



ORIGINAL ARTICLE

Effect of elemental sulfur in precursors on the pore structure and surface chemical characteristics of high-surface area activated carbon



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Abstract Analog sulfur-containing precursors (ASCPs) have been prepared by adding a certain amount of elemental sulfur (ES) into petroleum coke (PC) for synthesis of high-surface area activated carbon (HAC). ASCPs make it feasible to control the speciation and content of sulfur in ASCPs, so as to accurately investigate the influence of ES on the pore structure and surface chemical characteristics of the resultant HAC. The results indicate that ES in ASCPs can react with activator KOH and consume a part of KOH amount, thus leading to the deficiency of actual KOH amount for PC activation, eventually making a decrease in the specific surface area and pore volume of HAC. Interestingly, some of ES in ASCPs is transformed into organic sulfur thioether (C–S–C) and sulfate (C–SO₄–C) or sulfonate (C–SO₃–C) on HAC surface during the activation process. Therefore, the surface chemical characteristics of HAC are modified correspondingly.

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1. Introduction

High-surface area activated carbon (HAC) is well known as efficient material for its high specific surface area, developed pore structure and uniform pore size distribution. It has been widely used in the field of energy storage [1–5], gas separation [6], air purification [7] and environmental protection [8]. Nowadays, almost any carbonaceous material from biomasses

or minerals can be converted to HAC if properly treated. Mineral materials, due to their rich carbon content, have become highly attractive precursors for HAC preparation [9–11]. However, it is well known that mineral precursors usually contain sulfur-containing substances. Generally, minerals can be classified into three grades depending on their total sulfur content: low-sulfur, medium-sulfur, and high-sulfur minerals. Among them, the medium- and high-sulfur minerals are abundant and of low price, and most of them are stockpiled as industrial waste [12]. Therefore, the utilization of medium- and high-sulfur minerals as precursors for synthesis of HAC will promote an effective application of such minerals. Recent researches have demonstrated that HAC prepared from high sulfur minerals is of high adsorption capacity [13] and developed pore structure [14], and has been successfully applied to the removal of pollutants [12] and as catalyst support [15].

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Hence, high sulfur minerals as precursors for HAC preparation are practical and feasible. To date, a few reports have indicated that sulfur-containing substances in mineral precursors have an obvious influence on the pore structure and surface chemical characteristics of HAC [16–18]. Consequently, to investigate the influence of sulfur content and species in mineral precursors on the quality of HAC is necessary, which could provide deep insight into the use of sulfur-containing mineral precursors to produce HAC.

The sulfur species in mineral precursors is very complicated, mainly including inorganic sulfur, such as pyrite, sulfate and elemental sulfur (ES), and organic sulfur, such as aliphatic, aromatic and heterocyclic sulfides [19,20]. We have recently investigated the effect of organic sulfur dibenzothiophene (DBT) and inorganic sulfur FeS_2 on pore texture of HAC [21,22]. The results showed that the DBT in the precursors can react with the activation agent KOH, thus reducing the actual KOH/char ratio, eventually imposing a clear negative effect on the pore structure development of HAC. The FeS_2 in the precursors can also react with KOH and reduce the actual amount of KOH used to develop the porosity of HAC. However, different from organic sulfur species, such as DBT, the inorganic sulfur FeS_2 can be transformed into Fe_3O_4 during the activation process. Through our previous work, the conclusion can be drawn that different kinds of sulfur in mineral precursors have different mechanisms during the activation process. Therefore, to extend the studies to other sulfur species in mineral precursors is of significance [22].

In this work, by taking ES as the research object, the influence of ES in mineral precursors on the pore structure and surface chemical characteristics of HAC was investigated. Specifically, ES was added into petroleum coke (PC) to prepare analogous sulfur-containing precursors (ASCPs), and HAC was obtained from ASCPs by KOH chemical activation. The use of ASCPs can effectively avoid the differences in the precursor composition and content to interfere with the experimental results [21]. In addition, the obtained HAC was characterized by a variety of analytical methods such as X-ray adsorption near-edge structure spectroscopy (XANES), X-ray photoelectron spectroscopy (XPS), elemental analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), ion chromatography and N_2 physical adsorption/desorption. Correspondingly, the mechanism of ES on HAC structure and surface chemical characteristics is also proposed.

2. Experimental

2.1. Preparation of HAC

Different amounts of ES were added into 1.0 g PC with particle size 0.25–0.3 mm to prepare ASCPs by controlling ES/PC mass percentage ratio of 0%, 10%, 20%, 30% and 40%, respectively. Then, ASCPs and KOH were mixed in a nickel crucible at a KOH/PC mass ratio of 3:1, 4:1 and 5:1. The resultant samples were put into a muffle furnace and heated up to the pre-determined activation temperature at a heating rate of 5°C min^{-1} under N_2 atmosphere. The activation temperature varied from 20 to 800°C and was hold for 1 h at 800°C . After activation treatment, the samples were cooled naturally to room temperature and washed with deionized water until the pH value of lotion was neutral. Finally, HAC

was obtained by filtration and drying. HAC samples are designated as HAC-X-Y, where X and Y represent KOH/PC mass ratio and ES/PC mass percentage ratio, respectively. In this work, the mass ratio of KOH/PC is 3:1–5:1, and the mass percentage ratio of ES/PC is 0–40%. Therefore, the samples are called as HAC-X-0, HAC-X-10, HAC-X-20, HAC-X-30 and HAC-X-40, correspondingly.

2.2. Structural characterizations and sulfur analyses

S K-edge XANES measurement was performed using the soft X-ray micro characterization Beamline (SXRMB) at the Canadian Light Source. XPS analyses were carried out using ESCALAB 250Xi spectrometer (Thermo scientific, USA). The pore structure parameters of HAC samples were analyzed by N_2 adsorption/desorption at 77 K with ASAP 2020 instrument (Micromeritics, USA). The sulfur contents in HAC were determined by a Vario EL Cube element analyzer (Elementar, German). XRD spectra were obtained by the D8 ADVANCE diffractometer (Bruker, Germany) within the 2θ range from 10° to 80° with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The generator current and voltage were 200 mA and 40 kV, respectively. The concentration of sulfur-containing anions in washing solution was analyzed by ion chromatography system (ICS2100, Dionex Company, USA). The sample morphology was observed by the S-4800 II field emission SEM.

3. Results and discussion

3.1. Sulfur analyses

As listed in Table 1, S_g in HAC gradually increases with the increase in ES content in ASCPs, indicating that the more the ES content in ASCPs, the more the sulfur-containing substances in HAC, similar to the result of inorganic sulfur FeS_2 [22]. Meanwhile, it is worth noticing that the C content in HAC gradually decreases, while the O content gradually increases. This shows that some O-containing substances could be produced in HAC after activation process.

As Fig. 1a shows, the XRD patterns of unwashed samples have similar peak shape, suggesting that the species of activation products remain constant with the change of ES content in ASCPs. Furthermore, according to the PDF standard card and spectra analysis result, the characteristic peaks at $2\theta = 30.0^\circ, 31.7^\circ, 32.0^\circ, 32.1^\circ$ and 34.1° represent K_2CO_3 (71-1466); the characteristic peaks at $2\theta = 22.8^\circ, 30.0^\circ, 30.4^\circ, 35.2^\circ$ and 41.5° represent K_2SO_4 (85-0939); the characteristic peaks at $2\theta = 20.9^\circ, 24.1^\circ, 34.0^\circ, 49.0^\circ$ and 61.5° represent K_2S (77-2152). This indicates that K_2S , K_2SO_4 and other possible sulfur-containing products are generated during KOH activation reaction. As displayed in Fig. 1a, the characteristic peaks of K_2SO_4 , K_2S and K_2CO_3 completely disappear, demonstrating that they are basically removed after washing process. Moreover, the appearance of a diffraction peak at $2\theta = 43.5^\circ$ can be indexed to the (101) diffraction from the graphitic phase, indicating that HAC samples are partly graphitized [23].

The chromatogram charts of HAC-5-0, HAC-5-10 and HAC-5-40 washing solution undergoing 0, 10 and 10 times dilution treatment respectively are shown in Fig. 1b. The five kinds of anions can be observed in HAC washing solution,

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