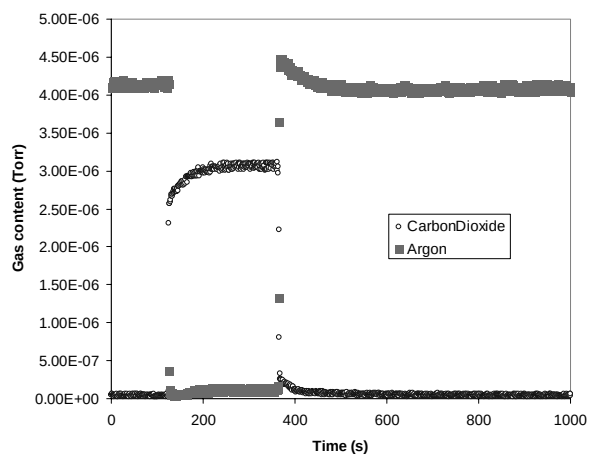

Figure 3. The mass spectrometer in an RGA shows the carbon dioxide breakthrough curve of the PMP anchor loaded onto multi wall nanotubes as flowing argon is switched to a 70% carbon dioxide/nitrogen mix and back.

Conclusions

Carbon nanotubes modified with molecular anchors are pursued as an attractive option for high capacity carbon dioxide sorbent materials. Model compounds based on pyrene anchors have been shown to modify the surface of multi wall carbon nanotubes and can efficiently be deposited using supercritical fluids. A pyrene-based anchor with amine functionality has been synthesized and initial attempts to characterize its effectiveness in capturing carbon dioxide have been made. Determination of the carbon dioxide isotherm of PMP anchors on multi wall carbon nanotubes, as well as the kinetics and magnitude of carbon dioxide uptake on the material, will enable an evaluation of the potential of this material system relative to other carbon dioxide sorbent systems. Alternative amine forms and alternate anchor moieties may be used to optimized performance of the promising molecular anchor on carbon nanotube approach.

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