A STUDY ON THE PREPARATION OF CARBON MOLECULAR SIEVES BY CHEMICAL VAPOR DEPOSITION

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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 [1]. One method used to obtain CMS is to carry out a process of pyrolytic carbon deposition onto a previously prepared CMS, in order to narrow its microporosity [2]. The pyrolytic carbon or pyrocarbon is obtained from the thermal decomposition of volatile insaturated hydrocarbons such as benzene, propene, isobutene, etc. [3,4]. The process is not simple, given that both homogeneous and heterogeneous reactions can be involved. In this way, the control of the experimental variables is of pristine importance to achieve good reproducibility and a controlled carbon deposition, this yielding CMS with the desired characteristics.

This communication reports a study on the preparation and characterization of CMS by carbon deposition from benzene; the effect of preparation variables (temperature, time and benzene partial pressure) are analyzed on the basis of the textural properties on the CMS prepared and their ability to separate gas mixtures.

Experimental

The starting material, DP_0, has been prepared from peach stones by carbonization in an inert atmosphere and further activation with carbon dioxide. Pyrolysis of benzene has been carried out in a fixed bed quartz reactor. The sample was heated in flowing helium (300 cm^3min^{-1}) up to the deposition temperature. Then, the gas flow was switched to a C_6H_6/He mixture prepared by flowing helium through a thermostabilized saturator containing benzene. After a given period of time, the gas flow was switched to pure helium and the sample allowed to cool down to room temperature.

The micropore volumes of the CMS prepared have been determined by CO_2 adsorption at 0°C and further application of the D-R equation; their micropore size distribution has been estimated by immersion calorimetry at 30°C into dichloromethane (0.33 nm) and benzene (0.37 nm). The adsorption kinetics of different pure gases have been measured at room temperature and atmospheric pressure in a glass volumetric system, after treating the CMS at 250°C for 4 h under vacuum.

Results and discussion

It has been previously shown that carbon molecular sieves can be prepared in a single activation step of chars if the appropriate raw material and activation conditions are used [5]. In this way, the starting CMS used in this study (DP_0) has been prepared with micropores narrower than 0.56 nm, as evidenced by immersion calorimetry into 2,2-dicholormethane. However, as reported in Table 1, micropores in this CMS are completely accessible to both dichloromethane and benzene, showing a similar immersion enthalpy for both liquids.

Table 1. Specific enthalpies of immersion, h_i (Jg^{-1}), into dicholoromethane (DCM) and benzene (BZ) and micropore volumes, Vo (cm^3g^{-1}).

Sample	h_i(DCM)	h_i(BZ)	Vo
DP_0	92.95	89.28	0.26
$DP_0$625-4-2	80.14	37.93	0.25
$DP_0$650-4-1	82.05	55.92	0.26
$DP_0$650-4-2	65.31	18.19	0.24
$DP_0$650-6-2	64.75	13.28	0.22
$DP_0$650-4-5	21.59	-	0.21
$DP_0$675-4-2	59.84	9.01	0.23
$DP_0$675-4-4	25.16	-	0.20
$DP_0$700-4-2	40.78	-	0.23
$DP_0$725-4-2	50.73	-	0.25

Table 1 reports the immersion enthalpies of the different CMS prepared into DCM and BZ, as well as their micropore volumes determined by CO_2 adsorption at 0°C. The nomenclature used, DP_0yyy-z-t, indicates the pyrolysis temperature (yyy), the %(v/v) of benzene in the reactive gas mixture (z) and the time allowed for the pyrolysis (t). Results in Table 1 show that the immersion enthalpies into DCM and BZ decrease with the pyrolysis temperature, although the decrease is larger for benzene.

In this way, samples prepared at 700°C and 725°C show immersion enthalpies into DCM which are nearly half of that of the starting CMS, but the immersion enthalpies into BZ are nearly nil. On the other hand, the micropore volume determined by CO_2 adsorption also decreases, but to a lesser extent than the immersion enthalpies. This shows the low sensitivity of this parameter to the evolution of the sieving properties of these CMS. Sample DP_0725-4-2 presents anomalous values for both immersion enthalpy and micropore volume, which can be due to a change in the mechanism of carbon deposition or benzene pyrolysis at this high temperature.

The increase of the deposition time also produces a decrease in the enthalpies of immersion in both liquids and, again, the decrease is higher for immersion in benzene. Furthermore, a linear relationship has been found between the decrease of accessibility of these two liquids to the microporosity of CMS and the deposition time. As can be seen in Figure 1, the slope obtained for deposition at 675°C is higher than the corresponding to the process at 650°C, as could be expected from results commented above. The slopes corresponding to immersion into benzene are much larger than for DCM, indicating that the pore blocking is not homogeneous and produce CMS with a narrower pore size distribution.

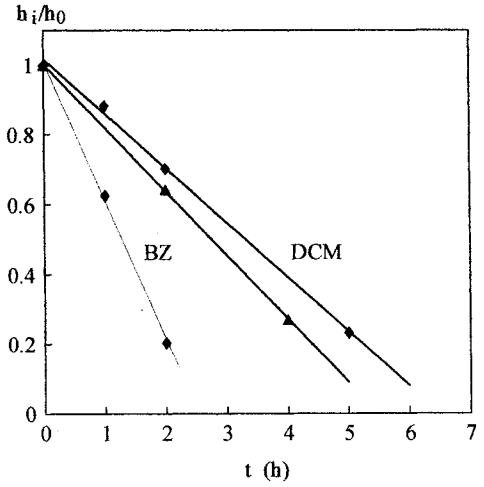

Figure 1. Evolution of the immersion enthalpy of CMS prepared, relative to DP_0, as a function of the deposition time at different temperatures: 650°C (◆) and 675°C (▲).

The separation ability of the different CMS prepared has been analyzed by measuring the adsorption kinetics of pure gases. It has been evidenced that sample DP_0 is not selective for the separation of N_2/O_2 and CO_2/CH_4 mixtures, but it can be achieved with CMS prepared by carbon deposition in the conditions used in this study. As an example, Figure 2 plots the adsorption kinetic curves of N_2, O_2, CH_4 and CO_2 obtained with the CMS DP_0650-4-5. It can be observed that oxygen adsorption is much faster than nitrogen adsorption and, also, carbon dioxide is adsorbed in a much higher extent that methane. In any case, the separation ability of the different samples can be related to the parameters obtained form their textural characterization.

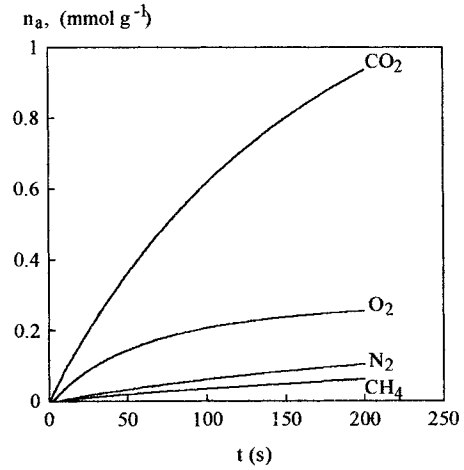

Figure 2. Adsorption kinetics curves of N_2/O_2 and CO_2/CH_4 in the CMS DP_0650-4-5

Acknowledgements

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