

MICROPORE SIZE DISTRIBUTIONS OF ACTIVATED CARBONS PREPARED WITH CARBON DIOXIDE AND STEAM

M. T. González, A. Sepúlveda-Escribano, M. Molina-Sabio and F. Rodríguez-Reinoso

Departamento de Química Inorgánica
Universidad de Alicante
Aptdo. 99, E-03080 Alicante (SPAIN)

INTRODUCTION

We have recently shown [1] that the porosity developed by carbon dioxide and steam when activating the same char is different: carbon dioxide mainly creates new microporosity whereas steam, from the early stages of the process, widens the micropores already present in the carbonized material.

The objective of this work is to determine the micropore size distributions of activated carbons prepared with both activating agents, and to relate them with the amount of oxygen surface groups formed during the activation process.

EXPERIMENTAL

The activated carbons used in this study have been prepared from carbonized olive stones. Three series have been prepared:

- Series D: by activation with CO₂ at 825 °C.
- Series W: by activation with steam at 800 °C.
- Series H: by activation with steam at 750 °C.

In series H, the gas flow and the activation temperature were adjusted to obtain the same reaction rate than in series D. Each series contains five activated carbons, with burn-off's ranging from 8 to 74 %.

The enthalpies of immersion of the activated carbons and the carbon black used as a reference (V3G) in different liquids, were determined with a Tian-Calvet type differential microcalorimeter. Three liquids with different molecular dimensions have been used: benzene (0.34 nm), 2,2-dimethylbutane (0.56 nm) and iso-octane (0.58 nm). The micropore volume has been derived from immersion enthalpies by using the equation proposed by Stoeckli et al. [2].

The oxygen surface groups on the activated carbons have been characterized by temperature programmed desorption (TPD) experiments. The amounts of CO and CO₂ evolved were measured by mass spectroscopy as a function of the temperature.

The integration of the TPD curves allows the calculation of the total amount of oxygen groups desorbed.

RESULTS AND DISCUSSION

The volumes of micropores which are accessible to each liquid for carbons with low, medium and high burn-off, are reported in Table 1.

For a given series (for example, series D), the micropore volume increases with activation. There is a regular increase for small molecules such as benzene, in contrast to what happens for bulky molecules such as 2,2-dimethylbutane or iso-octane, for which the accessible micropore volume sharply increases after the first activation stages. For lower burn-offs, the accessible micropore volumes decrease in the sequence benzene > 2,2-DMB > iso-octane, which corresponds to the increase in the minimal molecular dimension of the liquid molecules. Therefore, it is clear that activation, besides increasing the micropore volumes, produces a progressive widening of micropores: the ratio of accessible microporosity to total porosity increases with activation. For carbons with medium and high burn-offs (> 34%), the micropore volumes are the same irrespective of the liquid used. Maybe the micropore widening continues, but it can not be detected with these liquids because the microporosity is totally accessible to all of three. Carbons with low burn-off (D-8 and, to a lesser extent D-19) show 0.5-0.6 nm molecular sieve properties, which disappears when the activation progresses.

This discussion can also be applied to carbons in series W and H, although Table 1 shows that only a small increase of micropore volume is obtained when the activation degree is higher than 40% for carbons prepared with steam (Series W and H), whereas the increase is much larger for carbons in series D. The lower development of microporosity of carbons activated with steam is due to the widening from micro to mesopores, which is more important than when the activation

is carried out with carbon dioxide. Actually, the micropore volumes obtained from CO₂ adsorption at 273 K [1] remain practically unchanged as the activation with steam progress, and continuously increase in the case of activation with carbon dioxide. This different activating behaviour is also detected in the pore size distributions of carbons with activation degrees between 19 and 23 %. Those activated with carbon dioxide still show differences between the micropore volumes accesible to benzene and 2,2-DMB; no differences are observed when the carbons have been activated with steam.

Temperature programmed desorption.

The amount and stability of oxygen surface groups have been determined for three carbons in each series by temperature programmed desorption, by monitoring the evolution of CO and CO₂ as a function of the temperature. Table 1 reports the desorbed amount of both species, obtained by integrating the TPD curves. It can be seen that the amount of oxygen surface complexes is, in general, rather low. There are two main differences: First, CO-complexes in the carbons activated with carbon dioxide decompose at higher temperatures that those activated with steam. Furthermore, whereas the amount of CO₂-complexes only depends on the burn-off, the amount of CO-complexes is also affected by the activating agent, in such a way that the creation of this kind of complexes upon activation is much more important with carbon dioxide that with steam.

This behaviour correlates well with the micropore volumes obtained from immersion calorimetry with benzene (Table 1) and from CO₂ adsorption at 273K.

If one assumes that the C-CO₂ and C-H₂O reaction passes through the formation and further decomposition of oxygen surface groups on the active centres of carbon [3], the stability of the oxygen surface groups could determine if the activating agent would act by creating new microporosity or by widening the existing microporosity. If the activating agent forms thermally stable surface complexes, they could block the reaction centers and the reaction will mainly occur on other regions of the carbon structure, with no much micropore widening. On the contrary if the oxygen surface groups decompose with ease, there will be new active sites in the internal porosity for the attack by the activating agent and when the process proceeds the result will be the widening of micropores.

REFERENCES

1. F. Rodríguez-Reinoso, M. Molina-Sabio and M.T. González, *Carbon* **33**, 15 (1995)
2. H. F. Stoeckli and F. Kraehenbuel, *Carbon* **19**, 353 (1981).
3. N. M. Laurendau, *Prog. Energy Combust. Sci.* **4**, 221 (1978)

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Table 1. Micropore volume deduced from immersion calorimetry and oxigen surface groups of activated carbons.

Carbon	Micropore volume (cm ³ /g)			Surface groups (mmol/g)	
	Benzene	2,2 DMB	I-octane	CO ₂	CO
D-8	0.24	0.04	0.02	0.33	0.55
D-34	0.39	0.40	0.35	0.49	0.84
D-70	0.61	0.63	0.62	0.54	1.15
W-10	0.21	0.05	0.03	0.38	0.64
W-41	0.40	0.40	0.39	0.46	0.79
W-71	0.46	0.47	0.45	0.57	0.83
H-8	0.20	0.04	0.01	0.36	0.59
H-37	0.35	0.37	0.34	0.51	0.76
H-74	0.41	0.42	0.42	0.51	0.88