

MOLECULAR SIEVE PROPERTIES OF CARBONS OBTAINED FROM COALS

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Introduction

Actually, the manufacture of carbon molecular sieves from coals requires the development of the microporosity by carbonization and activation 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.

As reported previously [1,2], the coal oxidation allowed the size of the constrictions at the entrance of the micropores to be altered. Thus, 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. Additionally, the preoxidation of coal in air had a considerable influence on the microporosity distribution of the carbons obtained by subsequent activation with steam. These facts suggest that a controlled preoxidation of coal may be an alternative method to produce carbon molecular sieves.

The main aim of this study is to analyze the effect of coal rank, oxidation pretreatment of coal and burn-off degree on the molecular sieve properties of carbons obtained by carbonization and subsequent activation with steam.

Experimental

A high-volatile bituminous coal and an anthracite from the Asturian Basin (North of Spain) with particle diameters below 40 μm were used as starting materials. The coal particles were agglomerated under pressures of 2 and 3 Tn/cm^2 to obtain pellets of 13 mm in diameter and 1 mm in height. In the case of anthracite a phenolic resin was used as agglomerating agent. Prior to the pyrolysis the pellets were oxidized with air at 150°C and 250°C during 3 and 72 hours.

The oxidized pellets were carbonized under nitrogen at a heating rate of 15°C/min up to 850°C with a soaking time of 1 hour. The carbonized materials were treated at 600°C with a stream of nitrogen (flow rate of 400 l/min) and water vapor (12 % vol.) to burn-off of 3, 6 and 15 %.

The characterization of the samples included helium and mercury density measurement and mercury porosimetry. The microporosity of the carbons was

analyzed by immersion calorimetry at 20°C using molecular probes of different critical dimensions: dichloromethane (0.33 nm), benzene (0.41 nm), cyclohexane (0.54 nm) and carbon tetrachloride (0.63 nm). The technique and its theoretical basis have been described in detail elsewhere [3,4].

Results and Discussion

It has been observed that the carbons obtained under different oxidation conditions and burn-off degrees, show a quite similar porous structure. Thus, materials prepared by activation of the high-volatile bituminous coal show a porosity around 40 % and a total pore volume of 0.32 cm^3/g , approximately. On the other hand, carbons obtained from the anthracite have a porosity of 35 % with a total pore volume of 0.28 cm^3/g . In both cases, half of the total pore volume corresponds to pores larger than 7.5 nm, as deduced by mercury porosimetry.

The influence of the coal oxidation pretreatment on the microporous structure of the resulting activated carbons is reflected by their enthalpies of immersion into a series of liquids with different molecular sizes (see Table 1). As indicated by the increase in the enthalpy into dichloromethane, the preoxidation of the starting coal in air improved the yield of the subsequent activation by steam, although it remained low when the anthracite was used as precursor.

Immersion calorimetry can be used to follow the development of microporosity in series of carbons [3,4]. In the case of materials derived from the bituminous coal, we have been observed a development of the micropores with a size in the range 0.4-0.5 nm as coal oxidation degree increases, as suggested by the higher enthalpy of immersion into benzene. On the other hand, the values corresponding to the immersion into cyclohexane and carbon tetrachloride did not change significantly, indicating that the oxidation did not influence the micropores wider than 0.54 nm.

The evolution of the microporosity with burn-off is illustrated in Figure 1 by the profiles of the ratio $E_0W_0/(E_0W_0)_{\text{ref}}$ based on the enthalpies of immersion into liquids of various critical molecular sizes [4]. The liquid with the smallest molecular diameter (CH_2Cl_2) was used as reference. A decrease in the product E_0W_0 as the diameter of the molecular probe increases indicates that the

accessibility of the pores is limited either by gate effects or by the micropore distribution itself. It appears that the volume of the smallest micropores (0.35-0.55 nm) is larger as the activation progresses, whereas the porosity in the range 0.55-0.65 nm remains unchanged. At this stage, it is not possible to distinguish between open porosity and gate effects without the knowledge of E_o , related to the average pore width.

The influence of coal rank on the microporosity of the final carbon is shown in Table 1 and Figure 2. The activation of the anthracite by steam to a burn-off of 6% had limited success. The enthalpy of immersion into dichloromethane was small, even after the preoxidation of anthracite at 250°C during 72 hours. As reported previously[5], the distribution in the range 0.3-0.5 nm probably corresponds to the original microporosity of anthracite. The micropore volume of carbons obtained from the bituminous coal is much higher and it is mainly associated with micropores of 0.35-0.55 nm.

Conclusions

The carbons obtained by activation of an anthracite show a poor development of microporosity and it remains unchanged after oxidation treatments of the coal prior to carbonization and activation.

The active carbons prepared from bituminous coal correspond to potential carbon molecular sieves, the oxidation step being a key factor in the evolution of micropore volume and distribution of micropores.

Acknowledgments

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		- Δh_i (J/g of activated carbon)			
Initial coal	Oxidation	CH ₂ Cl ₂	C ₆ H ₆	C ₆ H ₁₂	CCl ₄
Bituminous coal	150°C-3 h	49.2	22.6	11.4	11.9
	150°C-72 h	74.5	58.1	13.1	14.4
	250°C-72 h	81.3	81.9	12.0	17.8
Anthracite	not oxidized	29.0	24.0	10.4	9.4
	250°C-72 h	36.9	22.1	14.0	16.8

Table 1. Enthalpies of immersion of activated carbons prepared from a high-volatile bituminous coal (15% b.o.) and an anthracite (6% b.o.) into liquids with different molecular diameter.

References

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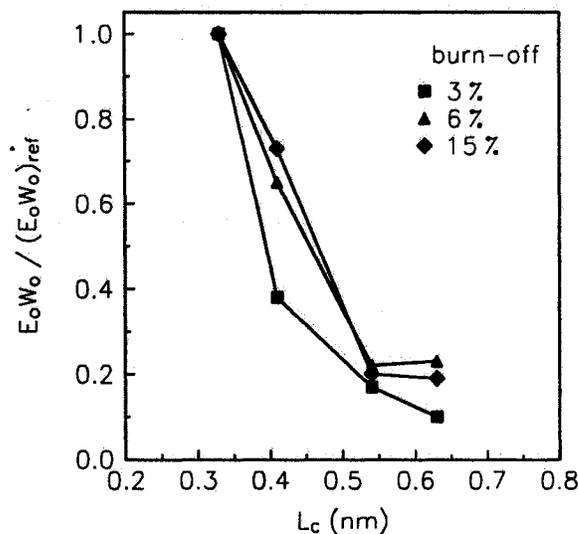


Figure 1. Plot of $E_o W_o / (E_o W_o)_{ref}$ as a function of the molecular size of the probes. Activated carbons obtained from a bituminous coal oxidized at 150°C during 72 hours.

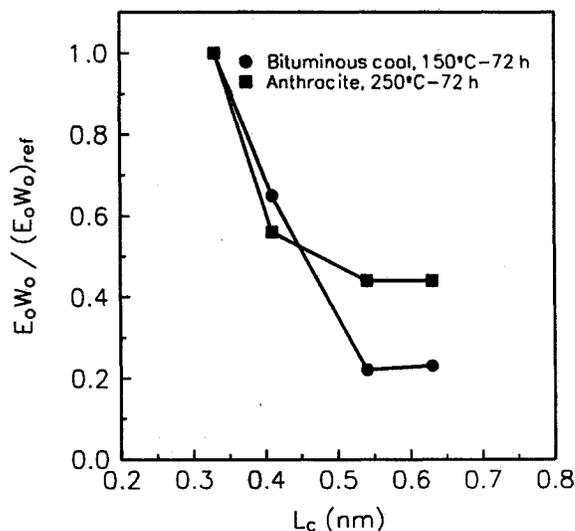


Figure 2. Ratio of $E_o W_o / (E_o W_o)_{ref}$ as a function of the molecular size of the probes. Carbons corresponding to 6% of burn-off by steam activation