

Carbon Fibre Monoliths: A study of water adsorption and Surface Chemistry

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Introduction

Active carbon granules and fibres possess a high degree of porosity and internal surface both of which can be used for fluid separation/purification applications. Selective adsorption with such materials can be achieved physically, by tailoring of the pore size distribution such that molecules are sifted according to size, or chemically by specific interactions at functional groups within the pore structure. The latter requires control of pore wall surface chemistry which also must be stable under the separation conditions used. It is also frequently desirable to present the filter material as a monolith or membrane for robustness and/or ease of handling. In this paper we present data for the surface chemical characterisation of a carbon fibre based monolith prepared at Oak Ridge National laboratory at 3 levels of burn off with and without additional oxidation

Experimental

The monolith materials were produced from a mix of pitch fibres and phenolic resin in an aqueous slurry drawn through a porous mould and the resulting material dried at 333K. This was then cured at 423K and carbonized at 923K. Samples were activated to 30.2, 50.3 and 56.8 wt.% burn-off at 1123K in Carbon Dioxide. Additional oxidation was carried out for two hours at 473K in Oxygen. Water adsorption isotherms were measured at 293 K using a Hiden IGA system after outgasing at either 378 K or 573 K.

Results and Discussion

The nitrogen adsorption data (Table 1) show that oxidation of the monolith leads to slightly increased adsorptivity at each burn-off value (Figure 1).

Sample	Oxidised	% Burn off	BET Area, m ² /g	DR Micropore Vol, cc/g	Mean DR Pore Width, nm
C1	No	50.3	1886	0.68	2.22
C2	Yes	50.3	2422	0.81	2.22
C3	No	56.8	2144	0.75	2.23
C4	Yes	56.8	2289	0.81	2.24
C5	No	30.2	1271	0.48	1.9
C6	Yes	30.2	1364	0.52	1.9
C7	No	0	99	0.03	1.7
C8	Yes	0	74	0.03	1.8

Table 1: Monolith Characterisation Data

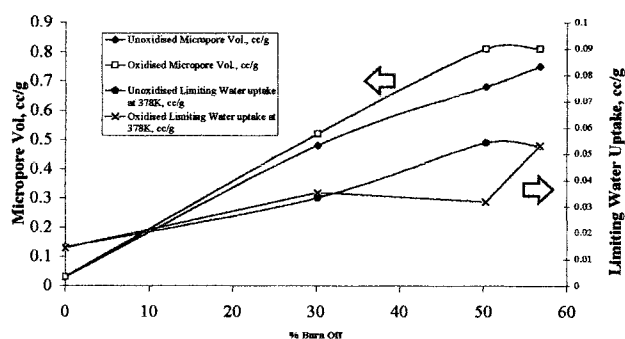


Figure 1: Variation of Micropore Vol. and Limiting Water uptake with activation.

Water isotherms measured at 293 K (Figure 2) give limiting values which follow the trend of increasing pore volume with burn-off observed for nitrogen but the water volumes adsorbed are significantly lower than those from nitrogen. There is also evidence in the isotherm data that low burn-off favours higher structural polarity whilst high burn-off leads to higher adsorption volumes but less carbon to support functional groups.

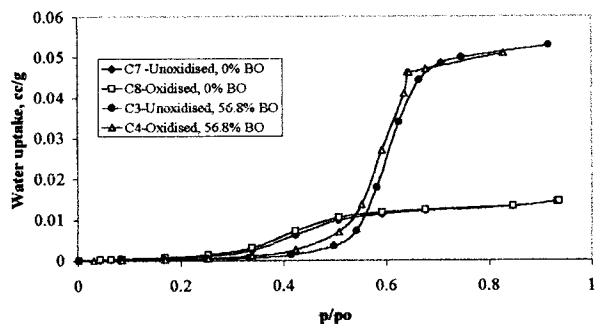


Figure 2: Comparison on the effect of Oxidation on the water adsorption isotherms for the unactivated and 56.8% BO samples (378K)

The chemical effects of oxidation are revealed by low pressure water adsorption data ($p/p_0 < 0.4$) which indicate that, at each burn-off value, the oxidised materials adsorb more water than the unoxidised i.e. the former are more polar due to the increase in chemisorbed oxygen (shown in Figure 3 for 0% and 56.8% burn-off).

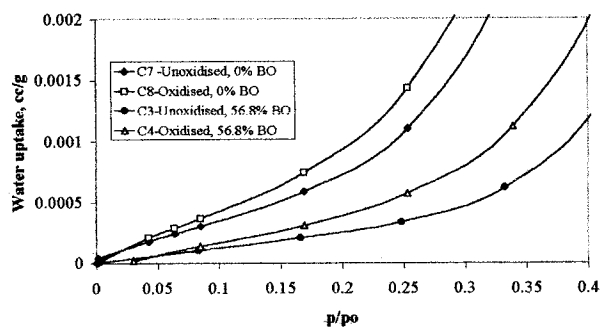


Figure 3: Comparison on the effect of Oxidation on the water adsorption Isotherms at low p/p_0 for the unactivated and 56.8% BO samples (378K).

Comparison of water isotherms measured at the different outgassing temperatures shows that the carbon surface chemistry is sensitive to the outgassing conditions (data not shown). Outgassing at 573 K makes the monolith more hydrophobic, due to the desorption of chemisorbed oxygen i.e. the primary water adsorption sites, than outgassing at 378 K. This

is also evident in heat of immersion data (ΔHi) shown in Figure 4 calculated using the method of Stoekli [2] which show that for each monolith sample the materials outgassed at 378 K have a higher ΔHi value than the corresponding material outgassed at 573 K. It is known from TPD studies that outgassing at temperatures < 573 K results primarily CO_2 evolution from the degradation of chemisorbed COOH groups. Outgassing temperature has no discernible effect on the limiting water adsorption volumes for these materials

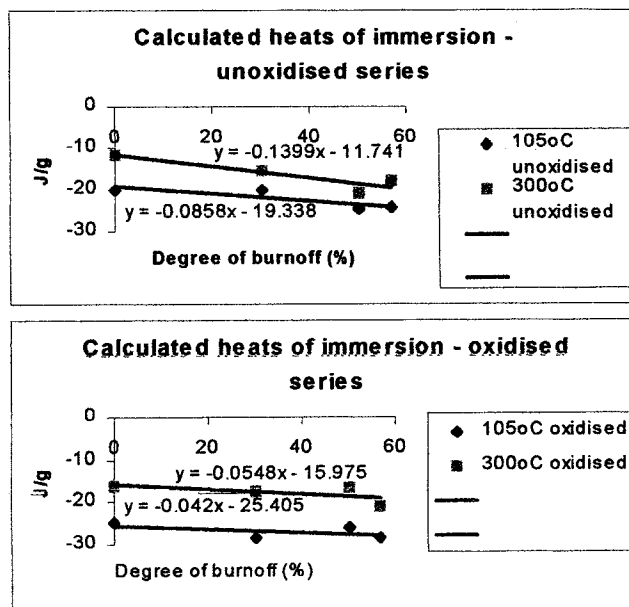


Figure 4: Calculated heats of Immersion for Unoxidised Samples (top) and Oxidised Samples (bottom).

Conclusions

Oxidation of the monoliths slightly increases nitrogen capacity at each burn-off. Oxidation also increases the levels of chemisorbed oxygen i.e. primary polar adsorption sites resulting in an increased ΔHi in water and also increased water adsorptivity at low relative pressures of water vapour. The chemisorbed oxygen is sensitive to outgassing temperature with structures outgassed at 378 K being more polar than those outgassed at 573 K. This is most likely due to the increased thermal desorption of COOH groups above 378 K.

References

- [1] Burchell TD, *et.al*, *Carbon*, **35**, 9, 1279-1294 (1997).
- [2] Stoekli F, *J.Chem. Soc. Faraday Trans.*, **19**, 24, 3689-3691 (1994).