

The strength and accessibility of acid surface sites in carbons and a pillared clay

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1. INTRODUCTION

New techniques of flow adsorption microcalorimetry were applied recently to determine simultaneously the heats and the amounts of adsorption and of desorption of an acid probe from carrier fluids. The magnitudes of the differential heats of adsorption indicated the strength of adsorption of the probe on specific functional groups, and how it changes with increasing coverage of the adsorbent's surface. The rates of heat evolution and uptake of the probes pointed to the kinetics of the displacement of the carrier fluids from the functional groups, on which the probes were preferentially adsorbed.

The degree of reversibility of the interactions was determined by carrying out two adsorption / desorption cycles. The heats and the amounts of the reversibly adsorbed probes were then subtracted from the heats and the amounts obtained in the first adsorption cycle, the difference representing reversible adsorption. The resulting differential molar heats of adsorption could then be related to surface coverage by the probes. Similar work was recently published by the author for zeolites and for pillared clays [1, 2].

2. EXPERIMENTAL

The microcalorimeter used in this work and its method of operation was fully described previously [1, 2]. A typical series of results obtained is illustrated in Figure 1, showing two adsorption / desorption cycles of NH_3 adsorbed from N_2 on a carbon black at 150 °C. The progress of the NH_3 uptake during the first adsorption cycle for all the adsorbents is shown in Figure 2.

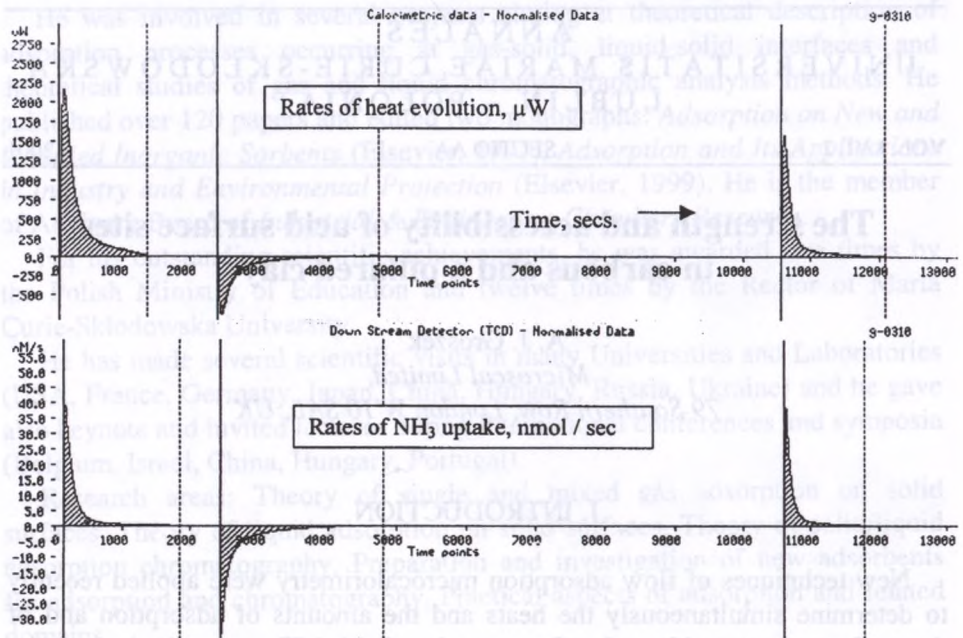


Fig. 1. The heats and amounts of adsorption of 5% vol. NH_3 / N_2 on 57 mg of DUKE CB determined concurrently by Flow Adsorption Microcalorimetry at 150 °C

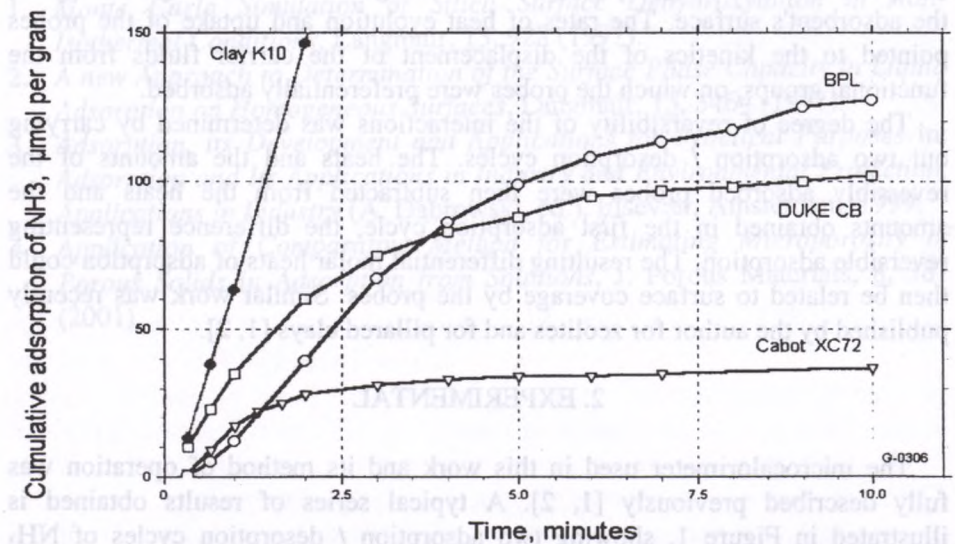


Fig. 2. The progress of NH_3 adsorption on carbons and a clay catalyst at 150 °C

The adsorbents used in this work are listed in Table 1. The interactions with the acidic sites were carried out using N_2 as the carrier, and a 5% vol. mixture

of NH_3 in N_2 as the probe. White-spot N_2 (99.9% pure) supplied by BOC was used as the carrier gas. The NH_3 / N_2 mixture was passed through the adsorbent at a constant rate of 1 cc per minute, containing 2.23 μmol of NH_3 per cc.

Tab. 1. Properties of the adsorbents used in these studies

Adsorbent type	Surface areas, m^2 per gram		
	BET(N_2)	Polar Sites	Accessible hydrophobic sites
Chemviron BPL	1000	56	145
Cabot XC72	221	21	59
DUKE CB	107	144	5.6
Cabot GRAPHON	85	0.14	85
Clay K10	279	270	0

**The polar and hydrophobic surface sites in the carbons have been determined by the Flow Adsorption Microcalorimetric methods described in [3, 4].

Any NH_3 that was not adsorbed passed directly to the thermal conductivity detector which monitored the concentration of the probe in the calorimeter's effluent. All of the experiments were carried out at 150 °C using a Mark 4Vms instrument, the FMCS 110.

3. RESULTS AND DISCUSSION

The two adsorption / desorption cycles shown in Figure 1 typify the results obtained for all of the adsorbents. The first peak represents a combination of reversible and irreversible adsorption. The irreversibly adsorbed NH_3 is not desorbed and therefore the second peak is smaller and represents predominantly reversible adsorption. The ratios of the heats and of the amounts of adsorption for the first and second cycles are different and reflect the reduction in the molar heats of adsorption after the retention of the irreversibly adsorbed NH_3 during the first cycle.

The heat evolution and the mass transfer peaks shown in Figure 1 represent the rates at which the heat of nitrogen displacement and the rate of the corresponding uptake of NH_3 take place as the NH_3 / N_2 mixture passes through the adsorbent bed in the calorimeter's cell. The shapes of the peaks are characteristic of each process and depend upon the accessibility of the adsorption sites, their strength, and their relative position on the surface of the adsorbent. For microporous adsorbents the acid site accessibility is an important factor. This aspect of the interaction of NH_3 with the acid sites can be

investigated by the determination of changes in the differential molar heats of adsorption as the surface of the adsorbent is saturated with NH_3 .

Slicing of the heat evolution and adsorption peaks' data produces heat evolution and NH_3 uptake occurring within any chosen interval of time, and the two quantities have been related by the analysis software to produce the differential molar heats as shown in Figure 3. These results represent the molar heats for the combined reversible and irreversible adsorptions of NH_3 . Similar plots for the irreversibly adsorbed NH_3 alone are shown in Figure 4. The latter results represent the adsorption on the strong acidic sites which might be expected to be catalytically active. Pillared clay K10 in an acid form, which is known to be an active catalyst for various oxidation processes, was also investigated to compare its acidity, as measured by the strength of NH_3 adsorption, to the carbon adsorbents.

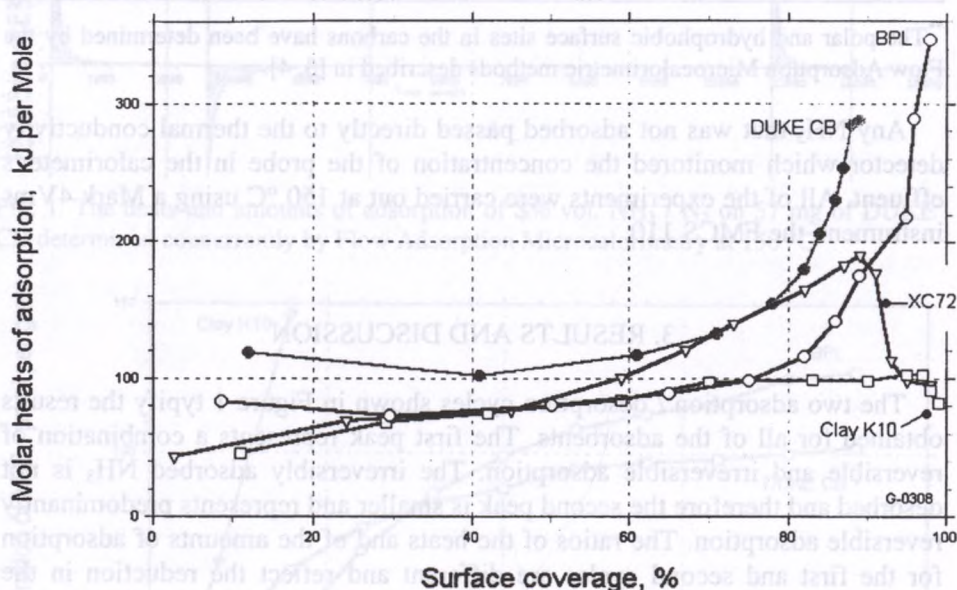


Fig. 3. Differential heats of total adsorption of NH_3 at 150 °C (total = reversible + irreversible)

The results shown in Figure 4 show how the clay catalyst compares with two of the carbons. Active carbon BPL produced similar high heats of adsorption over at least 60% of the surface coverage, but tended to give comparatively higher heats of adsorption at surface coverages exceeding 70%, and exceptionally high heats above 90% coverage. Similar results were obtained for DUKE CB and Cabot XC72 which gave the lowest amount of the strongly adsorbed NH_3 . It seems therefore that for the microporous carbons a certain critical surface coverage has to be reached before NH_3 can access the

strong acid sites. This is especially marked for active carbon BPL. The heats of adsorption on DUKE CB are exceptionally high and the sites adsorbing the NH_3 appear much more accessible than those on active carbon BPL. It has to be remembered, however, that the overall adsorption of NH_3 on the carbons ranges from about $50 \mu\text{mol}$ per gram to $150 \mu\text{mol}$ per gram, compared to the $500 \mu\text{mol}$ per gram for the clay catalyst K10 in which the acid sites are relatively more accessible than those present on the carbons. The clay adsorbent may, therefore, be more efficient in some catalytic processes than the carbons would be, in that they contain only a small proportion of the total $\text{BET}(\text{N}_2)$ surface in the form of polar sites. The latter adsorb NH_3 more strongly, however, than the polar sites of the clay catalyst. A special feature of the strong catalytic sites present in the microporous carbons is that a proportion of them exist in fine micropores and may, therefore, be more selective to shapes and sizes of reactant molecules, some of which may be small enough to penetrate the pores.

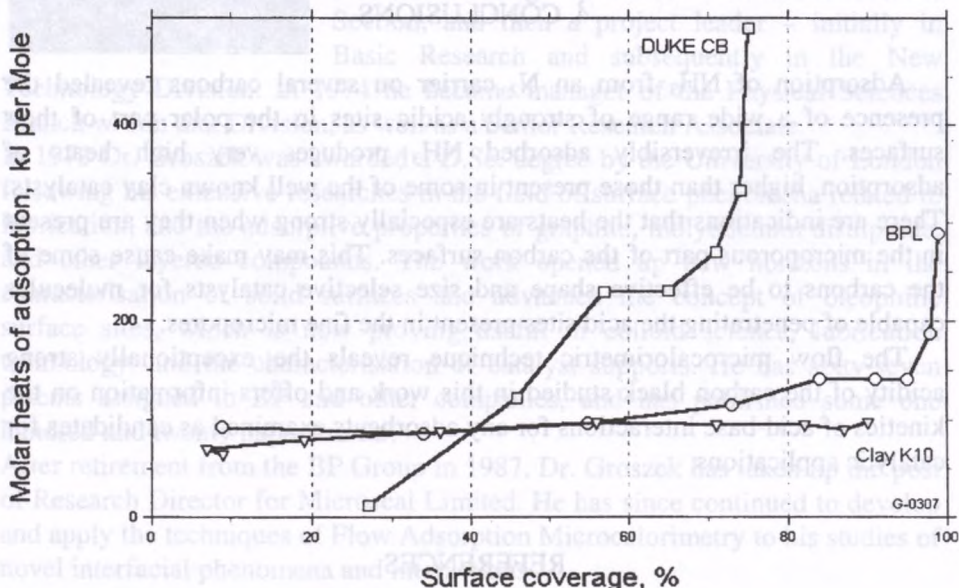


Fig. 4. Differential heats of irreversible adsorption of NH_3 at 150°C

It has to be emphasized, however, that only a small part of the $\text{BET}(\text{N}_2)$ surface of the carbons is polar in nature, as can be seen in Table 1, and only a proportion of them is acidic and capable of strongly adsorbing NH_3 . An overall picture of the relative acidities of the carbons may be obtained from the integral heats of NH_3 adsorption. The heats can be expressed as heats per m^2 of polar surface present in the carbons, as shown in Table 2 which clearly shows the exceptionally strong acidity of the carbon black.

Tab. 2. Integral heats of adsorption

Adsorbent type	Heats of NH ₃ adsorption	
	J per gram	J per m ²
ChemvironBPL	14.2	0.25
DUKE CB	9.1	0.63
Cabot XC72	4.0	0.19
Clay K10	45.0	0.17

The results indicate again the relatively high acidity of the polar sites in the carbons, with the carbon blacks showing the highest values, as indicated by their heats of adsorption.

4. CONCLUSIONS

Adsorption of NH₃ from an N₂ carrier on several carbons revealed the presence of a wide range of strongly acidic sites in the polar part of their surfaces. The irreversibly adsorbed NH₃ produces very high heats of adsorption, higher than those present in some of the well known clay catalysts. There are indications that the heats are especially strong when they are present in the microporous part of the carbon surfaces. This may make cause some of the carbons to be effective shape and size selective catalysts for molecules capable of penetrating the acid sites present in the fine micropores.

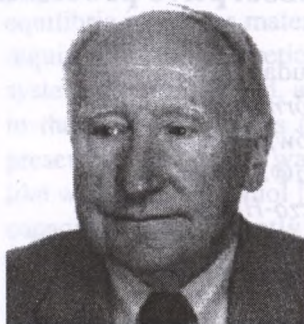
The flow microcalorimetric technique reveals the exceptionally strong acidity of the carbon black studied in this work and offers information on the kinetics of acid-base interactions for any adsorbents examined as candidates for catalytic applications.

REFERENCES

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CURRICULUM VITAE



Aleksander Groszek was born in Wilno (former north-eastern Poland) and was deported as a boy of twelve to Russia during the war and then evacuated to Iran, completing his secondary education there. By way of Lebanon and Egypt he came to Britain and graduated in chemistry in 1951 at the University of London.

He joined the BP Sunbury Research Centre in 1957, became a group head in 1958 in the Products Section, and then a project leader – initially in Basic Research and subsequently in the New

Technology Division. In 1974 he became manager of the Physical Sciences Branch within that Division, as well as a Senior Research Associate.

In 1973 Dr. Groszek was awarded a D.Sc. degree by the University of London following his extensive researches in the field of surface phenomena related to lubrication, and the adsorptive properties of graphite, molybdenum disulphide, and other layered compounds. The work opened up new horizons in the characterisation of solid surfaces and advanced the concept of oleophilic surface sites, which is now proving useful in colloid science, lubrication technology, and the characterisation of catalyst supports. He has sixty-seven patents assigned to BP and other companies, and has published some one hundred and twenty papers so far.

After retirement from the BP Group in 1987, Dr. Groszek has taken up the post of Research Director for Microscal Limited. He has since continued to develop and apply the techniques of Flow Adsorption Microcalorimetry to his studies of novel interfacial phenomena and interactions.