

# THE EFFECTS OF SURFACE FUNCTIONAL GROUPS ON THE ADSORPTION OF WATER VAPOR ON ACTIVATED CARBON

*Y. Uygur and K. M. Thomas*

*Northern Carbon Research Laboratories, Department of Chemistry, Bedson Building,  
University of Newcastle-upon-Tyne, Newcastle-upon-Tyne, NE1 7RU, U.K.*

## Introduction

The adsorption of environmentally unfriendly species from the atmosphere involves competitive adsorption between the target species and the oxygen, nitrogen and water vapor present in the atmosphere. The adsorption of water vapor on active carbons involves initial adsorption on surface functional groups followed by the development of clusters around the functional groups with eventual merging of the clusters leading to pore filling.<sup>1</sup> In this study the surface functional groups have been varied by chemical and heat treatment procedures. The effect of these procedures on the adsorption characteristics including the kinetics has been studied.

## Kinetic Model

Adsorption kinetics for water vapor adsorption usually follow a Linear Driving Force (L.D.F.) model,<sup>3-5</sup> which is described by:

$$M_t/M_e = 1 - e^{-kt} \quad (1)$$

where  $M_t$  is the uptake at time  $t$ ,  $M_e$  is the equilibrium uptake and  $k$  is the rate constant. The rate constant can be evaluated either from the gradient of a graph of  $\ln(1 - M_t/M_e)$  versus time or by fitting the  $M_t/M_e$  versus time graph to the above equation.

## Experimental

Carbon-G209, a coconut-based steam activated carbon (particle size fraction of 0.7-1.2mm) obtained from Pica, Vierzon, France and the following nomenclature was used for G209 subjected to the various chemical treatment procedures: Carbon starting material-Treatment procedure: 1) Reduction with red phosphorus and hydrogen iodide (G209-RPHI) 2) Chlorine at 400°C (G209-Cl<sub>2</sub>) 3) Nitric acid oxidation (G209-HNO<sub>3</sub>) 4) Hydrogen gas at 800°C (G209-H<sub>2</sub>) 5) Reduction with LiAlH<sub>4</sub> (G209-LiAlH<sub>4</sub>). Carbon G209-HNO<sub>3</sub> was heat treated to a range of sample temperatures up to 471°C at pressures of 10<sup>-7</sup> Pa, respectively. The porous structure was characterized by adsorption of nitrogen at 77K and carbon dioxide at 273K for each carbon sample. The water vapor adsorption measurements were carried out using the 'Intelligent Gravimetric Analyzer' (IGA) supplied by Hiden Analytical. The experimental procedure has been described previously<sup>3,4</sup>.

## Results and Discussion

As can be seen from CO<sub>2</sub> adsorption isotherms in Figure 1, N<sub>2</sub> adsorption isotherms in Figure 2 and Table 1, the microporous structure does not change with heat treatment but there are marked changes on the water vapor adsorption isotherms (Figure 3). The micropore volumes were very similar to each other with values between 0.25 and 0.26 cm<sup>3</sup>g<sup>-1</sup>. The total pore volumes are between 0.44 and 0.47 cm<sup>3</sup>g<sup>-1</sup>. The surface areas were between 663-677 m<sup>2</sup>g<sup>-1</sup>. The water pore volumes are lower than the total pore volumes for both the chemically and heat-treated carbons. This is ascribed to the inability of the water molecule to form a 3-dimensional structure in the pores. The chemically treated carbons have micropore volumes ranging between 0.24-0.43 cm<sup>3</sup>g<sup>-1</sup> and total pore volumes of 0.40-0.48 cm<sup>3</sup>g<sup>-1</sup>. Water pore volumes are less than the heat treated-samples with a maximum value of 0.41 cm<sup>3</sup>g<sup>-1</sup> for G209-HNO<sub>3</sub>. It is apparent that heat treatment has a negligible effect on pore structure but has a marked effect on the isotherms. Heat treatment results in a large loss of oxygen content which corresponds to loss in functional groups. The water vapor adsorption isotherms for the series of heat treated carbons are shown in Figure 3. All are Type V in the IUPAC classification scheme. The decrease in the amount of functional groups after each heat treatment shifts the isotherm to higher  $p/p^0$ . However, rate constants for the heat treated carbons show the same trend with respect to amount adsorbed expressed on a pore volume basis implying the rate constant is not markedly dependent on functional groups on the carbon surface. Figure 4 shows a graph of rate constant versus amount adsorbed (pore volume) for active carbons with modification of surface functional groups by both heat and chemical treatment procedures. The adsorption rate constants show similar trends with respect to amount adsorbed. Clearly, the extent of adsorption is the major factor in determining adsorption kinetics. The results show that modification of the functional groups by both chemical and heat treatment methods, alters the water vapor adsorption isotherms to a large extent without having a marked effect on the total pore volume. The large increase in oxygen content in G209-HNO<sub>3</sub> (21.9 wt% compared with 3.2 wt% in G209) shifts the isotherm towards lower  $p/p^0$  but the adsorption kinetics show the same trend with respect to relative pressure i.e. reaches a minimum rate around  $p/p^0 \sim 0.5$  with the rates having similar values for all chemically

modified carbons investigated. This may be reversed by heat treatment with the most marked change occurring for heat treatment up to 300°C. The rate constants for each pressure step for all the chemically modified and heat treated carbons when plotted against amount adsorbed can be represented with an experimental error by the same curve.

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## References

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## Acknowledgements

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Table: Gas/Vapor Characterization Data for Heat Treated Carbons

Samples	Pore volumes (cm <sup>3</sup> g <sup>-1</sup> )		Surface Area* (m <sup>2</sup> g <sup>-1</sup> )	Water/298 <sup>ρ</sup> (cm <sup>3</sup> g <sup>-1</sup> )
	CO <sub>2</sub> /273K <sup>α</sup>	N <sub>2</sub> /77K <sup>β</sup>		
250°C	0.258	0.438	677	0.426
350°C	0.255	0.449	668	0.396
400°C	0.254	0.457	665	0.399
450°C	0.253	0.459	663	0.400
505°C	0.255	0.471	669	0.402

\* Calculated from extrapolation of DR graph to p/p<sup>0</sup> = 1, using 1.87x10<sup>-19</sup> m<sup>2</sup> for area of CO<sub>2</sub> molecule

<sup>α</sup> Calculated from density of CO<sub>2</sub> = 1.023 gcm<sup>-3</sup> from extrapolation of DR graph to p/p<sup>0</sup>=1

<sup>β</sup> Calculated from density of N<sub>2</sub> = 0.8081 gcm<sup>-3</sup> from extrapolation isotherm to p/p<sup>0</sup>=1 using Langmuir equation.

<sup>ρ</sup> Calculated from density of water = 0.99707 gcm<sup>-3</sup> from extrapolation isotherm to p/p<sup>0</sup>=1.

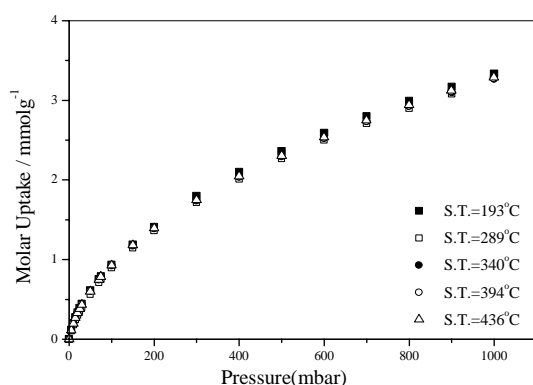


Figure 1: Carbon Dioxide Adsorption Isotherms of Heat Treated Carbons

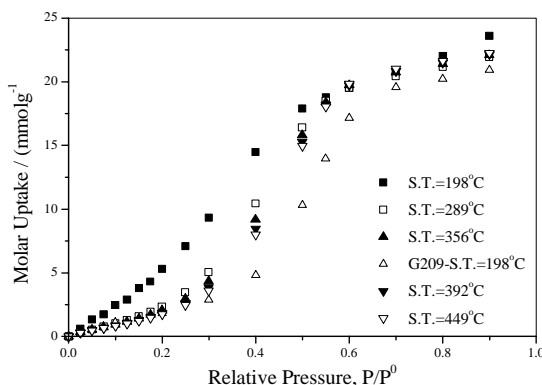


Figure 3: Water Vapour Adsorption Isotherms of Heat Treated Carbons

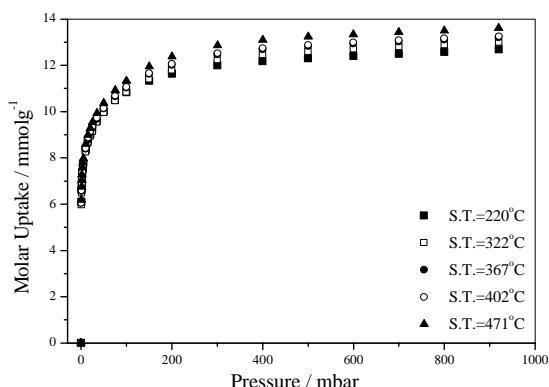


Figure 2: Nitrogen Adsorption Isotherms of Heat Treated Carbons

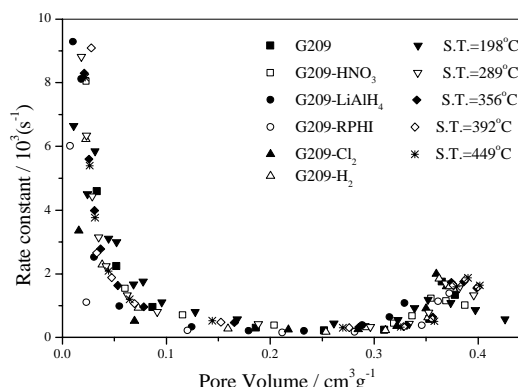


Figure 4: Variation in Rate Constant with Pore Volume for Chemically/Heat Treated Carbons