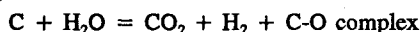# THE INFLUENCE OF SURFACE MODIFICATION OF BPL CARBONS ON AGING

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INTRODUCTION

The surface chemistry of an activated carbon is in many ways a dynamic characteristic which may be influenced by the method of storage. It is conceivable that exposure to atmospheric conditions could diminish the practical uses of the carbon by adding oxygen-containing functional groups to the carbon surface thus altering its adsorption properties. The oxidation of carbon at ambient temperatures in the presence of air and water has long been recognized and King [1] demonstrated the formation of oxalic acid. The oxidation reaction postulated in the literature by Pierce et al [2] was

$$C + H_2O = CO_2 + H_2 + C\text{-}O \text{ complex}$$

which was said to be dependant upon the reaction temperature. Two or more types of oxide complexes were later suggested, [3] the less stable decomposing to give CO_2 at low temperatures and a more stable complex decomposing at high temperatures with the evolution of CO. Indeed, accelerated aging of porous carbon, by exposure to 84% R.H. air for extended periods of time, results in an increased affinity for water vapour at lower relative humidities. Such a change in the general shape of the water vapour isotherm has been attributed to the creation of primary adsorption sites believed to be oxygen functional groups on the surface of the carbon. [4] [5] [6] A measure of these primary adsorption centres, designated a_o by Dubinin et al, [7] may be determined by a proposed extension of their isotherm model. [8] Accelerated aged, previously untreated, BPL carbons showed significant increases in the evolution of CO and CO_2 on thermal treatment, as well as an increased enthalpy of immersion in water, and also higher a_o values calculated from the modelled water isotherms. Samples stored in dry air and well sealed displayed no increase in thermally desorbable oxides and their water adsorption isotherms virtually overlapped isotherms determined months previously.

Treatment of the degassed carbon with Cl_2 or C_2H_4 at various temperatures may stabilize the surface thus diminishing the effects of high humidity aging on the adsorption properties. Aside from the simple physisorption of chlorine, the mechanisms of interaction of chlorine with the carbon surface involve the saturation of olefinic bonds, an exchange with chemisorbed hydrogen and dehydrohalogenation of the carbon to produce more olefinic bonds. [9]

Chemically treating carbon surfaces with various reagents, including ethylene, was studied by Schoderboeck et al [10] as a method of influencing microporosity. Although high temperature treatment resulted in a detrimental reduction of the surface area, infrared spectroscopy indicated a reduction in the population of alcohol functionalities on the surface and the disappearance of an IR active ketone band.

EXPERIMENTAL

Calgon BPL activated carbon was used throughout this study. The as received sample was washed, dried, and sieved to 16X20 mesh (US Standard) but otherwise untreated. The samples treated with either chlorine or ethylene gas were first evacuated at 110°C overnight in a stainless steel reaction vessel. The reaction vessel was enclosed in an oven at constant temperature for the duration of contact time of the gas with the carbon. Neither the heat of the reaction nor the change in temperature within the vessel were monitored. Chlorine treated carbon samples were washed with large quantities of methanol, some for a week in a soxhlet extractor, after which they were dried in air at 110°C. This extensive washing of the chlorinated carbons appeared to eliminate any reversibly held physisorbed chlorine from the samples. This was evident from desorption of the surface complexes to temperatures reaching 900°C. Chlorine was predominately released as HCl.

Ethylene treated samples were flushed with dry nitrogen and dried at 110°C. Portions of the treated carbons were sealed dry. To age, samples were place in a desiccator over saturated KBr solution delivering approximately 84% RH for an extended period of time. Laboratory temperatures varied from a low of 15°C to 30°C over the time period (up to 45 months). These samples were redried at 110°C after aging and before characterisation.

The apparatus for water adsorption and the temperature programmed desorption (TPD) procedure are both described elsewhere. [11] Nitrogen adsorption isotherms at -196°C were determined using a Micromeretics ASAP 2000 apparatus after evacuation of the samples at 110°C to $<7 \times 10^{-3}$ mbar. The nitrogen isotherms were fitted to both the BET equation [12] to determine surface area and the Dubinin-Radushkevich (D-R) equation to determine micropore volume [13] using 0.162 nm^2 for the area of a nitrogen molecule and 0.813 $g.mL^{-1}$ for the density of liquid nitrogen.

The enthalpy of immersion in water for the treated and aged samples was determined using a calorimeter also described elsewhere. [14]
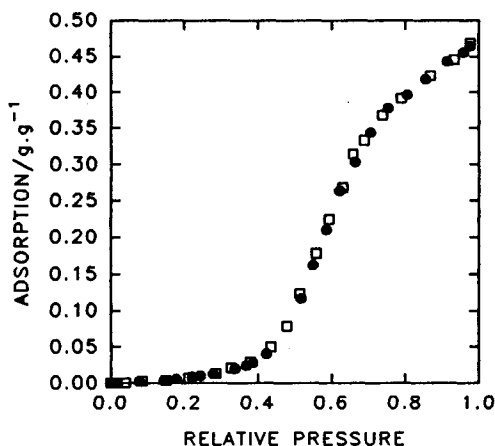

Figure 1 Water adsorption isotherms at 25°C on ● BPL (washed and dried) and □ BPL stored dry > 2 years.

RESULTS and DISCUSSION

Figure 1 shows the water adsorption isotherms at 25°C for the washed and dried BPL carbon and for the same carbon after dry storage at ambient temperatures for over two years. The water isotherms are almost identical, indicating little surface oxide change on dry storage over this time period. The calculated a_o values were 0.71 and 0.68 mmol.g^{-1} respectively. Adams et al report similar findings for samples stored sealed and dried for a period of 18 weeks. [15]

Figure 2 shows the water adsorption isotherms at 25°C on BPL carbon and on the same carbon aged for 45 months at 84% RH. The aged sample exhibits a greater affinity for water at low pressures indicating an increased concentration of primary sites on the surface. The aged carbon also showed a slightly lower adsorption capacity at high relative pressures.
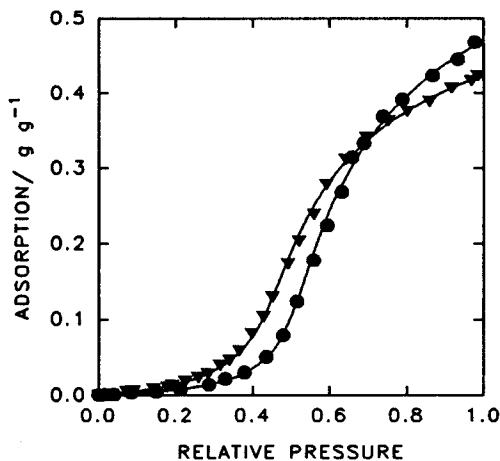

Figure 2 Water adsorption isotherms on BPL carbon at 25°C, ●, and the same sample aged 45 months at 84% RH, ▼.

TPD results on these two samples are shown in Figure 3 and indicate an increase in the measured amount of CO and CO_2 evolved from the aged sample (shown at the right in the figure) at each temperature up to 900°C when compared to the original sample. Similarly, the enthalpy of immersion in water for the aged sample increased to 58.3 J.g^{-1} from 47.2 J.g^{-1} for the unaged sample.
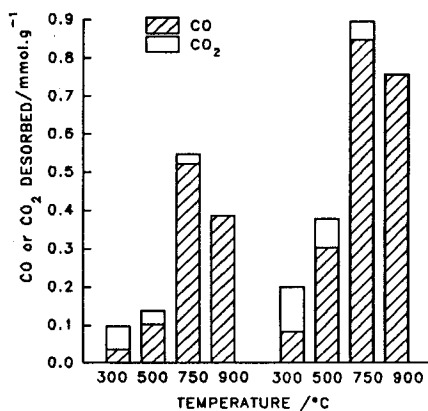

Figure 3 Temperature programmed desorption of surface oxides from BPL carbon (left side) and aged BPL carbon (right side).

Figure 4 shows the water adsorption isotherms for a sample of BPL carbon chlorinated at 170°C and for the same sample aged 11 weeks at 84% R.H. Admittedly, the aging of this sample was of a much shorter duration than the previous example, but no changes in the carbon were evident from the water adsorption isotherm or from TPD of the surface oxides. Preliminary studies on the ethylene treated BPL carbon indicate a higher susceptibility to similar aging.

No significant change in the measured surface areas from nitrogen adsorption measurements of the treated or aged samples was observed in this study.
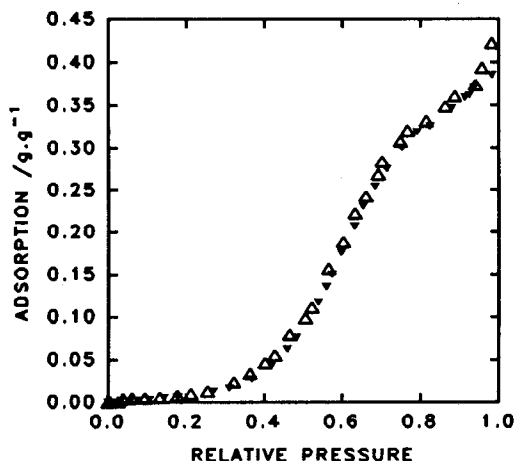

Figure 4 Water adsorption isotherms at 25°C on chlorinated BPL, ▲, and chlorinated BPL aged 11 weeks at 84% RH, ▼.

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