

# ENERGETIC HETEROGENEITY OF ACID AND BASIC SITES ON CARBON ADSORBENTS

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## Introduction

For most graphitic carbons large proportions of the surface are the graphitic basal planes, which are hydrophobic. The edge sites are, however, invariably combined with oxygen and are hydrophilic. As is well known, some of the functional groups responsible for the polarity of the carbons may have acidic or basic properties.

A method for the determination of total polar surface area in carbons has been developed by the author and is based on the preferential adsorption of butanol from a dilute solution in *n*-heptane [1]. This abstract describes methods based on preferential adsorption of ammonia from water which is assumed to occur only on the acidic surface sites.

Similarly the preferential adsorption of HCl has been used to measure the basic surface sites. In both cases the adsorption is determined on the adsorbents immersed in water using 0.05 molar solutions which are capable of forming an adsorbed monolayer on the acidic and / or basic surface sites. The preferential adsorption of gaseous ammonia from a nitrogen carrier was also investigated and the results compared with the adsorption from water.

## Experimental

The carbons investigated were commercial coal-based active carbon BPL, a coconut active carbon PICA210, and a peat-based NORIT carbon. The adsorption from nitrogen was measured only on carbon BPL.

Microscal flow adsorption microcalorimeters were used to measure simultaneously the adsorption and the heats of adsorption – an FMC-4014 for adsorption from water, and an FMC-4110 for adsorption from nitrogen. These instruments and their uses have been fully described [2].

## Results and Discussion

The results of adsorption of ammonia from nitrogen and water solutions are given in Tables 1 and 2. Figure 1 shows typical results obtained on adsorption of 5% NH<sub>3</sub> from a pure N<sub>2</sub> carrier.

In all the cases the first adsorption cycle produced higher heat of adsorption than the subsequent adsorption cycles, which were largely reversible. The irreversible adsorption occurred during the first cycle.

For carbon BPL the molar heats plotted against surface coverage peak at about 150 kJ mol<sup>-1</sup>, a value that approaches closely the heat of adsorption on acidic Zeolites.

Active carbons BPL, PICA210, and NORIT produce irreversible adsorption of HCl and high heats of adsorption, but the amounts of the strongly basic sites are different for each carbon – as shown in Table 2.

The distribution of strongly basic sites display a characteristic profile for each carbon. The acidity / basicity profiles are expected to be strongly correlated with the specific catalytic properties of the carbons and their application as selective adsorbents in gaseous and liquid environments.

## Conclusions

Cyclic flow adsorption microcalorimetry can be used to provide differential molar heats of irreversible adsorption of acidic or basic probes. High differential heats of the probes indicate the presence of strong basic or acid sites on the adsorbents. Changes of the values of the heats of adsorption with the amount of adsorbed probe is characteristic for each carbon adsorbent and can be used to predict its catalytic activity.

Kinetics of the preferential probe adsorption from selected carriers are obtained directly from the flow experiments and can be used to evaluate the efficiency of selective adsorption processes.

## References

- [1] Groszek AJ. Selective adsorption at graphite / hydrocarbon interfaces. Proc. Roy. Soc. Lond. 1970; A314; 473–498
- [2] Groszek AJ. Flow Adsorption microcalorimetry. Thermochemica Acta 1998;312;133–143

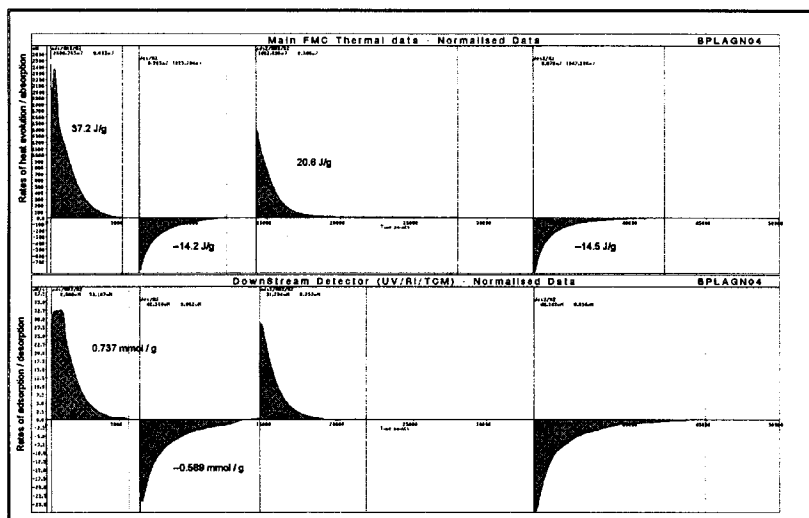
**Table 1.** Heats of adsorption / desorption of ammonia on active carbons from aqueous solution

Carbon	Heat of Interaction, J g <sup>-1</sup>		Reversibility %
	Adsorption	Desorption	
BPL	8.56	2.52	29.4
PICA210	6.8	5.4	80.6

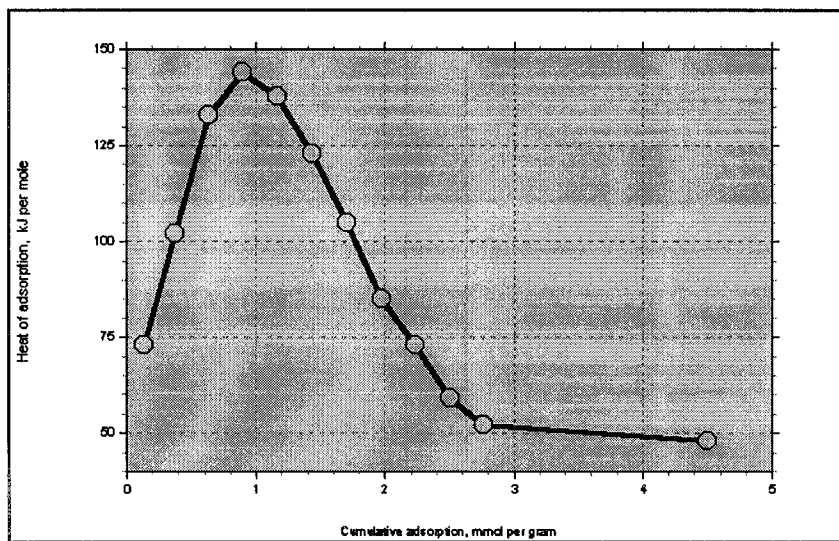
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**Table 2.** Heats of HCl interaction with active carbons  
Heat of Interaction, J g<sup>-1</sup>

Carbon	Heat of Interaction, J g <sup>-1</sup>		Reversibility %
	Adsorption	Desorption	
BPL	14.2	-5.2	36
PICA210	13.9	-1.4	10
NORIT	32.4	-4.4	14



**Figure 1** – Rates of heat evolution and adsorption of 5% NH<sub>3</sub> from N<sub>2</sub> carrier on 0.72 g of active carbon BPL  
The sample of carbon was mixed with 0.22 g of quartz sand to fill the volume of the adsorption cell



**Figure 2** – Heats of irreversible adsorption of NH<sub>3</sub> on carbon BPL