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RESEARCH PAPER

The catalytic role of aluminium trichloride in the polymerization and carbonization of coal tar

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Abstract: The polymerization and carbonization of coal tar was carried out at different temperatures from 633 to 1873 K using aluminium trichloride as catalyst. The polymerization degree, microstructures and optical texture of samples were analyzed by thermogravimetry, X-ray diffraction, Raman spectroscopy and polarized light microscopy. Results indicated that aluminium trichloride accelerated dehydrogenation during the polymerization of coal tar, and increased the toluene-insoluble fraction and carbonization yield. The presence of aluminium trichloride in the polymerized coal tar affected the microstructure of the coke by the formation of a quasi-isotropic structure.

Key Words: Coal tar; Aluminium trichloride; Catalytic carbonization; Microstructure; Optical texture

1 Introduction

Carbon materials are known for their high thermal and electrical conductivities, and excellent mechanical strength at high temperature, et al[1]. These unique properties are closely related to their microstructures and textures, which are strongly dependent on the carbonization to convert precursors into carbon. Therefore, carbonization is an important for production of carbon materials. There are three typical carbonization methods, gas phase carbonization, solid phase carbonization and liquid phase carbonization [2-6].

In 1961, Taylor [7] firstly attributed anisotropy of coke to the formation of nematic liquid crystals during pyrolysis of pitch and coal. Brooks [8] demonstrated the formation mechanism of mesophase in the liquid phase carbonization in 1964. Until then, more researches on preparation and application of mesophase pitch, mesocarbon mircobeads and needle coke were carried out [9-11]. In previous study, several papers reported the liquid phase carbonization of organic compounds with the aid of catalysts [12-21], which explored a new field for liquid phase carbonization. LV et al. [20, 21] modified naphthalene to obtain pitch using HF/BF_3 and SO_4^{2-}/ZrO_2 as catalysts. Mochida et al. [16-18] synthesized pitch derived from aromatic hydrocarbons with alkali metals and Lewis acid as catalysts. Rey et al. [19] found that hydrogen evolution rate reached a maximum with temperature around 653 K during the liquid phase carbonization of naphthalene catalyzed by aluminium trichloride ($AlCl_3$). The present work focused on effects of $AlCl_3$ catalyst on fundamental properties of the as-prepared coke.

In this work, the catalytic carbonization of coal tar was carried out using $AlCl_3$ as catalyst. The effect of $AlCl_3$ on polymerization degree, microstructures and optical texture of as-prepared samples were characterized by thermogravimetry (TG), X-ray diffraction (XRD) and polarized light microscopy. Moreover, the relationship between distribution of $AlCl_3$ and microstructures of the resultant coke was studied by Raman spectroscopy.

2 Experimental

2.1 Preparation of materials

Coal tar (Fujian Sangang Group Co., Ltd) and $AlCl_3$ (Sinopharm Chemical Reagent Co., Ltd, >99 wt.% purity) were used as carbonaceous precursor and catalyst, respectively. The coal tar mixed with 5 wt.% $AlCl_3$ was placed in an autoclave. The autoclave was first evacuated, and then pressurized with nitrogen to 4MPa. The autoclave was raised to a required temperature ranging from 633 to 673 K and maintained for 3 h to carry out polymerization. As-prepared samples at 673 K were further heated to 1173, 1623 and 1873 K in a tube furnace and kept at the final temperature for 2 hours to carry out carbonization. The C series samples catalyzed by $AlCl_3$ were signed as C-t and the N series samples without $AlCl_3$ as N-t, in which t represented the polymerization temperature.

2.2 Characterization

The content of carbon, hydrogen and nitrogen in the

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samples were analyzed by a vario MACRO CHN analyzer (Elementar, Germany). The carbon yield was measured by TG (Shimadzu DTG-60H) under nitrogen atmosphere from ambient temperature to 1073 K at a heating rate of 10 K /min. The crystal structures were analyzed by XRD (Rigaku SmartLab) operating at 40 kV and 30 mA, using Cu Kα radiation (k=0.15418 nm) with a step size of 0.01° and a scanning rate of 8°/min. The interlayer spacing (d_{002}), crystallite size (L_c) and graphitization degree (g) were calculated from the Bragg equation, Scherrer equation and Maire and Merings equation, respectively [22-24]. The internal silicon standard was used to correct the instrumental error. The Raman spectra were obtained by a Renishaw invia Raman Microscope with the 532 nm wavelength of a 50 mW Nd-YAG laser. The samples obtained below 673 K were easily charred, so the exposure time and laser power were different for different samples. Some samples were mounted in epoxy resin, then ground and polished by waterproof sandpaper, and finally their optical textures were observed using a polarized light microscope (Leica DM 2500P).

3 Results and discussion

3.1 Polymerization degree

The toluene insoluble (TI) content is related to the polymerization degree [25]. As seen in Fig. 1, samples without AlCl$_3$ held a low level of TI content (~20%). The TI contents of samples with AlCl$_3$ apparently increased with polymerization temperature to 96.4% at 673 K. The elemental analysis results of different samples are listed in Table 1. It could be seen that the value of H/C ratio was low for the samples with AlCl$_3$, indicating that AlCl$_3$ promoted dehydrogenation of coal tar during polymerization. In the presence of AlCl$_3$, multi-component aromatic hydrocarbons in coal tar were highly condensed and dehydrogenated, generating numerous high-molecular-weight aromatic hydrocarbons, which resulted in the increase of TI content.

Fig. 2 shows TG curves of C-673 and N-673 samples.The N-673 sample without AlCl$_3$ lost weight sharply from 450 to 800 °C with a maximum weight loss reached ~70%. However, the C-673 sample with AlCl$_3$ had a high weight of carbonaceous residues of 95.5%, a much lower weight loss than that of the N-673. The AlCl$_3$ catalyst could combine the aromatic planes via dehydrogenation, resulting in a sharp increase of the molecular weight.

3.2 Microstructures

The N series samples were black viscous liquid or semisolid. Only XRD patterns of the C series samples can be obtained, which are shown in Fig. 3 and Fig. 4. The prominent feature at all temperatures in XRD patterns was the 002 diffraction peak at ~25.6, which was identified as from turbostratic carbon [26]. The (002) diffraction peaks of the samples catalyzed below 673 K were broad and obscure, and

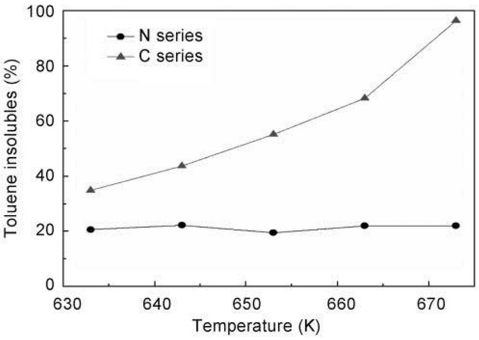

Fig. 1 Variation of TI contents with polymerization temperature.

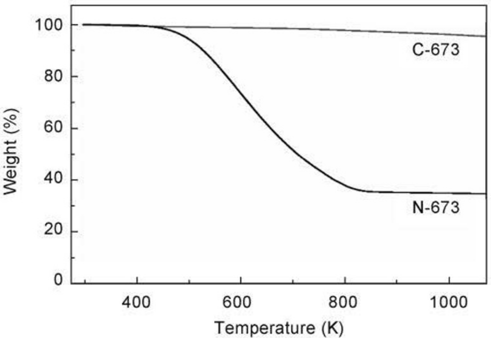

Fig. 2 TG curves of C-673 and N-673 samples.

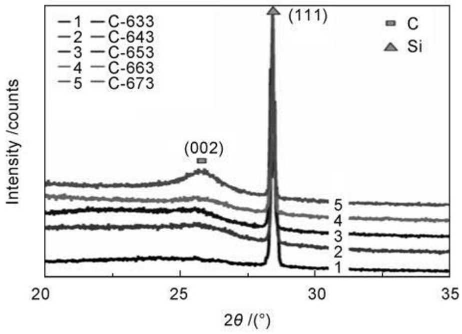

Fig. 3 XRD patterns of as-prepared samples catalyzed by AlCl3.

Table 1 Elemental analysis of different samples.

Samples	C (wt. %)	H(wt. %)	N (wt. %)	H/C ratio
Coal tar	90.81	5.45	1.17	0.72
N-633	91.05	5.32	1.09	0.70
N-653	91.34	5.13	1.01	0.67
N-673	91.57	4.97	0.96	0.65
C-633	91.89	4.24	0.46	0.55
C-653	92.90	3.21	0.39	0.41
C-673	94.26	1.76	0.28	0.22