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Effect of sonication and hydrogen peroxide oxidation of carbon nanotube modifiers on the microstructure of pitch-derived activated carbon foam discs

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ABSTRACT

We used carbon nanotubes (CNTs) as modifying particles and potassium hydroxide as a porogen to prepare mesoporous pitch-derived activated carbon discs (ACD) with high surface areas. The parameters investigated in this study included the concentration of CNTs (1%, 2%, 3.5% and 5%), the dispersion of the CNTs in the pitch using a 750 W sonic probe, the oxidation of the CNTs with H_2O_2, and the aspect ratio of the CNTs. The highest surface area ACD was obtained with 2% oxidized CNTs dispersed in the pitch with the ultrasonic probe (ACD-2%-SO, $S_{BET} = 2089\ m^2\ g^{-1}$). The ACDs prepared with the sonic probe and with 2 wt% or more of raw and oxidized CNTs exhibited larger mesopore volumes than those ACDs prepared with 1 wt% CNTs. A series of quench tests performed during the foaming process by withdrawal of the carbon from the tube furnace at 673 K, 773 K and 873 K revealed that mesopores in ACD develop at temperatures ranging from 773 K to 873 K, whereas micropores formed between 873 K and 1073 K. The adsorption capacities of N_2 and CO_2 on ACD-2%-SO were measured with a gravimetric apparatus at 298 K and 303 K at pressures up to 4000 kPa. The uptake of CO_2 on ACD-2%-SO at a temperature of 298 K was 3.33 mol/kg at 100 kPa and 11.51 mol/kg at 3496 kPa.

1. Introduction

Carbon foams with hierarchical pore structures, good thermal conductivity and electrical conductivity have been reported as promising materials for thermal management [1] and protection [2], cleanup of oil spills [3], electrochemical capacitors [4] and gas separation processes [5–8]. Carbon foams can be synthesized from a wide range of precursors such as coal [9,10], coke [11], pitch [12–14], polymers [15,16] and biomass [17,18]. One of the most widely studied carbon foam precursors is petroleum pitch because it is readily available at a low cost, it has a high carbon content, and when heated under controlled conditions pitch can produce a porous carbon foam. However, it may be challenging to control the pitch foaming process to produce a highly porous and mechanically strong foam. One of the challenges is forming the hierarchical microstructure, especially the mesoporous structure in the carbon foam. The open mesoporous structure connects between the micropores and macropores, which will significantly improve the adsorption capacity and reduce the pressure drop. High-pressure foaming processes [19] and the use of modifiers [20,21] are two strategies that have been reported to control carbon foam production. In this study, we explored the use of carbon nanotubes (CNTs) as modifying particles to produce carbon foams from tar pitch.

Modifiers in the form of particles may play multiple roles in the carbon foaming process including the stabilization of bubbles formed during foaming, and the supply of active catalytic sites during foam carbonization. Moreover, these particles may enhance the properties of the carbon product such as its surface area and/or electrical conductivity. Carbon foams have been produced with a number of particle modifiers, including coal [20,21], clay [22,23], carbon fibers [24–26], graphene [27] and CNTs [28–33]. Carbon nanotubes are also attractive reinforcing particles because CNTs have high aspect ratios, high elastic modulus and strength, and high specific surface area. In fact, Liu [31] reported that a carbon foam modified with acid-treated multiwall CNTs led to significant differences on the pore size and morphology, mechanical strength, thermal and electrical conductivity of the foams. Kim [32] also reported that the introduction of fluorinated CNTs increased the

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Table 1
Surface properties of pitch, raw CNTs and H_2O_2 oxidized CNT.

Sample	XPS		S_{BET}
	O 1s/At%	C 1s/At%	$(m^2 \cdot g^{-1})$
Raw CNTs	1.05	98.95	242.7
H_2O_2 CNTs	3.30	92.75	337.8
Pitch	3.96	92.75	–

compressive strength and thermal conductivity of an isotropic pitch-derived carbon foam.

The dispersion of modifying particles into the carbon foam precursor is a critical step in the preparation of reinforced carbon foams because CNTs tend to form aggregates. The uneven dispersion of CNTs in the carbon foam is not only a kind of waste of material, but also detrimental to the overall properties of the carbon foam, which typically displays microstructural defects. Several methods have been reported to disperse CNTs in polymers and pitch mixtures, including functionalization of the CNT-surface, use of surfactants, as well as melt-mixing the precursor and particles via extrusion during the molten stage of the foaming [34]. For instance, Datsyuk et al. [35] reported that grafting of carboxylate groups on CNTs imparts a negative charge that improves the dispersion stability of CNTs in polar media such as ethanol, methanol or water. In another approach, Andrews [36] used a high-power ultrasonic wand (Fischer Scientific 500 W) to disperse single wall CNTs in a solution of pitch in quinolone (this solvent was then removed by vacuum distillation in a subsequent synthesis step). These examples illustrate that sonication and surface functionalization may be effective methods to disperse CNTs in a carbon foam precursor.

Thus, we investigated the effects of (1) oxidation of CNTs with hydrogen peroxide (H_2O_2) and (2) sonication of the CNTs on the dispersion of CNTs into pitch to produce CNT-filled activated carbon discs in a low-pressure foaming process. We also studied the effect of concentration of CNTs in the pitch on pore development. The development of porous structures in carbon foams occurs in several temperature-dependent steps [20], and to gain a better understanding of the role of the CNT modifiers on pore development during pitch foaming, we performed a series of quenched foaming experiments in which the sample was withdrawn from the tube furnace at 673 K, 773 K and 873 K.

2. Experimental

2.1. Materials and carbon foam preparation

Here we used the same BP Bitumen Class 170 pitch and pitch pre-treatment procedures that we reported in our study on coal particles as carbon foam fillers [21]. According to the supplier's data sheet, the density of the BP Bitumen Class 170 pitch is 1.03 g cm^{-3} and its softening point is 320 K [37]. The softening point of the pitch was increased by adding dropwise 18 g of 15 M nitric acid (HNO_3) per 100 g of pitch while the pitch was stirred and heated at 393 K. The oil bath temperature was raised to 433 K and the pre-treatment continued until the impellor could no longer stir the pitch. The pre-treated pitch was a brittle solid at room temperature and this material was ground to a powder by hand with a mortar and pestle.

Carbon nanotubes (NC7000, Nanocyl, Belgium) were oxidized with 200 mL of 30 wt% H_2O_2 solution in an ultrasonic bath for 30 min, and then heated at 353 K for 5 h. The oxidized CNTs were washed with distilled water and dried at 373 K in a vacuum oven. Table 1 shows the concentration of oxygen on the surface of raw CNTs and the oxidized CNTs measured by X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI-560 ESCA operated at 15 kV), and the specific surface area (S_{BET}) of the CNTs determined from N_2 sorption analysis (experimental details described in section 2.3 Characterizations). The oxygen concentrations on the pitch are also included in Table 1.

The CNTs were dispersed in 80 mL of ethanol, then mixed with the pre-treated pitch at CNT concentrations of 1, 2, 3.5 and 5 wt%, and placed in an ultrasonic bath for 30 min. Three sets of CNTs + pitch mixtures were prepared in the next step of the activated carbon disc (ACD) synthesis: (i) raw CNTs + pitch labelled ACD-x%, (ii) raw CNTs + pitch mixtures treated for 30 min with an ultrasonic probe (Sonics, 40 Ampl, 750 W, 20 kHz) labelled ACD-x%-S, and (iii) H_2O_2 oxidized CNTs + pitch treated for 30 min with the Sonics probe ACD-x%-SO. Where x% stands for the CNT to pitch concentration by weight.

Prior to foaming, KOH was added as a chemical activator to each CNTs + pitch mixture at a KOH-to-pitch mass ratio of 1:1. Discs (14 mm diameter) were formed from about 1 g of the pitch + coal + KOH blend in a hydraulic press and dried in an oven at 353 K. Foaming was performed in argon gas in a horizontal tube furnace at 1073 K (10 K min^{-1}) with 1 h of soaking time. The foamed discs were washed with 0.2 M HCl, dried overnight at 353 K, and rinsed with distilled water several times until a filtrate pH of 7 was achieved. Table 2 lists the properties of the 12 ACDs prepared in the first part of this study. A photograph of ACD-5%-S is shown Fig. 1 as a representative sample of the ACDs produced. Interestingly, we previously attempted the pitch foaming experiment without any modifying particle, but the experiment did not produce a stable foam, instead the pitch overflowed the crucible in the tube furnace [21].

The carbon yield of the ACD was calculated from the weight of the treated-pitch (m_p), CNTs weight (m_{CNT}), and the weight of the washed ACD end product (m_f) according to:

$$Yield\ (\%) = \frac{m_f}{m_p + m_{CNT}} \times 100\% \qquad (1)$$

2.2. Quenching test

Carbon foam quenching tests were performed at temperatures of 673 K, 773 K and 873 K for the activated carbon discs prepared from the pre-treated pitch with 2% raw CNTs (ACD-2%-S) and

Table 2
Bulk density, skeletal density, porosity and carbon yield of the ACDs prepared with (a) raw CNTs, (b) raw CNTs dispersed in pitch using the 750 W ultrasonic probe, and (c) H_2O_2 oxidized CNTs dispersed in pitch using the 750 W ultrasonic prove. ACD-1%-SO did not produce a monolithic carbon disc.

Sample	Bulk density $(g \cdot cm^{-3})$	Skeletal density $(g \cdot cm^{-3})$	Porosity (%)	Carbon Yield (%)
(a) Raw CNTs (no ultrasonic probe)				
ACD-1%	0.20	1.96	90 ± 1.6	28.2 ± 2.0
ACD-2%	0.30	1.84	84 ± 2.5	32.0 ± 2.3
ACD-3.5%	0.30	1.88	84 ± 2.5	33.6 ± 2.5
ACD-5%	0.22	2.01	89 ± 1.7	39.7 ± 3.0
(b) Raw CNTs with 750 W ultrasonic probe				
ACD-1%-S	0.25	1.97	87 ± 1.9	28.9 ± 2.1
ACD-2%-S	0.31	1.92	84 ± 2.5	35.7 ± 2.6
ACD-3.5%-S	0.28	2.00	86 ± 2.1	39.6 ± 2.9
ACD-5%-S	0.33	2.03	84 ± 2.5	47.3 ± 3.5
(c) Oxidized CNTs with 750 W ultrasonic probe				
ACD-1%-SO	–	–	–	–
ACD-2%-SO	0.30	1.95	84 ± 2.4	30.2 ± 2.2
ACD-3.5%-SO	0.42	1.95	78 ± 3.3	41.4 ± 3.0
ACD-5%-SO	0.33	1.98	83 ± 2.6	48.0 ± 3.6