PREPARATION OF CARBON MOLECULAR SIEVES BY CHEMICAL VAPOR INFILTRATION OF LIGNIN BASED MICROPOROUS CARBONS

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Introduction

In a previous work we studied the influence of heat treatment on the molecular sieve properties of activated carbons prepared by chemical activation of lignin [1]. The thermal treatment modified the porous structure of the activated carbons, giving rise to solids that separate C_6H_6 from C_6H_{12}, CO_2 from CH_4 and O_2 from N_2 with a relative high selectivity. However, the heat treatment drastically reduced the adsorption capacity of these carbons.

The access to the micropores of the activated carbons can be modified by deposition of pyrolytic carbon on the micropore entrance to generate constrictions similar in size to some adsorbing species, allowing their selective adsorption [2-6]. In the present work, the preparation of carbon molecular sieves (CMSs) by deposition of pyrolytic carbon on lignin-based microporous chars has been studied.

Experimental

Microporous chars were prepared by chemical activation of lignin, followed by heat treatment [1]. Lignin was impregnated with $ZnCl_2$ at low (0.4) and high (2.3) $ZnCl_2$ to lignin weight ratios and the impregnated samples were activated by carbonization in a conventional horizontal furnace at 673 K for 2 h in an inert atmosphere [7]. After a washing process to eliminate the activation agent, the resulting carbons were further heat-treated at 1073 K during 2 h under N_2 flow.

Experiments to study the kinetic of the pyrolytic carbon deposition on the lignin-based microporous chars were carried out in a thermogravimetric analizer system. Benzene (5.5 vol %), in a stream of He at atmospheric pressure, was used as the pyrolytic carbon precursor. About 5 to 10 mg of char and a total flow rate of 200 cm^3 (STP)/min were used in each experiment. The reaction temperature for benzene cracking ranged from 973 to 1173 K.

CMSs were prepared by pyrolytic carbon deposition, from benzene cracking, on lignin-based micrporous chars in a conventional horizontal furnace. The experimental conditions were very similar to those used for the kinetic study in the thermogravimetric system, with the exception of the mass of char utilized, that in this case was of 500 to 600 mg.

Textural characterization of the carbons was carried out by N_2 (77 K) and CO_2 (273 K) adsorption. In order to analyze the sieving properties of the CMSs, the kinetics of adsorption of O_2/N_2 and CO_2/CH_4 were measured in a volumetric adsorption apparatus at room temperature.

Results and Discussion

Table 1 summarizes the effective micropore volume values and the apparent BET (N_2) and DR (CO_2) surface area values for the lignin-based microporous chars. The chars obtained by heat treatment of the activated carbons prepared at low and high impregnation ratios, 673L1073 and 673H1073, respectively, exhibit clearly a different micropore size distribution. The differences observed between the N_2 and CO_2 micropore volumes and surface areas for 673L1073, with higher values for those derived from the CO_2 adsorption data, can be attributed to the lack of achievement of true N_2 adsorption equilibrium, due to restricted diffusion through the pores at the low temperature of adsorption. This result suggests the existence of very narrow micropores in the structure of this carbon. An opposite behavior is observed for 673H1073, indicating that a considerable widening of the microporosity has been developed in the carbon prepared at higher impregnation ratio.

Table 1. Porous structure characteristics of lignin-based microporous chars prepared at low (L) and high (H) impregnation ratio.

Carbon	Microp. Vol. (cc/g)		A_{BET}	A_{DR}
	V_α (N_2)	V_{DR} (CO_2)	(m^2/g)	(m^2/g)
673L1073	0.210	0.263	451	720
673H1073	0.377	0.187	724	511

In an attempt to modify the molecular sieving properties of these carbons, they were infiltrated with pyrolytic carbon by cracking of benzene at different temperatures. Figures 1 and 2 represent the pyrolytic carbon deposited on 673H1073 and 673L1073 samples, respectively, as a function of the reaction time, for the experiments carried out in the thermogravimetric system. Blank experiments were carried out without char samples and no mass gain was observed. At low cracking temperature, the deposition proceeds initially at a high rate on 673H1073 carbon and after, approximately, a 3% of mass gain it decreases to a steady state. The initial rate of deposition substantially

increases with reaction temperature. However, the steady-state values and the total amount of pyrolytic carbon deposited decrease with chemical vapor deposition temperature. These results suggest that the cracking reaction of benzene take place on the internal surface of 673H1073 carbon. The pyrolytic carbon is deposited uniformily on the surface of the micropores and does not fill them at low cracking temperatures. At higher temperature, the reaction rate increase considerably and diffusion of benzene through the narrow micropores may limit partially the deposition process inside this pores [6]. This implies that the pyrolytic carbon is deposited preferentially on the surface of the wider micropores and the micropore entrance, blocking it shortly after the beginning of the deposition, that continues at a much slower steady-state rate on the external surface.
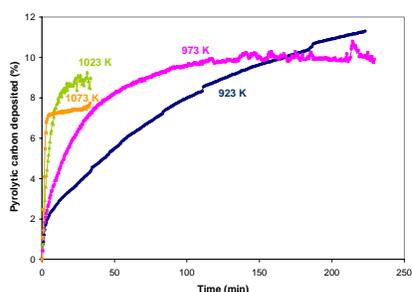

Figure 1. Pyrolytic carbon deposition on 673H1073 as a function of cracking reaction time, at different temperatures.

For 673L1073 carbon, with a narrow micropore size distribution, no appreciable pyrolytic carbon deposition was observed below 1073 K. At 1073 K this carbon presents a behavior very similar to that of 673H1073, although the amount of pyrolytic carbon deposited during the initial high rate step is quite lower. The blockage of the micropore entrance seems to take place in a shorter time for 673L1073 than for 673H1073. The small pore sizes of 673L1073 carbon do not allow the benzene to infiltrate the microporous structure before cracking [8,9]. The deposition proceeds, initially, on the micropore entrance, blocking off the pores quickly, and continues on the external surface at a very low rate. Above 1073 K linear relationship between the mass gain and the deposition time is observed and large amount of pyrolytic carbon were deposited on the surface of 673L1073. These results suggest that above 1073 K the cracking reaction of benzene takes place predominantly in the gas phase, once the micropore entrance is completely blocked shortly after the initiation of deposition, with no influence of the substrate on the formation of pyrolytic carbon.
CMSs were prepared from 673H1073 and 673L1073 carbons in a conventional horizontal tube furnace at the

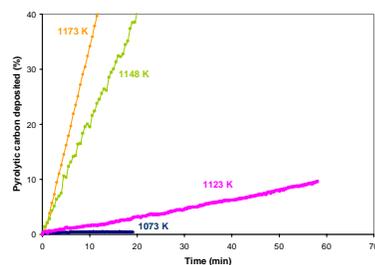same conditions as those used in the thermogravimetric experiments.

Figure 2. Pyrolytic carbon deposition on 673L1073 as a function of cracking reaction time, at different temperatures.

Figures 3 and 4 present the evolution of the N_2 and CO_2 adsorption derived surface areas for these two carbons subjected to various levels of deposition. Pyrolytic carbon deposition at 1023 K decreases gradually the N_2 surface area for 673H1073 carbon. About 50% of the N_2 micropore volume and surface area were reduced after 11,8% of pyrolytic carbon deposition. If the cracking process continues, the N_2 micropore volume and surface area drop steeply to very low values. The CO_2 surface area and micropore volume decrease a 50% after only 6% of pyrolytic carbon is deposited. However, these values remain relatively constant if the deposition process continues. Figure 4 shows that only 1% of pyrolytic carbon deposited at 1073 K on 673L1073 is enough to reduce drastically its N_2 surface area and micropore volume. However, the deposition process at this temperature does almost not affect the CO_2 surface area and micropore volume of this carbon, that remain constant even at higher deposition levels.
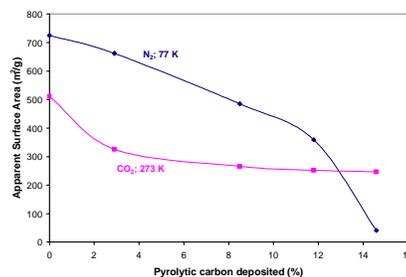

Figure 3. Evolution of the BET (N_2, 77 K) and DR (CO_2, 273 K) surface areas as a function of pyrolytic carbon deposition for 673H1073 carbon, at 1023 K

These results confirm the suggestions argued previously in the kinetic study. At high temperatures, the pyrolytic carbon deposition takes place primarily on the surface of the wider micropores and micropore entrance of 673H1073 carbon and only on the micropore entrance of 673L1073

carbon. Different sizes of micropore entrance can be obtained by controlling the temperature and time of benzene cracking, maintaining almost unaffected the micropore volume.
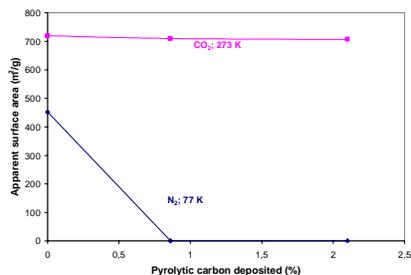

Figure 4. Evolution of the BET (N_2, 77 K) and DR (CO_2, 273 K) surface areas as a function of pyrolytic carbon deposition for 673L1073 carbon, at 1123 K.

Figures 5 and 6 show the adsorption kinetics of O_2/N_2 and CO_2/CH_4, respectively, for 673L1073 carbon and this carbon after different levels of chemical vapor deposition.
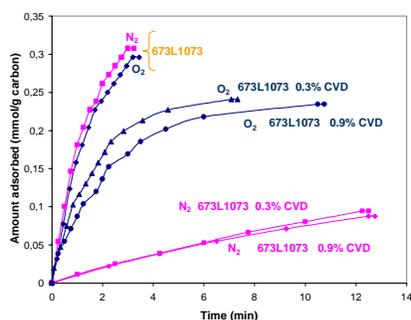

Figure 5. Kinetic of O_2/N_2 adsorption for 623L1073 carbon.

The O_2 and CO_2 adsorption capacities were decreased slightly with deposition. However, 0.3% of pyrolytic carbon deposited on 673L1073 at 1073 K was enough to reduce drastically the adsorption of N_2 and impede that of CH_4, improving considerably the molecular sieve properties of this carbon. The O_2 selectivity (ratio of O_2 to N_2 adsorbed in 2 min) increased rapidly to a value of 6 after 0.3% of pyrolytic carbon deposition, with a reduction of only 20% in adsorption capacity. The same behavior can be observed for CO_2/CH_4 adsorption.

Conclusions

Preparation of CMSs from lignin-based chars by pyrolytic carbon deposition from benzene cracking seems to be possible by controlling the cracking temperature and time and the microporous structure of the substrate, the principal parameters governing the deposition process. For

a lignin char with a relatively narrow microporosity, benzene cracking temperature of 1073 K and pyrolytic carbon deposition of 0.3% were enough to prepare a carbon with molecular sieve properties suitable for efficient separation of O_2 from N_2 and CO_2 from CH_4.
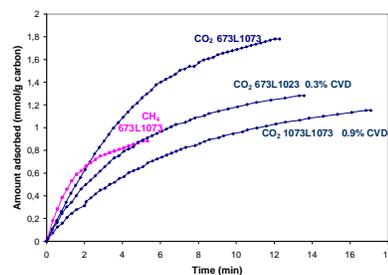

Figure 6. Kinetic of CO_2/CH_4 adsorption for 623L1073 carbon.

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