THE INFLUENCE OF HEAT TREATMENT TEMPERATURE ON THE INTERACTION OF PITCH- AND RESIN-BASED CARBONS WITH BROMINE

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Introduction

The interaction of bromine with carbon is mainly characterised by intercalation and surface adsorption. Studies of bromine intercalation in highly ordered graphitic carbons have been extensively reported [1-3]. In contrast, the interaction of bromine with carbons of a lower degree of structural order has not been so widely reported. This paper relates the uptake of bromine to structure by comparing the bromine vapour adsorption isotherms of both graphitising and non-graphitising carbons at various stages of their structural development.

Experimental

Samples of Ashland 'Aerocarb 80' petroleum pitch (graphitising) and Borden Cascophen P41 phenol formaldehyde resin (non-graphitising) were heat-treated at temperatures in the range from 600 to 2730 °C. The resulting carbons were characterised by gas adsorption (N_2 or Kr), helium pycnometry, XRD and elemental analysis (Table 1). For each sample, weight uptake of Br_2 vapour at 25 °C was measured over a range of partial pressures of bromine (P/P_o) using a McBain-type spring balance. Each carbon was also studied by raman spectroscopy, both in air and in a Br_2 vapour atmosphere.

Results and Discussion

Consider first the Br_2 isotherms for the pitch-based carbons (Figure 1). A wide variety of behaviour was observed. Despite having low surface areas and poorly ordered structures, the 600 °C and 750 °C samples both exhibited a very high uptake of Br_2, though the rate of uptake was very slow. Very different behaviour was observed for the 1200 °C sample; Br_2 uptake was minimal. At this heat treatment temperature much of the hydrogen and other heteroatoms, previously present in the structure, would have been removed. Further heat treatment to 1500 °C and 1750 °C resulted in incrementally higher levels of Br_2 uptake (~ 10 and 20 wt. %, respectively) as the structure of the carbon increased in order. At these higher temperatures of treatment the structure became more ordered. In addition, the carbons had higher surface areas, possibly due to the presence of defects arising from shrinkage and the evolution of volatile matter during treatment. A dramatic increase in the Br_2 uptake (~ 48 wt. %) was observed on heat treatment of the carbon to 2000 °C. There was strong evidence for the presence of a threshold pressure at $P/P_o = 0.6$. This feature, together with the appearance of a new (but poorly defined) peak at 1610 cm^{-1} in the raman spectra, indicated the onset of intercalation. Upon graphitisation at 2730 °C, X-ray diffraction revealed that the carbon structure had significantly increased in order. In this sample, the maximum Br_2 vapour uptake increased to ~ 72 wt. %; the shape of the resultant adsorption isotherm was characteristic of graphite-bromine intercalation. It was noted that the threshold pressure for intercalation to occur had reduced to $P/Po = 0.1$, which is typical for graphitic materials [1]. The raman spectrum was characterised by a decrease in size of the 1582 cm^{-1} 'g' peak and the presence of a well-defined 'intercalation peak' at a wavenumber of 1610 cm^{-1}.

The shapes of the Br_2 vapour isotherms for the non-graphitising carbons were typical of model adsorption behaviour. Weight uptake was rapid and most of the Br_2 was adsorbed onto the available surface at very low partial pressures. The 900 °C sample exhibited a relatively high Br_2 uptake (~ 74 wt. %), reflecting its large surface area. In contrast, the 2250 °C sample exhibited a very low Br_2 vapour uptake (~ 4 wt. %), reflecting the lower accessible surface area due to shrinkage and the closing of porosity on heat treatment.

Figure 2 illustrates a plot of the maximum weight per cent of bromine vapour uptake versus the stack height (L_c) for all of the carbons described above. There is a clear trend in behaviour which is a complex function of the degree of order in the structure.

Conclusions

In the graphitising carbon series, the low temperature treated samples exhibited low surface areas and poor structural order. Interaction of bromine with these materials was probably dominated by various interactions with hydrogen and other heteroatoms and surface groups. With higher temperatures of treatment, these species were removed and the material became more carbonaceous. Bromine vapour uptake was then minimal, as the structure was not ordered sufficiently to facilitate intercalation. Higher temperatures of heat treatment resulted in higher

degrees of structural order and slightly higher values of surface area. The degree of bromine uptake thus gradually increased with heat treatment temperature, due to surface adsorption and the onset of intercalation. Eventually, bromine uptake by intercalation was dominant and behaviour was similar to that of natural and synthetic graphite. In the non-graphitising carbons, the weight uptake was dominated by surface adsorption on the available surface area.

References

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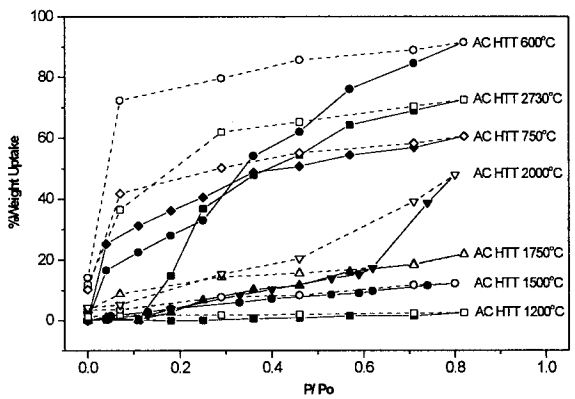

Figure 1. Bromine adsorption / desorption isotherms for the Aerocarb 80 graphitising carbon series at 25°C.

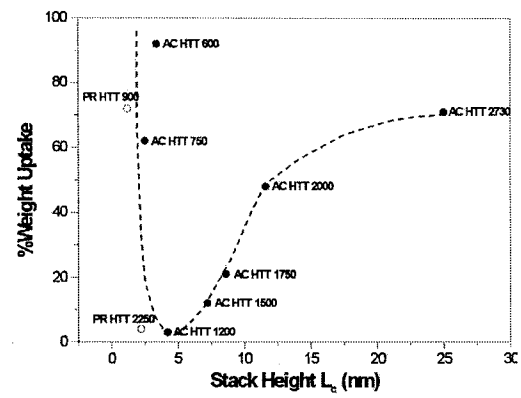

Figure 2. The variation in the maximum percentage weight uptake of bromine vapour versus layer stack height (L_c)

Table 1. Characterisation data for carbon samples prior to bromination

Sample	Elemental Analysis		X-Ray Diffraction			Physical Properties	
	C (%)	H (%)	d_{002} (nm)	L_c (nm)	L_a (nm)	He Density (gcm^{-3})	Surface Area (m^2g^{-1})
Aerocarb 80 Heat Treatment Series (Graphitising)							
AC HTT 600 °C	91.70	2.40	0.358	3.4	2.8	1.54	1.19
AC HTT 750 °C	93.45	1.55	0.356	2.5	4.2	1.80	0.88
AC HTT 1200 °C	98.65	-	0.353	4.2	4.2	2.06	2.05
AC HTT 1500 °C	98.75	-	0.348	7.2	12.4	2.06	2.12
AC HTT 1750 °C	100.1	-	0.345	8.6	6.4	2.15	5.06
AC HTT 2000 °C	99.80	-	0.342	11.6	27.1	2.18	4.27
AC HTT 2730 °C	100.6	-	0.339	25.0	49.3	2.29	6.96
Phenolic Resin Heat Treatment Series (Non-graphitising)							
PR HTT 900 °C	86.40	1.75	0.363	2.2	-	-	467
PR HTT 2250 °C	100.1	-	0.394	1.2	-	-	0.60