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Autocatalytic modification of coal tar pitch using benzoyl chloride and its effect on the structure of char

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ABSTRACT

Benzoyl chloride (BC) is used as both a modifier and a catalyst to successfully modify coal tar pitch (CTP). The char structure formed by the modified coal tar pitch (MCTP) was investigated in this study, and the results showed that the softening point, coking value, and β-resin content of MCTP increased in comparison with those of CTP. Effects of modification conditions, such as temperature, ratio of BC to CTP, and time on the char structure, were studied by polarized light microscopy, XRD, FT-IR, and ^{1}H NMR. Ordered, fibrous structures were produced at optimal conditions in char as a result of the carbonization of MCTP. The optimal conditions were as follows: modification reaction time of 15 h, reaction temperature of 150 °C, and BC to CTP ratio of 5 wt.%. Data from the XRD spectra indicated that the interplanar crystal spacing of the char, which was obtained after MCTP carbonization, was 0.339 nm, which is close to the crystal structure of graphite. The crystallite height of the MCTP char was higher than that of the CTP char. A possible reaction mechanism is therefore proposed in this paper.

1. Introduction

Coal tar pitch (CTP) is a byproduct of coal processing, and its yield accounts for 50 % to 60 wt.% of coal tar. With its high carbon content, CTP is an important precursor of many carbon materials. For example, CTP can be used to produce needle coke [1–3], carbon fibers [4], and mesocarbon microbeads [5]. Needle coke is an important material for the fabrication of electrodes that are used in steel production. The demand for needle coke is growing each year with the increase in iron and steel production. However, the structure of needle coke severely affects its heat transport, conductivity, and period of usefulness. Enhancing the structural degree of order of needle coke is considerably helpful to improve the previously mentioned properties. Microstructural analysis reveals that needle coke is composed of many highly ordered polycyclic aromatic compounds. The structure of needle coke is similar to grapheme, which has significant reduced resistance to current transmission. According to the related literature, careful control of carbonization conditions promotes mesocarbon microbead growth and then the subsequent melting [6,7], which creates a favorable environment for the formation of ordered char structures. This ordered char structure is an important prerequisite in producing high-quality needle coke [8,9]. Generally, the high aromaticity of the material contributes to its suitability to produce the ordered coke. Modification is an effective route. Thus, this study has explored modification issues. Previous studies have shown that the structure of char can be improved by adding polymers such as polystyrene [10] and PVC [11], divinylbenzene monomers [12], or benzaldehyde [13]. For the modification reactions of CTP, catalysts are required. The addition of catalysts not only introduces new impurities, but also increases production cost. Therefore, the promotion of autocatalytic behavior has higher practical significance in modifying CTP, which will consequently reduce the cost of production, improve char structure, and reduce the amount of impurities. In view of these considerations, benzoyl chloride (BC) was selected as modifier in this study. On one hand, the polar carbonyl group performs high reaction activity and benefits the modification reaction of CTP. On the other hand, protons that are generated during the electrophilic substitution between BC and benzene catalyze and sustain the reaction without introducing new catalytic components.

2. Experimental

2.1. Materials

CTP was obtained from a Hongfeng coking plant located at the municipality of Changzhi, Shanxi Province in China. The main properties of CTP are shown in Table 1. BC was purchased from a local chemical reagents corporation, with content of ≥ 98 % and boiling point from 195 °C to 198 °C.

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Table 1
Proximate and ultimate analyses (wt.%) of CTP and MCTP-15 h.

Sample	Proximate analysis			Ultimate analysis (dry basis)					H/C
	M_{ad}**	A_d	V_{daf}	C	H	N	S	Cl*	
CTP	0.14	0.2	65.5	93.00	4.53	0.94	0.83		0.585
MCTP-15 h	2.05	1.2	71.5	91.30	4.28	0.96	0.61	1.37	0.562

* Cl was determined by Chinese standard GB/T-3558(1996).
** M_{ad}, A_d, and V_{daf} respectively represent the contents of moisture, ash, and volatile matter in the samples on a dry ash-free basis. MCTP-15 h represents the sample produced by addition of 5 wt.% BC and reaction for 15 h at 150 °C.

2.2. Procedures

2.2.1. Modification of CTP

At the start of the experiment, 40 g of CTP treated to remove quinoline insolubles (QIs), as suggested by previous literature [14], were placed into a 250 ml two-necked flask under a nitrogen atmosphere. Different amounts of BC were then introduced to start the reaction. The mixture was subsequently heated to specified reaction temperatures. The solvent was removed by reduced pressure distillation. Finally, after the product was washed three times using toluene to remove the unreacted BC, the modified coal tar pitch (MCTP) was produced.

2.2.2. Carbonization

Carbonization was carried out in an autoclave. First, 10 g of MCTP was placed into the autoclave and then the autoclave was sealed, with the air displaced using an N_2 flow for 10 min to 15 min. A predetermined heating regime was subsequently introduced, and autoclave pressure was maintained at 0.5 MPa. The following carbonization process was implemented:

$$20\ ^\circ C \xrightarrow{10\ ^\circ C/\,min} 200\ ^\circ C \xrightarrow{2.5\ ^\circ C/\,min} 350\ ^\circ C \xrightarrow{3.0\ ^\circ C/\,min} 450\ ^\circ C\ (held\ 210\ min) \xrightarrow{3.0^\circ C/\,min} 550^\circ C\ (held\ 60\ min)$$

2.3. Analysis

2.3.1. Characteristics of samples

Toluene insoluble (TI), quinoline insoluble (QI), softening point (SP), and coking value (CV) for CTP and MCTP were measured, respectively, according to GB/T2292-1997, GB/T2293/1997, GB/T2294-1997, and GB8727-88 national standards of the People's Republic of China.

2.3.2. Optical texture

Polarizing microscope BK-POLR-type (Chongqing Optec Instrument Co., Ltd., China) was used to compare the micrographs obtained from the top of the block sample. Anisotropic content of the chars was assessed quantitatively from the polished surface by the point-counting technique that uses an attached point counter. The constituents were divided into three groups: (1) disordered group comprising areas with inclusions of isotropic matter, (2) isometric group comprising areas discriminated according to the average diameter of anisotropic units as mosaics M (<10 μm), large mosaics LM (10 μm to 30 μm), small domains SD (30 μm to 60 μm), and domains D (>60 μm), and (3) anisotropic group characterized by the further classification of elongated (length to width, l/w > 3) monochromatic units according to size and shape as flow domains FD (large, partly deformed units), short fibrous SF (l < 60 μm), coarse fibrous CF (l > 60 μm, w > 10 μm), and fine fibrous FF (l > 60 μm, w < 10 μm) [15].

2.3.3. Infrared spectroscopy

A TENSOR 27-type Fourier Transform Infrared Spectrometer was used in the experiments. Parameters were as follows: resolution of 4 cm^{-1}, scan frequency of 32 Hz, and scan range from 400 cm^{-1} to 4000 cm^{-1}.

2.3.4. X-ray diffraction

Powder XRD patterns were recorded with AD/max-2500-type X-ray (Rigaku) diffractometer. Sample granularity was below 40 μm. Parameters and conditions were as follows: copper target, Ni filter material, voltage of 40 kV, current of 100 mA, and scan angle from 10 ° to 80 °.

2.3.5. ^1H NMR spectroscopy

The instrument used in this experiment was a BRUKER AVANCE 600 MHz-type NMR spectrometer with a superconducting magnet. The resolution was less than 0.8 Hz. Deuterated chloroform served as the solvent and tetramethylsilane was used as the standard substance.

2.3.6. Thermogravimetry analysis

Thermogravimetric analysis (TG) was carried out in a NETZSCH STA409C analyzer. About 10 mg of sample (< 100 μm of particle size), placed in a platinum crucible, was heated to the designed temperature with a carrier gas (N_2) flow rate of 80 ml/min and heating rate of 10 °C/min.

2.3.7. Elemental analysis

The carbon, hydrogen, nitrogen and sulfur contents of the sample were performed using an Elementar Vario EL (Germany).

3. Results and discussion

3.1. Effect of different amounts of BC on the structure of char

CTP was first modified using different amounts of BC. The polarized light images of different chars after carbonization of CTP and MCTP were compared. As illustrated in Fig. 1(A), char prepared without BC showed extensive mosaic organization, indicating that mesophase spheres did not sufficiently grow during carbonization and the extensive mosaic organization is preserved. Fig. 1(B) presents the image of the char obtained by carbonizing MCTP after 5 wt.% BC modification. The texture of the char indicates its streamlined shape and organized structure. The figure also shows that the modification of BC for CTP promotes the formation of good char structures. The texture of char in Fig. 1(C) also reflects a fibrous shape. However, the structures obtained using 10 wt.% BC were no better than those shown in Fig. 1(B), which were obtained using 5 wt.% BC. Therefore, moderate amounts of BC for MCTP are necessary if a wide area of melting phenomenon is produced, which is beneficial for the formation of fibrous char structures. The reason behind this advantage is that the increased concentration of BC increases the number of macromolecular compounds in MCTP, resulting in heightened viscosity and softening point. If softening point are considerably high, it means the char has a high viscosity and the growth of mesophase spheres is affected. As listed in Table 2, the increase in viscosity is confirmed. In addition, coking value increased by adding a certain amount of BC, thus the increase in the degree of polymerization of CTP by BC is illustrated experimentally. The results after adding a dosage of 10 wt.% BC in CTP agreed with those reported by Brzozowska et al. [11]. The pitch-polymer containing 10 wt.% poly(vinyl chloride)-PVC composition clearly improved anisotropy during carbonization. This improvement demonstrates that chlorine hydride produced from the decomposition of PVC has a catalytic role.

3.2. Effect of reaction temperature on the structure of char

Reaction temperature has a significant effect on chemical reactions. After optimizing the concentration of BC, an attempt was made to determine the appropriate reaction temperature by fixing BC concentration and reaction time. As shown in Fig. 1(D), the large area of fiber textures is produced at 150 °C. Relatively, the areas of fiber texture shown in Figs. 1(B) and 1(E) are small. Given the considerable effect of temperature on the rate of modification reaction, an extremely high temperature produces an extremely high reaction rate. The formation of