

The use of microcalorimetry to assess the size exclusion properties of carbon molecular sieves

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Abstract

Carbon molecular sieves (CMSs) for separating gaseous mixtures have been prepared through chemical vapour deposition (CVD) of benzene on activated carbon fibres (ACFs) obtained from Nomex aramid fibres. The effect of the CVD treatment on the porous texture of the ACFs has been followed by immersion calorimetry into liquids of different molecular sizes (dichloromethane, benzene and cyclohexane). Both the kinetics of the immersion process and the equilibrium immersion enthalpies have been studied. Besides, the derived specific surface areas accessible to the different liquids employed have been calculated. The results show that the carbon deposition has taken place mainly at the pore entrances and the CVD treatment has succeeded to introduce selectivity without a significant loss of capacity.

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1. Introduction

Carbon molecular sieves (CMSs) are a special type of microporous carbonaceous materials whose pore size distribution is so narrow as to discriminate between molecules of similar sizes. Due to this fact, these materials have found use as adsorbents for the industrial separation of gas mixtures (pressure swing adsorption [1]) and as catalyst supports [2] and porous membranes [3]. A relatively uniform pore size close to the minimal size required to adsorb the smallest species in the gas mixture results appropriate for gas separations. It is therefore fundamental that a proper characterization of the porosity of these adsorbents is made to ensure their successful synthesis and application. However, the characterization of microporosity is a difficult task, most of all in the case of very narrow microporosity [4], which corresponds to the pore size involved in the separation of most gas mixtures with practical interest.

Immersion calorimetry, using liquids with molecules of different sizes as probes, is able to provide a direct measure-

ment of the amount of pores with different widths. Since Denoyel et al. [5] first proposed a method to calculate specific surface areas of activated carbons from immersion calorimetry experiments, this technique has been successfully applied to the analysis of microporous carbon materials [6,7].

Nomex-derived activated carbon fibres (ACFs) have attracted interest in recent years due to their outstanding homogeneity in pore width. The general conclusion of the studies performed [8–14] was that the development of porosity upon activation in these materials takes place mainly through creation of narrow micropores. For these features, they have been proposed as potential CMSs. Indeed, previous work has shown that the materials prepared through chemical vapour deposition (CVD) of benzene on Nomex-based ACFs could have similar or better performance than that found for commercial CMSs in gas separations of practical importance such as CO₂/CH₄ and O₂/N₂ [15,16].

The CVD of an organic compound on an activated carbon has been successfully employed as a method for preparing CMSs [17–22]. Carbon deposit is performed on a material with high adsorption capacity to narrow its pore mouths and thus introduce selectivity in the adsorption processes.

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However, the starting material and the conditions of cracking must be carefully chosen so that carbon deposition takes place at pore mouths and not elsewhere in order to avoid major losses in adsorption capacity [19].

The aim of this work was to assess the usefulness of immersion calorimetry as a means to follow the evolution of porosity during the CVD process on Nomex-derived ACFs and to characterize the size exclusion properties of the derived CMSs. To this end, the kinetics of the immersion process as well as the immersion enthalpies and accessible surface areas for the different liquids have been studied in parallel and compared with each other for the various adsorbents prepared.

2. Experimental

Nomex-derived carbon fibres activated to two burn-off (BO) degrees, namely, 21 and 42% BO, were chosen to be modified through CVD of benzene. CVD treatments were carried out at 1023 K by flowing 163 ml min⁻¹ of argon with a 2.3% C₆H₆ concentration by volume over 1 g of sample during different periods of time to deposit different amounts of carbon. The 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* (if present) specifies the period of time (in minutes) of the CVD treatment. Detailed information about the preparation and characterization of these series of samples is given elsewhere [13–16].

The porous 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 (analytical grade, Merck), were used as molecular probes. Prior to the experiments, the samples (~0.1 g) were outgassed overnight under vacuum at 523 K. The experimental procedure to determine immersion enthalpies has been described elsewhere [23]. The accessible surface areas of the samples were calculated from immersion calorimetry data by the method proposed by Denoyel et al. [5], using Vulcan 3 ($S_{\text{BET}} = 82 \text{ m}^2 \text{ g}^{-1}$) as reference material.

3. Results and discussion

3.1. Kinetics of immersion

The experimental calorimetric curves for the different liquids and adsorbents were normalized to compare the kinetics of immersion, which correspond to the diffusion through the porous network of the material. The brittle ends of the cells were wide enough to avoid the introduction of further diffusion problems.

Two types of thermograms were found: (i) thermograms which exhibited a strong initial rise until the maximum is reached (at short times), and quickly dropped afterwards; (ii) thermograms where both the initial rise and the final cooling were slow and the maximum was reached at long times. The former type of thermogram is ascribable to a material whose porosity is accessible to the immersion liquid; the latter one to diffusion-restricted immersion, due to the similarity between the pore widths of the adsorbent and the molecular size of the liquid.

Fig. 1 shows the normalized experimental curves for the immersion into the three different liquids of the materials derived from the ACF activated to the lowest BO (21% BO). Only the sample CVD-treated for the shortest period of time, and just for the case of the smallest probe (CH₂Cl₂), lacked diffusion problems. The rest of the samples showed thermograms that reflected a certain difficulty for CH₂Cl₂ molecules to access to their porous network. For the molecular probes bigger in size, all the samples showed similar thermograms, which clearly reflected the existence of diffusion limitations, most of all in the case for the biggest probe molecule tested (C₆H₁₂). Therefore, the kinetics of the immersion process shows that CVD treatments introduce selectivity from the early stages of the CVD process.

The results for the series derived from the fibre activated to 42% BO (not shown) were similar, except from the fact that the sample CVD-treated for the shortest period of time (sample 42-30) lacks diffusion problems even for the biggest molecule. Thus, sample 42-30 shows the most accessible porosity of the CVD-treated ACFs. This material comes from the fibre activated to the highest BO, which showed a certain widening of microporosity [13,14], and it is apparent that the short CVD treatment (30 min) performed has barely modified the original porous network.

3.2. Immersion enthalpy and accessible surface areas

The experimental immersion enthalpies of the two series of adsorbents under study are given in Table 1. For each of

Table 1
Experimental enthalpies of immersion of the two series of samples into different liquids at 298 K

Samples	$-\Delta H_{\text{imm}}$ (J g ⁻¹)		
	CH ₂ Cl ₂	C ₆ H ₆	C ₆ H 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

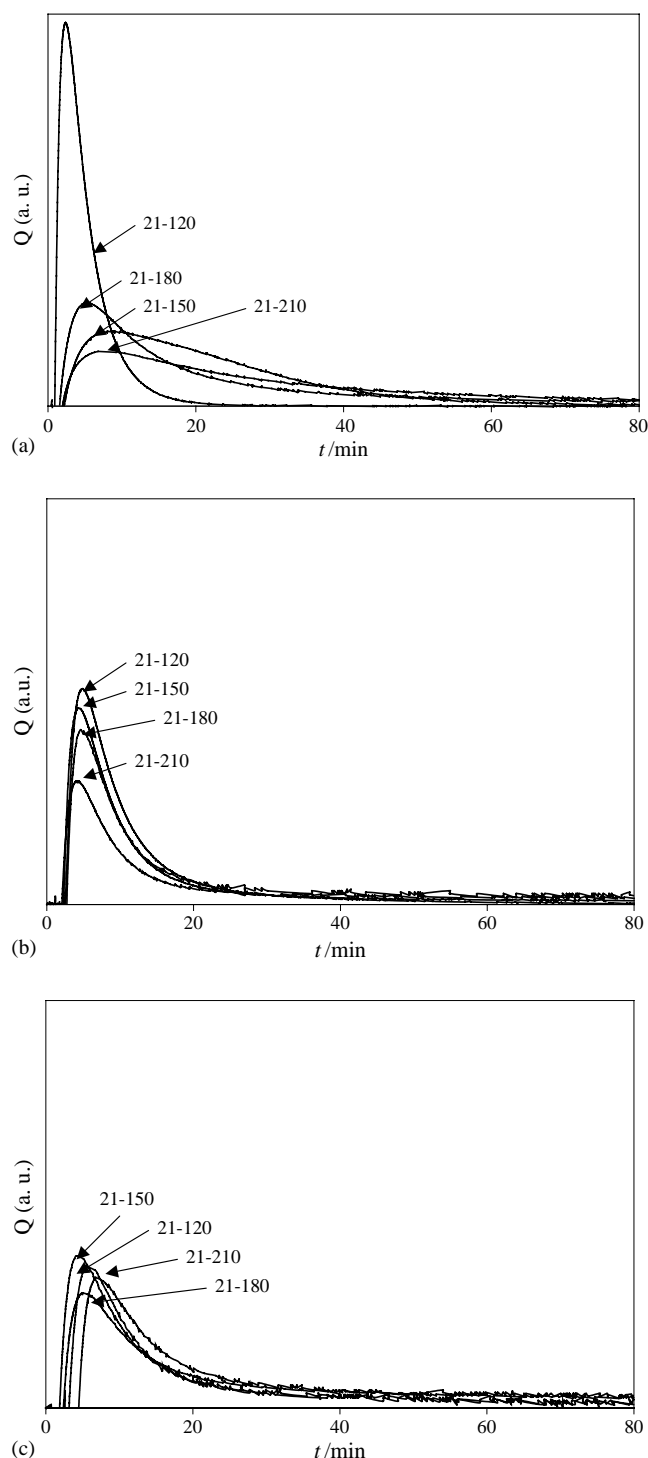


Fig. 1. Normalized kinetic experimental calorimetric curves for immersion into CH_2Cl_2 (a), C_6H_6 (b) and C_6H_{12} (c) of the series of materials derived from the fibre activated to 21% BO.

the three solvents a 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. However, the extent of this diminution

varies with the molecular size of the solvent. In general, the bigger the molecule, the more pronounced the decrease in the absolute value of immersion enthalpy for both series of materials. Certain irregularities found might be due to some heterogeneity in the activated carbon fibre precursors introduced by their preparation in different batches.

The evolution of the porosity of the materials under study during the CVD treatment can be followed with the help of Fig. 2, which shows the specific surface areas accessible to the different immersion liquids as a function of the duration of the CVD treatment for both series of materials. On the one hand, the surface areas accessible to the biggest probes (C_6H_6 and C_6H_{12}) drop to nearly zero as time of deposition increases. This indicates that the CVD process is able to narrow the pore mouth rendering the access of the biggest molecules difficult, thereby introducing selectivity. On the other hand, the surface areas accessible to the smallest molecule (CH_2Cl_2) are kept in the same order of magnitude. Therefore, the adsorption capacity for small molecules is preserved.

In summary, the calorimetric results confirm that the CVD treatments carried out in the conditions chosen modify the

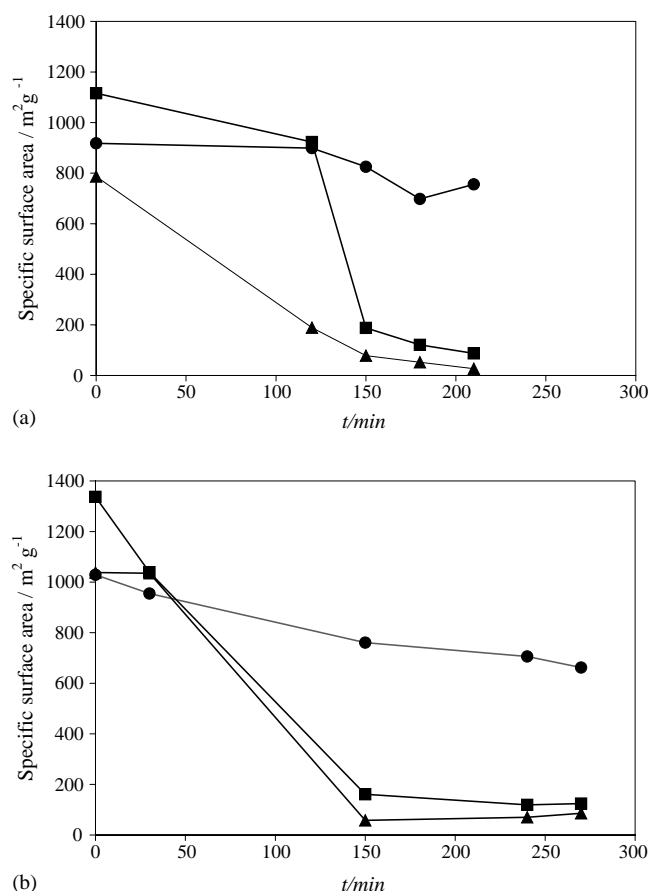


Fig. 2. Specific surface areas accessible to CH_2Cl_2 (circles), C_6H_6 (squares) and C_6H_{12} (triangles) for the samples derived from the fibre activated to 21% BO (a) and those prepared from the one activated to 42% BO (b).

ACF precursors in the desired way, i.e., introduction of selectivity and retention of adsorption capacity. It is thus apparent that carbon deposit has taken place mainly at pore entrances and not in the inner surface of pores. Kinetics of adsorption measurements for the CO₂/CH₄ and O₂/N₂ couples confirmed the good performance of these CMSs for the gas separations [15,16], constituting a further proof for the usefulness of immersion calorimetry to characterize the porosity in this type of materials.

4. Conclusions

Immersion calorimetry measurements has provided information about the size exclusion properties of the carbon adsorbents studied in this work both through the study of the kinetics of the experiment and through the assessment of immersion enthalpies and surface areas accessible to the different liquids employed. It has been shown that the CVD treatments have succeeded both to introduce adsorption selectivity for molecules of different sizes and to retain capacity for small molecules.

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