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A NOVEL CARBON FIBER BASED MATERIAL AND SEPARATION TECHNOLOGY

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ABSTRACT

Our novel carbon fiber based adsorbent material shows preferential uptake of CO₂ over other gases. The material has a unique combination of properties, which include a large micropore volume, a large BET surface area, and electrical conductivity. These properties have been exploited to effect the separation of CO₂ from a model gas (CH₄). Enhanced desorption is achieved using an electrical current passed through the material at low voltage. The manufacture, characterization, and CO₂ adsorption behavior of the materials is reported here, along with our novel electrical swing separation technology.

KEYWORDS

Activated carbon fibers, porous composites, gas separation, electrical swing adsorption.

INTRODUCTION

The removal of CO₂ is of significance to the combustion of fossil fuels which releases large volumes of CO₂ to the environment. Several options exist to reduce CO₂ emissions, including substitution of nuclear power for fossil fuels, increasing the efficiency of fossil plants, and capturing the CO₂ prior to emission to the environment. All of these techniques have the attractive feature of limiting the amount of CO₂ emitted to the atmosphere, but each has economic, technical, or societal limitations. Gas separation is, therefore, a relevant technology in the field of energy production. A novel separation system based on a parametric swing process has been developed that utilizes the unique combination of properties exhibited by our carbon fiber composite molecular sieve (CFCMS).

The CFCMS is a monolithic activated carbon composed of petroleum pitch-derived carbon fiber and a phenolic resin-derived binder (Burchell et al., 1994). The binder phase content is quite low and provides a monolithic structure by bonding the fibers at their contact points only, thus rendering the CFCMS macroporous. The CFCMS is a highly adsorbent material with very little resistance to bulk gas flow. Experiments conducted at ORNL have shown the CFCMS to have a high affinity for carbon dioxide compared to conventional granular activated carbons (Burchell and Judkins, 1996). Moreover, granular carbon systems are subject to attrition due to abrasive wear in service, and channeling of the gas being processed as a result of inhomogeneous

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packing in the beds. The use of the CFCMS would permit the employment of, for example, horizontally-oriented vessels with controlled flow of the gas with the contaminants/diluents to be adsorbed through the adsorbent without risk of channeling and bypass flows. Here, we present the results of several experiments which demonstrate the performance of CFCMS and the electrical swing adsorption process for CO₂ separation.

EXPERIMENTAL

The carbon fiber composite molecular sieve (CFCMS) synthesis route is illustrated in Fig.1. Isotropic pitch-derived carbon fibers are mixed with powdered phenolic resin and water to form a slurry. The slurry is transferred to a molding tank and the water drawn through a porous screen under vacuum. The resultant green artifact is dried, cured at 60°C in air, and stripped from the mold screen. The composite is cured at ~150°C in air prior to carbonization at 650°C in an inert gas. The final synthesis stage involves activation of the composite in moisture saturated He in the temperature range 800-950°C.

Porosity characterization was performed using nitrogen adsorption and mercury intrusion. Nitrogen adsorption isotherms were measured at 77 K using our Autosorb-1 instrument. Micropore size analysis used a variety of methods, including the Brunauer, Emmett, and Teller (BET) (Brunauer et al., 1938) method for surface area, the Dubinin-Astakhov (DA) (Bansal et al., 1988) method for micropore radius, and the t-method for micro-pore volume. CO₂ adsorption isotherms for CFCMS were obtained using the Autosorb-1 apparatus over the pressure range 0.1 to 760-mm Hg and at temperatures of 30, 60, and 100 °C. High pressure CO₂ adsorption data (850 psi max.) were obtained using a gravimetric apparatus, courtesy of Westvaco Corporation.

A schematic diagram of our experimental breakthrough apparatus is shown in Fig. 2. The feed gas flows through a CFCMS sample (25.4-mm diameter and 76.2-mm long) to a vent. A sample of the downstream gas is fed to a mass spectrometer allowing on-line monitoring of the exit gas composition. Flowmeters (F1 & F2) are positioned on the inlet and outlet sides of the CFCMS sample. Electrical leads are connected to each end of the sample creating an electric circuit through the sample. On saturation of the CFCMS with, for example, carbon dioxide, immediate desorption can be accomplished by application of very low voltages (in our experiments we have used 0.5-1 volt) across the CFCMS adsorbent.

Fig. 1. The CFCMS synthesis route.

Fig. 2. Schematic drawing of our breakthrough apparatus.

RESULTS AND DISCUSSION

A series of CFCMS cylinders were prepared and activated to burn-offs ranging from 9 to 36% and the BET surface area and micropore size/volume determined from the N₂ adsorption isotherms. Table 1 reports the mass and average burn-off for each of the four cylinders (25-mm diameter x 75-mm length), and their BET surface area, micropore volume (t-method), and mean micropore radius (DA method). Samples were taken from the top (T) and bottom (B) of each cylinder for analysis. Where the measured BET surface areas were widely different between the top and bottom of the cylinders a repeat measurement was performed.

Table 1. Micropore analysis data for activated CFCMS samples

Specimen	Mass (g)	Burn-off (%)	BET Area (m ² /g)	Pore Volume [t-method] (cm ³ /g)	DA Pore Radius (nm)
21-11 T	11.96	9	485	-	0.70
21-11 B	11.96	9	540	0.212	0.65
21-2B T	11.01	18	770	0.282	0.72
21-2B B	11.01	18	1725	0.603	0.70
21-2B B (repeat)	11.01	18	961	0.328	0.71
21-2D T	9.86	27	939	0.305	0.75
21-2D B	9.86	27	2470	0.866	0.75
21-2D B (repeat)	9.86	27	2477	0.791	0.75
21-2C T	8.86	36	923	0.235	0.87
21-2C B	8.86	36	2323	0.723	0.75
21-2C B (repeat)	8.86	36	856	0.270	0.75

At high burn-offs there was a tendency for one end of the cylinder to exhibit higher BET surface areas than the other end. The activation fixture used in this work was designed to distribute the saturated He along the length of the CFCMS cylinder. Despite this, activation to high burn-off does result in a non-uniform activation as indicated by the BET data. The BET surface area increases with burn-off, approaching 2500 m²/g at >25% burn-off. The micropore size (DA pore radius) is apparently less sensitive to burn-off (Table 1) and increases only slightly over the weight loss range reported here. The pore volume (t-method) varies with the BET surface area, increasing with burn-off. The observed variations in BET surface area and micropore volume and radius are in agreement with our previous data (Burchell and Judkins, 1996).

Adsorption isotherms were obtained at temperatures of 30, 60, and 100°C at pressures up to one atmosphere for CO₂ and typical data are shown in Fig. 3. All of the CFCMS samples analyzed adsorbed less CO₂ at 60 and 100°C than at 30°C. At 100°C the amount of CO₂ adsorbed was approximately one third that adsorbed at 30°C. Figure 4 shows CO₂ adsorption isotherms at 25°C for CFCMS specimens 21-11 and 21-2B over the pressure range 0.5-58 bar (8-850 psi).

The measured volumetric (Fig. 3) and gravimetric (Fig. 4) adsorption capacities at one atmosphere for CO₂ are in good agreement for the CFCMS specimens. At one atmosphere,

approximately 100 mg of CO₂ per g of CFCMS was adsorbed, rising to >490 mg/g (Fig. 4 specimen 21-2B).

Fig. 3. Carbon dioxide adsorption isotherms at 30, 60 and 100 °C on CFCMS (9% burn-off).

Fig. 4. Carbon dioxide isotherms at 298K on CFCMS activated to different burn-offs (9 and 18%).

The CO₂ adsorption data discussed above suggest that CFCMS might provide for the effective separation of CO₂ from gases such as CH₄ or flue gas mixtures. To determine the efficacy of CFCMS for this purpose, several steam-activated samples were tested in our breakthrough apparatus (Fig. 2). Figure 5 shows a breakthrough plot for CO₂ on CFCMS specimen 21-11. Initially the CFCMS sample is purged with helium to drive out any entrained air. The input gas is then switched to CO₂ at a flow of 0.1 standard liters per minute (slpm) and the He concentration falls to zero. The CO₂ concentration stays constant at a low level because the CO₂ is adsorbed. After approximately nine minutes, the CO₂ concentration begins to rise as the CFCMS becomes saturated with CO₂ (i.e., breakthrough occurs). The CO₂ adsorption capacity can thus be calculated from the gas flow rate and the breakthrough time. In this instance, specimen 21-11 adsorbed 0.9 liters of CO₂. A typical breakthrough plot for a CH₄/CO₂ mixture is shown in Fig. 6. Any entrained air is initially driven out with a He purge. The input gas is then switched to a 2:1 mixture of CH₄/CO₂ at a flow rate of 0.33 slpm. The outlet stream He concentration decreases and the CH₄ concentration increases rapidly (i.e., CH₄ breaks through). Adsorption of CO₂ occurs and, therefore, the CO₂ concentration remains constant at a low level for approximately six minutes before the CO₂ concentration begins to increase (i.e., "breakthrough" occurs). Breakthrough experiments were performed on four CFCMS samples with burn-offs ranging from 9 to 36%. In the case of the pure CO₂ gas experiments, the amount of CO₂ adsorbed exceeded 0.8 liters on 0.037 liters of CFCMS. The maximum CO₂ uptake during mixed gas breakthrough studies was observed for the lowest burn-off specimen, and was 0.73 liters of CO₂ adsorbed on a 0.037 liter CFCMS sample.

CFCMS has a continuous carbon skeleton which imparts electrical conductivity to the material. The carbon fibers used in the synthesis of CFCMS have, according to their manufacture, an electrical resistivity of 5 milliohm·cm. Figure 7 is a plot of the current-voltage and power-temperature characteristics of a 2.5-cm diameter, 7.5-cm long CFCMS cylinder. At an applied d.c. potential of one volt, approximately 5 amps flows through the CFCMS causing a temperature increase to 50-60°C. The CFCMS samples electrical resistance is thus 0.2 ohm and the resistivity is 131 milliohm·cm. This resistivity is considerably greater than that of the fibers, and is attributed to contact resistance and the lower electrical conductivity of the phenolic resin-derived carbon binder. We have utilized the electrical properties of CFCMS to effect a rapid desorption of adsorbed gases in our breakthrough apparatus. The process has been named electrically enhanced desorption, and the benefit of this technique is demonstrated in Fig. 8 where the CO₂ and CH₄ gas concentrations in the outlet gas stream of our breakthrough apparatus (Fig. 2) are shown. Three adsorption/desorption cycles are shown in Fig. 8. In the

first and second cycles (A and B in Fig. 8) desorption is caused by the combined effect of an applied voltage (1 volt) and a He purge gas. In the third cycle (C in Fig. 8) desorption is caused only by the He purge gas. A comparison of cycles B and C indicated that the applied voltage reduces the desorption time to less than one-third of that for the He purge gas alone (cycle C). Clearly, the desorption of adsorbed CO_2 can be rapidly induced by the application of an electric potential. A separation may thus be effected on the basis of an "electrical swing."

An "electrical swing" separation system would appear to have inherent advantages over both pressure and temperature swing adsorption systems because separation can be achieved without altering system pressure or applying external heat.

Fig. 5. Typical CO_2 breakthrough plot CFCMS sample 21-11 (9% burn-off).

Fig. 6. Typical CO_2/CH_4 breakthrough on plots on CFCMS sample 21-11 (9% burn-off).

Fig. 7. The current-voltage and power-temperature relationship for CFCMS (sample 21-2B, 18% burn-off, 25-mm diameter x 76-mm length).

Fig. 8. CO₂/CH₄ breakthrough plots on CFCMS showing the benefit of electrically enhanced desorption.

CONCLUSIONS

A porous monolithic activated carbon material (CFCMS) has been developed that is strong, rigid, and which overcomes problems associated with operation using granular adsorbents. The open structure of CFCMS results in a permeable material which offers little resistance to the free-flow of fluids. The material has a unique combination of properties, including reasonable compressive strength, electrical conductivity, and a large micropore volume. CO₂ isotherms have been obtained for samples of CFCMS both volumetrically and gravimetrically. At 30°C and atmospheric pressure the CFCMS material has a CO₂ uptake of >50 cm³/g (>100 mg/g). The CO₂ uptake is reduced at elevated temperature, and falls to approximately 20 cm³/g (40 mg/g) at 100°C. However, the adsorption of CO₂ increases with increasing pressure such that at 58 bar and 25°C the mass of CO₂ adsorbed increases to >490 mg/g. A series of breakthrough experiments were performed on CFCMS specimens and their ability to selectively remove CO₂ demonstrated. The unique combination of properties of CFCMS has been exploited to effect the rapid desorption of CO₂ from the material using electrically enhanced desorption under a low applied voltage.

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