

MODIFIED ACTIVATED CARBONS AS MOLECULAR SIEVES FOR GAS SEPARATION

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Introduction

Heat treatments and carbon deposition [1,2] from the pyrolysis of hydrocarbons such as propene [2,4,6] and benzene[3,7] onto activated carbons, are widely used methods for the preparation of carbon molecular sieves. The efficiency of these treatments depends on the pore size distribution of the starting material and on the extent and conditions of the treatment.

In the present work, we have studied the modification of the micropore structure of activated carbons with different textural properties, by heat treatment and by carbon deposition from the pyrolysis of benzene. These modifications were made in order to produce a material with molecular sieve properties for gas separation.

Experimental

Activated carbons were prepared in our laboratory from coconut shell to different extents of burn-off (BO): by carbon dioxide gasification at 1173 K BO=12.4% (ACA) and BO=63.3% (ACB); and by steam gasification at 1173 K, BO=51.4% (ACC). ACA is an activated carbon with narrow pore size distribution around a pore diameter of 0.6 nm, ACB and ACC are activated carbons with wide-open pore structures.

The heat treatment was performed in a tubular reactor externally heated by an electric furnace, under a nitrogen flow of 200 cm³.min⁻¹. ACA and ACB were heat treated at 1373, 1473 and 1673 K with a heating rate of 5 K.min⁻¹.

ACA and ACC were also used as substrates for carbon deposition from pyrolysis of benzene. The carbons were first degassed at 1173 K under nitrogen flow in order to remove any surface oxygen groups.

Carbon deposition was carried out in a CI Electronics Mk2B microbalance coupled with a flow reactor. About 150 mg of activated carbon were suspended from the balance by a silica filament, and carbon was deposited from a mixture of benzene and nitrogen at 1023 K. Benzene was introduced into the system by saturating a stream of nitrogen.

The weight gain was continuously monitored as a function of time.

The textural characterization of ACA, ACB and ACC before and after modification by heat treatment and by carbon deposition, was based on the determination of nitrogen and carbon dioxide adsorption isotherms at 77K and 273 K, respectively, with a Coulter Omnisorp 100 CX apparatus. The adsorption isotherm data were analyzed by the Dubinin equation and t-plot. The width of the micropores was estimated from the Stoeckli correlation [5]:

$$L \text{ (nm)} = 30/E_0 + 5705/E_0^3 + 0.028 \times E_0 - 1.49$$

Results and Discussion

Effect of thermal treatment

Tables 1 and 2 show the physical properties of the activated carbons before and after heat treatment. We can examine the effect of heat treatment on the pore structure when it is performed on activated carbons of different texture. ACB has pores of larger average size than does ACA. Therefore, these samples have different behaviors upon treatment as we can see on tables 1 and 2. The heat treatment of ACB up to 1673 K has little effect on its micropore volume measured by CO₂ and by N₂. The maximum decrease in the micropore volume was obtained at 1673 K, and it was only 11%. As we can see the micropore dimension (L) decreases with the heat treatment until 1473 K. ACA carbon shows significant selectivity for CO₂ over N₂, which suggests that it should show better results with heat treatment. The heat treatment of this carbon at 1373 K results in a small decrease of the micropore volume determined by N₂ and CO₂.

More severe heat treatments to 1473 and 1673 K effectively remove access to N₂ to most of the micropores. For the sample heated at 1473 K the access of CO₂ is reduced by 15.5% while the access of N₂ is reduced by 69.4%. When the sample is heat treated at 1673 K, the N₂ adsorption is almost null; however, with CO₂ adsorption we still find a micropore volume of 0.17 cm³.g⁻¹.

This reduction of pore volume at high temperatures is a result of the structure sintering, in agreement with findings of other authors [1]. It is important to determine the adsorption kinetics of O₂ and N₂ of the sample ACA treated at 1473 K in order to better clarify the selectivity of the material for this separation.

Effect of carbon deposition

The kinetics of carbon deposition from benzene onto particles of ACC ($W_0=0.553 \text{ cm}^3.\text{g}^{-1}$; $L=1.1 \text{ nm}$) was followed with the microbalance operating isothermally. From the carbon uptake vs. time at each temperature, the initial rate of carbon deposition was determined. From the Arrhenius plot we have identified clearly three kinetics regimes: chemical kinetics up to 998 K, pore diffusion from 998 to 1073 K, and external diffusion above 1073 K. The activation energy (154 kJ.mol^{-1}) determined in the chemical regime is similar to those reported by other authors [4]. From these results, carbon deposition to loadings of 5, 10 and 15% of the original weight of the sample heat treated at 1173 K, were made at 998, 1073 and 1123 K. These temperatures were chosen in order to deposit carbon at the pore mouth, therefore decreasing the entrance width. These treatments do not improve the sieving properties of ACC carbon. The preparation of a sample with a larger carbon loading (33.7%), at 1023 K, results in closure of some micropores, but at the same time the larger pores are narrowed. This sample shows significant selectivity for CO₂ over N₂.

The modification of ACA by deposition of 11.1% C, at 1023 K, also shows significant selectivity for CO₂ over N₂.

Conclusions

The potential for improving, by heat treatments, the molecular sieving characteristics of certain microporous carbons, specially those with a narrow pore size distribution, has been demonstrated.

In the present study it has been shown that carbon deposition from the pyrolysis of benzene can also be used to increase the molecular sieving ability of some carbons, depending on their particular pore structure. A carbon with a narrow pore size distribution is required for any of these techniques to be successful.

References

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Table 1- Textural characteristics determined by N₂ and CO₂ adsorption in ACA before and after HTT: 1- t method; 2- DR method.

	W_0 (1) ($\text{cm}^3.\text{g}^{-1}$)	S_{me} (1) ($\text{m}^2.\text{g}^{-1}$)	W_{01} (2) ($\text{cm}^3.\text{g}^{-1}$)	W_{02} (2) ($\text{cm}^3.\text{g}^{-1}$)	L (2) (nm)	W_{CO_2} ($\text{cm}^3.\text{g}^{-1}$)
ACA	0,307	14	0,306	0,010	0,60	0,367
HTT1373	0,249	13	0,242	0,016	0,87	0,332
HTT1473	0,094	33	0,074	0,019	2,2	0,310
HTT1673	0,024	15	0,019	0,006	2,1	0,167

Table 1- Textural characteristics determined by N₂ and CO₂ adsorption in ACB before and after HTT: 1- t method; 2- DR method.

	W_0 (1) ($\text{cm}^3.\text{g}^{-1}$)	S_{me} (1) ($\text{m}^2.\text{g}^{-1}$)	W_{01} (2) ($\text{cm}^3.\text{g}^{-1}$)	W_{02} (2) ($\text{cm}^3.\text{g}^{-1}$)	L (2) (nm)	W_{CO_2} ($\text{cm}^3.\text{g}^{-1}$)
ACB	0,742	43	0,646	0,100	1,30	0,554
HTT1373	0,686	30	0,584	0,105	1,15	0,548
HTT1473	0,658	36	0,527	0,130	0,98	0,504
HTT1673	0,661	47	0,511	0,181	1,0	0,497