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Research article

Effect of rheological properties of mesophase pitch and coal mixtures on pore development in activated carbon discs with high compressive strength

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ABSTRACT

We measured the rheological properties of mesophase pitch + coal mixtures at temperatures up to 873 K and used quench tests during carbonization to observe the effects of coal particles on foaming and pore development in activated carbon discs (ACD). We observed that high ratios of coal to pitch increased the mixture's viscosity in a low pressure foaming process, which restricted growth of large bubbles during foaming and produced stronger carbon monoliths. The highest strength ACD, with compressive strength of 56 ± 3 MPa, was obtained using a pitch to coal mass ratio of 1:2 (bulk density = 0.91 g·cm^{-3} and surface area = 579 ± 37 m^2·g^{-1}). The adsorption capacities of CO_2, CH_4, and N_2 of the ACDs prepared with a mesophase pitch to coal ratio of 1:2, measured on a gravimetric adsorption apparatus, at 298 K and pressures up to 4000 kPa were 3751 mol·m^{-3} CO_2, 2107 mol·m^{-3} CH_4, and 1691 mol·m^{-3} N_2. These adsorption results suggest the activated carbon discs have potential as structured adsorbents for gas separation or storage applications.

1. Introduction

Carbon foams with highly porous open cell structures, low density, good thermal stability, and controllable thermal and electrical conductivity have potential applications as catalyst supports [1–3], electrode materials [4,5], thermal insulation [6,7], thermal energy storage devices [8–10], sponges for recovery of spilled oil [11,12], and as adsorbents in gas separation and storage processes [13,14]. Desirable properties in carbon foams for gas separation and storage applications include high specific surface areas, tailored micropore size distributions and surface functionalizations for enhanced selectivity for the target gas molecules, and connected macroporous channels for fast sorption kinetics and low pressure drops. However, a consequence of producing foams with these properties is that these highly porous carbons tend to be weak and brittle, which can lead to mechanical failure during pressurization cycles [15]. Breakage of the carbon foam into fine particles and fragments will lose the potential advantages of structured adsorbents such as low pressure drop, high mass transfer, good heat management and high chemical stability [16]. Therefore, several techniques have been investigated to improve the robustness and mechanical strength of carbon foams; the two most common approaches are to select high yield carbon precursors and to use modifier or filler particles such as carbon nanotubes (CNT).

Carbon foams can be prepared from a variety of raw materials such as coal tar pitch [17–19], mesophase pitch [20,21], coal [22], polymers [23,24], and bio-materials [25,26]. Among these precursors, several studies have shown precursors that lead to high yields of carbon foams also produce strong carbons compared to low yield precursors [27]. For example, Liu et al. [28] produced carbon foams at a carbon yield of > 80 wt% with compressive strength of 25.5 MPa (and a high strength/density ratio of 43 MPa·g^{-1}·cm^3) using polyarylacetylene. In another example, Li et al. [29] demonstrated that extraction in toluene of more volatile components from mesophase pitch reduced the length of cracks formed during carbon foaming and improved the compressive strength of the carbon foam (up to 9 MPa).

In the second common approach to improve carbon foam strength, particles such as coal [30], CNTs [31–33], carbon nanofibers [34], clays [35], and mesocarbon microbeads [36] have been reported as foam modifiers. Kim et al. [37] added fluorinated CNTs to isotropic pitch and improved the compressive strength of their foams up to 2.42 ± 0.22 MPa at a bulk density of 0.50 g·cm^{-3}. Wang et al. [35] added 10 wt% montmorillonite clay particles to mesophase pitch to produce foams with compressive strength up to 12.8 MPa, and explained the improvement was due to the clays effect to create a densely packed foam structure reinforced that exhibited less shrinkage during heat treatment and consequently fewer micro cracks developed in the carbon foam. In a third example, Li et al. [36] mixed mesocarbon microbeads (MCMBs) with a mesophase pitch to prepare carbon foams,

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and observed the compressive strength of the foams increased significantly from 2.8 MPa to 23.7 MPa with an increase in the MCMB concentration from 0 to 50 wt%.

In this study, mesophase pitch was selected as the carbon precursor because mesophase pitch has a high concentration of carbon (> 80 wt %), long polymer chains, and a low concentration of volatile materials [38,39]. Previous studies, such as that by Klett et al. [40], have concluded that mesophase pitch can lead to well-ordered carbon macrostructures supported by cell ligaments that may help to improve the overall mechanical strength of foamed carbon monoliths. We added coal particles to change the viscosity of the carbon precursor and control the pitch bubbling during foaming and carbonization process. The effects of coal to pitch ratio on rheological properties of carbon precursors and on development of pore structures were investigated using a high-temperature rheometer and quenching tests, respectively. The relationship between factors like proportion of filler particles, viscosity of foaming precursor, development of pores and compressive strength of ACDs was investigated. The adsorption capacities of CO_2, CH_4 and N_2 on prepared ACDs were measured on a high-pressure gravimetric adsorption apparatus and compared with other adsorbents in literature.

2. Experimental

2.1. Materials and activated carbon discs preparation

Mesophase pitch (MP, 074608) was obtained from Bonding Chemical (US) and the properties are listed in Table 1. Coal filler from the Blackwater coal mine in Queensland's Bowen Basin (Australia) was ground and screened to recover particles < 53 μm. The carbon precursor blends for activated carbon discs were prepared by mixing MP, coal particles, and the chemical activator KOH at mass ratios of 1:1:1, 2:4:3, and 4:2:3 (pitch + coal mass to KOH mass was 2:1 in all three experiments). These precursor blends stirred in 50 ml ethanol at 350 rpm for 10 min and sonicated in an ultrasonic bath (Model FXP12DH Unisonics, Australia) for 30 min. After sonication, the precursor blends were stirred again at 350 rpm on a hot plate at 353 K to evaporate ethanol, dried in an oven at 353 K overnight, and then ground to a powder in a hand mortar and pestle.

Approximately 1 g of the MP + coal + KOH precursor blends were pressed into 14 mm diameter discs at 2.4 t in a cold, isostatic press (Model YLJ-CIP-15 MTI, USA). The precursor discs were heated under a flow of argon gas in a horizontal tube furnace at 10 K·min^{-1} from room temperature to 1073 K with a 1 h soak time at 1073 K. 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. The activated carbon discs prepared with KOH are labeled ACDMP*x*C*y*, where *x*:*y* is the MP:coal ratio; for example ACDMP1C2 identifies the carbon prepared from the 2:4:3 MP:coal:KOH blend. The ACDs prepared without KOH are labeled ACDMP*x*C*y**, for example ACDMP1C1* was prepared from a 1:1 MP:coal blend without any KOH.

2.2. Carbon quench test

Carbon quench tests were performed at temperatures of 500 K, 550 K, 600 K, and 650 K using the 2:4:3 blend of MP + coal + KOH (as for ACDMP1C2) and 1:2 MP + coal without KOH (ACDMP1C2*). The procedures for quench tests were the same as the preparation of ACDs described above, but quenched samples were pulled quickly from the center of furnace tube to the inlet end of the tube once the furnace reached the quench temperature. The flow of argon gas is maintained during this procedure. The quenched ACDs are labeled as ACDMP1C2-*TTT*K where *TTT*K indicates the quench temperature as in ACDMP1C2-500 K for the carbon removed from the tube at 500 K.

Table 1
Properties of mesophase pitch.

Softening point (K)	Toluene insoluble (wt%)	Quinoline insoluble (wt%)	Volatile constitution (wt%)	Ash (wt%)	Content of mesophase (%)
533–553	76–80	66–70	18–20	0.02–0.04	About 85

2.3. Characterization

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out with a Perkin-Elmer STA 6000 instrument at a heating rate of 10 K·min^{-1} up to 823 K under a N_2 flow of 20 ml·min^{-1}. Scanning electron microscopy (SEM) images were collected with a JSM-7001 instrument (JEOL Ltd., Japan). Compressive strength was measured by uniaxial compression testing using an Instron 5584 material testing system with a cross-head speed of 0.05 mm·min^{-1}. The bulk or apparent density (ρ_{Hg}) of the carbon discs was measured by mercury intrusion porosimetry (MIP, Micromeritics PoreSizer 9320) and the skeletal density (ρ_{He}) by helium pycnometer (Micromeritics AccuPyc II 1340). The disc porosity (ϕ) was calculated with Eq. (1):

$$\phi(\%) = \frac{\rho_{He} - \rho_{Hg}}{\rho_{He}} \times 100 \quad (1)$$

The carbon yield of the ACDs was calculated from the weight of the mesophase pitch (m_p), coal weight (m_c), and the weight of the washed ACD end product (m_{ACD}) according to:

$$Yield\ (\%) = \frac{m_{ACD}}{m_p + m_c} \times 100 \quad (2)$$

Sorption isotherms of N_2 at 77 K and CO_2 at 273 K were measured with a TriStar II 3020 apparatus (Micromeritics, USA) after degassing the ACD at 473 K and a pressure of 10^{-5} Torr for 24 h. The N_2 isotherms were used to determine the Brunauer Emmett Teller (BET) specific surface area at a relative pressure in the range of P/P_0 = (0.05–0.35); total pore volumes at P/P_0 = 0.99; micropore volumes using the t-plot method and mesopore volumes from the Barrett Joyner Halenda (BJH) method. The pore size distributions were also calculated from the N_2 adsorption on TriStar II 3020 determined by non-local density functional theory (NLDFT) model. Limiting micropore volumes were calculated from the CO_2 isotherms measured at 273 K with the Dubinin-Astakhov (DA) equation [41].

High pressure adsorption equilibrium capacities of CO_2, CH_4 and N_2 were measured at 298 K and 308 K with pressure up to 4000 kPa on a Belsorp-BG apparatus (BEL, Japan) equipped with a magnetic floating balance (Rubotherm, Germany). Details of the Belsorp-BG apparatus and its operation are described in our lab's previous articles [42,43].

Rheological measurements were performed using a Rheometrics AR 2000ex rheometer with an oven temperature up to 873 K and a steady N_2 flow of 10 ml·min^{-1} to sweep the volatiles away. Samples were prepared for the rheometry by pressing 1 g of each of the coal, mesophase pitch, or carbon precursor blends at 2.4 t to 25 mm discs approximately 1.8 mm thick. Two parallel 25 mm diameter plates were used to hold the samples to either maintain a fixed gap of the original height of the pressed discs (normal force measurement), or a constant normal force of 2 N with a 0.1% strain at a frequency of 1 Hz (viscosity and phase angle measurement). Viscosity and phase angle are two key properties obtained from the rheological measurements. Viscosity is a measure of the specimen's resistance to displacement under an applied strain. Phase angle is a measure of how solid-like the specimen is whereby 0° is a completely Hookean solid and 90° is a completely Newtonian liquid. In between, the 45° point is an indicator of the transition between solid-like and liquid-like behavior which is known as the gel-point [44].