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Short communication

Coal tar residues based activated carbon: preparation and characterization

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ABSTRACT

Coal tar residues (CRT) are a toxic and carcinogenic waste from coal tar processing unit that need extensive post-treatment before their safe disposal. This study prepared activated carbon from coal tar residues using activating H_3PO_4 at 650–1200 °C. At 850 °C, the yielded activated carbon has an iodine value of 793.5 mg/g, total pore volume of 0.286 cm^3/g and micropore volume of 0.255 cm^3/g, which can have feasible usage as mediate quality activated carbon. Kinetic model fitting reveals that the presence of H_3PO_4 increases effective reaction collision rate and decreases activation energy of pyrolysis reactions.

1. Introduction

Coal tar is a by-product of coke or coal-gas making industries which is a highly viscous liquid enriched with hydrocarbons. Besides being used as pavement, ingredients in coal tar can be separated and used as raw materials for chemicals and pharmaceuticals. Coal tar residues (CTR) are a reclaimable waste produced from post-processing of coal tar, which is regarded as toxic and carcinogenic to human health [1,2]. Although activated carbon (AC) can be produced from carbon material, to produce AC from CTR is environmentally friendly and possibly cost-effective pathway for handling this specific coal industry waste [3,4].

Activated carbon (AC) is prepared with physical or physicochemical activation [5]. Physicochemical activation is generally a two-step method that can be implemented at relatively lower temperature and shorter activation time in the presence of chemical activating agents such as KOH, NaOH, and H_3PO_4 [6–12]. Both activation temperature and activating agents used significantly affect the pore size and volume, yield, surface properties, iodine value, and adsorption capacity of the so-yielded AC [13–17]. In application, AC with mesopores should be feasible for removing large-molecular weight pollutants from wastewaters [18–20]. AC with manipulated mesopores is of practical interests to be synthesized [21].

This study prepared AC from CTR using physiochemical activation method with H_3PO_4 as the activating agent. The nitrogen adsorption isotherm and thermogravimetry (TG) were applied to characterize the obtained AC. The paper focused on the effects of activation temperature on the pore volume and pore size of synthesized AC.

2. Material and methods

2.1. Raw material

CTR is provided by Yulin Coal Tar Plant, Shaanxi Province, China, that has the elemental composition as (C/H/O/S/N) = (80.18%/1.41%/10.16%/0.59%/1.66%) [3]. The CTR was grounded and sieved into 75 μm size and dried at 105 °C for 2 h as raw material for AC making. Coal based commercial activated carbon (CAC) was purchased from Chongqing Zhongshan Activated Carbon Manufacturing Co., Ltd., China as control.

2.2. Preparation of coal tar residues based activated carbon

CTR was carbonized and activated in a horizontal oven (SJK-16-10, Luoyang Shenjia Ceramic Industry Co., Ltd., China), equipped

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Table 1
Physicochemical composition of CTR and the yielded activated carbons.

Sample	Element C (%)	Iodine value (mg/g)	Total pore volume V_{pore} (cm^3/g)	Micropore volume V_{micro} (cm^3/g)	Burn off (%)
CTR	80.8	237.6 ± 4.0	0.030	0.000	NA
CTR 1000	78.8	457.2 ± 3.0	0.174	0.130	56.1 ± 0.9
CTRP 600	87.6	347.8 ± 1.1	0.026	0.025	17.1 ± 1.0
CTRP 850	91.2	793.5 ± 2.1	0.286	0.255	28.9 ± 1.0
CTRP 900	91.5	787.9 ± 6.3	0.252	0.210	29.5 ± 2.0
CTRP 1000	91.0	656.8 ± 8.1	0.250	0.232	48.3 ± 2.9
CAC	89.9	735.0 ± 1.0	0.359	0.331	NA

with an alumina tube of volume 0.2 L. The CTR was dipped in 1 M H_3PO_4 solution for 24 h and then was removed and dried at 110 °C for 24 h. The dried product was put into the oven under 0.09 L/min nitrogen flow with heating rate of 10 °C/min with temperature being kept at 400 °C for 30 min and then was increased at 10 °C/min to 600, 850, 900, 1000, or 1200 °C for another 180 min for activation. The so yielded products were washed by hot water till reaching neutral pH, which are termed as CTRP600, CTRP850, CTRP900, CTRP1000 and CTRP1200 in this work. The activated carbons prepared using the same protocol but with no H_3PO_4 at 1000 or 1200 °C are respectively named as CTR1000 or CTR1200.

2.3. Characterization of coal tar residues based activated carbon

Elemental analysis of solid samples was carried out with Elemental Analyzer (a Vatio EL CUBE Model 611B, CH Instruments, Austin, TX, USA) after being dried at 130 °C overnight. Burn-off value of sample was defined as the fraction of weight lost in carbonization and activation. The iodine value of AC was measured according to China National Standard 12496.70 [3]. The specific surface area of solid samples was obtained using nitrogen adsorption isotherm measured by the automatic surface porosity analyzer (Autosorb-1MP, Quantachrome Instruments, Boynton Beach, FL, USA), from which the total pore volume (V_{pore}) and the microspore volume (V_{micro}) [22], and pore size distribution were estimated [23].

The TG tests of CTR and CTRP samples were performed from 25 °C to 1200 °C in N_2 atmosphere with heating rate of 10 °C/min by thermogravimetric analyzer (Netzsch, Germany). From the TG data, the conversion α is derived and the α–T and $d\alpha/dt$–T curves are subsequently obtained. An FTIR analyzer (Nicolet 5700) was connected next to TG so the adsorption spectra of emitted gas from pyrolyzed sample were extracted online.

3. Results

3.1. Characteristics of CTR based activated carbons

Table 1 lists the properties of CTR, yielded AC at different activation temperatures, and commercial AC. The iodine value and the total pore volume of CTRP samples were low at 600 °C, but reached a high value at 850 and 900 °C. At 1000 °C, both iodine value and V_{pore} dropped, suggesting deterioration of the carbon quality. The correspondingly high burn off (48.3%) suggests a similar conclusion. Therefore, the optimum activation temperature for producing AC from the CRT can be assigned as 850 °C. The CTRP850 with iodine value of 793.5 ± 2.1 mg/g can be classified as a medium quality AC [24].

Fig. 1 shows the pore size distributions of CTR, CAC and CTRP samples, with major pore sizes at < 30 nm. The total pore volumes of CTR and CTRP600 are the lowest, suggesting that activation at 600 °C is ineffective. The CTRP850 and CTRP900 have similar pore size distributions. The ratio of V_{micro}/V_{pore} for CTRP1000 was close to 0.9 [25], suggesting that micropores are present principally inside CTRP1000. Pore deterioration at high temperature can also be observed from the lower total pore volumes for CTRP900 and CTRP1000 (approximately 0.25 cm^3/g) compared with CTRP850 (0.286 cm^3/g, Table 1).

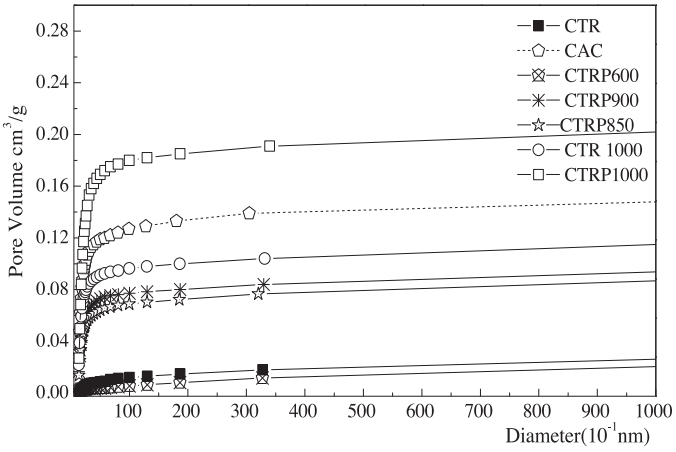

Fig. 1. Pore size distributions of CTR and tested activated carbons.

3.2. Thermal analysis on CTR and CTRP

The TG curve (Fig. S1a) and DTG curve (Fig. S1b) up to 1200 °C of CTR1200 and CTRP1200 reveal that the presence of H_3PO_4 (CTRP1200) has a larger down slope of weight loss than CTR1200, confirming the activation role of the added H_3PO_4. One platform and three obvious pyrolysis peaks at 122, 584 and 899 °C were identified for CTRP1200 sample (Fig. S1b). Compared to CTR1200, H_3PO_4 delays the first pyrolysis peak (about 100 °C), probably by covering the sample surface to inhibit reactions, and H_3PO_4 shifts the two latter pyrolysis peaks to lower temperature regime, indicating the incorporation of H_3PO_4 inside solid matrix and participate in reactions. The platform of CTRP1200 was shifted to lower temperature regime and was shorter compared to CTR1200 (Fig. S1b), indicating that H_3PO_4 affects the activation energy of reactions. Meanwhile the down slope of weight loss at 600–1000 °C is larger than that of 400–600 °C, suggesting that pore formation is completed at > 600 °C range.

3.3. TG-FTIR spectrum of CTRP850

Strong peaks at 1200–1600 cm^{-1} were noted on the TG-FTIR spectra (Fig. S2), corresponding to stretching vibration of C–O–C, C–O or bending vibration of O–H which exists in the lactone, phenolic and carbonyl functional groups [26,27]. These peaks may be relating to methane, carbon dioxide and carbon monoxide. Two narrow bands at near 1000 cm^{-1} are the significant peaks of ammonia [26]. Nitric oxide could be found as the main evolution