Adsorption 11: 663–667, 2005

Preparation of Carbon Molecular Sieves by Pyrolytic Carbon Deposition

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Abstract. The effect of different preparation parameters (pyrolysis temperature, process time, benzene concentration and residence time) on the properties of carbon molecular sieves obtained by pyrolytic carbon deposition from benzene on a microporous activated carbon, has been studied. For a fixed process time of 2 h, the increase of the pyrolysis temperature from 525 to 700°C produced a strong increase of the CO_2/CH_4 selectivity, reaching a maximum value of 13 for pyrolysis at 700°C. Selectivity also increased with process time (up to 5 h, with the pyrolysis temperature fixed at 650 and 675°C), yielding values as high as 28. The obtained results have allowed to find the optimal preparation parameters for the preparation of CMS with high selectivity.

Keywords: carbon molecular sieves, carbon deposition, adsorption, separation

1. Introduction

Carbon molecular sieves (CMS) are carbonaceous materials characterized by a very narrow micropore size distribution, which produces high adsorption selectivity. These materials are receiving increasing attention because of their practical interest in fields such as catalysis and separation of gas mixtures, where they show some advantages over zeolites (greater thermal stability in non oxidizing atmospheres, higher chemical stability and larger adsorbate packing density in their slit-shaped micropores). A great variety of methods have been used for the preparation of CMS's: thermal and chemical activation of chars (De Salazar et al., 2000; Hu and Vansant, 1995), deposition of pyrolytic carbon (Cabrera et al., 1993), controlled oxidation of chars (Gómez-de-Salazar et al., 2000), etc. This contribution presents the results obtained in a study on the effect of different preparation parameters on the properties of carbon molecular sieves produced from peach stones by a carbonization-thermal activation process followed by deposition of pyrolytic carbon. The pyrolytic carbon or pyrocarbon is generally obtained from the thermal decomposition of volatile unsaturated hydrocarbons such as benzene (used in this piece of work), propylene, isobutylene, etc. (Becker and Hüttinger, 1998). The process is not simple, given that both homogeneous and heterogeneous reactions can be involved. In this way, the control of experimental variables is of pristine importance to achieve good reproducibility and controlled pyrocarbon deposition, this yielding CMS with the desired properties.

2. Material and Methods

The starting material was an activated carbon obtained from peach stones. The raw material was ground and sieved to obtain particles in the range 2.0–2.8 mm, treated with a diluted sulfuric acid solution and thoroughly washed with distilled water. It was carbonized under flowing N_2 ($80\ cm^3 \cdot min^{-1}$) at 850°C for 2 h and then activated with flowing CO_2 ($110\ cm^3 \cdot g^{-1}$) for 8 h. The activated carbon prepared will be referred as sample DP_8.

Pyrolytic carbon deposition was carried out in a fixed bed quartz reactor, using benzene as the carbon source. The sample was heated under a helium flow ($330\ cm^3 \cdot min^{-1}$) up to the pyrolysis temperature

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(550–725°C) and then a gas stream containing benzene and helium was fed to the reactor. After a given period of time, the sample was cooled under flowing helium. The preparation parameters analyzed were the pyrolysis temperature, the process time, the benzene partial pressure in the benzene/helium gas stream and the residence time.

The characterization of the porous texture of the prepared samples was carried out by CO_2 adsorption at 0°C, by application of the Dubinin-Radushkevich equation. The pore size distribution of the samples was determined by immersion calorimetry into liquids with different molecular sizes: dichloromethane (DCM, 0.33 nm), benzene (Bz, 0.37 nm) and 2,2-dimethylbutane (2.2DMB, 0.56 nm). Finally, their sieving properties were evaluated by comparing the adsorption kinetics of O_2 (kinetic diameter: 0.346 nm) and N_2 (kinetic diameter: 0.364 nm), and of CO_2 (minimal dimension: 0.33 nm) and CH_4 (kinetic diameter: 0.4 nm) at 25°C, in a glass manometric system.

3. Results and Discussion

The activated carbon (DP_8) used as starting material for the preparation of the sieves contained mainly micropores narrower than 0.56 nm, as evidenced by immersion calorimetry. Thus, the specific immersion enthalpies of DP_8 into DCM and Bz were similar, around 90 $J \cdot g^{-1}$, but a value of only 2.8 $J \cdot g^{-1}$ was obtained when 2,2DMB was used as wetting liquid, this indicating the lack of accessibility of the large 2,2DMB molecule to the inner porosity. On the other hand, its micropore volume, measured by CO_2 adsorption at 273 K, was 0.26 $cm^3 \cdot g^{-1}$ (DR equation). This sample was used to study the effect of several parameters on the properties of CMS prepared by carbon deposition.

The variables controlling the mechanism of pyrolytic carbon deposition (temperature, time, benzene concentration in the gas stream and residence time) will be discussed separately.

3.1. Effect of Pyrolysis Temperature

To study the effect of the pyrolysis temperature other parameters were fixed as follows: process time, 2 h; residence time, 0.002 min; benzene concentration, 4.5 vol.%.

The effect of the pyrolysis temperature on the porosity development of the CMS is presented in Fig. 1, where the natural logarithm of the ratio between the immersion enthalpies into DCM (squares) and Bz (circles) of the CMS's and those of the starting activated carbon are plotted as a function of 1/T. A good linear correlation has been obtained. The dependence with the temperature is higher for the porosity which is accessible to benzene, in such a way that porosity accessible to benzene (the larger molecule) decreases to a larger extent that the porosity which is accessible to DCM when the pyrolysis temperature is increased. This indicates that porosity is being gradually narrowed, although the pore volume is only slightly decreased. In fact, the micropore volume (V_0) measured by CO_2 adsorption decreases from 0.26 $cm^3 \cdot g^{-1}$ for the starting activated carbon (DP_8) to 0.22 $cm^3 \cdot g^{-1}$ for the CMS prepared by benzene pyrolysis at 700°C.

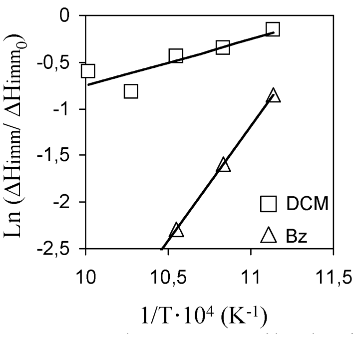


Figure 1. Effect of the pyrolysis temperature on the porosity accessible to liquids with different molecular sizes (DCM and Bz).

The adsorption kinetics of CO_2, CH_4, O_2 and N_2 were determined on these CMS's at 25°C, and the CO_2/CH_4 and O_2/N_2 selectivities at 2 min are plotted in Fig. 2. The selectivities have been calculated from the amounts adsorbed after 2 min of starting the adsorption process. The highest CO_2/CH_4 selectivity is obtained for the sample prepared at 700°C. The lower selectivity obtained for the sample prepared at 725°C may be due

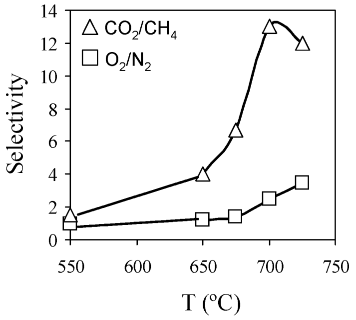


Figure 2. CO_2/CH_4 and O_2/N_2 selectivities of CMS prepared at different pyrolysis temperatures, measured at 2 min.

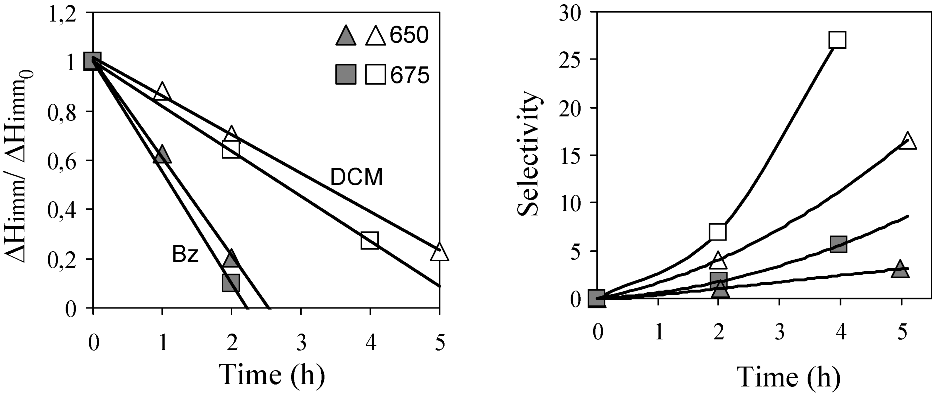
to a change in the carbon deposition process because of the higher pyrolysis temperature. In this sense, it is likely that the deposition of pyrolytic carbon at high temperature takes place at the more external porosity (Benzinger and Hüttinger, 1996), this decreasing the accessibility of gas molecules to the more internal microporosity. Similar results have been reported by other authors (Kawabuchi, et al., 1996). Under strong conditions such as high pyrolysis temperature, the reaction step is favored over the diffusion step, and pyrocarbon is formed at the pore mouth; however, under milder conditions the diffusion step is favored, and the pyrolytic carbon is deposited inside the pores. In fact, the adsorption kinetic curves (amount adsorbed vs. time) on the CMS prepared at the higher temperature, 725°C, show less pronounced curves, this indicating the slower diffusion of gas molecules to the inner porosity.

On the other hand, the O_2/N_2 selectivity increases with the pyrolysis temperature in the range studied. In this case, although the amounts of O_2 and N_2 adsorbed by the sample prepared at 725°C are smaller than those adsorbed by the sample prepared at 700°C, the decrease of N_2 adsorption is more important and, in this way, selectivity still increases.

3.2. *Effect of Process Time*

Deposition of pyrolytic carbon on the starting DP_8 activated carbon was carried out during different periods of time at 650°C or 675°C, residence time of 0.002 min and a benzene concentration of 4.5 vol.% in helium. The obtained results show that immersion enthalpies into DCM and Bz both decrease with exposure time, although the decrease is more important for Bz. Thus, CMS's prepared during 4 and 5 h of pyrolysis time show immersion enthalpies into DCM which are nearly a quarter of that showed by the starting DP_8 sample, but the immersion enthalpies into benzene are nearly nil. On the other hand, the amount of CO_2 adsorbed also decreases, but to a lesser extent than immersion enthalpies. This demonstrates the low sensitivity of the CO_2 micropore volume to the evolution of the sieving properties of the carbon molecular sieves. Fig. 3(a) shows that there is a good correlation between the evolution of microporosity, measured by the ratio between the immersion enthalpies of the CMS's prepared and that of the starting activated carbon, and the exposure time. Again, the effect is more important for the porosity accessible to Bz (higher slope in the plot), what is important to achieve good sieving properties. Furthermore, Fig. 3(a) also shows the effect of the temperature at which pyrolysis has been carried out which, as expected, correlates with results discussed above.

The adsorption kinetics of CO_2, CH_4, O_2 and N_2 at room temperature allowed for the calculation of the O_2/N_2 and CO_2/CH_4 selectivities after 2 min, which are plotted in Fig. 3(b) as a function of the process time. Both values increase with time in the range studied (up to 5 h), and are also higher when the deposition was carried out at 675°C. The effect of the process time is more important for the CO_2/CH_4 selectivity, in such a



(a) (b)

Figure 3. (a) Evolution of microporosity accessible to DCM and Bz in the CMS's, referenced to that in the starting material, as a function of process time. (b) CO_2/CH_4 (empty symbols) and O_2/N_2 (full symbols) selectivity of CMS as a function of process time at 650°C (△) AND 675°C (□).

way that values as high as 28 have been achieved after 4 h of treatment at 675°C.

3.3. Effect of the Benzene Concentration

To study the effect of the benzene concentration in the gas stream in the 4–10 vol.% range, the temperature was fixed at 650°C, the exposure time was 2 h and the residence time was 0.002 min. As the benzene concentration increases, the surface areas accessible to DCM and to Bz, measured by immersion calorimetry, decrease. The values are much lower for benzene. Thus, the CMS prepared with 4% v/v Bz had a surface area accessible to Bz of only 150 $m^2 \cdot g^{-1}$, whereas the value obtained for DCM was 600 $m^2 \cdot g^{-1}$. When a gas stream containing 10% v/v Bz was used, the surface area accessible to DCM decreased to 380 $m^2 \cdot g^{-1}$, whereas for Bz it was of only 70 $m^2 \cdot g^{-1}$. The effect of benzene concentration is more evident on the accessibility of benzene, the larger molecule, but it is also important for DCM. These results indicate that as the amount of benzene in the gas phase increases the amount of pyrolytic carbon deposited is higher, resulting not only in the narrowing of the micropores but also in a decrease of the total micropore volume as detected by immersion calorimetry into DCM. It is worthy to indicate that the micropore volume measured by CO_2 adsorption remains unchanged, this remarking the low sensitivity of this parameter to analyze the sieving properties of these materials.

Figure 4 plots the evolution of the O_2/N_2 and CO_2/CH_4 selectivities at 2 min with the amount of benzene in the cracking gas stream. It seems clear that the benzene concentration has an important effect on the CO_2/CH_4, which increases as the %Bz increases whereas the effect is nearly nil on the O_2/N_2. However, the CO_2/CH_4 selectivity values are too small in the range of %Bz studied. Furthermore, the analysis of the adsorption kinetic curves reveals that the diffusional limitations to the adsorption of both gases increase with the benzene concentration in the gas stream. This makes the adsorption process being too slow for practical purposes. It can then be concluded that better selectivities with practical applicability can be achieved by the control of other parameters such as cracking temperature and time.

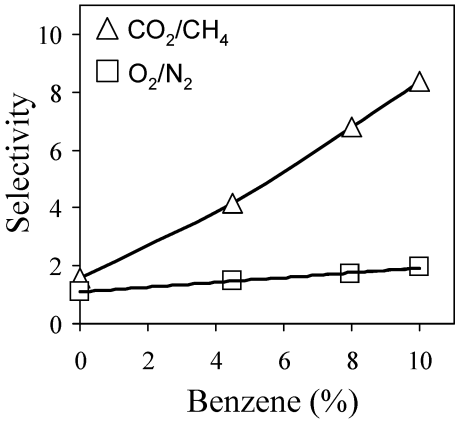


Figure 4. CO_2/CH_4 and O_2/N_2 selectivities of CMS prepared at different benzene concentration in the gas stream, measured at 2 min. (*T*: 650°C, *t*: 2 h).

3.4. Effect of the Residence Time

To study the effect of the residence time on the properties of the CMS prepared, the pyrolysis temperature was fixed at 650°C, the process time was 2 h and the benzene concentration in the gas stream was 4.5 vol.%. The effect of the residence time on the surface areas accessible to DCM and Bz, measured by immersion calorimetry, is shown in Fig. 5. It can be seen that the surface areas accessible to both test molecules increase with increasing residence time, and that the differences in accessibility for both liquids are not modified by this parameter. As the residence time is defined as the ratio between the adsorbent bed volume and the volumetric gas flow, the results indicate that a higher amount of pyrocarbon is deposited when the pyrolysis process is carried out at higher flow rates, this decreasing the accessible surface area in a similar way for both the small (DCM) and larger (BZ) probe molecules. In this way,

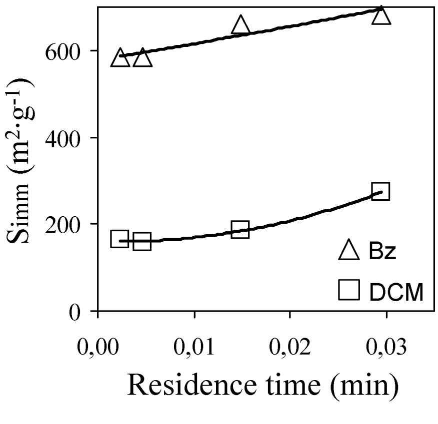


Figure 5. Correlation between the surface areas accessible to DCM and Bz and the residence time (*T*: 650°C; *t*: 2 h).

the modification of the residence time has no effect on the separation properties of the CMS prepared.

4. Conclusions

It has been shown that carbon molecular sieves can be prepared by pyrolytic carbon produced from benzene on a microporous activated carbon prepared by physical activation. Several variables that control the deposition rate and the mechanism of the reactions on the carbon surface have been analyzed. An increase in the pyrolysis temperature in the 550 to 700°C range produces a strong increase of the CO_2/CH_4 selectivity, which decreases when the carbon deposition is carried out at higher temperatures (725°C). This result can be explained on the basis of a different mechanism taking place at high temperatures by which pyrolytic carbon is deposited at the outer porosity. Another important parameter is the process time. A continuous increase in selectivity has been obtained with time on stream in the range studied (up to 4–5 h at 650 and 675°C).

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