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Electrically renewable carbon fibers composites for CO_2 adsorption

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An efficient CO_2 adsorbing monolith structure is obtained. The monolith is based on blended petroleum-pitch-derived carbon fibers and phenolic resin in weight ratio of 3:1. The measured CO_2 adsorption capacity of the adsorbent is about 2.34-2.87 moles CO_2/kg at 1 bar and 273 K. Due to its good electrical conductivity, the adsorbed CO_2 can be desorbed quickly and efficiently by direct electro-thermal desorption, at the passage through the monolith of an electric current at low voltage. The measured rate of CO_2 desorption of the steam activated sample FCN400a at environmental pressure is 0.273 moles/h at 393 K (18 A/6.8 V).

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1. Introduction

During the past decade, there has been much interest in CO_2 capture and sequestration technologies due to the emerging need for green-house gas mitigation. Adsorption of CO_2 by solid adsorbents from gas mixtures gives one possible solution to the problem. The most widely used solid adsorbent reactors are conventionally based on packed beds loaded with various types of zeolite, carbon, polymer, organic-inorganic hybrid or inorganic oxide adsorbent materials [1-19].

Large amounts of data have been published concerning the CO_2 adsorption capacity of different materials like active carbons and zeolites. The literature reports on CO_2 adsorption capacity of activated carbons were between 0.06 moles/kg (298 K, 1 bar) and 3.5 moles/kg (275 K, 2 bar), while on zeolites register values between 0.09 moles/kg (298 K, 1 bar) and 4.9 moles/kg (273 K, 0.1 bar CO_2 partial pressure) [8].

In terms of achieving high adsorption capacities, activated carbons and zeolite-based molecular sieves have shown much promise. Activated carbon is widely used in adsorption separation processes because of its attractive adsorption properties [9]. Activated carbons generally give higher additional capacity at pressures greater than atmospheric pressure in comparison to zeolites. CO_2 adsorption capacities of activated carbons depend on their pore structure but also on the surface chemistry properties.

The interest in using monolithic structures for the adsorption process is increasing due to their practical advantages, such as rapid cycle pressure swing adsorption, volatile organic compounds removal, desiccant and other processes where pressure drop has a significant economic impact [10].

There is a growing interest in using activated carbon fibers for the adsorption and recovery of organic vapours, for removing CO_x, SO_x and NO_x from gases, and improves air quality [11-17]. Difficulties in using activated carbon fibers in monolithic forms can be overcome by incorporating them into a composite structure.

The objective of our work is to design a material for CO_2 adsorption that is simple, cost-effective and can be easily regenerated. Having a good electric conductivity, the adsorbent should be regenerated by direct electro-thermal desorption.

2. Experimental

Petroleum-pitch-derived carbon fibers were purchased from Asbury Graphite Mills Inc. Milled carbon fibers of 13 µm diameter and an average length of about 200, 400 and 800 µm were used. Phenolic resin powder type Steron F-VIII NVD from Dynea Chemicals Oy was used.

The monoliths were fabricated by blending carbon fibers and powdered phenolic resin via a slurry moulding process. The weight ratio of carbon fibers to phenolic resin was 3:1. The fibers and phenolic resin powder were mixed with water to obtain slurry. The slurry was transferred into a mould and the water was removed under vacuum. The green forms which were obtained were dried in air atmosphere at 333 K for 16 hours and cured at 423 K for 4 hours. Cured monolithic composites (FCN200, FCN400 and FCN800) were then carbonized up to 923 K. The carbonized forms were held at 923 K for 3 hours under continuous nitrogen flow of 0.5 L/min, in order to convert the phenolic resin into carbon. The obtained carbonized composite monoliths were activated by steam injection at 1073 K for 1 hour, at a 0.5 L/h flow rate, in order to develop micropores within the carbon fibers and resin-derived carbon binder. The activated samples (FCN200a, FCN400a and FCN800a) were finally obtained [17].

Porosity development and void volume were analysed using a Carl Zeiss Auriga Scanning Electron Microscope (SEM).

Low-pressure nitrogen (N_2) and carbon dioxide (CO_2) adsorption measurements up to 1 bar were performed on the Autosorb-1 (Quantachrome) volumetric analyzer, at 77 K using liquid nitrogen. CO_2 isotherms were also collected at 273 K using pure carbon dioxide gas (purity ≥ 99.5%). Parameters such as the BET surface area and total pore volume were determined from the N_2 adsorption isotherms. Micropore volume was determined from the CO_2 adsorption isotherms at 273 K, after applying the Dubinin-Radushkevich (DR) equation (1) [20]. DR equation can be represented as follows:

$$\ln W = \ln W_0 + (R/E)^2[T\ln(P_0/P)]^2, \qquad (1)$$

where W is the amount of adsorbed CO_2, W_0 is the microporous volume and E is the characteristic adsorption energy. W is given by equation (2):

$$W = \Delta n{*}M/\rho, \qquad (2)$$

where Δn is the amount of CO_2 adsorbed in mol/g, M is the molecular weight (M = 44 g) and ρ is the density of the CO_2 adsorbate at the temperature T ($\rho = 0.85$ g/cm^3 at 298 K).

CO_2 adsorption capacity at low pressure was also evaluated from the isotherms.

The monolith adsorbents' regeneration capacity was measured by passing the electric current at low voltage directly through the monolith. A special designed adsorption cell according to Burchell [15] was used. Prior to the measurement, the monolith was saturated with CO_2 from pure carbon dioxide gas (purity ≥ 99.5%), using a continuous gas flow of 30 L/h CO_2 for about 40 minutes at 298 K and atmospheric pressure. The FCN400a monolith sample with a mass of 193.5 g and geometric size of 90 mm in diameter and 130 mm in height was tested. The adsorption efficiency of CO_2 was measured by the difference between output and input of CO_2 concentrations. A tool probe type TESTO 535 with two IR channels and measuring range between 0-9999 ppm was fixed on the output gas circuit.

3. Results and discussion

3.1. Porosity development characterization

Fig. 1(a) shows an image of the synthesized monoliths. As it can be observed, well defined cylinder-shape monoliths were obtained.

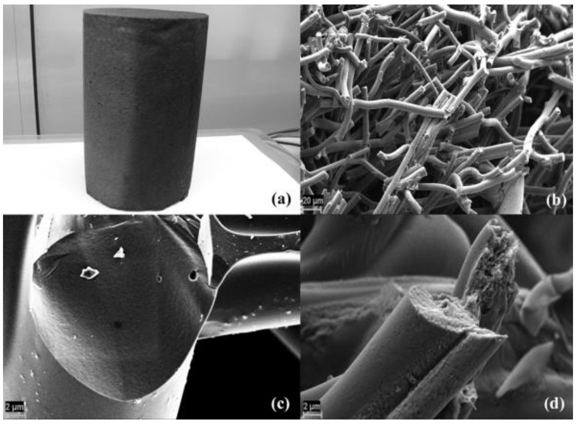

Fig. 1. Images of the carbon fibers based monolith FCN400a: (a) Monoliths image; (b) SEM - steam activated monolith (1000x); (c) SEM - non activated monolith (10000x); (d) SEM - steam activated monolith (10000x)

The porosity development and void volume were observed using a Carl Zeiss Auriga Scanning Electron Microscope (Figs. 1(b, c, d)). By activation, the surface area of the monolith increased and the pore structure was developed, thus improving the surface area, pore volume, respectively adsorption capacity. A highly developed porosity can be observed on the steam activated samples, in comparison to the non-activated sample in Figs. 1(c) and 1(d). The random arrangement of the fibers assures an interconnected structure of voids. The resulting open structure allows the free flow of fluids through the monoliths so that gases can reach the micropores where they may be selectively adsorbed.

3.2. Low-pressure N_2 and CO_2 adsorption

Low-pressure N_2 adsorption (up to 1 bar) was performed at 77 K in liquid nitrogen. Prior to the experimentation, the samples were degassed under vacuum (< 10^{-6} atm) for 4 hours at 573 K. Parameters such as the BET surface area, and total pore volume were determined from the N_2 adsorption isotherms, according to the Brunauer-Emmett-Teller (BET) theory.

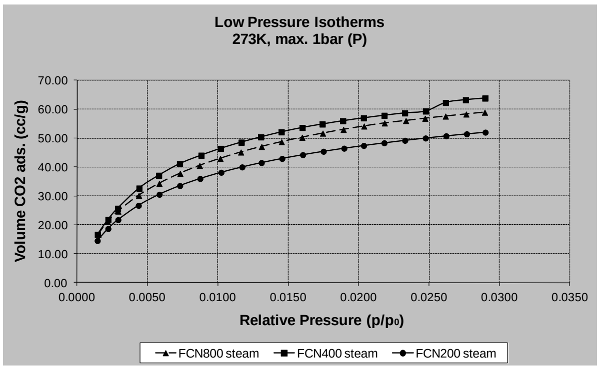

Fig. 2. Adsorption CO_2 isotherms at low pressure (< 1 bar) on steam activated FCN200, FCN400 and FCN800 samples

Table 1. Porosity characteristics of non-activated and steam activated composites

Sample	BET surface area [m^2/g]	Total pore volume [cm^3/g]	DR micropore volume [cm^3/g]	CO_2 ads. at 273K, 1 bar [cm^3/g]	CO_2 ads. at 273K, 1 bar [moles/kg]
FCN200	10.86	$7.087 \cdot 10^{-3}$	-	-	-
FCN400	16.82	$7.519 \cdot 10^{-3}$	-	-	-
FCN800	3.46	$6.425 \cdot 10^{-3}$	-	-	-
FCN200a	226.37	$1.17 \cdot 10^{-1}$	$1.974 \cdot 10^{-1}$	52.001	2.340
FCN400a	379.15	$1.73 \cdot 10^{-1}$	$2.749 \cdot 10^{-1}$	63.777	2.870
FCN800a	506.08	$4.45 \cdot 10^{-1}$	$2.309 \cdot 10^{-1}$	62.302	2.803

Table 1 includes the results of the BET surface area and total pore volume determinations of the non-activated and steam activated composites. As it can be observed, the apparent surface area of the synthesized monoliths ranges from 3.46 m^2/g to 16.82 m^2/g for the non-activated samples, and from 226.37 m^2/g to 506.08 m^2/g for steam activated samples. The large differences in BET surface area between non-activated and steam activated samples show that the steam activation has a great influence on porosity development. In the case of non-activated composites, the FCN400 sample shows the highest values for surface area of 16.82 m^2/g and a total pore volume of $7.519 \cdot 10^{-3}$ cm^3/g.

In the case of steam activated composites, BET surface area and total pore volume vary proportionally with the increase of carbon fibers length. After steam activation, the surface area increases about 20 times in almost all types of composites. In the case of FCN800a sample, the surface area increased from 3.46 m^2/g to 506.08 m^2/g, which is about 146 times. The FCN400a sample shows the best developed micropore structure even though the BET surface area and the total pore volume are higher for FCN800a sample. This could be an indication that the microporosity is developed especially at the edges of the fibers, which can be observed in figure 1(d).

Low pressure CO_2 adsorption was performed on steam activated samples and CO_2 adsorption isotherms were collected. The micropore volume is determined from the CO_2 adsorption isotherms and the results are presented in table 1.

Carbon dioxide molecules are slightly thinner than nitrogen molecules (3.3 Å radius vs. 3.6 Å) and will fill the narrow micropores (below 0.7 nm) [21]. Nitrogen measures the whole amount of micropores whereas carbon dioxide at $p/p_0 < 0.03$ is used for the determination of narrow micropores volume. The best value for the DR micropore volume of $2.749 \cdot 10^{-1}$ cm^3/g was obtained for the FCN400a sample.

CO_2 adsorption capacity at low pressure (up to 1 bar) was also evaluated from the isotherms, which are presented in figure 2. Only steam activated samples have been taken into account for characterization. The best adsorption capacity was developed by the steam activated FCN400 sample, which is about 2.34-2.87 moles/kg at 273 K and atmospheric pressure. The variation of CO_2 adsorption capacity between the three samples corresponds directly with the variation of the micropore volume.

The isotherms shape shows a linear behaviour in the p/p_0 range of 0.01-0.025, which is correspondent to the adsorption process in micropores. The absence of slope in the middle region indicates that only a monolayer of CO_2 gas has been adsorbed on the fibers surfaces at a pressure of up to 1 bar [22]. As the maximum adsorption corresponds to a relative pressure p/p_0 of less than 0.3, at the equilibrium pressure of 1 bar, it indicates that the monolayer is not totally formed. This aspect is also sustained by the calculation of the monolayer capacity from the isotherms by applying the BET theory. The calculated monolayer capacity was 65 cm^3/g (0.0029 moles/g) for FCN200a, 71 cm^3/g (0.0031 moles/g) for FCN400a, respectively 73 cm^3/g (0.0033 moles/g) for FCN800a sample. The slight measured difference in adsorption capacity between the FCN400a and FCN800a samples could also be explained from the isotherms' behaviour. In the case of FCN400a the isotherm shows a small slope change after the relative pressure p/p_0 of 0.025, which corresponds with the formation of the first multilayer in the micropore structure.

3.3. Regeneration capacity evaluation

Regeneration capacity of the FCN400a sample was measured by passing the electric current at low voltage directly through the monolith. The adsorption efficiency of CO_2 was measured through the difference between output and input of CO_2 concentrations. The experimental results showed an efficiency of CO_2 uptake up to 98.84–99.03%.

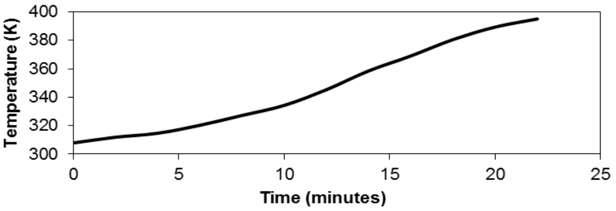

Fig. 3. Heating rate under continuous loading (18 A/6.8 V) on steam activated FCN400a sample

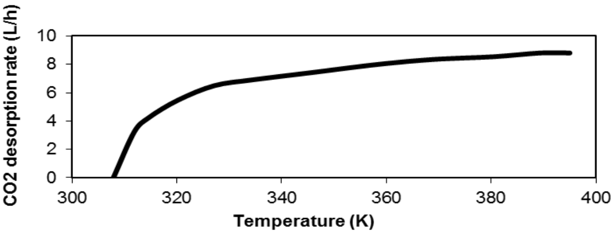

Fig. 4. CO_2 desorption rate under continuous loading (18 A/6.8 V) on steam activated FCN400a sample

A light exothermic effect during the CO_2 uptake was observed. The monolith temperature increased from 302.4 K (environmental adsorption cell temperature) up to 308.7 K in about 15 minutes, after which it decreased gradually back to 302 K. Such behaviour indicates that the CO_2

uptake was complete after about 20 minutes, also considering the residual time for finalizing the adsorption. The thermal effect may be attributed to the increased interaction of the CO_2 gas molecules with the functional groups and the pores at the surface of functionalized fibers in the monolith.

In order to evaluate the regeneration capacity of the monolith adsorbent, an electric current at low voltage of 18 A/6.8 V was applied. Under resistive loading, the monolith temperature started to increase and the volume of CO_2 desorbed was measured, in the range of 303-393 K (Fig. 3). By applying a current of 18 A at 6.8 V, the monolith temperature increases with a rate of about 5 K/minute. The experimental measured rate of CO_2 desorption was about 8.8 L/h (0.273 moles/h) at 393 K (18 A/6.8 V), at environmental pressure (Fig. 4). The experimental data shows that the volume of desorbed CO_2 is directly dependent on the temperature. By increasing the monolith temperature, the rate of desorption will also increase.

4. Conclusions

An efficient CO_2 adsorbing monolith structure was obtained. The monolith is based on blended petroleum-pitch-derived carbon fibers and phenolic resin-derived carbon binder, in a weight ratio of 3:1. Adsorption experimental results show that the amount of CO_2 adsorbed at 273 K and atmospheric pressure is mainly defined by the volume of micropores.

The adsorbed gas may be quickly and efficiently desorbed by passing the electric current at low voltage directly through the monolith. The measured rate of CO_2 desorption of the steam activated sample FCN400a is 0.273 moles/h at 393 K, atmospheric pressure, corresponding to 18 A/6.8 V.

Acknowledgments

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