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Can highly activated carbons be prepared with a homogeneous micropore size distribution?

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Abstract

From a practical point of view, microporous activated carbons with high surface area and a homogeneous micropore size distribution (MPSD) are very interesting materials. However, according to the results found in the literature, up to now, the preparation of activated carbons with high surface areas (BET>2000 m^2/g) produces a widening of the microporosity in all the activation methods. In the present work, chemically activated carbons from several coal precursors have been prepared using KOH as activating agent. A deep study of the effect of the different preparation variables in the porous texture of the activated carbon has been carried out. After this analysis, the selection of the suitable coal precursor and preparation conditions has lead to obtain a highly activated carbon (BET>2000 m^2/g) and a homogeneous MPSD.

Keywords: Activated carbons; Chemical activation; Microporosity; Homogeneous micropore size distribution

1. Introduction

From a practical point of view, microporous activated carbons, which have, simultaneously, high surface area and a homogeneous micropore size distribution (MPSD) are very interesting materials for different applications. Our research group has found that these materials are suitable for applications such as CH_4/CO_2 separation, CH_4 storage, VOC abatement, SO_2 removal, etc. [1–3]. A material with a homogeneous MPSD

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presents similar values of the micropore volume calculated by N_2 adsorption at 77 K (V_{N_2}) and by CO_2 adsorption at 273 K (V_{CO_2}) [4,5]. It must be noted that V_{CO_2} is obtained from the CO_2 adsorption at low relative pressure ($P/P_0 < 0.03$). Then, the porosity analyzed by this method corresponds to pores size smaller or equal than about 0.7 nm. Thus, samples with $V_{N_2} \approx V_{CO_2}$ have pore size about 0.7 nm. According to the results found in the literature, up to now, the preparation of activated carbons with high surface areas (BET>2000 m^2/g) produces a widening of the microporosity in all the activation methods. This fact is reflected by an increase of V_{N_2} with the activation degree, while V_{CO_2} reaches a maximum, which cannot be exceeded.

In the present work, chemically activated carbons from several coal precursors have been prepared using KOH as activating agent. According to a deep study carried out by our research group, where the effect of the different preparation variables in the porous texture of the activated carbons was carefully analyzed [6–10], in the present paper, the suitable coal precursor and preparation conditions have been chosen to prepare microporous activated carbons with high surface area and a homogeneous micropore size distribution (MPSD). Thus, in order to know if highly activated carbons can be prepared with a homogeneous micropore size distribution, the objective of this work is to prepare activated carbons with the highest V_{N_2} and V_{CO_2}.

2. Experimental

A series of activated carbons have been prepared from a Spanish anthracite (UA) and from a bituminous coal (UB), using KOH as the activating agent. The precursor was ground and sieved to a particle size range of 600–1000 μm and mixed with KOH. The resulting mixture was pyrolyzed in a horizontal furnace using nitrogen atmosphere. The details of the process have been described elsewhere [7,8].

As mentioned in the Introduction, the preparation conditions (KOH/coal ratio, method of mixing KOH and coal, pyrolysis temperature and time, N_2 flow rate during the pyrolysis, etc.) have been chosen in such a way that activated carbons with narrow pore size distribution can be prepared. All the samples have been prepared by the impregnation method [7], except for one of the sample (KUA21701-800a), where the incipient impregnation [8] has been used.

The nomenclature of each sample includes the activating agent (K), the coal name (UA or UB, for anthracite or bituminous coal, respectively), the KOH/coal ratio (i.e. a 2:1 ratio would be 21), the pyrolysis temperature (for example, 750 °C would correspond to 75), the pyrolysis time in hours and the nitrogen flow rate. Thus, for an activated carbon prepared with a KOH/anthracite ratio of 2:1 and which has been pyrolyzed at 700 °C for 1 h with a nitrogen flow rate of 200 ml/min, the nomenclature would be KUA 21751-200.

Porous texture characterization of all the samples has been carried out by physical adsorption of gases (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6, Quantachorme). The micropore volume has been calculated from the application of the Dubinin–Radushkevich (DR) equation to the N_2 adsorption at 77 K. The volume of narrow micropores (pore size smaller than 0.7 nm) has been assessed from CO_2 adsorption at 273 K [4,5].

3. Results and discussion

Fig. 1 presents the N_2 adsorption isotherms at 77 K corresponding to all the samples of this study. All the activated carbons have Type I isotherms according to the IUPAC classification [11], characteristic of microporous solids. It can be observed that samples with different nitrogen adsorption capacities have been prepared. Table 1 contains the BET surface area calculated from N_2 adsorption and the micropore volume of these samples obtained from both N_2 and CO_2 adsorption data. According to these characterization results, it can be said that, changing the preparation variables, activated carbons with BET surface area from around 700 m^2/g to more than 2000 m^2/g have been prepared. It must be emphasized that for all these samples the total micropore volume (calculated from N_2 adsorption data) and the narrow micropore volume (calculated from CO_2 adsorption data) are very similar, being the difference $(V_{N_2} - V_{CO_2}) < 0.05$ cm^3/g in all the cases. It must be noted that to reach these high values of surface area, keeping V_{N_2} similar to V_{CO_2} is not usual at all.

Fig. 2 presents the total micropore volume evaluated from N_2 adsorption data and the narrow micropore volume (obtained from CO_2 adsorption) vs. the BET surface area. It can be observed that the plot of the total micropore volume (V_{N_2}) vs. the BET surface area values is linear, as it happens for most of the microporous activated carbons. Interestingly, for this series of samples, the plot for the narrow micropore volume (V_{CO_2}) vs. the BET

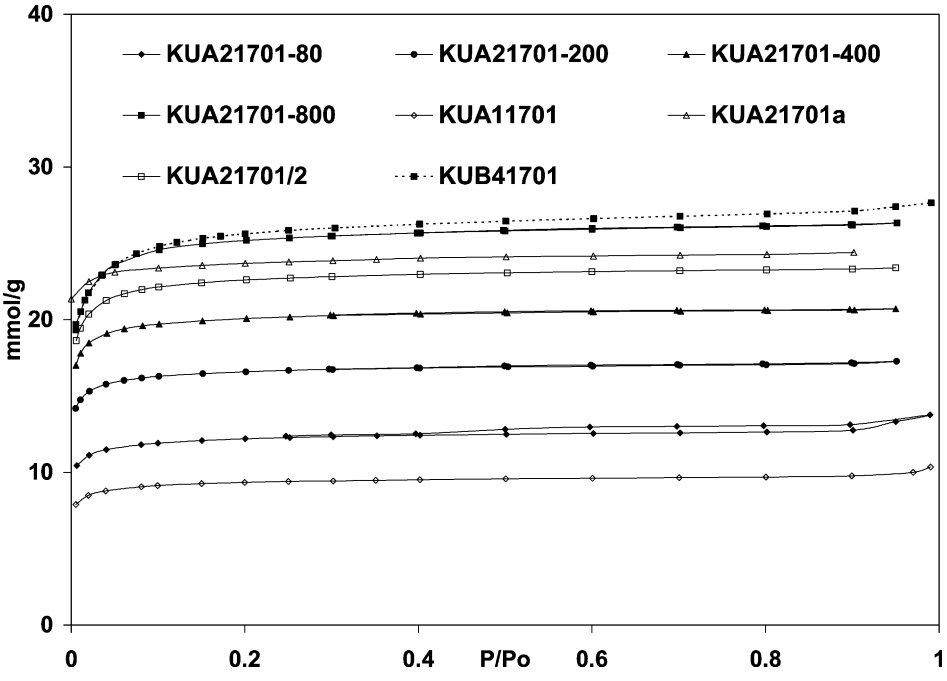

Fig. 1. N_2 adsorption isotherms corresponding to the chemically activated carbons.

Table 1
Porous texture characterization results for the chemically activated carbons

Sample	S_{BET} (m^2/g)	V_{DR} (N_2) (cm^3/g)	V_{DR} (CO_2) (cm^3/g)
KUA21701-80	945	0.43	0.43
KUA21701-200	1305	0.61	0.58
KUA21701-400	1580	0.73	0.71
KUA21701-800	2021	0.89	0.86
KUA11701-800	726	0.33	0.37
KUA21701-800a	1883	0.83	0.80
KUA21701/2-800	1784	0.80	0.80
KUB41701-800	2123	0.93	0.92

surface area is also linear, even for highly activated carbons. These dates constitute new and important results as they correspond to activated carbons with surface areas higher than 2000 m^2/g and a very homogeneous micropore size distribution (mean pore size around 0.7 nm) that can be prepared by chemical activation.

To reach BET surface areas as high as 2000 m^2/g is not easy, and it is even more difficult if this surface area corresponds mainly to narrow microporosity (V_{CO_2}). This type of microporosity cannot be obtained by physical activation because the increase in surface area occurs together with pore widening. In order to compare the results obtained with

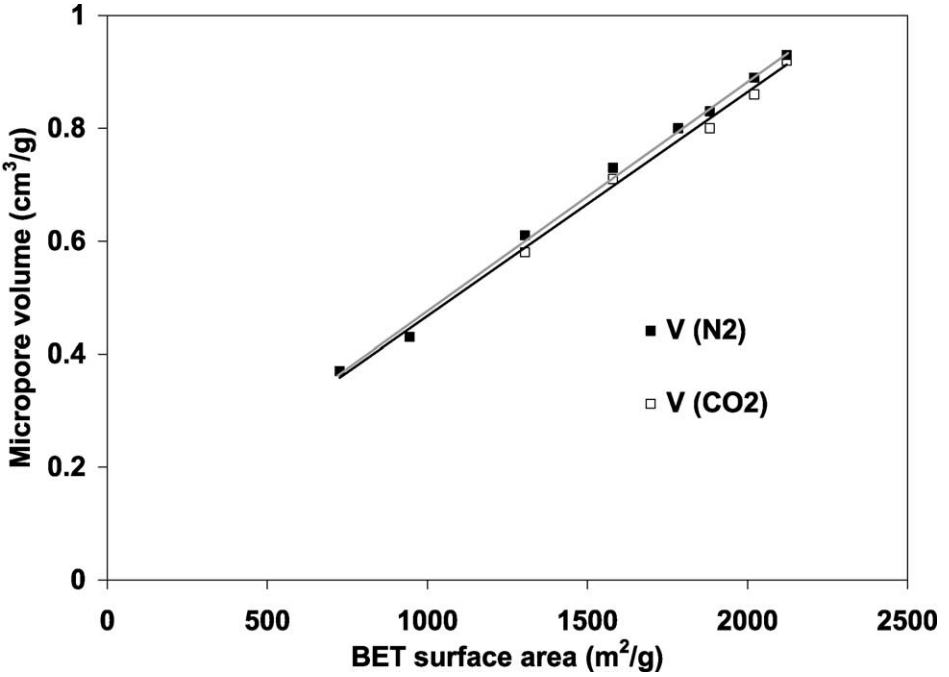

Fig. 2. Relationship between the total micropore volume (V_{N_2}) and the narrow micropore volume (V_{CO_2}) with the surface area for the chemically activated carbons.

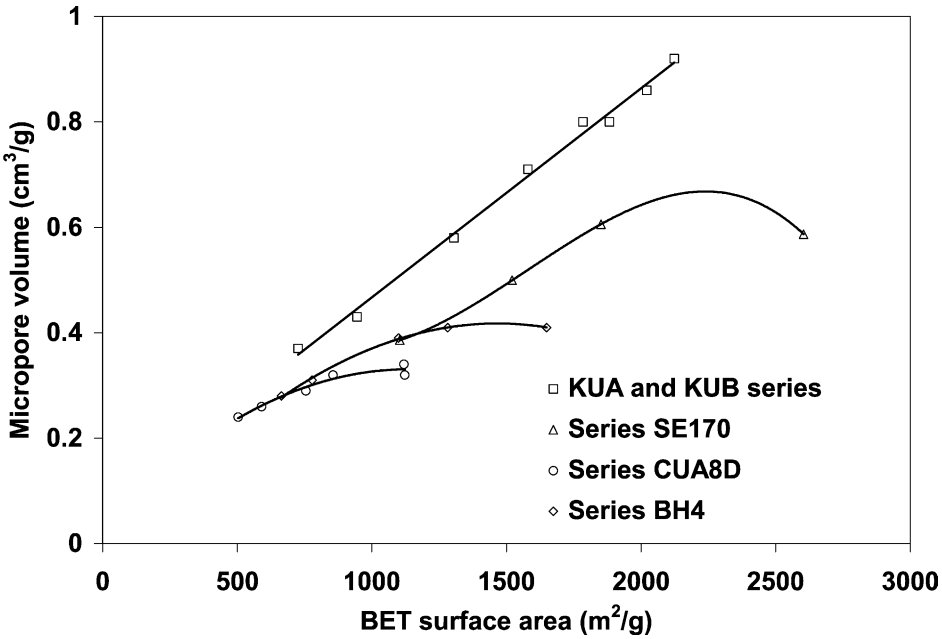

Fig. 3. Relationship between the narrow micropore volume (V_{CO_2}) with the surface area for the series of chemically activated carbons and three series of physically activated carbons.

chemically activated carbons and other materials, Fig. 3 presents the same type of plot as Fig. 2, but it includes only V_{CO_2}, because V_{N_2} is directly related to BET surface area, so that the plot of V_{N_2} vs. BET is linear for all the cases. In this figure, in addition to the chemically activated carbons, it has been included, as an example, results obtained in previous studies [12–14], where very different precursors were used (i.e. Saran char (series SE170) [12], bituminous coal (series CUA8D) [13] and almond shell char (series BH4) [14]). These materials were activated using CO_2 and steam as activating agents. In Fig. 3, it can be observed that, except from the chemically activated carbons series, the narrow micropore volume (V_{CO_2}) for all the materials is below 0.6 cm^3/g, approximately, and reaches a maximum. That means that for physical activation, even though high surface area activated carbons can be obtained, the development of narrow microporosity reaches a maximum, which cannot be exceeded. From this maximum, further increase in micropore volume results in an increase of the pore size. On the other hand, activated carbons with very high micropore volumes and very narrow micropore size distributions can be prepared by KOH activation of coals, choosing the suitable preparation conditions.

4. Conclusions

The deep analysis of the preparation variables of a chemical activation process has allowed us to prepare activated carbons with very narrow micropore size distribution

($V_{N_2} \approx V_{CO_2}$), which cover a wide range of surface area (from 700 to 2000 m^2/g). An activated carbon with a BET surface area of 2000 m^2/g and a narrow micropore volume (V_{CO_2}) as high as 0.92 cm^3/g has been prepared. Highly activated carbons with this type of porosity cannot be prepared by physical activation, and have not been obtained by chemical activation up to the moment.

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