

USE OF PECVD TO PRODUCE HYDROPHOBIC CARBONS WITH CONTROLLABLE MOLECULAR GATE EFFECTS

R. H. Bradley, M. Falco, M. R. Davidson and J. McConnachie, Materials Research Centre, School of Engineering, The Robert Gordon University, Aberdeen, AB10 1FR, United Kingdom.

Abstract

Plasma enhanced chemical vapour deposition (PECVD) of silane or fluorocarbon precursors has been used to coat atomic/molecular clusters and nanoscale thin films onto the surfaces of a commercial granular active carbon. These treatments lead to materials with decreased enthalpies of immersion in water ($-h_i / \text{mJm}^{-2}$) and water adsorption isotherms which are displaced to higher relative pressures which indicate that the treated carbons are relatively hydrophobic. Nitrogen adsorption data measured at 77 K exhibit decreased micropore volumes compared to the untreated base carbon whereas data measured for hydrocarbon vapours at ambient temperatures show no such decreases. The data indicate that pore entry by nitrogen at low temperature is restricted in the PECVD materials most probably by the formation of constrictions at pore openings which act as kinetic energy gates which are controllable using the PECVD process parameters. The available open internal porosity remains largely unaffected and is accessible to the organic vapours at ambient temperatures. These materials are therefore of interest for a variety of selective adsorption and vapour enrichment applications and for adsorption uses in humid environments and for a range of biomedical applications.

Keywords: Active carbon, Water adsorption, Selective vapour adsorption, Vapour separation

Introduction

Activated carbons are characterised by high adsorptive capacity, most of which occurs in micropores ($<2\text{nm}$ width) and a high affinity for organic vapours. However, even though some control over the mean pore width of the materials may be possible by heat treatment and activation during manufacture, it is extremely difficult to produce materials with sufficiently defined adsorption properties to facilitate the controlled molecular separations required for ultrafiltration applications in, for example, hydrogen recovery, bioseparations, CO_2 sequestration and breathing apparatus. Further, although the surfaces of activated carbons are essentially non polar, making them hydrophobic, their adsorption properties are often strongly influenced by the presence of large amounts of adsorbed oxygen. This gives increased hydrophilicity and means that in use they adsorb water which leads to pore blocking and loss of filtration capacity. In practical applications this frequently means that the performance of the adsorbent toward a specific adsorptive is compromised. Ideally carbons which give adsorptive selectivity but which are also hydrophobic are required.

In this paper we present data for the adsorption of nitrogen and a small group of organic vapours by active carbons which have been modified using plasma enhanced chemical vapour deposition (PECVD) to selectively control adsorptive entry into the pore structure and to control the chemistry of the granule surfaces in order to influence adsorption and diffusion, particularly of water molecules.

Theoretical

Adsorption data for nitrogen and organic vapours have been analysed using the Dubinin-Radushkevich equation (Dubinin, 1989; 1947):

$$W = W_0 \exp[-(A / \beta E_0)^2] \quad [1]$$

where W is the volume of liquid like adsorbate within the pore structure at relative pressure p/p^s and W_0 is the micropore volume. $A = RT \ln p^s/p$ is the thermodynamic adsorption potential required to bring 1 mole of adsorptive to the state of the bulk liquid at the temperature, T . R is the gas constant and E_0 the characteristic adsorption energy which is a function of the adsorbent. β is the so called affinity coefficient which depends on the adsorptive. By convention $\beta(\text{C}_6\text{H}_6) = 1$. On the basis of molecular sieve experiments it has been shown that for active carbons the characteristic energy E_0 (KJ mol^{-1}) is related to the average width of the slit shaped micropores L/nm (Stoeckli, 1995) by:

$$L(nm) = 10.8/(E_0 - 11.4) \quad [2]$$

For slit shaped micropores as found in active carbons, the surface area of the pores is related to their volume and their width through:

$$S_{mi}(m^2 \cdot g^{-1}) = 2 \cdot 10^3 \cdot W_0(cm^3 \cdot g^{-1}) / L(nm) \quad [3]$$

Experimental

Plasma Enhanced Chemical Vapour Deposition (PECVD) has been used to modify the external surface chemical and energetic properties and the pore entrance characteristics of commercial granular active carbons (BPL is discussed here). The chemical vapour sources used were hexamethyl disiloxane (HMDSO) and perfluorohexane (PFH) at three levels of treatment 1, 5 and 10 minutes, which represent a small range of the final properties which can be achieved using this method.

The surface chemical composition of the base and treated BPL was studied using a Kratos Axis HSi 5 channel imaging X-ray photoelectron spectrometer using monochromated AlK_α radiation (energy 1486.6 eV). A Setaram/Calvet 80C calorimeter has been used to measure the heat of immersion data in water at room temperature (298K ±2).

Nitrogen isotherms were measured at 77 K in an automated volumetric gas adsorption apparatus (ASAP 2010) after outgassing for 22 hours at 353K. Adsorption isotherms for methanol, ethanol, propanol, carbon tetrachloride and toluene have been measured at 303 K using a Hiden/IGA gravimetric system after outgassing under similar conditions as above. Equilibrium adsorption for each point of p/p^s was defined from kinetic data such that no effective weight changes occurred.

Results And Discussion

The adsorption isotherm of nitrogen at 77 K on BPL and the three PECVD treated BPL samples give isotherms with Type I character although considerable positive slope is present in the higher pressure region of each plot indicating adsorption in wider micropores. As previously discussed in detail (Falco, 2006), analysis of the data using the Dubinin-Radushekevich equations leads to plots which are linear over much of the pressure range measured but which have an upward deviation at high values of relative pressure, or at low values of Ln²p^s/p. Table 1 contains the characteristic parameters from the D-R analysis of the data and also application of the BET equation over the p/p^s range 0.01-0.2. Most noticeable is that the micropore volumes (W₀) for the treated materials are 40 % smaller than the value obtained for the BPL base material and a decrease in both the BET surface area and the surface area in micropores (S_{mi}), derived using equation (3), is observed. The total pore volumes, obtained from N₂ adsorption at p/p^s=0.95 also show a slight decrease with treatment.

Table 1. Comparison of characteristic parameters from nitrogen adsorption at 77 K.

Sample	V _T [cm ³ /g]	W ₀ [cm ³ /g]	E ₀ [KJ/mol]	L [nm]	S _{mi} [m ² /g]	BET Surface Area [m ² /g]
BPL-0	0.46	0.40	20.47	1.19	674	1049
BPL-1	0.41	0.22	16.84	1.98	284	672
BPL-2	0.42	0.21	16.84	1.98	215	659
BPL-3	0.37	0.19	17.95	1.64	235	618

The characteristic adsorption energy E₀ for BPL modified carbons decreases in comparison to the BPL base carbon indicating adsorption in pores of higher average width (1.64—1.98 nm) as calculated using equation (2). This decrease in adsorption capacity can be attributable to the loss of adsorption capacity in the narrower supermicropores.

The isotherms for adsorption of organic vapours (alcohols, toluene and carbon tetrachloride) are also Type I and the D-R plots show positive curvature at higher pressures but also negative deviations at low relative pressures which are sometimes interpreted as being due to activated diffusion (Falco, 2006). A general feature of the alcohol isotherms is that, as previously reported (Bradley and Rand, 1987; 1991) the knee becomes tighter as the alkyl chain length increases causing a commensurate increase in the dispersion contribution to the adsorption force within the micropores in relation to the specific interaction of the hydroxyl group. This knee is even more pronounced in the isotherm for toluene adsorption where only dispersion forces occur and the D-R plots do not contain the Type A deviations.

The most interesting finding is that the adsorbed volumes derived from the isotherms for the organic vapours show only very small decreases in adsorption capacity, most noticeable for the adsorbates with the highest molecular size (Table 2) and, as previously reported, the corresponding E_0 and L values show that these small losses in porosity occur in the narrower supermicropore region so that adsorption is occurring mainly in supermicropores toward the top end of this size group (Table 3).

Table 2. Total (V) and micropore (W_0) volumes from organic vapours at 303K.

Carbon	Adsorption Volumes ($\text{cm}^3 \text{g}^{-1}$)							
	Methanol		Ethanol		Propanol		Toluene	
	V	W_0	V	W_0	V	W_0	V	W_0
Base	0.45	0.42	0.44	0.41	0.49	0.45	0.48	0.42
1	0.44	0.41	0.42	0.39	0.45	0.40	0.43	0.38
5	0.44	0.41	0.41	0.37	0.40	0.36	0.43	0.38
10	0.42	0.39	0.40	0.37	0.41	0.36	0.42	0.36

The data indicate that, in physical terms, the major effect of the PECVD modification occurs at the entrances of the pores where deposition results in constriction of their openings. This means that nitrogen at 77 K is excluded from volumes of otherwise open and unmodified porosity because it does not have sufficient kinetic energy to overcome the activation energy of diffusion through the constriction. Clearly the majority of the pore volume is unaffected by the modification as seen from the adsorption volumes from the alcohols, toluene and CCl_4 data (the latter not given here).

Table 3. Characteristic energies and micropore widths (L/nm) from alcohol and toluene adsorption data.

Carbon	Characteristic energies (kJ mol^{-1}) and micropore widths (nm)							
	Methanol		Ethanol		Propanol		Toluene	
	E_0	L	E_0	L	E_0	L	E_0	L
Base	18.47	1.52	18.78	1.46	17.11	1.89	22.12	1.00
1	16.87	1.97	17.50	1.76	17.11	1.89	22.12	1.00
5	16.87	1.97	17.26	1.84	18.74	1.47	20.99	1.12
10	16.42	2.14	16.94	1.94	19.09	1.40	21.76	1.04

In terms of hydrophilic/hydrophobic character, immersion calorimetry measurements show that the enthalpies of immersion in water ($-\Delta H_i \text{H}_2\text{O}$) decrease from -40.56 J g^{-1} for the base BPL to -15.51 , -17.20 and -12.06 J g^{-1} for the PECVD treated materials at the respective treatment times indicating that the treatment produces an increasing degree of hydrophobicity on the granule surfaces. This is confirmed by the water adsorption isotherms (Figure 1) which show that the HMDSO and PFH treated materials both adsorb less water than the base material.

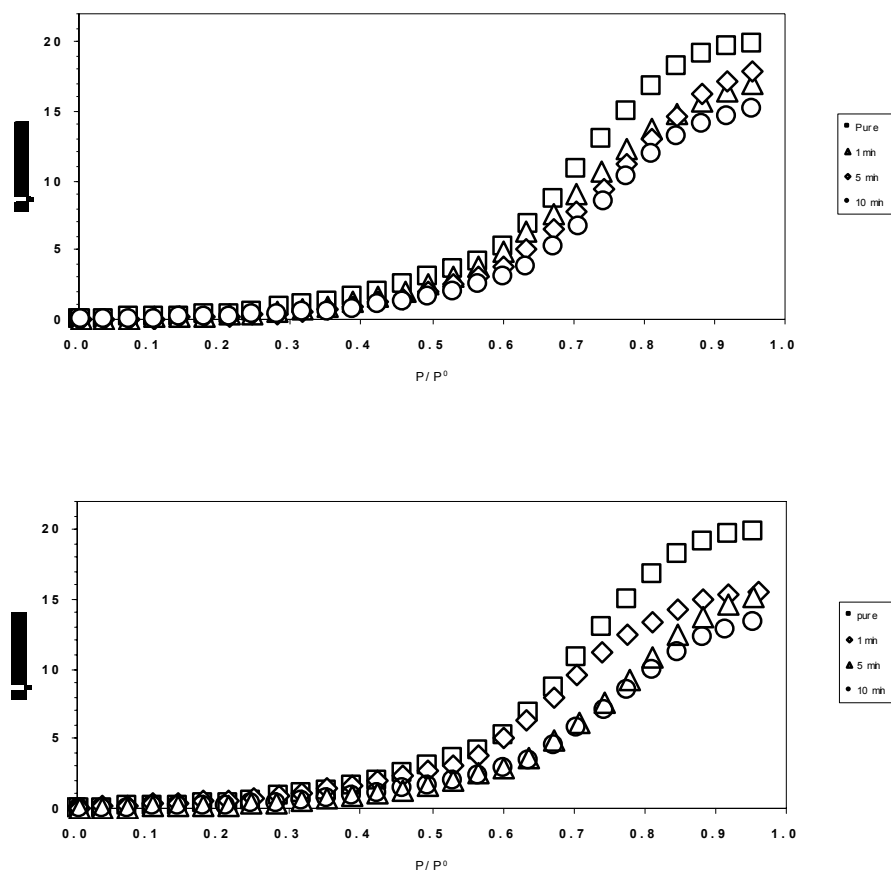


Figure 1. Water isotherms for BPL and BPL PECVD treatment times of 1, 5 and 10 mins with HMDSO (top) and PFH (bottom) showing the respective decreases in uptake as a function of treatment time.

Conclusions

The adsorptive properties of a PECVD modified granular active carbon (Pat.Appl. GB0114081.8) have been probed using the adsorption of N_2 at 77 K and organic vapours at 303 K. Total open pore volumes have been evaluated using standard liquid density data at T_{ads} and p/p^s 0.95 and W_0 values have been obtained using the Dubinin equation. The hydrophilic/hydrophobic character of the new materials has been investigated using water adsorption and immersion calorimetry.

PECVD treated carbons show no significant loss of adsorption capacity for the range of organic vapours tested, relative to the untreated base BPL carbon. However, a dramatic decrease in W_0 occurs when N_2 is the adsorptive indicating that the modification influences the pore entrances, probably by depositions which cause constrictions which act as kinetic energy ‘gates’ through which N_2 at 77 K cannot diffuse; the deposition process is highly controllable using the plasma process variables. This effect is not observed for the organic vapours at 303 K. The PECVD treatment offers a method of controlling pore entry as a function of adsorptive size but does not compromise the total internal pore volume available for adsorption.

Heats of immersion in water decrease from about 40 mJm^{-2} for the base carbon to $10\text{-}15 \text{ mJm}^{-2}$ for the treated materials indicating a marked increase in hydrophobicity which is confirmed by the water isotherms which show suppressed water adsorption for the treated carbons.

Acknowledgements

MF acknowledges the financial support of SFC and The Robert Gordon University, both authors acknowledge the help of Mr Aurik Andreu in preparing this manuscript.

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