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Preparation and characterization of pitch-based nanoporous carbons for improving CO_2 capture

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ABSTRACT

Pitch is considered a promising low-cost carbon precursor. However, when pitch is pyrolyzed, it forms polycrystalline graphite, which is non-porous, and therefore, not useful for CO_2 adsorption. In this work, pitch was chemically activated to obtain a large specific surface area and micropore volume. Varying weight ratios of KOH (*i.e.*, 0, 1, 2, and 3) were used as the activating agent. The characteristics of the samples were investigated using scanning electron microscopy (SEM), N_2/77 K adsorption isotherms, and X-ray diffraction (XRD). The CO_2 adsorption performance was studied by isothermal adsorption/desorption measurements. The results showed that an increase in specific surface areas and total pore volumes of pitch-based nanoporous carbons, resulted in an enhancement of CO_2 adsorption capacity.

1. Introduction

One of the foremost technological challenges today concerns the development of environmentally friendly, efficient, and low-cost industrial processes for the recovery of carbon dioxide (CO_2). Removal of acidic gases like CO_2 is an important industrial operation. CO_2 is produced in large quantities by many important industries such as fossil fuel-fired power plants, steel production, chemical and petrochemical manufacturing, cement production, and natural gas purification. CO_2, one of the greenhouse gases (GHG), is currently responsible for over 60% of the enhanced greenhouse effect. Environmental concerns such as global climate change are among the most important and challenging issues facing the world and have motivated intensive research on CO_2 adsorption and sequestration [1,2].

To reduce the amount of CO_2 released into the atmosphere, four main methods are being developed for CO_2 capture and separation (CCS). They are solution absorption, adsorption, membrane diffusion, and cryogenics [3]. The absorption of CO_2 by alkanolamine solvents is a well-tested method that can be used on a large-scale [4]. However, this process suffers from several drawbacks such as high-energy consumption, corrosion of the equipment, and toxicity that hamper its implementation. It is therefore highly desirable to develop alternative capture methods.

Capture methods based on solid adsorbents are one of the most promising options owing to their low energy consumption, low equipment costs, and ease in implementation [5–8]. This method utilizes highly porous solids as adsorbents for capturing CO_2 by employing of pressure, temperature, or vacuum-swing adsorption systems [9–13].

Over the past few decades, many types of porous materials have been used in CO_2 adsorption, such as zeolite [14], porous silica [15,16], metal oxides [17], metal–organic frameworks (MOFs) [18], and activated carbons [19].

Among the adsorbents mentioned above, activated carbons offer several advantages such as their low cost, availability, large surface area, an easy-to-design pore structure, hydrophobicity (insensitiveness to moisture), and low energy requirements for ease of regeneration [20–23].

Activated carbons are porous materials prepared using specific methods in order to acquire certain specific properties. Lignocellulosic materials are one of the most widely used materials for the production of activated carbons. Wood and coconut shell are the major precursors for obtaining activated carbons. Lignocellulosic materials are responsible for the production of more than 300,000 t of activated carbons every year [24]. Pitch materials with high-density graphitizable precursors of carbon materials can be suitably activated to use in the fields of adsorption, catalysis, energy storage or conversion in recent years [25,26]. They also have high-aromatic and low-aliphatic carbons contents and give high yields on carbonization.

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However, most activated carbons exhibit low CO_2 uptakes, which render them unsuitable for this application. In this study, we used KOH as the activation agent in order to improve the CO_2 adsorption capacity of activated carbons. Recent research has shown that activated carbons with a large population of 1–2 nm sized pores exhibit a better CO_2 adsorption performance than those with narrower microporous pore network [27,28].

In this work, we prepared activated carbon from pitch using different ratios of the activation reagent. The pore structures, surface morphologies, and CO_2 adsorption properties of the activated carbons were determined. The main objectives of the present work were to prepare activated carbons with high pore volumes for CO_2 adsorption and to study the effect of KOH on the textural properties of the final activated carbons.

2. Experimental method

2.1. Radical vulcanization derived isotropic pitch precursor

Isotropic pitch precursors were prepared by the condensation of pyrolyzed fuel oil (PFO) with H_2O_2 at 150 °C for 5 h, after which the pitch precursor was heated at 360 °C for 5 h to prepare the precursor of pitch-based nanoporous carbon. The process was carried out under a flow of N_2 at atmospheric pressure. The chemical reactions are presented in Fig. 1.

2.2. Preparation of pitch-based nanoporous carbons

Next, we chemical activated the pitch precursors to obtain the activated carbons. The precursors were finely grounded and mixed with the required weight ratios (*i.e.*, 1, 2, and 3) of an aqueous solution of KOH and maintained for 5 h at 60 °C. The mixture was vacuum-dried for 12 h and then placed in a horizontal cylindrical furnace. Then, it was heated to 800 °C at a rate of 2 °C/min and held for 2 h under a N_2 flow rate of 200 ml/min. The activated products were then washed with diluted hydrochloric acid to get rid of the alkaline compounds. The pH value was adjusted to 7 using distilled water. Activated carbons named AC-*x* ('*x*' represents the weight ratio of KOH) were finally obtained after drying for 12 h at 120 °C.

2.3. Characterization

Scanning electron microscopy (SEM, Hitachi/S-4300) was used to characterize the morphologies of the untreated and KOH-treated AC-*x* samples. All the samples were characterized by recording their X-ray diffraction (XRD) patterns on a Rigaku X-ray diffractometer (Model D/MAX 2200V/PC) using a CuKα radiation. The wide-angle XRD patterns were collected over the scanning range, $2\theta = 10–90°$, with a step width of 0.05° and a time per step of 0.5 s. The porous texture of the samples was examined by N_2/77 K adsorption/desorption isotherms using a gas adsorption analyzer (BET, BERSORP/Max). The Brunauer–Emmett–Teller (BET) equation was used to estimate the specific surface area from the values of N_2 adsorbed on the samples. The total pore volume was estimated by converting the amount of N_2 gas adsorbed at a relative pressure or about 0.99 to liquid volume of the nitrogen. The micropore size distribution was determined using the Horvath–Kawazoe (H–K) method. The peak of the pore size distribution was used as the average pore diameter (D_p).

A CO_2 adsorption test was carried out under ambient conditions at 298 K and low (1 bar) pressure (BEL, Japan). In each experiment, approximately 0.3 g of the sample was loaded into a glass cell. Prior to the measurements, the samples were degassed at 473 K for 24 h to obtain a residual pressure. After cooling the glass cell to room temperature, CO_2 was introduced until a pressure of 1 bar was attained. Ultrahigh purity grade (99.9999%) CO_2 was used to exclude the effects of moisture and other impurities. Finally, a volumetric measurement method was used to determine the CO_2 adsorption capacity.

3. Results and discussion

The pitch precursors used in this study were prepared by the condensation of pyrolyzed fuel oil (PFO) with H_2O_2. H_2O_2 accelerates ozone decomposition and results in a high concentration of OH radicals, which produce water and alcohol as a byproduct of radical vulcanization. This eco-friendly method affords pitch precursors (24–30% yield) with a softening point between 280 and 290 °C.

Fig. 2 shows the SEM images of the samples before and after the KOH treatment. It has been noted that the KOH treatment changed the sample′s pore structure and surface morphology. No pores were observed in the untreated sample (Fig. 2a). It could be seen that the KOH treatment led to increased pore formation in the samples (Fig. 2b–d).

This suggested that pore formation in the activated carbons was strongly dependent on the precursor-to-KOH ratio. The mechanism of activation by the precursor-KOH has been reported previously [29–31] and is summarized below:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad (1)$$

$$K_2CO_3 + C \rightarrow K_2O + 2CO \quad (2)$$

$$K_2O + C \rightarrow 2K + CO \quad (3)$$

Potassium metal (K) is produced during K_2O activation at high temperature and it was found that the formation of pores was due to the loss of carbon (C).

Figs. 3 and 4 show the nitrogen adsorption/desorption isotherms and the corresponding micropore size distribution (PSD) curves, respectively. Type I adsorption isotherms (IUPAC classification) were observed for all the samples [32]. It was evident that most of the pores were filled below a relative pressure of about 0.1, indicating that these samples are highly microporous.

As shown in Table 1, untreated sample had a low BET surface area of 2 m^2/g. In contrast, the AC-*x* materials synthesized in this study showed BET surface areas of 950–1442 m^2/g. The AC-2 sample exhibited a large total pore volume (0.593 cm^3/g), with

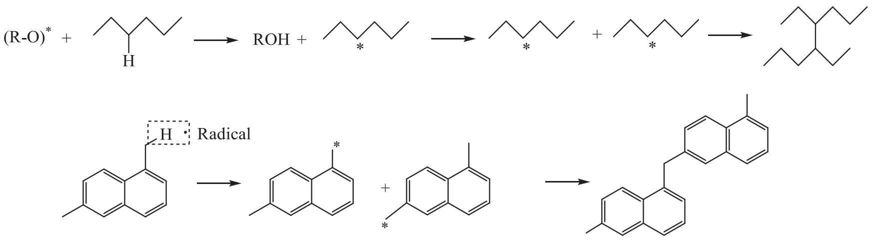

Fig. 1. Chemical reactions for the preparation of radical vulcanization derived isotropic pitch precursors.