CARBON MOLECULAR SIEVES FROM CVD OVER ACTIVATED CARBONS

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Introduction

Carbon molecular sieves (CMS) are carbon microporous materials which have an amorphous structure, micropore mouths similar in dimensions to small molecules and a narrow micropore size distribution. Gas separation in PSA systems is their main industrial application. Overlapping of the potentials that the pore walls produce over the adsorbed particles, makes the diffusion process so difficult that separation of gases is produced by the different rates of diffusion of their molecules to the inside of micropores. The present work describes a process of carbon vapour deposition, by pyrolysis of benzene, over activated carbons from coals in order to obtain carbon molecular sieves. The main aim of the work is to study the process of carbon vapour deposition (CVD) over activated carbons from four different rank coals and to analyse the influence of the CVD degree on the porous texture and the molecular sieve effect of the materials.

Experimental

A high-volatile bituminous coal -Pumarabule- and an anthracite -Tineo- from the Asturian Basin (North of Spain) and a medium-volatile bituminous coal -Jastrzebie- and a semianthracite -JastrzebieS- from Poland were used as starting materials. The four coals were ground to particle diameters below 45 μm and agglomerated under pressure to give pellets 13 mm in diameter and 1 mm in height. Prior to pyrolysis, the pellets were oxidized with air at 250°C for 72 h and carbonized under nitrogen at a heating rate of 16°C/min up to 850°C, with a soaking time of one hour. The carbonized material was subjected to a stream of nitrogen (200 ml/min) and water vapour (12% vol.) at a temperature of 800°C to 20% burn-off. The activated pellets were treated at 725°C with a flow of N_2 and benzene of 150 $ml.min^{-1}$and 1% benzene content [1], causing the pyrolysis of the organic molecule and the deposition of carbon atoms onto the carbon structure.

Textural characterisation of the samples included helium and mercury density measurements, mercury porosimetry and CO_2 and benzene adsorption at 25°C [2]. The micropore size distribution of the carbons was analysed by immersion calorimetry at 20°C, using molecular probes of different critical dimensions: dichloromethane (3,3 Å), benzene (4,1 Å), cyclohexane (5,4 Å), carbon tetrachloride (6,3 Å) and 1,5,9-cyclododecatriene (7,6 Å). The technique and its theoretical basis have been described in detail elsewhere [3]. The adsorption kinetics of N_2, O_2, CO_2 and CH_4 were carried out in order to study the posibilities of using the materials obtained as molecular sieves for the separation of gases

RESULTS AND DISCUSSIONS

CVD of carbon over activated carbons produces materials with a lower real density, a higher apparent density and as a consequence a decrease in their pore volume, basically micropores and mesopores in the range smaller than 7.5 nm .
The evolution of micropore accessibility with the CVD process is illustrated by the profiles of the ratio $E_0W_0/(E_0W_0)_{ref}$ (E_0 characteristic energy; W_0 micropore volume) based on immersion studies [4]. A decrease in the product E_0W_0 as the CVD process progressed (Figure 1) indicates that the accessibility of the pores was limited by formation of constrictions on the micropore mouths or walls. A 3.6% of CVD reduces the volume of the narrower mesopores and the wider micropores, accessible to CDDT and CCl_4. After 5% of CVD the sample showed little microporosity accesible to molecules larger than 5.4 Å. The deposition of 8% carbon produced samples with microporosity ranging between 3.3 and 4.1 Å, showing molecular sieve properties. The sample obtained by deposition of 10% of carbon had an insignificant volume of micropores with a diameter greater than 3.3 Å.
Materials with a narrow micropore size distribution between 4.1 and 5.4 Å (Figure 2) and volumes of micropores between 0.20-0.25 $cm^3.g^{-1}$ (Table 1) were obtained by 5% carbon deposition over activated Pumarabule and JastrzebieS, 6% over activated Jastrzebie and 2-3% over activated Tineo. An 8% carbon deposition over activated bituminous coals produces molecular sieves with a preferential micropore size distribution between 3.3 and 4.1 Å (Figure 3) and micropore volumes of 0.23 $cm^3.g^{-1}$(Table 1). Materials from high rank coal with a similar micropore size distribution showed a smaller amount of micropores accessible to dichlorometane.

Kinetics of O_2 and N_2 adsorption in samples with micropore size distribution between 3.3-5.4 Å are similar. Samples obtained by a higher degree of carbon deposition make it possible to separate O_2/N_2 (Figure 4) and CO_2/CH_4.

Conclusions

Deposition of carbon atoms by pyrolisis of benzene over activated carbons produces a gradual closing of micropores due to the formation of constrictions on their mouths and walls. As a result materials with a narrow micropore size distribution of around 3.5-5 Å can be obtained. Samples with micropore diameters smaller than 3.3 Å,. obtained by a higher degree of deposition, can separate O_2/N_2 and CO_2/CH_4.

References

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Table 1. Mesopore and micropore volumes obtained by the isothermes of CO_2 and benceno at 25°C in carbon molecular sieves with narrow micropore size distributions prepared by CVD over carbons activated to 20% burn-off.

		Micropore Volume (cm^3g^{-1})		Mesopore Volume (cm^3g^{-1})			
Coal	**CVD (%)**	**diameter d < 0,41 nm**	**diameter 0,41<d< 2 nm**	**diameter 2-3 nm**	**diameter 3-5 nm**	**diameter 5-10 nm**	**diameter 10-50 nm**
Pumarabule	**6**	0,038	0,178	0,011	0,006	0,005	0,018
Jastrzebie	**5**	0,046	0,183	0,009	0,007	0,004	0,016
JastrzebieS	**6**	0,037	0,199	0,016	0,005	0,005	0,007
Tineo	**3**	0,083	0,138	0,007	0,005	0,005	0,019
Pumarabule	**8**	0,159	0,112	0,005	0,002	0,001	0,010
Jastrzebie	**8**	0,150	0,077	0,003	0,002	0,002	0,016

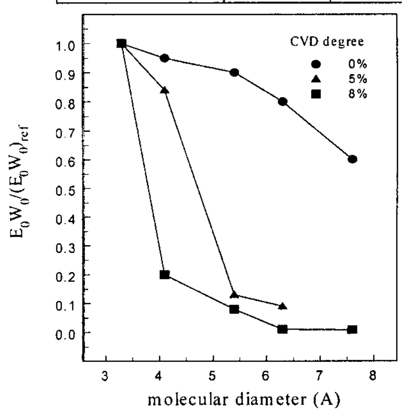

Figure 1. Micropore accesibility of Pumarabule samples

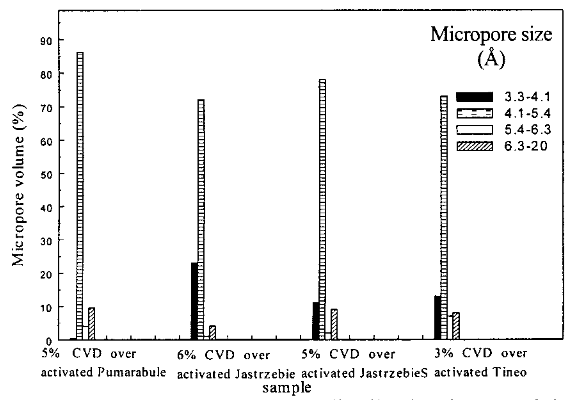

Figure 2. Micropore volume distribution in materials obtained by pyrolysis of benzene at 750°C over 20% activated carbons.

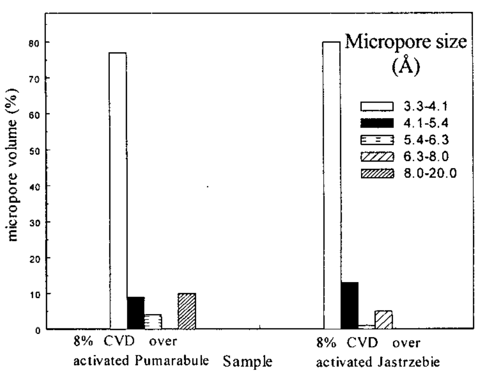

Figure 3. Micropore volume distribution in samples obtained by 8% CVD over 20% activated bituminous carbons

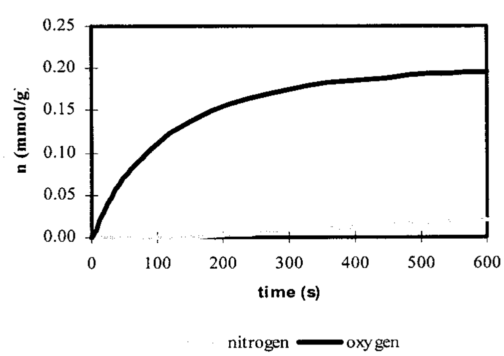

Figure 4. Kinetics of adsorption of nitrogen and oxygen in a CMS obtained by 10% CVD over 20% activated Pumarabule