SELECTIVE ADSORPTION OF PLATINUM AND MERCURY COMPOUNDS ON GRAPHITIC CARBONS

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Introduction

It is now realised that strong adsorption of transition metal compounds on catalyst supports, such as alumina and graphitic carbons can lead to metals being highly dispersed on these supports after the adsorbed metals are reduced at high temperatures to their metallic state (1). Recent work by the author established that compounds such as chloroplatinates and mercury nitrate are strongly adsorbed on the graphitic basal plane and are likely therefore to become especially effective catalysts after the reducing treatments (2). Most active carbons contain a high proportion of graphitic basal plane surface, but also contain significant amounts of polar groups which could act as adsorption centres for the metal compounds. It was decided therefore to investigate the adsorption of potassium chloroplatinate on graphitized carbon blacks in which there was only a negligible amount of polar sites compared with commercial active carbons. The adsorption of mercury nitrate was also investigated to establish whether there is any generality in the adsorption patterns of the heavy transition metal compounds on the graphitic carbons.

Experimental

The adsorptions and the heats of adsorption were determined in a new model of Microscal Flow Adsorption Microcalorimeter(FMC) which was recently described(3). All the reagents had purities exceeding 99% supplied by Aldrich Chemicals. Graphitized active carbons, supplied by Cabot Co. had BET N_2 surface area of 85 m^2/g (Graphon) and 70 m^2/g (V3G) respectively. Their polar surface areas were 0.20m^2/g and 0.14m^2/g respectively. The active carbon was a commercial material Chemviron BPL having a BET N_2 surface of 1000m^2/g and a polar surface area of 53.6m^2/g. The polar surface areas were determined microcalorimetrically (3)

Results and Discussion

Results obtained by the FMC are exemplified by Figure 1 showing graphical representation of the adsorption and desorption processes occurring on percolation of 1 milimolar K_2PtCl_6 solution through 0.0278 of Graphon powder mixed with 0.08g of PTFE. Heat evolutions due to adsorption/desorption are represented on the same time scale. It can be seen that some 90% of the adsorbed K_2PtCl_6 is retained by the adsorbent i.e. not eluted by water percolating through the adsorbent bed for 93 minutes. The total Pt adsorbed is 25.2$\mu m/g$. Therefore, each adsorbed molecule occupied 560 $Å^2$ which corresponds to about 10%

of the surface that would be occupied if a close-packed monolayer was formed on adsorption. However, the very small polar areas in graphitized carbons are insufficient to accommodate all the adsorbed Pt. The same applies to Hg adsorptions shown in Table 1. I conclude is that a proportion of graphitic basal planes is more active than the rest of that surface i.e. that the basal plane surface in the carbon is not homogenous. This is further confirmed by variations in the heats of adsorption in relation to surface coverage for the Pt and Hg compounds, as shown in Figures 2 and 3 respectively. Figure 2 also includes adsorptions on aluminium adsorbent which is often used as a support for Pt in catalysis. There is clearly a strong decrease in the heats of adsorption with increasing surface coverage for all the carbons.

For both Pt and Hg the adsorption on the graphitized carbons gives much higher heats of adsorption, for the same amount of adsorption per unit surface area, than the adsorptions on the active carbon - the adsorbent with 5% of its surface being constituted by its polar sites. It can be concluded therefore that the polar sites do not play an important role in the adsorption of the Pt and Hg compounds from aqueous solutions. In this context it is interesting to compare the heats of adsorption K_2PtCl_6 on alumina with those on carbons which had a surface area of 90m^2/g, i.e. close to that of Graphon. For surface coverages from 0 to 200mmol/m^2, the graphitized carbon gives very much higher heats of adsorption than alumina and may be expected, therefore, to produce catalysts with much higher degrees of dispersion than alumina. There is not too much difference between the active carbon and alumina suggesting that these two supports would give similar Pt dispersions and, consequently, less effective catalysts than the Pt adsorbed on the active basal plane sites of the graphitized carbons.

There are differences between V3G and Graphon. The adsorptions of K_2PtCl_6 and $Hg(NO_3)_2$ on V3G from 1 mmol solutions indicate that it contains a lower proportion of the total surface in the form of "active" basal planes than Graphon. It is also evident that saturation of the graphitic carbons with the dilute K_2PtCl_6 solutions produces extended heat evolution and downstream detector response suggesting decomposition of the adsorbate, especially on active carbon BPL.

References

1. M.C. Roman-Martinez, D.Casoria-Amoros, A.Linares-Solano, C. Salinas Martinez de Lecca H. Yamashita & M. Anpo, Carbon 13, 1995, pp 3-13
2. A.J. Groszek, Proc.of Carbon 92, Essen, June 22-26 1992, pp 278-280
3. A.J. Groszek & S.Partyka ,Langmuir, 9 1993 p2721-2725

Table 1

Adsorption of K_2PtCl_6 and $Hg(NO_3)_2$ from 1mmol Aqueous Solutions on Carbon Adsorbents at 20°C

Carbon	Adsorption/Desorption, mmol g-1			
	K_2PtCl_6		$Hg(NO_3)_2$	
	Ads	Des	Ads	Des
Graphon	25.2	2.3	20.3	1.5
V3G	14.0	2.8	8.2	0.4
AC BPL	743	472	176.4	41.4

Fig 1: Adsorption of K_2PtCl_6 from 1 mmol Solution in Water on 0.0278g of Graphon at 20°C

Calorimeter Monitoring - Graphical Output - Relative Data 43

Experiment Name: d172
Start Time: 120:00   Sample weight   Resolution time 4.000s
                    TITLE: Ads/KPtCl6/H2O   0.0278g   Stop Time: 320:40min

Heat of Adsorption 2.97 Jg⁻¹

Desorption − 0.52Jg⁻¹

Adsorption   25.2 μumol g⁻¹

Desorption   2.3 μumol g⁻¹
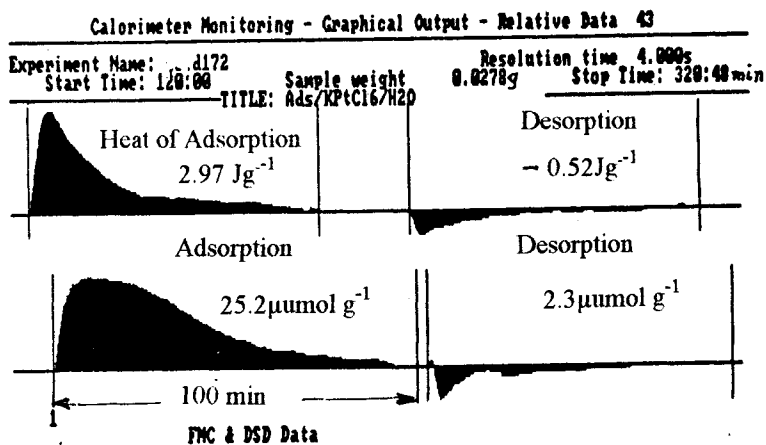
100 min

FMC & DSD Data

Fig. 3: Variation of Differntial Heats of Adsoprtion of $Hg(NO_3)_2$ with Surface Coverage

Graphon

V3G

Chemviron BPL

Differential Heat of Adsorption, mJ
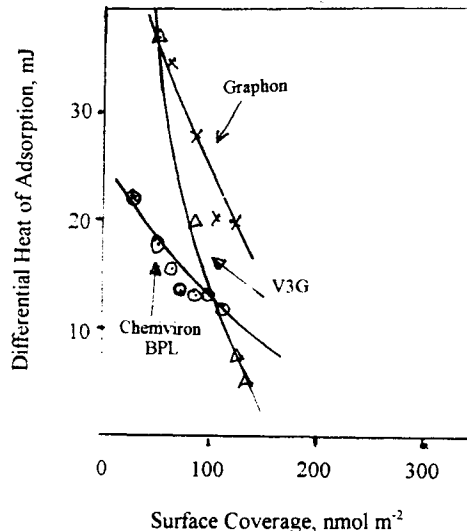
Surface Coverage, nmol m⁻²

Fig 2: Variation of Differential Heats of Adsorption of K_2PtCl_6 with Surface Coverage

Graphon

Alumina

CHEMVIRON BPL

Differential Heat of Adsorption, mJ

Surface Coverage nmol/m²

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