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THE OXIDATION OF AN ASTURIAN BITUMINOUS COAL IN AIR AND ITS INFLUENCE ON SUBSEQUENT ACTIVATION BY STEAM

TERESA A. CENTENO* and FRITZ STOECKLI
Chemistry Department of the University, Avenue de Bellevaux 51, CH-2000, Neuchatel, Switzerland

Abstract—It is shown that the oxidation of an Asturian bituminous coal by air, at 150° and 270°C, has a considerable influence on the microporous structure of the carbon obtained by subsequent carbonization and steam activation to 50% burn-off. The direct activation of the coal leads to an open micropore system of 0.2 cm^3/g, with an average pore size near 0.8 nm. On the other hand, much larger systems of micropores can be obtained in the final products, depending on the temperature of pretreatment in air. The oxidation at 270°C eventually leads to supermicropores (W_0 = 0.4 cm^3/g) and to a small system of narrow micropores near 0.3–0.5 nm. Molecular sieving experiments indicate that these micropores are part of the constrictions leading into 50–60% of the larger pores.

Key Words—Bituminous coal, pretreatment, activation, microporosity.

1. INTRODUCTION

It has been shown recently that various pretreatments applied to cokes[1] and to anthracites[2] can influence, to some extent, the physical properties of the material obtained by subsequent activation by steam near 850°C. In the case of an Asturian anthracite, for example, preoxidation in air at 270°C improved the yield of the active carbon, although it remained relatively low. With respect to the carbon obtained from the non-oxidized coal, the micropore volume and the external surface areas were, respectively, 20% and 30% higher. Moreover, development of micropores smaller than 0.4 nm was observed while the porosity in the range of 0.4 to 0.6 nm was reduced.

As shown elsewhere[3,4], the coal oxidation process influences markedly the development of the microporous structure of the carbonized materials obtained from bituminous coals. The coal oxidation temperature and time both allowed the size of the constrictions at the entrances of the micropores to be altered. In this way, the micropores of chars from oxidized bituminous coals were more accessible, in spite of being narrower than those of the carbonized material obtained from unoxidized coal. In the present study, we show that in the case of a bituminous coal from Asturias, preoxidation in air and, in particular, its temperature, have a considerable influence on the microporosity of the carbon obtained by subsequent activation with steam. As illustrated below, the physical properties differ considerably from those of the carbon obtained by direct activation of the untreated coal. These differences are revealed by the use of combined adsorption and immersion techniques developed in our laboratory[5–8].

*On leave from Instituto Nacional del Carbón, Oviedo (Spain).

The theoretical background is provided by Dubinin's theory for the volume filling of micropores[5,6,9]. It makes a clear distinction between the micropore volume, W_0, and the external surface, S_e. The classical BET surface area corresponds to the sum of S_e and the monolayer equivalent of W_0. The actual surface area of the micropores, S_{mi}, depends on the average pore width, L. It follows that S(BET) and S_{mi} are often different.

2. EXPERIMENTAL

2.1 *Raw material*

A high-volatile bituminous coal from the Asturian Basin, Lieres (North of Spain), was used as the starting material. The raw coal had the following chemical composition: ash, 5.3% (d.b.); V.M., 41.4% (daf); C, 85.0% (daf); H, 5.1% (daf); N, 1.7% (daf); S, 0.6% (daf); O(by diff.), 7.6% (daf). It is interesting to point out the low ash yield of the raw material, since it will increase markedly during the carbonization and activation processes.

The coal was ground and sieved, the size fractions of 125–180 and 710–1000 μm being used in parallel, in order to investigate the possible effect of the grain size on the properties of the subsequent materials.

2.2 *Sample preparation*

2.2.1 *Coal oxidation[3].* The oxidation of the coal (40 g) was carried out in an oven with forced circulation of air at 270° and 150°C during 6, 12, and 72 hours.

2.2.2 *Carbonization[3].* The fresh and oxidized coal samples (4 g) were pyrolyzed in a tubular quartz reactor under a stream of N_2 at 850°C. The heating rate was around 100°C/min, with a soaking time of 1 hour. Finally, the samples were cooled in N_2 to room temperature.

2.2.3 *Activation[1,2,8].* The carbonized materials were treated in batches of 2 g at 850°C in a stream of N_2 (0.5 l/min) with water vapor (29% vol.) provided by a bath at 70°C. The activation took approximately 1.5 hours and the final degree of burn-off, relative to the ash-free char, was around 50% for all samples.

2.3 *Sample characterization*

The main characteristics of the carbonized materials have already been discussed elsewhere[3] and, for the sake of clarity, they are shown in Table 1. In the present study, we also determined the enthalpies of immersion into benzene and water at 293 K.

The different active carbons prepared in this study were characterized as described in detail previously[2, 5–7]. The techniques include the adsorption of CH_2Cl_2 vapour at 293 K and immersion calorimetry, at the same temperature, using molecular probes of different critical dimensions: dichloromethane (0.33 nm), benzene (0.41 nm), carbon tetrachloride (0.63 nm), tetrabutylurea (0.93 nm), and tri-2,4-xylylphosphate (1.50 nm). Immersion into water provided further information about the hydrophilic/hydrophobic character of the carbon surface. As shown below, the combination of these techniques, based on Dubinin's theory and its extensions[5,6,9], provides useful and complementary information on the structure of the carbons (micropore volume W_0; average micropore width L; external, microporous, and total surface areas S_e, S_{mi}, and S_{tot}).

The properties of the solids, given in Table 2, correspond to 1 g of the material as received (carbon + ashes) and no correction was made. This means that scaling factors have to be applied to obtain the values for 1 g of the pure active carbons. These factors are 1.1 for sample L6BC-A, 1.2 for samples L4-A, L4DM-A, L4D3-A, and L4BC-A and 1.4 for L4B3-A. The pore widths and specific enthalpies of immersion into water ($h_i(J/m^2) = \Delta h_i(J/g)/S_{tot}(m^2/g)$) are not affected by this scaling.

3. RESULTS AND DISCUSSION

The direct activation of the carbonized bituminous coal by steam at 850°C to 50% burn-off leads to a typical active carbon (sample L4-A). The yield is relatively low in comparison with other precursors[8]. However, the development of microporosity is better than that observed for the Asturian anthracite examined previously[2] or obtained from bituminous coals with a lower volatile matter content[10]. Different activation conditions can also play a role[8,11]. The Dubinin-Radushkevich plot, shown in Fig. 1, leads to $W_0 = 0.24$ cm^3/g and to an average pore width of 0.8 nm, derived from E_0 (The so-called characteristic energy E_0 of the system is related to the average micropore width[5,7]). From the enthalpies of immersion Δh_i into liquids of different molecular sizes L_c, it is possible to derive the limiting micropore volumes $W_0(L_c)$ filled by the probes, as shown in Fig. 2. The profile for sample L4-A suggests that the average micropore size should be around 0.8–0.9 nm, in agreement with the value derived from the CH_2Cl_2 isotherm. This agreement also indicates the absence of "gate" effects at the entrance of the larger pores.

The specific enthalpy of immersion into water, 0.045 J/m^2, is typical for carbons activated without preliminary treatment[1,2].

The oxidation of the coal in air at 150°C during 12 and 72 hours, followed by carbonization and steam activation, leads to samples L4DM-A and L4D3-A. The former is similar to the active carbon obtained without preoxidation, as suggested by the data of Table 2 and by the accessibility of the micropore volume shown in Fig. 2. The only difference is a downward deviation in the D-R plot at low pressures (Fig. 1), which indicates the presence of some constrictions in the microporous system of this sample.

In the case of sample L4D3-A, on the other hand, the micropore volume obtained for the same degree of burn-off (50%) is larger (0.43 cm^3/g as received, or theoretically 0.51 cm^3/g of pure carbon). This indicates a strong influence of the 72-hour pretreatment on the structure of the precursor and, consequently, on the course of subsequent activation. Moreover, as shown in Fig. 3, the D-R plot of the CH_2Cl_2 isotherm is slightly curved, which corresponds to a Dubinin-Astakhov eqn.[5,6,9] with $n = 1.7$. This behaviour reflects a relatively broad micropore distribution around 1.2 nm, as confirmed by the variation of the accessible volume $W_0(L_c)$ shown in Fig. 2.

The larger microporosity of the active carbons, resulting from the preoxidation stage, can be related to earlier observations on the properties of the Lieres coal[2]. It has been shown that, during the pyrolysis

Table 1. Main characteristics of the carbonized materials (850°C), following preoxidation in air[3] (The data correspond to dry ash-free material)

Coal oxidation temperature	No treatment	150°C		270°C	
Coal oxidation time	–	12 hours	72 hours	6 hours	72 hours
W_0 (cm^3/g) (CO_2; 273 K)	0.12	0.17	0.18	0.21	0.24
L (nm) (E_0 of CO_2; 273 K)	1.2	0.8	0.8	0.9	0.9
S_{mi} (m^2/g)	200	425	450	467	533
$-\Delta h_i$ (C_6H_6) (J/g)	2	1	1	3	7
$-\Delta h_i$ (H_2O) (J/g)	6.5	30.3	29.6	36.7	47.4

Table 2. Main characteristics of the active carbons obtained from Lieres coal (values per gramme of material as received)

	Sample								
	L4-A	L4DM-A	L4D3-A	L4BC-A		L4B3-A		L6-A	L6BC-A		L6B3-A
Particle diameter (μm)	125–180	125–180	125–180	125–180		125–180		710–1000	710–1000		710–1000
Coal oxidation temperature	–	150°C	150°C	270°C		270°C		–	270°C		270°C
Coal oxidation time	–	12 hours	72 hours	6 hours		72 hours		–	6 hours		72 hours
W_0 (cm^3/g)	0.24	0.28	0.43	[1] 0.03	[2] 0.43	[1] 0.06	[2] 0.32		[1] 0.06	[2] 0.33	
E_0 (kJ/mol)	24.8	27.2	20.2	42.9	13.2	32.6	15.8		34.6	16.0	
L (nm)	0.81	0.68	1.2	0.3–0.5	2–3	0.3–0.5	2–3		0.3–0.5	2–3	
S_{mi} (m^2/g)	593	823	717	165	300	235	256		255	287	
S_{ex} (m^2/g)	52	small	68	189		159			121		
S_{tot} (m^2/g)	645	823	785	654		650			663		
$-\Delta h_i$ (CH_2Cl_2) (J/g)	83.6	95.8	120.8	117.3		113.3		68.1	112.0		113.6
$-\Delta h_i$ (C_6H_6) (J/g)	79.1	102.0	113.7	112.2		108.1		60.5	111.5		116.5
$-\Delta h_i$ (CCl_4) (J/g)	70.1	79.5	106.4	105.0		98.9		56.2	92.4		106.6
$-\Delta h_i$ (TBU) (J/g)	53.3	44.4	71.7	84.9		60.3		52.8	74.0		63.6
$-\Delta h_i$ (TXP) (J/g)	23.6	15.0	19.7	25.0		11.5		26.7	21.1		18.6
$-\Delta h_i$ (H_2O) (J/g)	29.3	37.9	46.4	36.4		57.2		29.9	41.0		53.2
$-h_i$ (H_2O) (J/m^2)	0.045	0.046	0.059	0.056		0.088		–	0.063		–

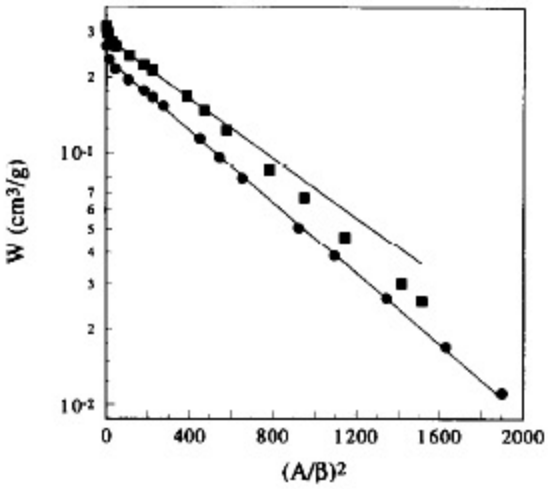

Fig. 1. D-R plot for the adsorption of CH_2Cl_2 vapour at 293 K by samples L4-A (●) and L4DM-A (■).

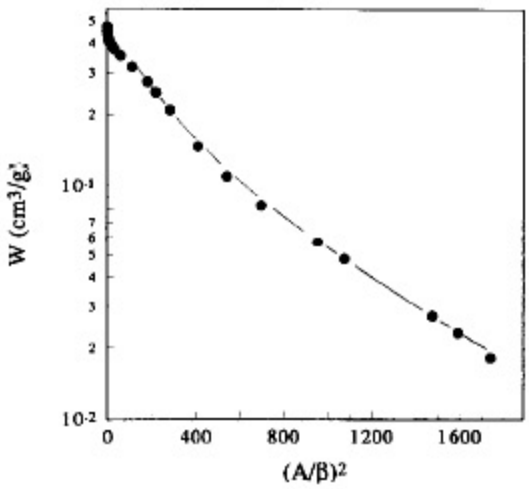

Fig. 3. D-R plot for the adsorption of CH_2Cl_2 vapour at 293 K by sample L4D3-A.

step, the untreated coal displays thermoplastic properties. As a consequence, the carbonized material has some microporosity around 1.2 nm, as indicated by the adsorption of CO_2 at 273 K (see Table 1). However, as suggested by the low adsorption of N_2 at 77 K and by the low enthalpy of immersion into benzene $\Delta h_i(C_6H_6)$, the micropore system is virtually inaccessible, owing to the presence of constrictions. Water, itself, has a limited interaction with the solid, as suggested by $\Delta h_i(H_2O) = 6.6$ J/g.

On the other hand, the preoxidation of the coal reduces its thermoplasticity during the carbonization stage and one observes a larger micropore system (CO_2 at 273 K). Its accessibility also increases, as indicated by nitrogen adsorption and by the enthalpies of immersion into benzene and water. As shown in Table 1, these effects increase with the time and the temperature of oxidation. The initial porosity and its increasing accessibility provide better conditions for the subsequent activation of the chars by water.

The effect of a longer preoxidation in air is clearly shown in the case of samples L4BC-A and L4B3-A, where pretreatment was carried out at 270°C for 6 and 72 hours, respectively. The micropore volumes are similar to that of sample L4D3-A (pretreatment at 150°C for 72 hours), but an important modification, probably due to the higher temperature, is observed in the microporous structure. As illustrated in Figs. 4–5, the D-R plots of the CH_2Cl_2 isotherms display two sections. As discussed elsewhere[12], this situation may correspond either to the coating of the walls of large micropores or to the primary filling of small micropores[13] (section 1), followed by the filling of a distinct system of larger micropores (section 2).

As shown below, it appears that section 1 corresponds to a mechanism of primary micropore filling. The presence of two distinct systems of micropores is relatively rare, but it has been observed and investigated by Dubinin *et al.* [9,14–16]. Under these circumstances, the overall adsorption isotherm is a sum of contributions from sections 1 and 2,

$$W = W_{01}\exp\{-(A/\beta E_{01})^2\} + W_{02}\exp\{-(A/\beta E_{02})^2\} \quad (1)$$

It follows that the enthalpy of immersion of the carbon into various liquids is given by

$$-\Delta h_i\,(\mathrm{J/g}) = (E_{01}W_{01} + E_{02}W_{02})\beta(1+\alpha T)\pi^{1/2}/2V_m - h_i Se \quad (2)$$

provided that volumes W_{01} and W_{02} are both accessible to the molecular probe.

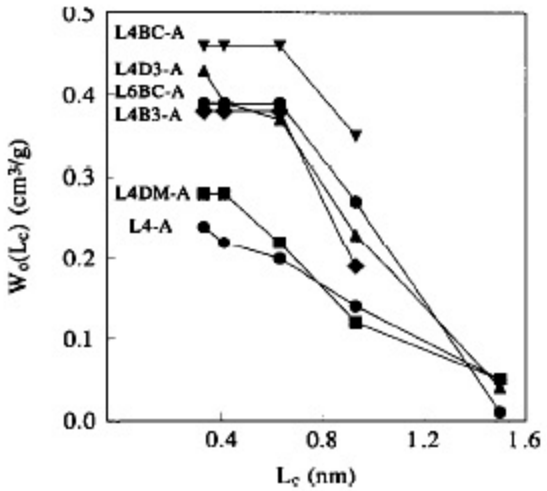

Fig. 2. The micropore volume $W_0(L_c)$ of samples L4-A, L4DM-A, L4D3-A, L4BC-A, L4B3-A, L6BC-A filled by liquids with different molecular sizes L_c.

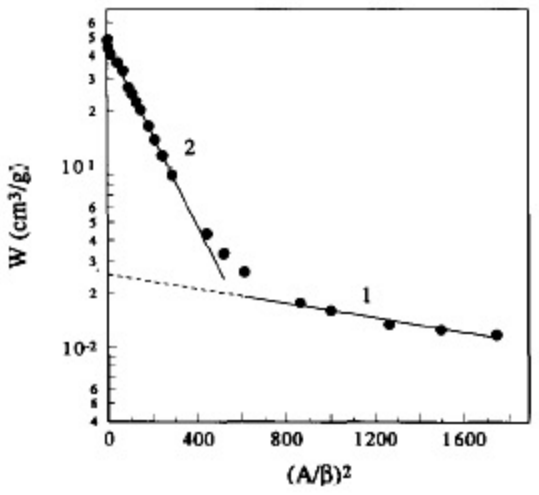

Fig. 4. D-R plot for the adsorption of CH_2Cl_2 vapour at 293 K by sample L4BC-A.

For the carbons derived from our bituminous coal treated at 270°C, the first system has micropore widths in the range of 0.3–0.5 nm. The second system, on the other hand, corresponds to supermicropores with an average width around 2 nm (this dimension is an approximation, since these pores are not necessarily slit-shaped).

As shown by immersion calorimetry into liquids of different molecular dimensions, active carbons with average pore widths beyond 1.2–1.5 nm no longer display molecular-sieve effects and the enthalpies of immersion are numerically similar[6]. However, in the present case, the values obtained for tetrabutylurea (TBU) and tri-2,4-xylyl phosphate (TXP) are low (Table 2), which indicates a gate effect for these molecules.

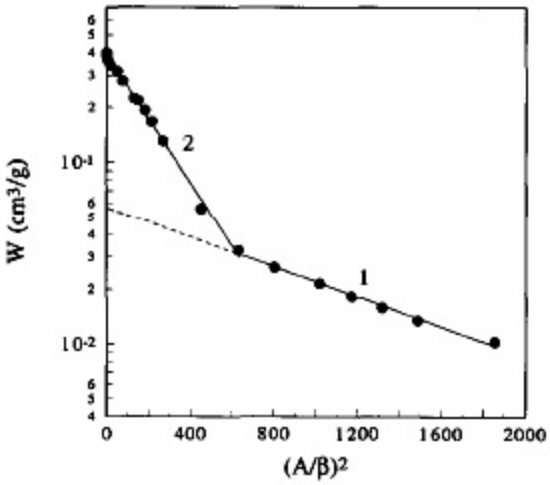

Fig. 5. D-R plot for the adsorption of CH_2Cl_2 vapour at 293 K by sample L4B3-A.

Equation (2) can be used first to calculate S_e from the data obtained for CH_2Cl_2. In a second stage, one obtains the micropore volumes $W_0(L_c)$ filled by the larger molecules (it is assumed that the first system is not accessible to TBU and TXP). As shown in Fig. 2, in the case of samples L4BC-A and L4B3-A these molecules only fill a fraction of W_{02}. The cut-off begins near 0.7 nm, whereas the average pore size suggested by the characteristic energy E_0[7] is around 2 nm. Therefore, the profiles shown in Fig. 2 do not reflect the real microporosity, but the molecular-sieve effect resulting from constrictions at the entrance of the supermicropores. These constrictions may be represented, partly at least, by the smaller micropore system. As a consequence, only half of the volume W_{02} is accessible to larger molecules.

Since the initial microporosity in the chars increases with the coal oxidation temperature (see Table 1 and refs. [3,4]), the subsequent activation process may produce a larger and wider porosity in activated carbons derived from the coal oxidized at 270°C than that oxidized at 150°C.

As illustrated by the data of Table 2, the effect of the particle diameter of the bituminous coal on pretreatment is negligible and one obtains a similar behaviour for the D-R plot of sample L6BC-A (particles of 710–1000 μm). Moreover, the enthalpies of immersion of samples L6BC-A and L6B3-A into the different liquids, including water, are also similar to those of samples L4BC-A and L4B3-A. The $W_0(L_c)$ profile of sample L6BC-A shown in Fig. 2 is similar to that of the samples obtained with particles of 125–180 μm.

The increasing values of $\Delta h_i(H_2O)$ and, in particular, of the specific enthalpy of immersion, $h_i(H_2O)$, are also a clear reflection of the effect of oxygen on the final carbons. As shown in Table 2, $h_i(H_2O)$ increases from 0.045 J/m^2 for active carbon L4-A (direct activation of the bituminous coal) to 0.088 J/m^2 in the case of carbon L4B3-A, where the coal has been treated at 270°C for 72 hours. In spite of the 50% activation by steam at 850°C, the effect of preoxidation (shown in Table 1) is still observed in the final product. This comparison also illustrates the advantage of immersion calorimetry in the study of a series of related carbons.

4. CONCLUSIONS

The present study shows that, in the case of the Asturian bituminous coal, the preoxidation in air can influence in two ways the microporous structure of the carbons obtained by subsequent carbonization and activation with steam. The temperature plays the key role in the process. First, a mild treatment around 150°C increases the yield in microporosity, with respect to the direct activation, but retains a relatively open structure. Secondly, a treatment at a higher temperature (270°C) also induces a change in the structure, leading finally to supermicropores and to a considerable "gate" effect. This corresponds, in fact, to a potential molecular sieve carbon with a relatively

large micropore volume W_0 (approximately 0.50 cm^3/g of pure carbon at a 50% burn-off). At the present time, the manufacture of this type of carbon requires the development of the microporosity and the subsequent reduction of the width at the entrance of the pores. The latter is typically achieved by carbon deposition resulting from the pyrolysis of hydrocarbons adsorbed in the solid[17,18]. As a result, the pore size decreases, as well as the pore volume, and a substantial fraction of the adsorption capacity is lost. This suggests that it may be more convenient to produce carbon molecular sieves by the controlled treatment outlined in the present paper.

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