

ECONOMICAL MONOLITHIC COAL MOLECULAR SIEVES

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Introduction

Activated Carbons (AC) are carbonaceous materials with a large micropore volume (pore size < 2 nm). This property is an advantage for their application in gas storage [1,2] and gas separation [3,4]. The AC used for gas separation have to be selective to the adsorption of gases with different molecular sizes; these materials are known as carbon molecular sieves (CMS). They contain both narrow microporosity and pore size distribution. The preparation of CMS with high adsorption capacity is difficult because of the specific porosity needed. Thus, the preparation process of these materials uses to involve well defined macromolecular precursors and the selection of several steps in their preparation methods [3].

The objective of this work is to analyze a different CMS preparation method using a low cost raw material and a simple preparation process. For that, a low rank coal and a low cost binder (coal tar pitch) are used. The pore size modification and the molecular sieve properties of these CMS materials are analyzed. Commercially available CMS samples (from Takeda) are also used for comparative purposes.

Experimental

The preparation process consists of several steps: i) steam activation of a high ash content (20% wt) bituminous coal, ii) impregnation of the AC with a suitable solution of a coal tar pitch (AC/pitch: 60/40 weight), iii) molding in a monolithic form and iv) carbonization. The conditions of the heat treatment and the effect of maximum temperature (from 700 to 1200°C) have been studied. The monoliths obtained were characterized by TGA, XRD and SEM and the porous texture analysis was carried out by N₂ adsorption at 77 K and CO₂ adsorption at 273 K (Autosorb 6. Quantachrome). Molecular sieve properties were analyzed through the measurement of CH₄ and CO₂ adsorption kinetics (kinetic diameter 0.38 and 0.33 nm, respectively). These experiments were carried out in a DMT high pressure microbalance (Sartorius 4406) at 0.1 MPa and 298 K.

Results and discussion

The preparation methodology used in this study gives a suitable process for the preparation of hard pellets. The

TGA study has observed that during the pyrolysis process the pitch behaves differently in the pitch-AC mixture, used for monolith preparation, than when it is alone. This different behaviour is reflected in a lower weight loss, in a decomposition temperature shift and in a different softening behaviour (the pitch as a binder in monoliths did not melt during heat treatment). The latter observation is important because it permits that the monoliths can be carbonized without any previous stabilization step.

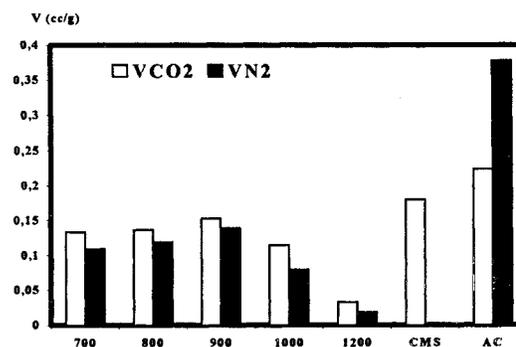


Figure 1. Micropore volumes of the samples used.

Figure 1 shows the micropore volumes corresponding to: the original AC, the monoliths prepared at different temperatures and the commercial CMS. The comparison between the micropore volumes obtained from N₂ adsorption isotherms (V_{N2}) (total micropore volume) and the micropore volume obtained from CO₂ adsorption isotherms (V_{CO2}) (narrow micropores, i.e., pore size < 0.7 nm) provides information about the pore size distribution. The AC has both, a high micropore volume and a wide micropore size distribution, as it is clearly shown by its higher V_{N2} than its V_{CO2}. The results of this figure denotes that this preliminary monolith preparation process produces noticeable changes in the AC porosity. Thus, the monoliths present much lower micropore volumes but, positively, they have narrower micropore size distribution than the original AC (note that their V_{CO2} is now higher than their V_{N2}). This type of narrow pore size distribution can be more suitable for the use of these materials as CMS. The changes in the porosity has shown to be dependent on the maximum temperature used on the carbonization process, reaching a maximum at 900°C. New variables of the preparation process have been tested in order to get a narrow pore size distribution without loosing that much micropore volume.

Figure 2 shows, as an example, the kinetics results of CO₂ and CH₄ adsorption obtained in the characterization of the molecular sieve properties of monolith treated at 700°C (CB7), the original AC, and the commercial CMS. It can be observed that the AC adsorbs both gases, CO₂ and CH₄, after a short period of time, indicating that it does not present molecular sieve properties. On the contrary, the monolith prepared using the AC and pitch mixture up to 700 °C (CB7) behaves as a molecular sieve. It adsorbs the smaller molecule, CO₂, while CH₄ adsorption is very low (not shown in the Figure).

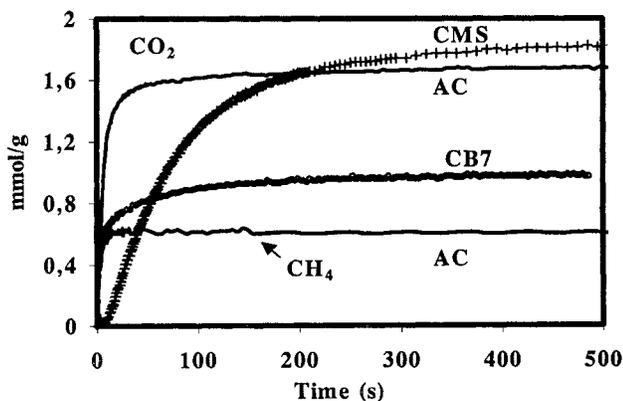


Figure 2. Kinetics of CO₂ and CH₄ adsorption

Although the comparison with the commercially available CMS shows that the monolith adsorption capacity is lower, an important difference, related to the kinetics of adsorption, has to be pointed out. The kinetics of CO₂ adsorption in the monolith sample is faster than the commercial CMS. That is in agreement with its smaller micropore volume and wider pore size distribution (see Figure 1).

This different kinetics behaviour can be important from an economical point of view, for example the commercial use of CMS for gas separation in PSA (Pressure Swing Adsorption) systems. This process consists of a cyclic sequence of adsorption and desorption steps where one of the components in the gas mixture is selectively adsorbed and subsequently desorbed by decreasing the partial pressure, the adsorption kinetics (high adsorption in a small period of time) is, amount other factors, a key parameter. As it can be seen in Figure 2, if a small period of time is considered (the time suitable for PSA applications) the volumetric capacities of both, the commercial CMS and the monolith sample can be comparable.

Further comparison between CMS and the monolith samples has been extended carrying out changes in the particle size of the sample studied. Thus, the same molecular sieve test was carried out with both the powdered CMS and the monolith. The kinetics results obtained show a decrease in the molecular sieve properties for the case of the monolith sample, whereas the kinetics properties of the commercial CMS is not affected in the powdered form. This indicates that in the case of commercial CMS the molecular sieve properties are not affected by the binder used in the process, whereas in the case of the monoliths prepared, the molecular sieve properties are strongly influenced by the binder. This observation suggests that further variables, as lower pitch/AC ratio mixture or higher amount of solvent, have to be studied.

Conclusions

A different process for the preparation of carbon molecular sieve monolith from coal has been described. The pitch plays a double role in monoliths preparation. It acts as a binder and modifies the porosity of the raw activated carbon, producing a material with molecular sieve properties. The pitch seems to produce an efficient blockage of the pore mouth.

Acknowledgments

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