

GRANULAR CARBON MOLECULAR SIEVES FROM LIGNOCELLULOSIC MATERIALS

C. Gómez de Salazar, F. Coloma, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso
Departamento de Química Inorgánica. Universidad de Alicante
Apto. 99, E-03080 Alicante (SPAIN)

Introduction

Carbon molecular sieves (CMS) are microporous materials that are able to discriminate between adsorbing molecules on the basis of shape and size and thus, can be used in gas separation processes such as the pressure swing adsorption [1]. They have some advantages over molecular sieve zeolites in terms of shape selectivity for planar molecules, high hydrophobicity, high resistance to both alkaline and acid media and thermal stability under inert atmosphere at higher temperatures. Furthermore, carbon molecular sieve membranes can be easily prepared which show better performance than polymeric membranes for separation of gas mixtures [2]. There are some suitable methods for preparing CMS; among them, the deposition of carbonaceous material on a previously prepared activated carbon, in order to narrow its porosity, is widely used [3,4]. However, the preparation process would be improved if CMS could be obtained in only one step, by using the appropriate raw material and preparation conditions. This communication reports the results obtained in the preparation of granular CMS from lignocellulosic materials, peach stones and coconut shells, by one activation step under different experimental conditions.

Experimental

Carbon molecular sieves have been prepared from lignocellulosic materials, peach stones and coconut shells, by carbonization in an inert atmosphere and further activation with carbon dioxide. The effect of the mineral matter in the precursors on the activation process and on the micropore size distribution has been analyzed by using precursors which had been subjected to washing treatments with deionized water and with diluted sulfuric acid. The micropore volumes of the samples have been determined by CO₂ adsorption at 273 K and further application of the D-R equation; their sieving properties have been evaluated by immersion calorimetry at 303 K into liquids with different molecular sizes (dichloromethane, 0.33 nm; benzene, 0.37 nm; methanol, 0.43 nm; 2,2-dimethylbutane, 0.56 nm, etc.). The adsorption kinetics of CO₂, CH₄, N₂ and O₂ have been measured at room temperature (298 K) and atmospheric pressure in a volumetric system, in order to evaluate the gas separation capacity

(CH₄/CO₂ and N₂/O₂ mixtures) of the prepared CMS.

Results and discussion

The choice of the appropriate raw material and activation conditions can lead to the production of carbon molecular sieves of the desired pore size distribution. As an example, Table 1 reports the surface area which is accessible to molecules with different molecular size in granular CMS's prepared from the same raw material, peach stones, by using a number of activation procedures (activating agent, activation time and temperature, spacial velocity and concentration of activating agent).

Table 1. Surface area (m²g⁻¹) accessible to liquids of different molecular sizes, as measured by immersion calorimetry.

Sample	Dichloro- methane	Benzene	2,2-Dimethyl- butane
P14	260	30	----
P15	510	30	----
P16	720	130	----
P17	710	350	20
P19	820	725	30
P24	730	80	----

These results clearly show the molecular sieve properties of all the samples for molecules larger than about 0.56 nm, as the surface accessible to 2,2-dimethylbutane is lower than 5% the surface accessible to the smaller molecule, dichloromethane. It can be also seen that samples P14, P15, P16, P24 and, to a lower extent, P17, show molecular sieving properties for molecules of about 0.4 nm. These data allow to estimate that these CMS will be able to separate efficiently methane and carbon dioxide mixtures, and even nitrogen and oxygen from the air.

The main components of the mineral matter in the lignocellulosic materials used in this study to prepare carbon molecular sieves are potassium and calcium, as obtained from X-Ray Fluorescence analysis. These metals are well known catalysts for the gasification reaction of carbon with carbon dioxide, the activation agent used in this study. Thus, the presence of K and Ca in the starting material will affect both the rate of activation and the pore size distribution, given that the latter will be highly dependent on the distribution of the catalysts all over the precursor. As mentioned above, the precursors have been subjected to two different washing treatments; that with water removes only the dust and water soluble impurities, but that with H_2SO_4 can remove nearly all the mineral matter in the precursors, thus eliminating the catalysts for the activation process.

A first example of the effects of the inorganic impurities is shown in Figure 1, where the reactivity of both precursors (% burn-off) are plotted as a function of the activation time for a given set of activation conditions with carbon dioxide. Thus, the activation rate of the water-washed precursor is about five times higher than that of the acid washed precursor.

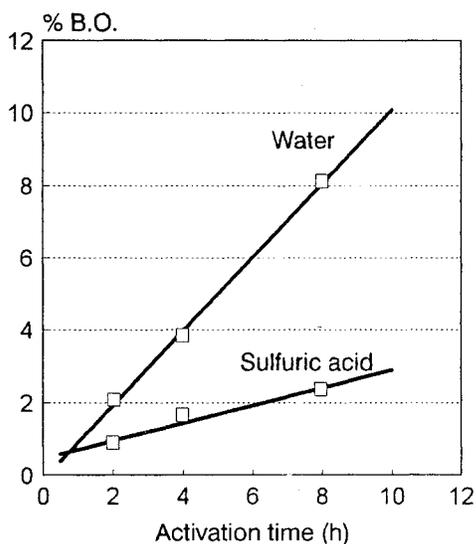


Figure 1. Reactivity of chars prepared from water-washed and acid-washed lignocellulosic precursor for a given set of activation conditions.

The mineral matter is expected to affect not only the reactivity of the chars but also the porosity development, since the reaction between carbon and the activating agent will take place preferentially in the vicinity of the catalytic sites. Figure 2 plots the surface area accessible to dichloromethane, benzene and 2,2-dimethylbutane as a function of their molecular sizes, for CMS prepared from coconut shell subjected to water- and acid-washing treatments, respectively, and activated under the

same experimental conditions. The total porosity is much more developed in the activated carbon obtained from the water washed precursor, which shows a nearly nil surface accessible to 2,2-dimethylbutane (0.56 nm) but a relatively high surface accessible to smaller molecules. On the other hand, the CMS obtained from the acid-washed precursor shows a lower surface accessible to dichloromethane (0.33 Å), but the access of benzene (0.37 nm) to the porosity is restricted. Thus, this activated carbon has very narrow porosity which is not accessible to benzene, but the surface area accessible to carbon dioxide at 273 K is about $500 \text{ m}^2\text{g}^{-1}$. This makes this carbon useful for the separation of gas mixtures with components of similar sizes like oxygen and nitrogen (kinetic diameters, 0.346 nm and 0.364 nm, respectively) [5].

Acknowledgements

This work was supported by DGICYT (Project No. PB94-1500). C. Gómez de Salazar acknowledges a grant from M.E.C. (Spain).

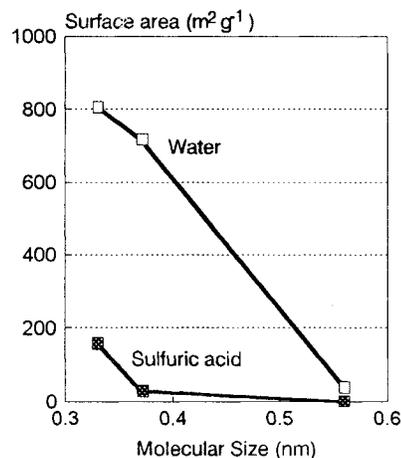


Figure 2. Surface area accessible to different liquids, as a function of their molecular size, in CMS's prepared from water- and acid-washed lignocellulosic precursors.

References

- [1] Foley, H.C., *Microporous Materials*, 1995, 4, 1717.
- [2] Suda, H., and Haraya, K., *Chem. Commun.*, 1997, 93.
- [3] Cabrera, A.L., Zehner, J.E., Coe, C.G., Gaffney, T.R., Farris, T.S. and Armor, J.N., *Carbon*, 1993, 31, 969.
- [4] Nguyen, C., Do, D.D., *Carbon*, 1995, 33, 1717.
- [5] Breck, D.V.; in *Zeolite Molecular Sieves*, John Wiley & Sons. New York, 1974, p. 636.