

MESOPOROUS ACTIVATED CARBONS FROM PHENOLIC RESINS

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Abstract: Activated carbons were prepared from carbonized phenolic resins by steam-activation. Three different novolak type phenol formaldehyde resins were synthesized under different formaldehyde (*F*) to phenol (*P*) molar ratios ($F/P = 0.3, 0.5$ and 0.8) and were used as the precursors for activated carbons. The activated carbons obtained from resins synthesized under typical F/P ratios were microporous, which is characteristic for activated carbons derived from phenolic resins. However, it was found that by decreasing the F/P ratio of the precursor resin to values lower than those usually adopted for commercial phenolic resin production, i.e., values lower than 0.5 , activated carbons with developed mesopores could be obtained. Structural information of the precursor resins obtained from Raman spectroscopy indicated that although typical novolak resin structures could be found in all the resins, the resins synthesized at lower F/P ratios included larger amounts of phenol and lower molecular weight substances. This is thought to have led to a large difference in their thermoplastic natures. The existence of low molecular weight substances was also confirmed through thermogravimetric analysis of the resins during carbonization. CO_2 , C_2H_6 , $n\text{-C}_4\text{H}_{10}$ and $i\text{-C}_4\text{H}_{10}$ adsorption isotherms of the prepared activated carbons were also measured at 298 K for the better understanding of micropore development within the samples. The obtained data suggested that micropore development was not so much influenced by the F/P ratio of the precursor resin.

Keywords: activated carbon; activation; adsorption; mesopore; phenolic resin.

INTRODUCTION

Activated carbon is an adsorbent which is widely used in various fields. It is recognized that the most important property of activated carbons is its pore structure (Wigmans, 1989). Activated carbons usually have a very wide range of pores within their structure, from angstrom-sized micropores, to micrometer-sized macropores. Their applicability to various purposes highly depends on their porous properties. Therefore the development of pore size controlling techniques is one of the major challenges in the production of activated carbons.

It is well known that the porous properties of activated carbons highly depend on the structure of its precursor (Bansal *et al.*, 1988). Natural sources such as woods, coconut shells, coal, lignite, peat *etc* and so on, are widely used for the production of activated carbons, due to their low cost and abundance (Rivera-Utrilla *et al.*, 1991; Girgis *et al.*, 1994; Toles *et al.*, 1997; Lua and Guo, 1998; Rodoriguez-Reinoso and Molina-Sabio, 1992; Shopva *et al.*, 1997; Nakagawa *et al.*, 2002). Activated carbons

can also be obtained from synthetic sources, such as plastics. Although such precursors tend to be more expensive, activated carbons with well-controlled structures and a low amount of impurities can be obtained (Merchant and Petrich, 1993; Bota *et al.*, 1996; Laszlo *et al.*, 1998; Ariyadejwanich *et al.*, 2003; Nakagawa *et al.*, 2003). Phenolic resin is one of the well-used synthetic precursors for the production of activated carbons. Although many researchers have reported that various types of activated carbons can be prepared from various types of phenolic resins, the obtained activated carbons are mostly microporous (Lenghous *et al.*, 2002; Centeno and Fuerted, 1999; Tennison, 1998; Mangun *et al.*, 1998; Daley *et al.*, 1997). Indeed, there are several reports that show that mesoporous activated carbons can also be produced from phenolic resins through catalytic activation (Yang *et al.*, 2002; Oya *et al.*, 1995).

In this work, we attempted to produce mesoporous activated carbon from phenolic resins through steam-activation by controlling structural properties of the precursor resins. Phenolic resins can be obtained from various

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combinations of phenols and aldehydes, but we used the most conventional combination, phenol and formaldehyde. Both thermosetting and thermoplastic type resins can be obtained from this combination by using either a base or acid as the catalyst for polymerization. The usage of a base catalyst results in the formation of a thermosetting resin, resole. When an acid catalyst is used, a thermoplastic resin, novolak, is obtained. As novolak resins can be transformed to thermosetting resins using a cross linking agent, such as hexamethylenetetramine, we used novolak type resins in this work, as a wide variety of resins can be expected by simply adjusting synthesis conditions. When novolak type resins are produced commercially, the formaldehyde to phenol molar ratio in the starting material, F/P , is usually set to values in the range of 0.5–1.0. Therefore we used resins synthesized under the conditions of $F/P = 0.8$ and 0.5 as precursors for activated carbons. We also intentionally decreased this value to 0.3 and synthesized a resin to be used as the precursor. The obtained resin cannot be used for typical purposes that phenolic resins are suitable for, as it is likely to include a large amount of unreacted phenol and/or low molecular weight substances, but can be used as a precursor for activated carbons. The existence of phenol and/or low molecular weight substances is expected to lead to the development of unique pore structures upon carbonization followed by steam-activation. Structural information of the prepared resins was obtained from Raman spectroscopy. Weight loss that occurs during carbonization and steam-activation was traced by thermogravimetric analysis to clarify whether their carbonization and activation behaviors differ among each other. Finally, the porous properties of the resulting activated carbons were evaluated through gas adsorption experiments.

EXPERIMENTAL

Preparation of Phenolic Resins

Novolak type phenol formaldehyde resins, which were used as the precursors in this work, were synthesized through the following procedure. First, three mixtures of phenol (Wako, Japan) and aqueous formaldehyde solution (36 wt%; Wako, Japan) were prepared. The formaldehyde to phenol molar ratios (F/P) of the mixtures were respectively adjusted to 0.3, 0.5 and 0.8. To these mixtures, 1 N hydrochloric acid (Wako, Japan) was added as the catalyst at amounts of 1 wt% of each mixture. The solutions were stirred and transferred to Erlenmeyer flasks equipped with reflux condensers, and heated to 373 K. The changes in the Raman spectra of each solution was traced using a Raman spectrometer (Kaiser Optical Systems, Inc., Hololab 5000). After 4 h hexamethylenetetramine was added as the cross-linking agent at amounts of 5 wt% of each mixture, and the obtained mixtures were heated in air at 423 K for 8 h. The obtained resins were ground into fine powder by an electric blender. Finally, three types of phenol formaldehyde resins PS, PM and PH (respectively prepared under the conditions of $F/P = 0.3, 0.5$ and 0.8) were obtained. It should be noted that PS was soft even though it was cross-linked by hexamethylenetetramine.

Preparation of Carbonized Resins

Ten grams of the prepared resin was set in a quartz reactor and carbonized using an electric furnace. The reactor was kept under an inert atmosphere by a N_2 flow of $100 \text{ cm}^3 \text{ min}^{-1}$. The reactor was heated from room temperature to 823 K at a heating rate of 10 K min^{-1} , and kept at 823 K for 1 h. Weight loss during carbonization was recorded using a thermogravimetric analyzer (Shimadzu Co., TGA-50). Finally, three groups of carbonized resins were obtained, i.e., PS derived cPS, PM derived cPM and PH derived cPH.

Steam-Activation

Activated carbons were prepared from the obtained carbonized resins by steam-activation. Half a gram of the carbonized resin was placed in a quartz reactor, and heated under a N_2 flow of $200 \text{ cm}^3 \text{ min}^{-1}$ using an electric furnace from room temperature to 1123 K at a heating rate of 27 K min^{-1} . When the temperature reached 573 K, steam was introduced into the reactor at a flow rate of 0.5 g min^{-1} . This gives a steam partial pressure of 0.46 atm. Activation time (i.e., the holding time at 1123 K) was changed from 0 to 150 min in order to prepare carbons with different burnoffs. Burnoff is defined as $1 - (\text{weight of obtained activated carbon})/(\text{weight of char})$. Weight loss during steam-activation was recorded using a thermogravimetric analyzer (Shimadzu Co., TGA-50). Through this procedure, three series of carbons were prepared from each precursor. The '0A' series corresponds to samples with burnoffs around 0.1, '1A' series around 0.5 and '2A' series about 0.8.

Characterization of Activated Carbons

N_2 adsorption-desorption isotherms of the obtained activated carbons were measured at 77 K using a volumetric adsorption apparatus (BEL Japan, Inc.; BELSORP28). The BET method was applied to the adsorption isotherms and the specific surface areas of the activated carbons were evaluated. Mesopore range pore size distributions (range of pore radii = 1.0–20 nm) were estimated by applying the method of Dollimore and Heal (1964) to the desorption isotherms, and the mesopore volumes of the samples were also determined. The micropore volumes of the samples were evaluated by the t -plot method (Lippen and Boer, 1965). The N_2 adsorption isotherm of Spheron 6 was adopted as the standard isotherm. Adsorption isotherms of CO_2 , C_2H_6 , nC_4H_{10} , iC_4H_{10} were also measured at 298 K using the same adsorption apparatus.

RESULTS AND DISCUSSION

Raman Analysis of Prepared Phenolic Resins

Raman spectra of the prepared phenolic resins PS, PM and PH are shown in Figure 1. Their measurements were finished before the addition of cross-linking agent (hexamethylenetetramine) to the resins. Although it is well known that strictly quantitative data cannot be derived from Raman spectra, qualitative data, such as which sample tends to have certain chemical bonds within their structure, can be obtained by normalizing the spectra using the intensity of a standard peak. We normalized the spectra using the peak corresponding to the

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