

PREPARATION AND CHARACTERIZATION OF CARBON MOLECULAR SIEVES FROM LIGNIN

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Introduction

Lignin has gained an increasing interest as a potential raw material for the chemical industry in the last two decades. ALCELL lignin, a by-product in the organosolv pulping process (ALCELL process), presents many physical and chemical properties (hydrophobicity, lack of inorganic contaminants, low molecular weight, etc.) that differentiate it from lignins produced by the kraft and sulfite processes [1]. In previous works we have studied the physical [2] and chemical [3] activation of eucalyptus kraft lignin to produce activated carbon. The results of these studies revealed that activated carbons prepared by chemical activation of kraft lignin with $ZnCl_2$ presented substantially higher yield values, a more developed micropore structure and a fairly lower mesoporosity than activated carbons prepared by physical activation with CO_2 of the same precursor.

In the present work, the influence of heat treatment on the molecular sieve properties of carbons prepared by chemical activation of ALCELL lignin has been studied.

Experimental

ALCELL lignin was supplied by Repap Technologies Inc. The lignin was impregnated with $ZnCl_2$ in a rotary evaporator at 303 K for 1 h. The concentration of $ZnCl_2$ and the weight of lignin were adjusted to obtain $ZnCl_2$ /lignin weight ratios (i.e., impregnation ratios, IR) of 0.4 and 2.3. Impregnated samples were activated by carbonization in a conventional horizontal furnace in an inert atmosphere at 623, 673 and 773 K for 2 h. The resulting carbons were washed with aqueous HCl solution until no Zn^{2+} was detected. These washed samples were further heat-treated at 1073 K during 2 h under N_2 flow, in the same furnace system.

Textural characterization of the carbons has been carried out by N_2 (77 K) and CO_2 (273 K) adsorption. In order to analyze the sieving properties of the carbons, the kinetics of adsorption of O_2/N_2 and CO_2/CH_4 were measured in a volumetric adsorption apparatus at room temperature. The kinetics of adsorption of benzene and cyclohexane were measured at 293 K, using a microgravimetric system. Desorption experiments were also performed in the microbalance system at the adsorption temperature under an inert atmosphere.

Results and Discussion

Chemical activation of ALCELL lignin with $ZnCl_2$ produces activated carbons with a predominantly microporous structure and high surface areas. Figure 1 shows the evolution of the BET (N_2) and DR (CO_2) surface areas with activation temperature (AT) for activated carbons prepared with impregnation ratios of 0.4 and 2.3. An increase of the activation temperature and of the impregnation ratio leads to an increase of both the surface areas measured with N_2 and with CO_2 , reaching values of 1500 and 680 m^2/g , respectively, for a temperature of 773 K and a impregnation ratio of 2.3. The differences observed between the N_2 and CO_2 surface areas for carbons prepared at 0.4 impregnation ratio, with higher values for those derived from the CO_2 isotherm data, indicates the existence of a narrow microporosity in the structure of these carbons. At 2.3 impregnation ratio an opposite behavior is observed. A considerable widening of the microporosity and an important development of mesoporosity takes place at this higher impregnation ratio.

In order to modify the molecular sieving properties of these carbons, they were heat-treated at 1073 K for 2 h. Table 1 summarizes the effective micropore volume values and the apparent BET (N_2) and DR (CO_2) surface area values for the activated carbons heat-treated at 1073 K. Heat treatment of the activated carbons prepared at 673 and 773 K with the higher impregnation ratio, 2.3, reduces both their BET surface area and N_2 micropore volume and the DR CO_2 surface area and micropore volume. The A_{DR}/A_{BET} ratio for these carbons shows a value close to 0.7, similar to that of the activated carbon precursors, indicating that both narrow and wide microporosity have been reduced to the same extent with temperature and that useful molecular sieving properties were not developed by the thermal treatment. On the contrary, the carbons obtained by heat treatment of the activated carbons prepared at 0.4 impregnation ratio exhibit a substantial increase of the micropore volume and surface area derived from the CO_2 adsorption data, with almost no increase for the N_2 derived values. The fact that the values of A_{DR} and V_{DR} are higher than those of A_{BET} and V_{α} , respectively, 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 77 K. This result suggests the existence of very narrow micropores in the structure of these carbons. The kinetic benzene/cyclohexane adsorption curves for 773-L-1073 and 773-H-1073 carbons, shown in Fig. 2, reveal the different behavior of these carbons for the efficient C_6H_6/C_6H_{12} separation. Adsorption of benzene and cyclohexane on 773-H-1073 takes place at a similar rate, although the amount adsorbed of benzene is larger than that of cyclohexane. Both gases are partially desorbed at the adsorption temperature and an appreciable amount of them remains adsorbed on the carbons, most likely, on the narrower micropores. A different picture is observed for 773-L-1073 carbon. This carbon would be suitable for separation of these two gases, given that, it adsorbs significant amount of benzene, a flat molecule, and negligible amount of cyclohexane. It is also interesting to note, that almost all the amount of benzene adsorbed remains retained by the carbon in the desorption cycle. This amount retained in the narrower micropores is larger than that observed in the case of carbon 773-H-1073. Carbon 773-L-1073, however, does not separate efficiently CO_2 from CH_4 , which suggests the existence of slit-type narrow micropores with size of around 3.7 \AA , the molecular size of benzene in thickness. A similar behavior was observed for 673-L-1073 carbon. Only carbon 623-H-1073 is able to separate efficiently CO_2 from CH_4 (in addition to separate C_6H_6 from C_6H_{12}), as can be observed from Fig. 3. However, the benzene and CO_2 adsorption capacity of this carbon is significantly lower than that of the carbons activated at higher temperature.

References

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Acknowledgments

The authors acknowledge the Spanish CICYT for financial support through the research project QUI97-0872. C.P. expresses her gratitude to that institution for a research grant.

Table 1. Porous structure characteristics of activated carbons prepared by chemical activation of ALCELL lignin heat treated at 1073 K.

Carbon	IR	AT (K)	Microp.	Vol. (cc/g)	A_{BET} (m^2/g)	A_{DR} (m^2/g)
			V_{α} (N_2)	V_{DR} (CO_2)		
673-L-1073	0.4	673	0.210	0.263	451	720
773-L-1073	0.4	773	0.263	0.299	536	818
623-H-1073	2.3	623	0.149	0.197	322	539
673-H-1073	2.3	673	0.377	0.187	724	511
673-H-1073	2.3	773	0.499	0.188	854	512

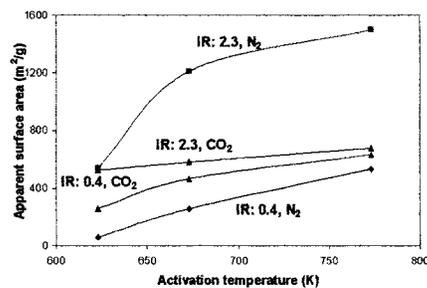


Figure 1. Evolution of the BET (N_2 , 77 K) and DR (CO_2 , 273 K) surface area with activation temperature for activated carbons prepared at different impregnation ratios.

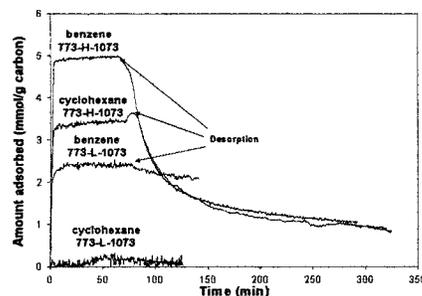


Figure 2. Kinetics of C_6H_6/C_6H_{12} adsorption on activated carbons prepared at different impregnation ratios, heat-treated at 1073 K.

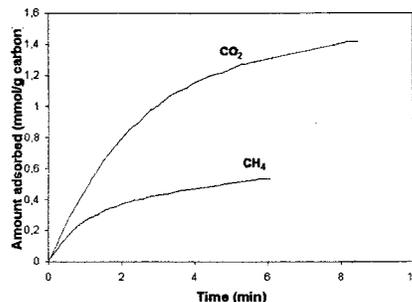


Figure 3. Kinetic of CO_2/CH_4 adsorption on 623-H-1073 carbon.