

Diversity of Carbon Pore Structures Obtained by KOH Activation

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Abstract

Wood-based activated carbons were subjected to a second stage of activation using potassium hydroxide. The high surface area products obtained exhibited a wide spectrum of porous structures, from exclusively microporous to predominantly mesoporous. Alkali metal-activation of carbon or carbonaceous precursors is a multi-factorial process in which the effects of all process parameters are not fully understood. Nevertheless, it was demonstrated through this work that the influence on pore structure of the mass ratio of alkali activant to carbon precursor can be distinguished from other process variables and accurately described in a mathematical model. The model can be used to set process conditions for the production of activated carbons possessing specific pore structure characteristics.

Key Words

KOH Activation Process, Characterization of Carbon Pore Structure, Pore Size Distribution, Nitrogen Adsorption Isotherm.

Introduction

The production of very high surface area, “super-active” carbon products using an alkali activation procedure was demonstrated in the mid-70’s by the Standard Oil Company (1), but the process was not successfully commercialized until the late-80’s by Toshiro Otowa (2) of the Kansai Coke and Chemicals Company (Japan). Nevertheless, the production method is still referred to as the “AMOCO Process.” In this process, coal coke, petroleum coke, coconut char or their mixtures are blended with KOH at high ratios of activant to precursor. The mixture is subjected to a two-stage, high-temperature treatment in an inert atmosphere, to produce activated carbon exhibiting an apparent BET surface area in excess of $3000 \text{ m}^2\text{g}^{-1}$. It was later demonstrated that the micropore volume of an activated carbon material, *per se*, could be substantially enhanced through a second stage of alkali activation of the carbon (3). In fact, the second stage of activation of an existing activated carbon resulted in a “mutation” of porosity, in which mesopores and macropores were largely removed and replaced by micropores. This was most notably observed with wood-based carbons produced through chemical activation with phosphoric acid, but a similar response to the second stage of alkali activation was also found with coal and coconut-based carbons produced through thermal activation. The work published earlier (3) on this two-stage activation approach was directed to obtaining ultra-microporous carbons (UMC) for the storage of natural gas at low pressure (500 psi). The work discussed here highlights the relationship between KOH/carbon ratio and the pore structure of the subsequent carbon, and demonstrates that a wide range of pore size distributions can be obtained through control of this process parameter.

Experimental

The activated carbon precursor, such as Westvaco's WV-A 1100 product, was obtained through the conventional chemical activation of wood with phosphoric acid. The activated carbon was subjected to a second stage of chemical activation with potassium hydroxide, at KOH/carbon weight ratios in the range of 1:1 to 4:1, in which the temperature of the alkali/carbon blend was raised from ambient to 930°C over a period of about 4 hours under an atmosphere of nitrogen. The alkaline char was thoroughly washed with water to remove the spent alkali, and the activated carbon product dried at 110°C overnight. The pore structure of the carbon obtained was characterized in terms of its pore size distribution (PSD) calculated from nitrogen adsorption isotherm data using software (4) based on the Density Functional Theory, DFT (5). Replicate runs under a given set of activation conditions were made to ensure a high degree of reproducibility of product properties.

Results and Discussion

A visual illustration of the influence of KOH/C ratio on the pore structure of the final activated carbon product is shown in the form of a 3D plot in Figure 1. The plot is based on the raw differential PSD of the carbon and shows a progressive development of carbon porosity with increasing KOH/C ratio.

To quantitatively assess the variation of carbon pore size distribution as a function of KOH/C ratio, a simple model is proposed in which the carbon pore structure is represented by the cumulative PSD data, v_i , calculated for selected pore widths of 8, 10, 15, 20, 30, 40, 80, 160, and 320 Å. A satisfactory fit is obtained by using the following exponential cubic polynomial as the model equation:

$$v_i = \exp\{a_i + b_i q + c_i q^2 + d_i q^3 + \dots\} \quad (1)$$

where q is the KOH/C activation ratio, and a_i , b_i , c_i , and d_i are the best-fit parameters for the i -th pore width. Using this model, the variation of the cumulative PSD of the carbons as a function of KOH/C ratio is shown in Figures 2-4. In Figures 2 and 3, the original PSD data points are included to illustrate the agreement with the model. Using the contour plot shown in Figure 4, explicit values of cumulative pore volumes can be obtained for activated carbons obtained using a specific KOH/C ratio. The lines in this plot represent equal values of cumulative PSDs.

In Figure 5, the effect on pore size distribution of multiple activation of an activated carbon with KOH is shown schematically. Starting with Westvaco's WV-A 1100 with the PSD shown in Figure 5a, a second stage of activation using a KOH/C ratio of 2:1 yielded a product with the pore size distribution shown in Figure 5b. Clearly, all pores in the WV-A 1100 carbon with a width of greater than about 30 Å were eliminated and replaced with micropores. Yet another stage of alkali activation of this carbon with a 4:1 KOH/C ratio yielded a product with the PSD shown in Figure 5c. It is apparent that the micropore volume of the Figure 5b carbon was retained, but also that a significant volume of small mesopores was introduced. A qualitatively similar result was obtained by a single stage of activation of the WV-A 1100 carbon with a 4:1 KOH/C ratio, but with a much greater volume of mesopores than micropores (Figure 5d). In

general, higher KOH/C ratios lead to wider pore size distributions characterized by larger pore widths. Similar findings have been reported recently by Linares-Solano, et al, for carbons prepared by the activation of anthracite with either KOH or NaOH (6,7).

Conclusions

The alkali (KOH) activation process is a powerful and flexible means of producing activated carbons exhibiting a broad spectrum of pore structures, both from carbonaceous precursors and from carbon materials. A second stage of alkali activation of an existing activated carbon material results in the “mutation” of porosity in the carbon, whereby relatively large pores can be replaced with much smaller pores, thereby greatly enhancing the micropore volume of the carbon; e.g., for gas storage applications. Further manipulation of the pore structure of the carbon can be made through yet more stages of alkali activation. Despite its multi-factorial character where the effects of all factors are not fully understood, the activation process is highly reproducible. The alkali to carbon mass ratio is a strong controlling factor of the process, which largely determines the pore structural characteristics of the resultant carbon. A mathematical model was derived to describe the relationship between KOH/C ratio and the pore size distribution of the activated carbon product. The work described here was carried out on a Westvaco, wood-based activated carbon product (WV-A 1100), but qualitatively similar results have been obtained on other carbonaceous precursor-based carbons, including coal, coconut, and pitch.

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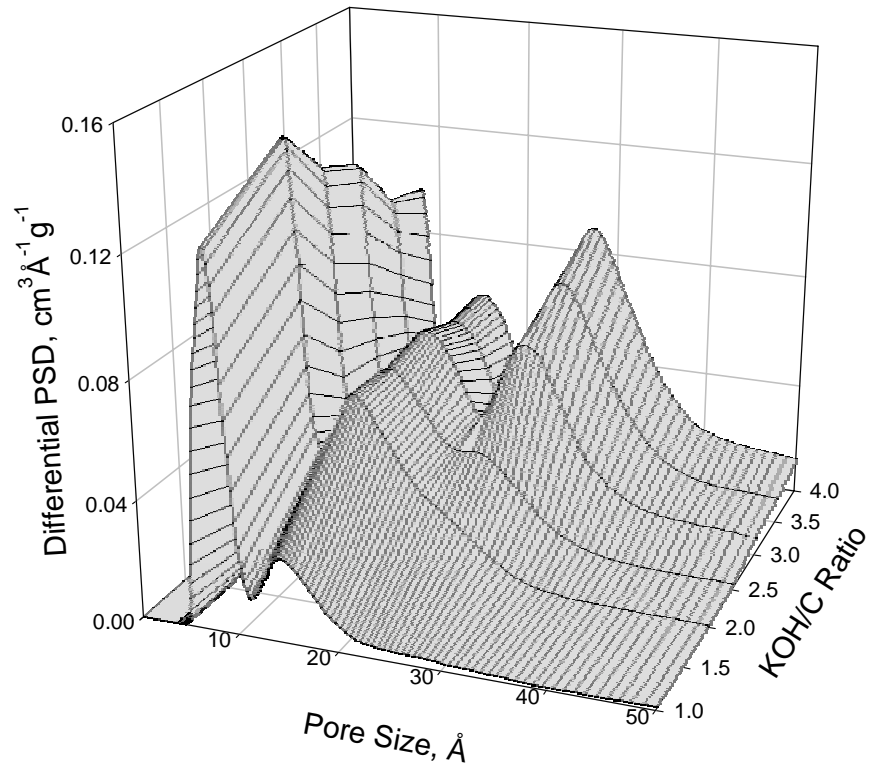


FIGURE 1. Dependence of PSD on KOH/C ratio for carbons obtained from WV-A 1100 precursor

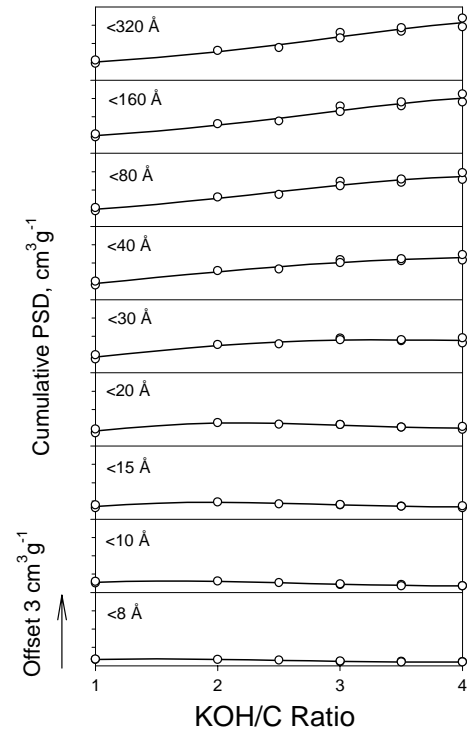


FIGURE 2. Fit of the mathematical model to cumulative PSD data.

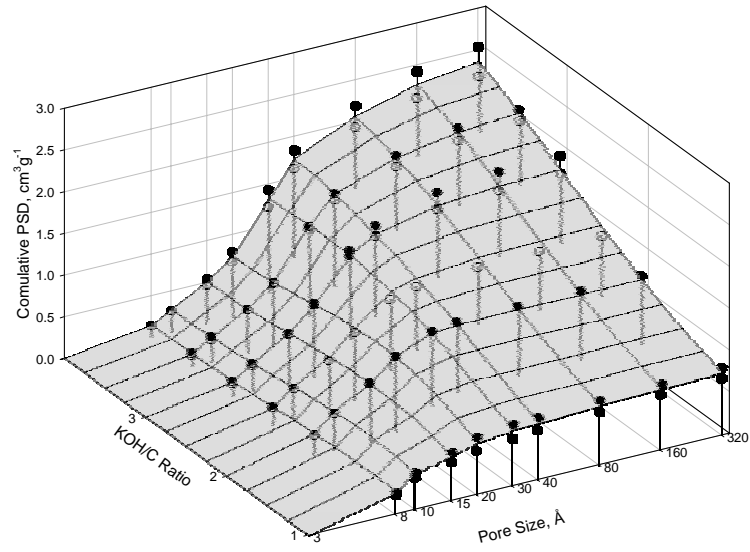


FIGURE 3. Cumulative PSDs calculated for individual carbons (data points). 3D surface represents the model.

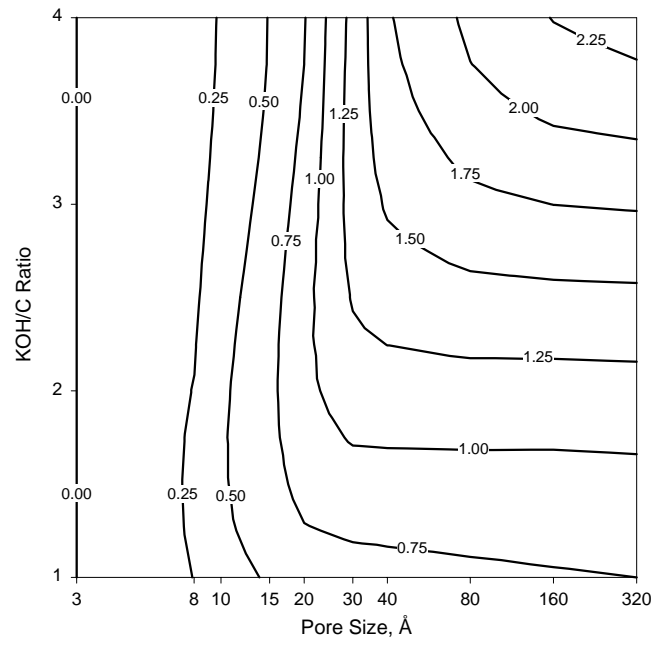


FIGURE 4. Variation of cumulative PSD with KOH/C ratio. Contour lines represent equal pore volumes (cc/g).

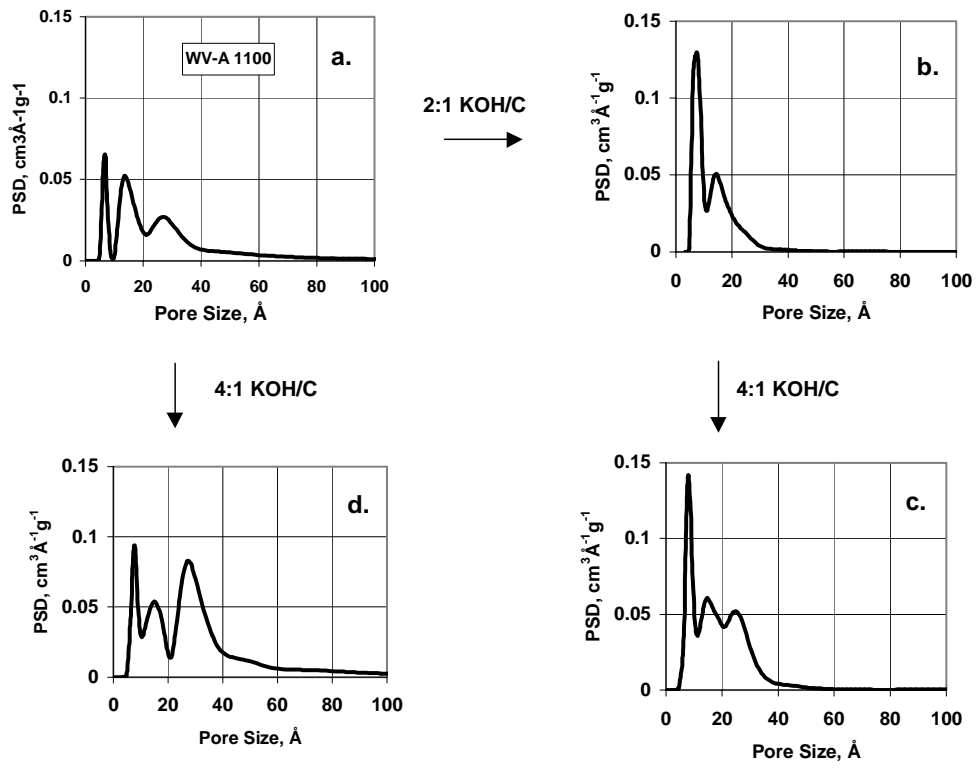


FIGURE 5. Change in carbons PSDs as a result of various activation processes.