On the Characterization of Microporous Carbon Blacks by Various Techniques

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Abstract. It is shown that the combination of different techniques, based on the adsorption of vapors and on calorimetry, can lead to the unambiguous characterization of carbonaceous materials. The case of a microporous carbon black, with pores in the range 0.35–1.2 nm, is used as an example.

1. Introduction

Carbonaceous materials exist in a variety of forms, ranging from highly porous active carbons and active carbon fibers, to virtually nonporous graphitized carbon blacks. However, a number of carbon blacks present some degree of microporosity, which can be characterized by adsorption and calorimetric techniques used and developed in our laboratory [1–4]. The differential heat of adsorption of vapors, measured with a calorimeter of the Tian-Calvet type, appears to be a very useful technique [4]. The standard approach, based on the BET method alone is not sufficient and in some cases it can be misleading. This point is illustrated by the study of sample XC-72, a microporous carbon black of industrial origin which has been studied extensively in our laboratory.

2. Theoretical

Adsorption by microporous carbons is described by the equation of Dubinin and Astakhov [1]

\[
W = W_0 \exp \left\{ - \frac{A}{E_0} \beta^m \right\} \tag{1}
\]

where \( W \) represents the volume filled at temperature \( T \) and relative pressure \( p/p_0 \); \( W_0 \) is the total volume of the micropores, \( A = RT \ln(p_0/p) \) and \( n, E_0 \) and \( \beta \) are specific parameters of the system under investigation. For a variety of active carbons, \( n = 2 \) and Eqn. 1 becomes the classical expression of Dubinin and Radushkevich. A plot of \( \ln(W) \) vs. \( (T/E_0)^{1/2} \) leads to parameters \( W_0 \) and \( E_0 \).

It has been shown [2], that parameter \( E_0 \) the so-called characteristic energy of the micropore system given in kJ/mol, is related to the average micropore-size \( L \) of the system by

\[
L [\text{nm}] = 10.8/(E_0 - 11.4) \tag{2}
\]

If one assumes slit-shaped micropores, the surface area of their walls \( S_{\text{mi}} \) is

\[
S_{\text{mi}} [\text{m}^2/\text{g}] = 2 \times 10^3 W_0 [\text{cm}^3/\text{g}] / L [\text{nm}] \tag{3}
\]

Microporous carbons often contain a non-microporous or external surface area \( S_e \). It can be obtained either from the decomposition of the overall isotherm, by subtracting the contribution of the micropores, or from the enthalpy of immersion into an organic liquid (e.g. \( \text{CH}_2\text{Cl}_2 \), whose vapour can be used for the adsorption isotherm). From Eqn. 1, one can derive an expression for the enthalpy of immersion [1].

\[
\Delta h [\text{J/g}] = -\beta E_0 W_0 \pi^{1/2} (1+\alpha T) / 2 V_m + h S_e \tag{4}
\]

where \( \alpha \) and \( V_m \) are the thermal expansion coefficient and the molar volume of the liquid, and \( \Delta h \) is the enthalpy of wetting of the surface by the liquid. The two techniques are usually in good agreement [1]. Eqn. 4 can also be used to determine the micropore distribution from the limiting volumes \( W_0 \) filled by liquid molecular probes in the range of 0.35 to 1.5 nm [1][2]. Fig. 1 shows the distribution obtained for sample XC-72. The cumulative surface area leads to \( S_{\text{mi}} = 120 \text{ m}^2/\text{g} \) if one postulates slit-shaped micropores.

As shown recently, the total surface of a microporous carbon, \( S = S_{\text{mi}} + S_e \), can also be obtained from the enthalpies of immersion into aqueous solutions of caffeine [2] or ammonia [4]. In the case of caffeine, however, the technique is limited to pores larger than 0.6–0.7 nm, approximately.

A complementary picture is also pro-

Fig. 1. The micropore distribution of carbon black XC-72. obtained from adsorption and immersion experiments. The continuous curve corresponds to a theoretical model [2].
3. Results and Discussion

The different techniques, and in particular calorimetry from the vapor phase, were applied to sample XC-72, a microporous carbon black of industrial origin. This solid has already been investigated extensively and the results were part of a study leading to Eqn. 2 [1-3].

Prior to adsorption and calorimetric experiments, the solid was prepared following standard procedures [1-3]. For the adsorption from the gas phase, we used $N_2$ at 77 K and $C_6H_6$, $N_2O$, and $CH_2Cl_2$ at 293 K. Their respective affinity coefficients $\beta$ are 0.38, 1.00, 0.46, and 0.66 [1]. As shown in Fig. 2, one obtains practically a single linear logarithmic plot of Eqn. 1 and, with the exception of the nitrogen similar limiting volumes $W_0$ given in the Table. This is not too surprising, in view of the dimensions of these molecules (0.35-0.40 nm) and the width of the micropore distribution shown in Fig. 1.

The enthalpies of immersion into various liquids at 293 K and Eqn. 4 lead to an average external surface area $S_0 = 121 \pm 20$ m$^2$/g. It is in good agreement with the value of $120 \pm 30$ m$^2$/g obtained from the analysis of the $N_2$, $C_6H_6$, and $CH_2Cl_2$ adsorption isotherms (decomposition and/or $t$-plot). The $\alpha_p$ plot technique for $N_2$ (77 K), using the data of Carrott and Sing [6], leads to $S_0 = 127 \pm 10$ m$^2$/g. On the other hand, the micropore volume of 0.044 cm$^3$/g is too small. The discrepancies observed for nitrogen are not understood yet.

The solid has, therefore, a total micropore volume $W_0$ close to 0.060 cm$^3$/g ($L > 0.35-0.4$ nm) and a total surface area of ca. 240 m$^2$/g. As shown recently [4], the technique based on the immersion of carbons into aqueous solutions of $NH_4$ leads to a total surface area of 234 m$^2$/g (uncertainty of 10-15%).

The combination of the cumulative surface area $S_{cum} = 120$ m$^2$/g (derived from the histogram of Fig. 1) with $W_0$, through Eqn. 3, leads to $L = 1$ nm for the average micropore width. This data has been used to derive Eqn. 2, on the basis of results obtained with various samples [1][2].

The classical BET treatment [7] of the $N_2$ (77 K) and $C_6H_6$ (293 K) isotherms leads to 195 and 214 m$^2$/g. This information is relatively limited, since no distinction is made between the internal and external surface areas of the solid.

The variation of the differential heat of adsorption of $CH_2Cl_2$ at 293 K, obtained from gas-phase calorimetry, confirms the general picture derived from adsorption and immersion experiments. As seen in Fig. 3, the process begins with the filling of the smaller micropores where $q_{diff}$ is around 60 kJ/mol, as observed for active carbon CAF-B [5]. In the present case, the amount of 0.4 mmol/g would correspond to the micropores having width $L < 0.8$ nm, approximately.

The decrease in the heat of adsorption and the plateau near 38 kJ/mol correspond to the coating of the walls and the filling of the larger micropores. In view of the pore-size distribution shown in Fig. 1, the two processes overlap to some extent. In the region of $N_2 = 1$ mmol/g, corresponding to $W_0$ one observes a final drop in $q_{diff}$. Beyond this stage, adsorption occurs exclusively on the external surface.

The present study shows that the combination of adsorption and calorimetric techniques provides complementary information for the study of microporous carbon blacks, along the same lines as for active carbons.

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