

THE ROLE OF ACTIVE SURFACE SITES IN THE EFFECTIVENESS OF MILITARY CARBON

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Introduction

The adsorption properties of current in-service single pass filters change on exposure to humid air, due to a process known as ageing. Research at CBD has demonstrated that modification of the carbon surface using a high temperature chlorination technique can reduce the detrimental effects of chemisorbed water on filter performance. However, basic data on the nature and role of the surface oxide sites, which are known to be preferential sites for water adsorption and hence likely sites for surface modification effects, is lacking. The aim of this work is to gain a better fundamental understanding of the nature of surface oxide sites present on carbon surfaces, and their role in adsorption process.

Experimental

Two model carbon substrates (Vulcan 3 and carbon black) were chosen and their surfaces were modified using a range of solution and gaseous phase oxidation techniques. The carbons were treated with carbon dioxide (150ml min^{-1} , 185°C , 2 hours), an equal carbon dioxide and nitrogen mixture (150 ml min^{-1} , 120°C , 2 hours) and air (1000ml min^{-1} , 185°C , 2 hours). Carbons were also treated with solutions of nitric acid (150ml of 8.625, 17.25, 34.5 or 69% w/w, 25°C , 2 hours), ammonium persulphate saturated in 1M HCl (150ml, 24 hours) and hydrogen peroxide (30% w/w, 150ml, 25°C , 24 hours). The modified carbon samples were characterised using the techniques discussed in the next section.

Results and Discussion

Nitrogen adsorption isotherms were analysed using the Brunnauer, Emmett and Teller (BET) equation in order to determine the surface area of the carbon samples. Figure 1 shows that any changes in surface chemistry of the carbon samples resulting from oxidation with nitric acid have been made without significantly affecting the textural properties of the carbons. The surface area of the ammonium persulphate and hydrogen peroxide treated carbons were also not affected.

Water adsorption isotherms were analysed using the Dubinin-Zhavarina equation [1] in order to obtain values of a_0 , the number of primary adsorption (oxide) sites on the surface of the carbons. Figure 2 shows that oxidation with a range of nitric acid concentrations has produced carbons with differing degrees of surface oxidation. It was not possible to calculate a_0 values for the oxidised carbon black samples because the small amounts of water adsorbed on these low surface area substrates prevented the measurement of meaningful water adsorption isotherms.

It has been demonstrated that there is a linear relationship between the total oxygen content of an oxidised carbon black and its heat of immersion in water [2]. Flow calorimetry, using heat of adsorption of n-butanol from n-heptane, has also been used to obtain a measure of the surface polarity of carbons [3]. This method has been found to be very sensitive to changes in surface chemistry [4] and was subsequently used in characterising the modified carbons. Figure 3 confirms that the experimental techniques employed, successfully produced two series of samples with different degrees of surface oxidation.

X-ray Photoelectron Spectroscopy analysis was used to determine the identity of the surface functionalities on the carbons. Only the C-O type functionalities found in either ether/hydroxyl groups were present on the base Vulcan 3 sample, whilst both C-O and carboxylic C=O functionalities were observed on the carbon black base. The room temperature oxidation reactions on the two carbons resulted in increases in both types of functional group. The data indicates that the two substrates clearly had different reactivities, which rendered them more susceptible to oxidation by different oxidising agents.

The thermal stability of surface complexes was assessed using TG/DSC. By varying the carrier flow from inert Helium to reducing Hydrogen (5%)/Helium gases the reduction of surface oxides on the carbon could be studied. This reduction was shown to occur between 400 and 650°C . Surface groups are thought to decompose producing CO_2 (ca. 200 - 600°C), CO (ca. 450 - 1000°C), water vapour and free hydrogen (ca. 500 - 1000°C).

Dynamic breakthrough profiles of hexane (RH 80%) through the modified carbons (Figure 4) were measured using Inverse Gas Chromatography (IGC). The breakthrough times of the nitric acid treated carbons decreased as the strength of the acid increased. This is thought to be due to the increase in the number of surface oxygen groups as a function of acid strength. This observation confirms previous work by Holmes [5] and Meech [6], who demonstrated that when adsorption took place in competition with water vapour, the adsorption of a non-polar vapour was determined by the rate at which water was displaced from the surface of the carbon. This work has shown that dynamic performance of carbon filters under humid conditions is ultimately dependent on the surface chemistry of the carbon.

Conclusions

A systematic series of active surfaces with different degrees of surface oxidation have been prepared for the two model carbons using a number of controlled oxidation techniques. The XPS analysis gave qualitative and quantitative information regarding the nature of the surface functional groups introduced from the oxidation techniques. An increase in surface oxygen functional groups resulted in a significant decrease in the adsorption performance of the carbons under humid conditions. Results show that the spatial location, strength of interaction, and availability of surface oxygen groups to adsorbate molecules play an important part in determining the dynamic adsorption performance of the carbons.

References

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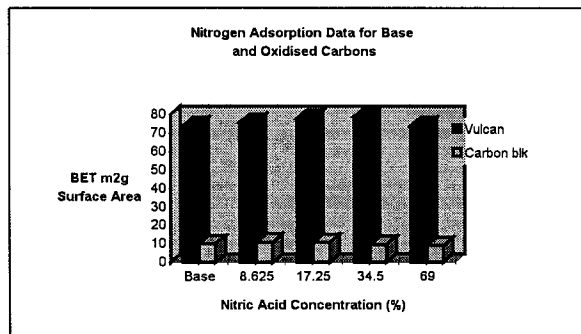


Figure 1

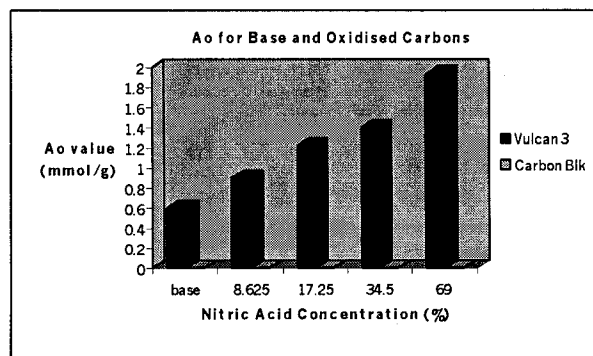


Figure 2

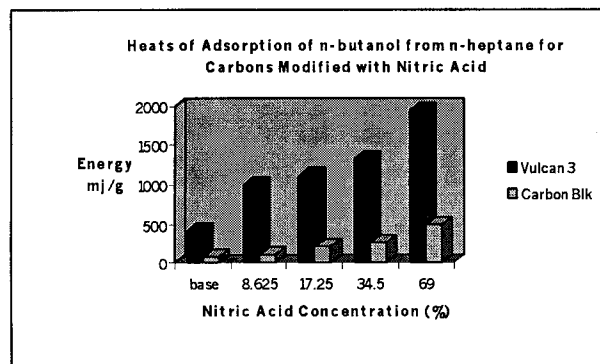


Figure 3

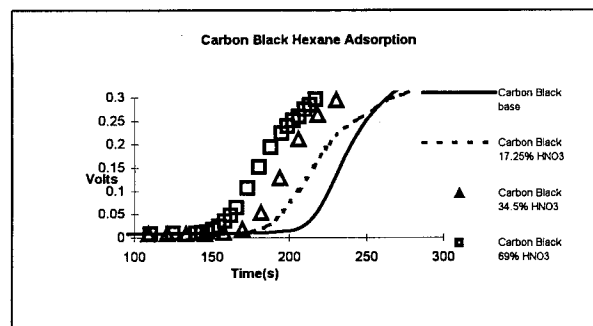


Figure 4