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Oxidation of acetylene black by nitric acid in hermetically sealed condition

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ABSTRACT

Acetylene blacks were oxidized with nitric acid to obtain some insight into the mechanism of oxidative degradation in sealed condition. Changes in the morphologies and structures of acetylene blacks in the course of oxidation were investigated using transmission electron microscopy, X-ray diffraction, Raman, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and nitrogen adsorption and desorption isotherms. Time-dependent experiments were carried out to investigate the degree of oxidation. It was found that, with the increase of acid steaming duration ranging from 2, 4, 6 to 8 h, the yield of oxidized product decreases from 87.5%, 64.4%, 51.0% to 27.5%. Experimental results demonstrated that the prolonged treatment led to an increased hollow ratio and an enhanced degree of oxidation. The functionalized hollow sample was characterized and it was observed a well developed microporous and mesoporous structure.

1. Introduction

Carbon blacks are an industrially manufactured fluffy powder composed of fused aggregates having complex configurations and quasigraphitic in structure, with a range of size between 10 and 1000 nm. Their features include the extreme fineness and high surface area [1,2]. Carbon blacks are extensively used for the reinforcement of rubber, as a black pigment, and as an additive to improve electric conductivity of electrode materials in dry cell batteries due to their specific physical and chemical properties. According to the processes by which they are made, carbon blacks can be divided into oil-furnace blacks, lampblacks, thermal blacks, acetylene blacks, and channel blacks. Among them, acetylene blacks, made by the decomposition of acetylene, are the most crystalline or graphitic of the commercial carbon blacks [3,4].

It is well known that chemical oxidation of carbon materials (such as graphene, carbon nanotubes and carbon nanofibers) by acid is a common chemical method to purify original samples and to get functionalized products, which enables chemical covalent bonding between carbon nanostructures and the other materials of interest [5–8]. Many researches concerning the oxidation of carbon blacks were also carried out by heating the mixture of carbon blacks and concentrated nitric acid. Conventionally, the use of nitric acid is an efficient agent to dissolve the impurities from carbonaceous materials, but long time treatment is required in an open reactor [9,10].

In the present work, we propose a nitric acid steaming process occurred in a closed-vessel system without the direct contact between nitric acid solution and acetylene blacks powder for the oxidation of acetylene black. The changes in crystallographic structures, morphologies, functional groups on the surface and pore structures during the oxidation of acetylene black by nitric acid in hermetically sealed condition are investigated on the basis of transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Raman, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption and desorption isotherms. The mechanism is also discussed briefly.

2. Experimental

2.1. Sample preparation

The acetylene blacks used in this study were obtained from TIMCAL, Sweden. The acetylene blacks were air-dried at 393 K for 12 h prior to the experiments. The acid steaming process was carried out in a conventional Teflon-lined vessel which could be sealed into a matched stainless steel autoclave and the representative experimental apparatus was shown in Fig. 1. Typically, 1 g of

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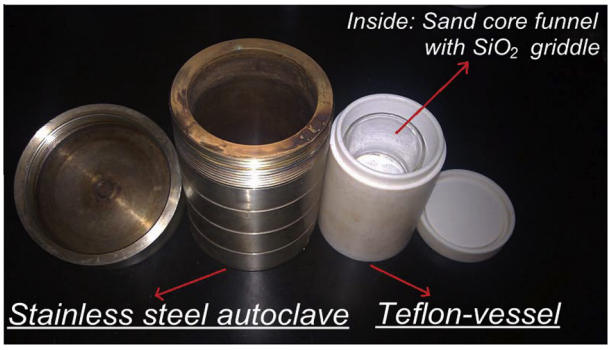

Fig. 1. Representative experimental apparatus.

pristine acetylene blacks (p-ABs) powder were placed on the silica griddle of a sand core funnel, and then put the sand core funnel into a Teflon-vessel, the bottom of which has added 20 ml concentrated HNO_3 (65–68 wt%). After been sealed into a stainless steel autoclave, the experimental apparatus was placed into an oven at 423 K for prescribed periods (2, 4, 6, and 8 h). After cooling down to room temperature the oxidized acetylene blacks (oxi-ABs) were dissolved in deionized water and filtered on a membrane filter, washed with abundant deionized water until neutral, dried at 393 K for 12 h, and weighed. The samples obtained with different steaming durations are denoted as oxi-ABs-2, oxi-ABs-4, oxi-ABs-6 and oxi-ABs-8. (Caution: in order to avoid the hurting of released gases, the cooled stainless steel autoclave was opened in fume hoods to get the oxidized acetylene blacks.)

2.2. Characterization

Field emission scanning electron microscopy (NOVA NANO SEM230, JAPAN) and field emission transmission electron microscopy (FETEM, JEM-2100F, JAPAN) were used to characterize the materials. The structures of samples were measured by XRD (Rigaku-TTRIII, Cu Kα, at a scanning rate of $10^\circ\ min^{-1}$), Raman spectroscopy (LabRAM Hr800, HORIBA JOBIN YVON) and FT-IR (Nicolet 6700). XPS were recorded using an X-ray photoelectron spectrometer (K-Alpha 1063) with a monochromatic Al Kα X-ray source. The porous texture of the samples was characterized through nitrogen adsorption and desorption isotherms obtained at 77 K using a Micromeritics ASAP 2020 system. Specific surface areas were determined according to the Brunauer–Emmett–Teller (BET) method. The pore size distribution (PSD) plot was recorded from the adsorption branch from the isotherm based on the non-local density functional theory (NLDFT) method.

3. Results and discussion

The crystallinity of carbon materials can be determined by XRD and Raman spectroscopy. Fig. 2A displays the XRD patterns of p-ABs and oxi-ABs-8. The presence of (002) and (101) reflections indicated the partial graphitic nature of the materials, demonstrating the existence of sp^2 carbon-bonded graphite crystals although with a lower degree of crystallization [11,12]. The parameters derived from XRD as reported in Table 1 indicate that p-ABs consist of well-developed graphite platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers. While the graphite interplanar distance is 0.335 nm, the interplanar distance of p-ABs is 0.358 nm as a consequence of the random planar orientations or so-called turbostratic arrangement [3]. After the acid steaming, the (002) peak shown in Fig. 2A became sharper and intenser. Compared with p-ABs, oxi-ABs-8 have a smaller d_{002}

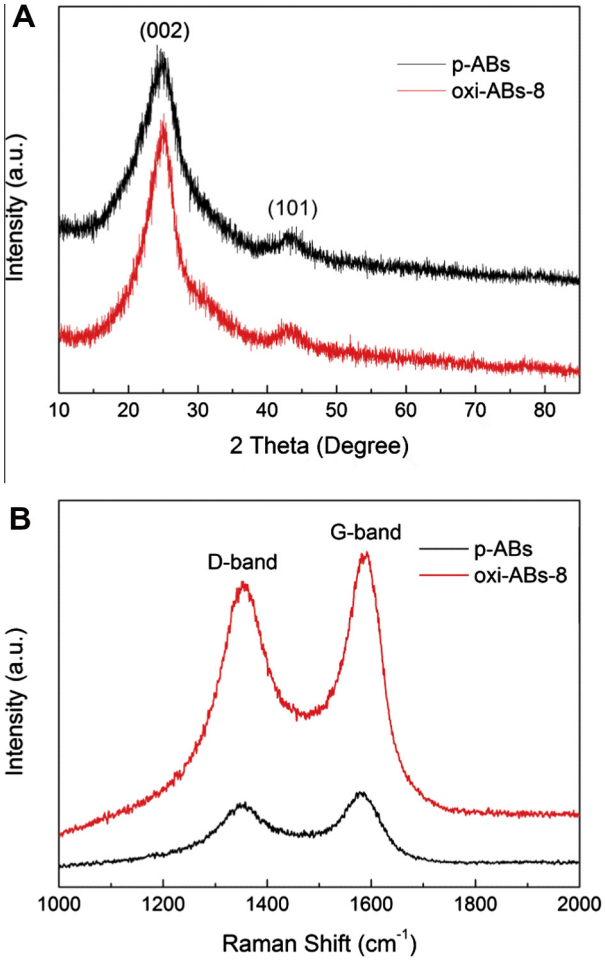

Fig. 2. (A) XRD patterns and (B) Raman spectra of p-ABs and oxi-ABs-8.

Table 1
Physical properties derived from XRD patterns.

Sample	(002)/°	d_{002}/nm	Peak FWHM/°	L_c (002)/nm
p-ABs	24.74	0.358	5.876	2.886
oxi-ABs-8	25.11	0.353	3.786	4.518

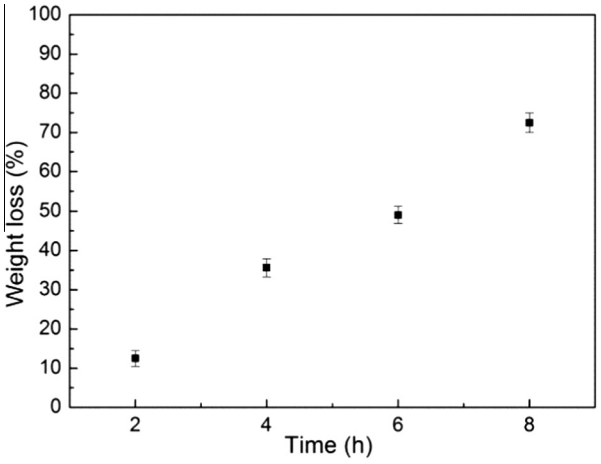

Fig. 3. Weight loss of p-ABs through varying the acid steaming time.