Fibrous Carbon Molecular Sieves by Chemical Vapor Deposition of Benzene. Gas Separation Ability

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Activated carbon fibers (ACFs) prepared from highly ordered polymers, such as aramid fibers, have been proven to possess an outstanding homogeneity in pore size. Taking advantage of this feature, microporous carbon molecular sieves for separating gaseous mixtures such as CO_2/CH_4 and O_2/N_2 (air separation) have been prepared through chemical vapor deposition (CVD) of benzene on ACFs obtained from Nomex aramid fiber. Two batches of carbon fibers steam-activated to different burnoffs (BOs), namely, 21% and 42%, were subjected to CVD of benzene for different periods of time. The micropore size distribution of the resulting materials was assessed by immersion calorimetry into liquids of different molecular sizes (dichloromethane, benzene, and cyclohexane). Their validity for separating CO_2/CH_4 and O_2/N_2 was tested by performing the corresponding kinetics of adsorption experiments. Carbon molecular sieves with good selectivity for these two separations and showing acceptable adsorption capacities were obtained from ACFs activated to the two chosen BOs.

1. Introduction

Pressure swing adsorption (PSA) processes exploiting the distinctive textural features of carbon molecular sieves (CMSs) have found widespread application for gas purification and separation. Besides their use in air separation (O_2 from N_2),[1] CMSs are also employed in other separation processes such as CO_2 from CH_4 in the presence of H_2O, applicable for CH_4 sources with high concentrations of CO_2 and H_2O.[2]

CMSs are microporous carbon materials whose special textural characteristics enable kinetic separation of gas mixtures, i.e., separation as a result of differences in the diffusion rates of the species involved. For a CMS to be useful for gas separation, it must possess a narrow pore size distribution (PSD) consisting of pores or, to be more precise, pore mouths of molecular sizes and a relatively high micropore volume, features which confer them selectivity and capacity, respectively. Besides, it must show high adsorption and desorption absolute rates[3] as the performance for a PSA cycle designed for kinetic separation is usually optimal for cycles with short time duration.[4]

CMSs can be prepared from a broad variety of carbonaceous precursors through different methods. The development of the porosity of carbonaceous materials begins in the pyrolysis process, and a subsequent mild oxidation treatment (known as activation) enhances this development through the creation of new pores and the widening of the preexistent ones. If the precursor material is a polymer, the pore network developed is relatively uniform.[5] Thus, through pyrolysis or pyrolysis and activation to low burnoff (BO) degrees of polymeric materials, it is possible to interrupt the textural development when the narrowest pores have widths of the order of molecular diameters. This can be a valid method for the preparation of CMSs,[6,7] taking into account that the selectivity in these materials is determined by the predominance of pore mouths similar to the molecular widths of the species to be separated. The CMSs obtained through this method show in general high purity and relatively narrow PSDs. However, this method also has disadvantages. One of them is the usual low carbonization yield obtained for this type of precursor material, which can increase the costs of the process, making it not viable.[8] Another disadvantage is the low adsorption capacity that the resultant molecular sieves show in general. This last feature comes from the fact that BO must be low not to widen the mouth of the pores, which determines the selectivity of the porous solid; generally, the rest of the dimensions of the pore also remain in low values, bringing about low micropore volumes and, hence, low adsorption capacity.

An alternative method is the preparation of CMSs from activated carbons with high adsorption capacity to which selectivity is conferred through narrowing of the pore mouths by chemical vapor deposition (CVD) of

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an organic compound.[9-14] However, care must be taken in the choice of the organic and the conditions of cracking so that pore mouths are narrowed without major losses in adsorption capacity.[9] Moreover, some kind of homogeneity is desirable in the pore network of the activated carbon precursor. If its PSD is too wide, the carbon deposit could merely cause a continuous shrinkage of pores of all sizes, therefore simply shifting the distribution downward to a smaller average pore size without achieving the uniform pore size required for good selectivity.[14]

Activated carbon fibers (ACFs) derived from Nomex polyaramid fibers have attracted interest in recent years due to their outstanding homogeneity in pore width.[15-20] The general conclusion is that the development of the porosity in these materials takes place mainly through creation of narrow micropores, the resulting materials having outstandingly narrow PSDs, even at high BOs. This suggested that the pyrolyzed material and the fibers activated to low BOs could be directly useful for gas separation, whereas those activated to higher BOs, which still contain relatively narrow micropores with a narrow PSD, could be good precursors through CVD treatments.[20] Indeed, CMSs of fibrous nature have been recognized as the best type of adsorbent for PSA applications[12] because of their high adsorption—desorption rate and ease of handling. The already mentioned drawback of high costs when polymeric materials are used as precursors could be overcome in this case by using low-value byproducts of Nomex fiber fabrication as raw material,[17] most of all, when the carbonization yields are high in this case.[21,22] As regards the usual problem with low micropore volumes for CMSs made through carbonization of polymers, those obtained for the Nomex pyrolyzed material and the samples activated to low BOs are comparable to the ones given in the literature for commercial and noncommercial CMS materials,[23,24] so they could be acceptable in principle from the point of view of capacity. However, a direct evaluation of the separation ability of these materials is still lacking.

The present investigation deals with the evaluation of the separation ability for the gas mixtures O_2/N_2 and CO_2/CH_4 of the Nomex-derived pyrolyzed material and ACFs as well as the preparation, characterization, and testing of CMSs obtained from them through CVD treatment. The textural characterization of the latter has been carried out through immersion calorimetry with probes of various molecular dimensions. Kinetics of adsorption of O_2, N_2, CO_2, and CH_4 have been assessed to investigate the selectivity and capacity of these materials in O_2/N_2 and CO_2/CH_4 separations. The results are of interest in connection with the possible application of Nomex-derived carbonaceous materials as CMSs, but also in the field of ACF application in general as, to our knowledge, there are few reports of successful preparation of ACF-based CMSs useful for air separation.[13]

2. Experimental Section

ACFs coming from pyrolysis and activation to two different BOs (21% and 42%) of a variety of Nomex polyaramid fiber [poly(*m*-phenyleneisophthalamide)] known as crystalline Nomex (T450 2.2 dtex.) were used as precursors. Several batches of each of them were prepared to have the necessary amount for further treatments made in this work. Detailed information about the preparation and characterization of these materials is given elsewhere.[20]

CVD treatments were carried out in a tubular quartz reactor. The samples ($\sim$1 g) were heated at 10 K min^{-1} up to 1023 K under an Ar flow of 50 mL min^{-1}. At that temperature, a gas flow of 163 mL min^{-1} with a 2.3% C_6H_6 concentration by volume in Ar was introduced into the reactor during different periods of time to deposit different amounts of carbon. After this, the samples were cooled to room temperature in an Ar flow of 50 mL min^{-1}. Samples prepared in this way will be referred to as BO-*t*, where BO will indicate the BO (%) of the precursor material (either 21% or 42%) and *t* will specify the period of time (in minutes) of the CVD treatment.

The textural characterization of the materials was accomplished by immersion calorimetry measurements carried out at 298 K in a Tian-Calvet differential microcalorimeter (Setaram, model C80D). Liquids of different molecular sizes, namely, dichloromethane, benzene, and cyclohexane (Merck, analytical grade), were used as molecular probes. Prior to the experiments, the samples ($\sim$0.1 g) were outgassed overnight under vacuum at 523 K. The experimental procedure to determine immersion enthalpies has been described elsewhere.[25] The accessible surface areas of the samples were calculated from immersion calorimetry data by the method proposed by Denoyel et al.,[26] using Vulcan 3 ($S_{BET} = 82$ m^2 g^{-1}) as reference material.

Separation ability properties of the samples for the gas mixtures O_2/N_2 and CO_2/CH_4 were tested from the adsorption kinetics of these gases at 298 $\pm$ 0.1 K. They have been determined gravimetrically in a CI Electronics vacuum microbalance with a sensitivity of 10^{-7} g. Prior to every adsorption experiment, the samples ($\sim$0.05 g) were degassed overnight at 523 K after a vacuum better than 1 $\times$ 10^{-6} bar was reached. After the samples were cooled under vacuum, the gas was admitted into the system to a pressure of 1 $\pm$ 0.01 bar. The experimental results have been corrected for buoyancy effects.[27]

3. Results and Discussion

Immersion Calorimetry Results. Table 1 shows the experimental immersion enthalpy of the two series

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Table 1. Experimental Enthalpies of Immersion of the Two Series of Samples into Different Liquids at 298 K

	$-\Delta H_{imm}$ (J g^{-1})		
sample	CH_2Cl_2	C_6H_6	C_6H_{12}
21-120	120.6	101.3	18.7
21-150	110.6	20.6	7.7
21-180	93.6	13.3	5.3
21-210	101.5	9.5	2.6
42-30	128.1	114.0	102.3
42-150	102.1	17.6	5.7
42-240	94.7	13.0	7.0
42-270	88.8	13.6	8.5

Table 2. Specific Surface Areas Derived from the Experimental Enthalpies of Immersion at 298 K into Different Liquids

	specific surface area (m^2 g^{-1})		
sample	CH_2Cl_2	C_6H_6	C_6H_{12}
pyrolyzed	338	100	96
21	918	1116	787
21-120	899	923	189
21-150	825	188	78
21-180	698	121	52
21-210	756	87	27
42	1029	1337	1038
42-30	955	1039	1035
42-150	761	161	58
42-240	706	119	70
42-270	662	124	86

of samples studied in this work. For each of the three solvents, the expected decrease in the absolute value of the immersion enthalpy as the time of carbon deposition increases is observed within each series; i.e., the accessibility to the microporous texture diminishes as the amount of deposited carbon increases. Certain irregularities found might be due to some heterogeneity in the activated carbon fiber precursors introduced by their preparation in different batches. In general, the bigger the probe molecule, the more pronounced the diminution in the absolute value of the immersion enthalpy for both series; i.e., while the values for dichloromethane remain in the same order of magnitude throughout the treatment, those for benzene and cyclohexane fall significantly with increasing CVD time.

The derived accessible surface areas can be seen in Table 2 where data for the samples not subjected to CVD, i.e., the pyrolyzed carbon fiber and the two activated carbon fiber precursors,[20] have been added for comparison. As regards these materials, prepared in previous work, the surfaces for all the solvents follow the same trend as adsorption capacity, pyrolyzed sample < sample 21 < sample 42; i.e., the surfaces accessible to all the probe molecules increase with BO, as the pore development through activation brings about further adsorption. Differences in the PSDs can be inferred from the comparison of the ratios of the surfaces for each sample for the different solvents, these also indicating the order in average pore width, pyrolyzed sample < sample 21 < sample 42 (for example, comparing samples 42 and 21, the ratios of the surfaces are 1029/918 (dichloromethane) < 1337/1116 (benzene) < 1038/787 (cyclohexane)). Thus, the development of the porosity takes place through widening of the micropores though it has been shown that this only occurs to a certain extent.[20]

It must be noted how the CVD treatment affects the largest pore size range of the PSD. The most significant

changes are evidenced in the surface areas accessible to the biggest molecules. This can be ascertained by comparing the values for the ratios of the surfaces for each solvent among themselves. While the ratio for the surface areas calculated from dichloromethane immersion for samples 21 and 21-180 has a value around 1.3, the corresponding ratios for benzene and cyclohexane surfaces are 9.2 and 10, respectively. The same happens with samples 42 and 42-150, the ratios being 1.5 (dichloromethane), 11.2 (benzene), and 14.8 (cyclohexane). Thus, whereas the surface area accessible to the smallest molecule is rather maintained, the surface areas accessible to the bigger ones decrease by an order of magnitude. This suggests that the CVD treatment in these conditions succeeds in narrowing the mouths of the pores to restrict the entrance of the bigger molecules, putting forward higher selectivity while preserving a good capacity, which is reflected in the admittance of dichloromethane.

The use of a fiber activated to a higher BO as starting material does not seem to introduce any advantage. Introducing selectivity through the CVD treatment by diminishing the surface area accessible to the biggest molecules (benzene, cyclohexane) also decreases the surface area accessible to the smallest molecule (dichloromethane), loosing adsorption capacity. Besides, some lower limit is found in the value for surface area in cyclohexane for the fibers activated to the highest BO (while the surface area for cyclohexane steadily diminishes from 787 to 27 m^2 g^{-1} in the series prepared from sample 21, for samples 42-150 through 42-270, it fluctuates around 60–90 m^2 g^{-1}).

Adsorption Kinetics. Figure 1 shows the pure gas adsorption kinetic curves for CO_2, CH_4, O_2, and N_2 at 298 K on selected samples. The initial 30 s period of time is not included because it does not yield reliable data due to the finite interval required to flush the gas into the system and to stabilize the balance after the rapid weight change.

The textural characterization of the pyrolyzed material[20] suggested that it could be a good molecular sieve for gas separations, both from the point of view of selectivity and from that of capacity. The validity of this material for the CO_2/CH_4 separation is apparent from these graphs (Figure 1a). However, selectivities are greater for the CVD-treated samples (Figure 1b,c) as CH_4 uptakes are not appreciable in the first minutes of adsorption, especially for sample 42-150. Figure 1d shows that long CVD treatments put forward further selectivity in both separations so that neither N_2 nor CH_4 uptakes are observed in the first 10 min on sample 42-270. But, on the other hand, too long carbon deposition times bring about drastic losses in the capacity for O_2 (compare parts a–c with part d), which would be unacceptable from a practical point of view.[11]

Table 3 shows parameters for CO_2/CH_4 and O_2/N_2 separations deduced from the adsorption kinetics experiments on the two series of samples studied in this work as well as on the pyrolyzed material. A commercial CMS—Takeda 3A—used for air separation has been tested under the same conditions in our laboratory for comparison. The selectivities for CO_2/CH_4 and O_2/N_2 separations have been defined here as the ratio of the uptakes for the corresponding gases at 2 min, and the
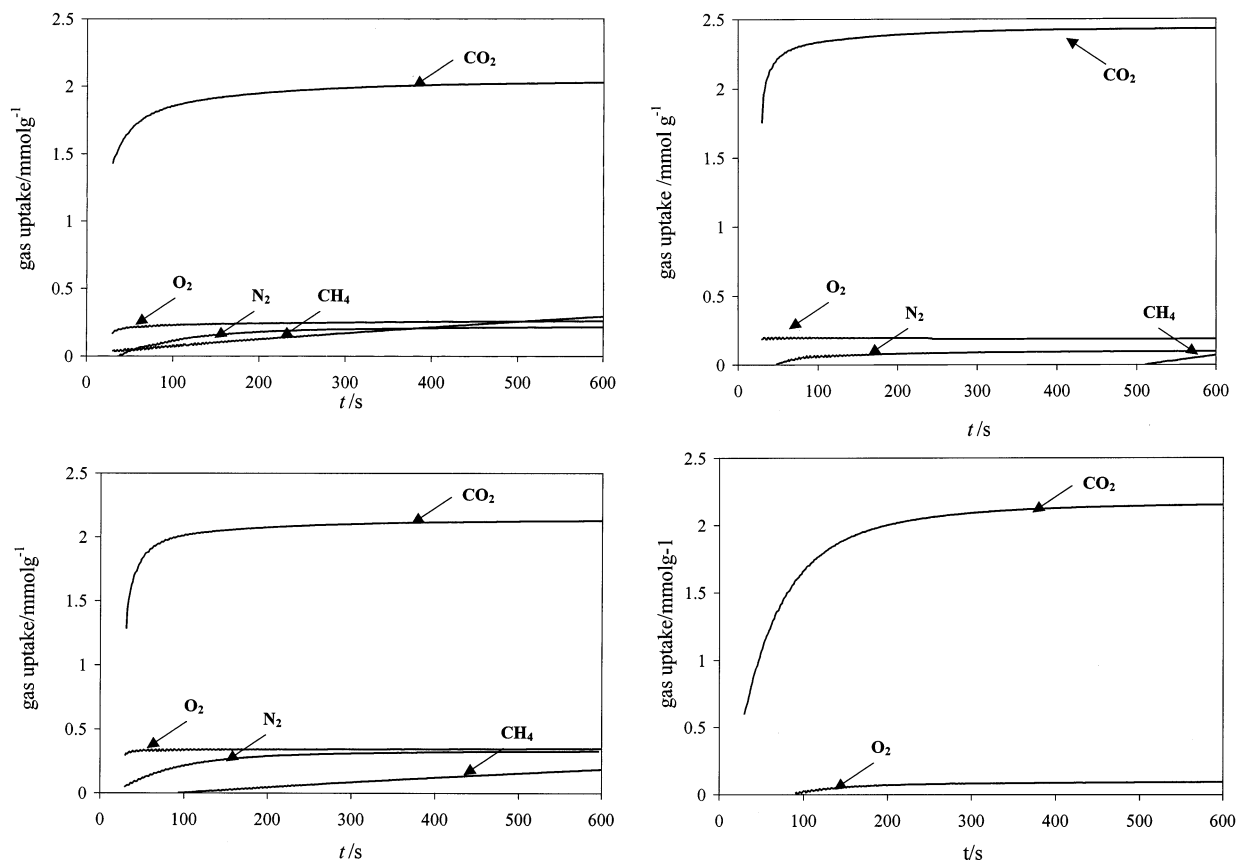
Figure 1. Adsorption kinetics of CO_2, CH_4, O_2, and N_2 at 298 K on the samples (a, top left) pyrolyzed material, (b, top right) 21-150, (c, bottom left) 42-150, and (d, bottom right) 42-270. Initial pressure 1 bar.

Table 3. CO_2/CH_4 and O_2/N_2 Selectivities (s) as Well as CO_2 and O_2 Capacities (c) on the Samples 2 min after the Admission of Gas in the System in Adsorption Kinetics Experiments[a]

	$s(CO_2/CH_4)$	c_{CO_2} (mmol g^{-1})	$s(O_2/N_2)$	c_{O_2} (mmol g^{-1})
Takeda 3A	149.2	1.68	5.5	0.32
pyrolyzed	29.4	1.87	1.8	0.22
21	2.5	2.38	~1	0.23
21-120	2.2	2.36	~1	0.36
21-150	∞[b]	2.34	4.5	0.24
21-180	∞[b]	2.12	∞[b]	0.26
21-210	∞[b]	2.16	∞[b]	0.37
42	2.2	2.43	1.8	0.26
42-30	2.4	2.83	1.2	0.29
42-150	919.6	2.03	1.4	0.32
42-240	∞[b]	1.94	6.8	0.40
42-270	∞[b]	1.77	∞[b]	0.03

[a] The commercial carbon molecular sieve Takeda 3A is included for comparison. [b] Adsorption of CH_4 or N_2 is not detected at this time.

capacities are given by the amounts of CO_2 and O_2 adsorbed in the same period of time following the same criterion as Kawabuchi et al.[12] This definition of capacity has been chosen instead of the equilibrium capacities in the experimental conditions as being more appropriate given the short duration of the PSA cycles[4] and the fact that O_2 and N_2 show close values for their boiling and critical temperatures and similar kinetic diameters; the equilibrium uptakes for these two gases on any carbonaceous material under specific conditions should be similar.

The task of obtaining a CMS good for CO_2/CH_4 separation is not as difficult as that of achieving one for the pair O_2/N_2. The difference in kinetic diameter between the pair O_2/N_2 being 1 order of magnitude below that of the pair CO_2/CH_4, the O_2/N_2 separation performed by CMS is only kinetically favored whereas CO_2/CH_4 separation is helped by both kinetic and equilibrium factors. Thus, the requisite of a narrow PSD is not as critical for the latter separation: it suffices to have pores below a certain pore size. As can be ascertained from Table 3, the merely pyrolyzed sample is really more selective than the two activated samples (samples 21 and 42) for the CO_2/CH_4 separation but it does not possess a better selectivity for the O_2/N_2 couple. The CO_2 capacity for the pyrolyzed material is comparable to that of the commercial CMS Takeda 3A. However, its selectivity is worse.

As has been explained, the two ACFs prepared at 21% and 42% BO have been subjected to CVD to improve their selectivity. This improvement for both separations as the time of deposition increases can be observed within the two series of ACFs in Table 3. Good selectivities for CO_2/CH_4 separation are achieved in both series for samples subjected to CVD treatments longer than 150 min. Furthermore, the CO_2 uptakes are comparable (better than) to those obtained at similar times for the commercial CMS used in this work or those in other studies.[23] The aforementioned fact that CO_2/CH_4 separation is helped by both kinetic and equilibrium factors is reflected in the diminution of CO_2 capacity in the two series as longer times for CVD treatment are used. As the capacities for CO_2 and O_2 as defined in Table 3 are close to the equilibrium capacities, they diminish as the pore network becomes blocked. Comparing both series,

Table 4. CO₂, CH₄, O₂, and N₂ Kinetic Rate Constants (*k*) and Selectivities for CO₂/CH₄ and O₂/N₂ Calculated with the LDF Model for the Pyrolyzed Material and Selected CMSs Prepared through CVD of Nomex ACFs[a]

	$k \cdot \pi^2$ (s⁻¹)				$k \cdot \pi^2$ (s⁻¹)			
	CO₂	CH₄	$k(CO_2)/k(CH_4)$	e_{CO_2} (mmol g⁻¹)	O₂	N₂	$k(O_2)/k(N_2)$	e_{O_2} (mmol g⁻¹)
Takeda 3A	8.06×10^{-3}	4.56×10^{-4}	17.7	1.99	1.32×10^{-2}	9.76×10^{-4}	13.5	0.34
pyrolyzed	1.04×10^{-2}	3.77×10^{-4}	27.6	2.04	9.32×10^{-3}	4.41×10^{-3}	2.11	0.28
21-150	1.91×10^{-2}	$0 \ (t < 500 \ s)^b$	∞^b	2.43	6.62×10^{-3}	6.48×10^{-4}	9.79	0.25
21-180	9.1×10^{-3}	$0 \ (t < 600 \ s)^b$	∞^b	2.26	8.33×10^{-3}	$0 \ (t < 120 \ s)^b$	∞^b	0.28
21-210	8.59×10^{-3}	$0 \ (t < 600 \ s)^b$	∞^b	2.35	8.59×10^{-3}	$0 \ (t < 120 \ s)^b$	∞^b	0.41
42-150	1.53×10^{-2}	$0 \ (t < 100 \ s)^b$	∞^b	2.13	1.44×10^{-2}	4.35×10^{-3}	33.1	0.36
42-240	1.12×10^{-2}	$0 \ (t < 600 \ s)^b$	∞^b	2.06	1.66×10^{-2}	1.4×10^{-3}	11.8	0.42

[a] Equilibrium uptakes (*e*) for CO₂ and O₂ are also reported. The commercial carbon molecular sieve Takeda 3A is included for comparison.
[b] Adsorption of CH₄ or N₂ is not detected at this time.

with similar selectivities, the adsorption capacities for the samples in the series derived from the fiber activated to 42% BO are lower than those for the samples in the other series (compare, for example, samples 21-180 and 42-240).

The order in molecular sizes being CO₂ < O₂ < N₂ < CH₄, attaining selectivity for the O₂/N₂ separation implies possessing it for CO₂/CH₄, and therefore, longer CVD treatments are needed for that purpose. While 150 min of treatment is enough for imparting a good selectivity for the CO₂/CH₄ separation in both series, at least 180 min is necessary for a good value for the O₂/N₂ separation in the case of the series based on the fiber activated to 21% BO. Once again, comparing the selectivity and capacity of the samples under study with those of the commercial CMS Takeda 3A, samples 21-180, 21-210. and maybe 42-240 seem adequate for O₂/N₂ separation. Comparing both series, longer CVD treatments are needed for the samples derived from the fiber activated to higher BO to reach similar selectivities. Moreover, this is not achieved without a major loss in capacity for O₂ (compare samples 21-210 and 42-270). However, for samples with selectivities similar to that of Takeda 3A (21-150, 42-240), the capacities are larger for the material coming from the ACF activated to a higher burnoff.

Absolute adsorption rates, together with the capacity, define the overall efficiency of the PSA process.[3] For the most interesting samples, the adsorption kinetics of the different gases have been compared in terms of kinetic rate constants. These rate constants have been determined by fitting experimental curves to the linear driving force (LDF) mass-transfer kinetic model,[11] described by the following equation:

$$M_t / M_e = 1 - \exp(-kt)$$

where M_t is the mass uptake at time *t*, M_e is the mass uptake at equilibrium, and *k* is the kinetic rate constant. The rate constants *k* can be determined from the gradient of the graphs of $\ln(1 - M_t/M_e)$ versus time, and they are offered in Table 4, together with a complementary value for selectivity, calculated as the ratio of rate constants for each gas couple (note that this concept of selectivity differs from that established in Table 3). These calculations have also been performed on Takeda 3A for comparison.

Whether the adsorption kinetics follows a LDF model or not depends on the kinetic diameter of the adsorbate relative to the porosity of the porous material. When the rate-determining step is diffusion through the barrier at the pore entrance, the model is applicable,

but the adsorption kinetics is expected to deviate from this model when other factors become significant. Thus, the degree of fitting of the data to the LDF model gives an indication of the evolution of the porous texture of the samples. Table 4 does not show parameters for untreated ACFs as none of the studied adsorbates follow the LDF model because even the biggest molecule is admitted in the porosity of these materials without restricted diffusion problems. This is in agreement with other results in the literature.[28] As carbon deposition at the entrance of the pores takes place through CVD treatments, thereby introducing restricted diffusion, the adsorption kinetics of the adsorbates come about to fit the LDF model: the bigger the adsorbate, the better the fitting. Thus, graphs of $\ln(1 - M_t/M_e)$ versus time (not shown) are linear for methane, nitrogen, and oxygen in the materials with marked molecular sieve behavior (those shown in Table 4), while there is a curvature in the case of the smallest molecule (CO₂). As a matter of fact, carbon dioxide does not fit this model even for the samples treated for the longest periods. Reid et al.[29] found something similar for CO₂ adsorption on a commercial CMS. Nevertheless, the parameters calculated for CO₂ through the LDF model are included for comparison as an overall value for the adsorption kinetics.

The pyrolyzed sample would have a performance similar to that of Takeda 3A according to this criterion (high adsorption rate and selectivity). Besides, it has been shown that, from the point of view of capacity, the pyrolyzed material is good enough. The CMSs prepared through CVD treatments on ACFs also have acceptable adsorption rates, comparable to those of commercial CMSs. For all these reasons, these materials could be useful in both separations from an application point of view.

Finally, combining the results from immersion calorimetry and adsorption kinetics, one can conclude that good selectivity for the CO₂/CH₄ separation is achieved in both series when the surface for benzene (also for cyclohexane) drops significantly. While the two ACF precursors lead to a good CMS for the less difficult CO₂/CH₄ separation with comparable treatment times (samples 21-150 and 42-150), the one activated to 42% BO needs longer CVD treatment times than the one activated to 21% BO to attain a molecular sieve selective for the O₂/N₂ separation (compare samples 21-180 and 42-240, or samples 21-210 and 42-270). Moreover, such

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selectivity is not achieved without a major loss in capacity, already indicated by the lower surface for dichloromethane in the adsorption calorimetry results. The wider PSD of the sample activated to higher BO makes more difficult the task of closing the mouth of the pores to a precise size.

4. Conclusions

This is, to our knowledge, the first report on successful modification through CVD of benzene of ACFs to yield CMSs valid for air separation. CMSs prepared from Nomex-derived ACFs are found to be appropriate for CO_2/CH_4 and O_2/N_2 separations from the point of view of both selectivity and capacity. An intermediate BO of 21% is convenient for this purpose, a higher BO not introducing further improvements in the separation ability. Thus, the lower BO precursor would be preferable from a practical point of view as it provides better results and higher yields in the global activation−CVD process.

Immersion calorimetry has been proven to be a very valuable technique for following the evolution of CVD-treated ACFs. The information provided by immersion calorimetry about the textural evolution of the materials under study and their separation ability based on adsorption kinetics were found to be consistent with each other.

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