Base adsorption calorimetry for characterising surface acidity: a comparison between pulse flow and conventional "static" techniques

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Abstract

A pulsed flow adsorption microcalorimeter (pulse-FMC) has been developed by modifying a Setaram 111. It is tested in comparison with a conventional pulsed static adsorption microcalorimeter (pulse-SMC) for characterising surface acidity of solid acid catalysts. Small pulses of 1% ammonia in helium are delivered to an activated catalyst sample and its surface acidity is differentially profiled in terms of the molar enthalpy of ammonia adsorption (ΔH_{ads}°) using a combination of differential scanning calorimeter (DSC) and a downstream thermal conductivity detector (TCD). The pulsing action and its sequences are controlled by in-house developed software and the TCD output also is logged into a PC. Thus, the pulse-FMC is fully automated. Two sulfonated polystyrene resin-type catalysts, Amberlyst 15 and Amberlyst 35, a zeolite of the type H$^+$-ZSM-5 (CT 410) and an acid activated clay (Fulcat 220) are characterised at appropriate temperatures using both the new technique and the conventional static base adsorption method. ΔH_{ads}° versus surface coverage profiles of all the four catalysts obtained from both pulse-FMC and the conventional method are found to be comparable. Results are interpreted in terms of the extent to which NH$_3$ adsorption on the catalysts surface is under thermodynamic control in the two methods.
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1. Introduction

Solid acids comprise a group of very important heterogeneous catalysts having wide industrial applications. It is generally believed that their surface acidities can be correlated with their catalytic activities [1–4]. There are many spectroscopic and thermo-chemical methods that are being used for characterising surface acidity of solid acid catalysts. However, there is no universally applicable single method for measuring the surface acidity of these materials. Much of the recent research effort [5–9] in this area has been dedicated to design hyphenated techniques capable of simultaneously assessing the number, strength and nature of acid sites.

Titrating the solid acids with a gaseous base, such as ammonia, is an easy and convenient method for characterising the surface acidity. Progress of such a titration can be monitored using a gas burette and the enthalpy of the reaction can be measured with a calorimeter. This is the basis for the conventional static (equilibrium) calorimetric adsorption technique for solid acid characterisation. The sample is activated under vacuum and then the probe gas is introduced progressively to the sample, necessarily at a very low pressure and the adsorption process is allowed to reach equilibrium after each pulse of probe gas. A disadvantage of this technique, however, is that these conditions are very different to those that prevail when the catalysts are used in industrial processes. Other gases, some of which may 'poison' the catalyst, can be present during the practical application of catalysts. Thus, the validity of correlating acidity data measured under "ideal" conditions with the catalytic activity is often questioned. Another possible disadvantage associated with the conventional calorimetric adsorption techniques is that they often fail to separate the contribution to the measured adsorption of the gaseous base from physical adsorption, while titrating the acid sites. Thus, the adsorption enthalpy obtained

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is generally an average value from chemisorption and a contribution from physisorption, and the enthalpy of interest (enthalpy of chemisorption on acid sites) is not determined unambiguously.

Recently, dynamic methods in which adsorption from a flowing stream of gases have been gaining attention [5,7,8,10]. In flow adsorption techniques, the catalyst is activated in an inert gas flow at an elevated temperature. Then, the carrier gas flow is changed to a mixture of probe and carrier gases and a downstream detector is used to monitor probe gas concentration [7,10]. Flow adsorption microcalorimetry (FMC) has advantages, such as its flexibility to allow changes in composition of the carrier gas and to vary the gas flow rate, and as a result it can be used to mimic industrial processes more realistically [7].

As far as we know, applications of FMC techniques (base adsorption from a flowing gas stream) to date have adopted an integral approach to characterise the surface acidity. So, enthalpy measured using the integral approach for any catalyst effectively gives only an average value for the molar enthalpy of base adsorption on the active sites and gives no indication of any heterogeneity of acid site strength on the surface of a catalyst.

We have now designed a pulse-FMC method to differentially characterise surface acid sites on solid acid catalysts. In this communication, we report a comparative study of the results from the well-established pulsed static microcalorimetric technique [1] and those from our new pulse-FMC method.

The questions concerning whether the observed adsorption in pulse-FMC is under kinetic or thermodynamic control and whether adsorbed ammonia is able to achieve an equilibrium distribution after each pulse are also addressed. We have studied a range of solid acid catalysts and the results suggest that our new pulse-FMC is a valuable tool for characterisation of these materials.

2. Experimental

2.1. Materials

The following solid acid catalysts were used: (1) macroporous sulfonated polystyrene resins Amberlyst 15 and Amberlyst 35; (2) an H^+-ZSM-5 zeolite, namely CT 410 with a Si/Al ratio of 55 from Catal International Ltd.; (3) an acid activated montmorillonite clay (Fulcat 220) supplied by Rockwood Additives Ltd. All these catalysts were used as supplied. Helium and 1% ammonia in helium mixture were from BOC Ltd.

2.2. Pulse-FMC

We have modified a Setaram Calvet type differential scanning calorimeter (DSC) 111, which has a specially designed flow-through sample tube for studying adsorption from flowing gas. The sample tube (167 mm long) has a central sintered
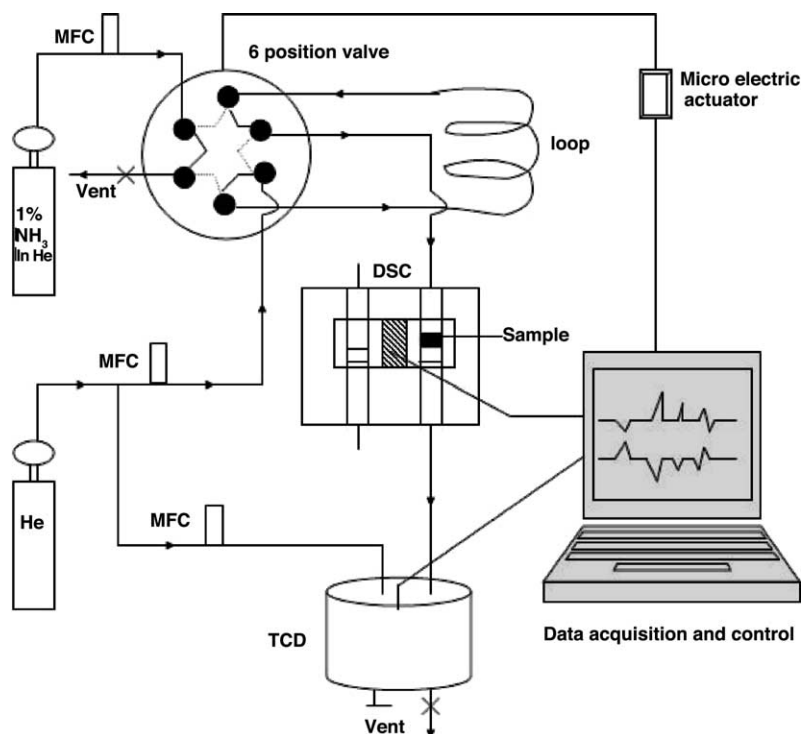

Fig. 1. Pulsed flow adsorption calorimeter system.

silica glass frit, on which the sample is loaded. When this tube is positioned inside the calorimeter, the sample bed is in the centre of the 20 mm long thermopile sensor surrounding it. This allows the heat changes during adsorption and desorption processes to be recorded without significant loss. We have modified the carrier gas supply as shown in Fig. 1. A steady gas flow across the sample is maintained through an MKS mass flow controller (MFC). Helium is used as the carrier gas and the 1% NH_3/He mixture is used as the probe gas. A blank sample tube in static air atmosphere is used as a reference for recording DSC thermal curves. Pulses of probe gas are delivered to the carrier gas stream from a calibrated sample loop using a Vici Valco® 6 position valve with microelectric actuator. The positioning and the sequencing of the actuator are controlled by in-house developed software.

The ammonia concentration in the gas stream is detected by a downstream thermal conductivity detector (TCD) from Gow-Mac. It is a differential type TCD and an independent steady flow of helium through the reference side is maintained by a MFC. The signal from the TCD is continuously fed to a PC using a data-logger.

In a typical experiment, an accurately weighed sample is transferred to the DSC sample tube and activated under a steady flow of helium at an elevated temperature. The desorption of moisture or any other physically adsorbed gases during activation is followed with the TCD. Completion of activation is detected as the TCD baseline for pure helium is restored. A sequence of pulses of probe gas is then passed through the sample and the DSC detects any heat changes. The downstream TCD continuously detects NH_3 and the amount of NH_3 adsorbed is calculated from a comparison with the TCD signal from an NH_3 pulse of same size through a blank DSC sample tube. Time is allowed between each pulse to allow reversibly adsorbed NH_3 on the sample to desorb and for the baselines to be re-established. In this way, the amount of any physisorbed ammonia is measured by the TCD and the corresponding heat absorbed as this is lost from the sample recorded by the DSC. Thus, net heat evolved during each pulse and net amount of ammonia adsorbed irreversibly can be calculated for each pulse. The molar enthalpy of adsorption associated with irreversibly adsorbed NH_3 from each pulse is plotted against the total amount of NH_3 irreversibly adsorbed per gram of the sample or surface coverage. Multiple experiments were performed on each sample, keeping the conditions same and satisfactory reproducibility was achieved for both DSC and TCD peak integrations.

2.3. Pulsed static adsorption microcalorimeter (pulse-SMC)

Acidity measurements by conventional base adsorption static calorimetry were performed using a Tian-Calvet type differential microcalorimeter (Setaram C80). The gas handling unit or gas burette was developed in-house and the typical experiments were performed as reported earlier [1]. Five or more experiments were performed on each sample under the same conditions and the average enthalpy of adsorption was found to be reproducible within less than 2%. The exact conditions for both pulse-FMC and pulse-SMC experiments on each sample are summarised in Table 1.

3. Results

3.1. Amberlyst 15 and Amberlyst 35

Typical pulse-FMC data for ammonia adsorption on Amberlyst 15 are shown in Fig. 2. The TCD signals for each pulse recorded downstream of the sample are subtracted from that due to a pulse of probe gas (1% mixture of NH_3 in He) of the same volume (10 ml) passed through a blank sample tube. This means that, if no adsorption or desorption of NH_3 by the sample occurs, a flat baseline is recorded. Net adsorption shows up as a peak below the baseline and net desorption a peak above.

Completion of activation (generally dehydration) of the catalyst under the experimental conditions can be easily ascertained from the pulse-FMC data as described earlier, when the TCD output returns to its baseline. Activation of both the resin catalysts was completed in ~3 h. A further 2.5 h was allowed for the activated sample to equilibrate under the flow of helium, before the first pulse of ammonia was introduced. Both Amberlyst 15 and Amberlyst 35 irreversibly adsorbed more than 90% of the initial pulses of ammonia (4.13 μmol), to which they were exposed. The adsorption events were observed as exothermic peaks in the DSC output as shown in Fig. 2. The extent of irreversible adsorption decreased gradually with subsequent pulses and the corresponding heat release also showed this decreasing trend up to the ninth pulse. The amount of ammonia adsorbed per gram of the sample up to this stage roughly corresponds to the known concentration of acid sites in Amberlyst 15 [1,3,4]. Starting from the ninth pulse each adsorption event was followed by desorption of

Table 1
Conditions under which NH_3 adsorption experiments were carried out

Sample	Temperature (K) (for activation and subsequent adsorption)		Flow rate (ml min^{-1})	Sample mass (mg)	
	Pulse-FMC	Pulse-SMC		Pulse-FMC	Pulse-SMC
Amberlyst 15	373	373	2	3–5	12–15
Amberlyst 35	373	373	2	8–10	12–15
H$^+$-ZSM-5	423	423	2	40–60	140–160
Acid clay	423	423	2	40–60	40–50

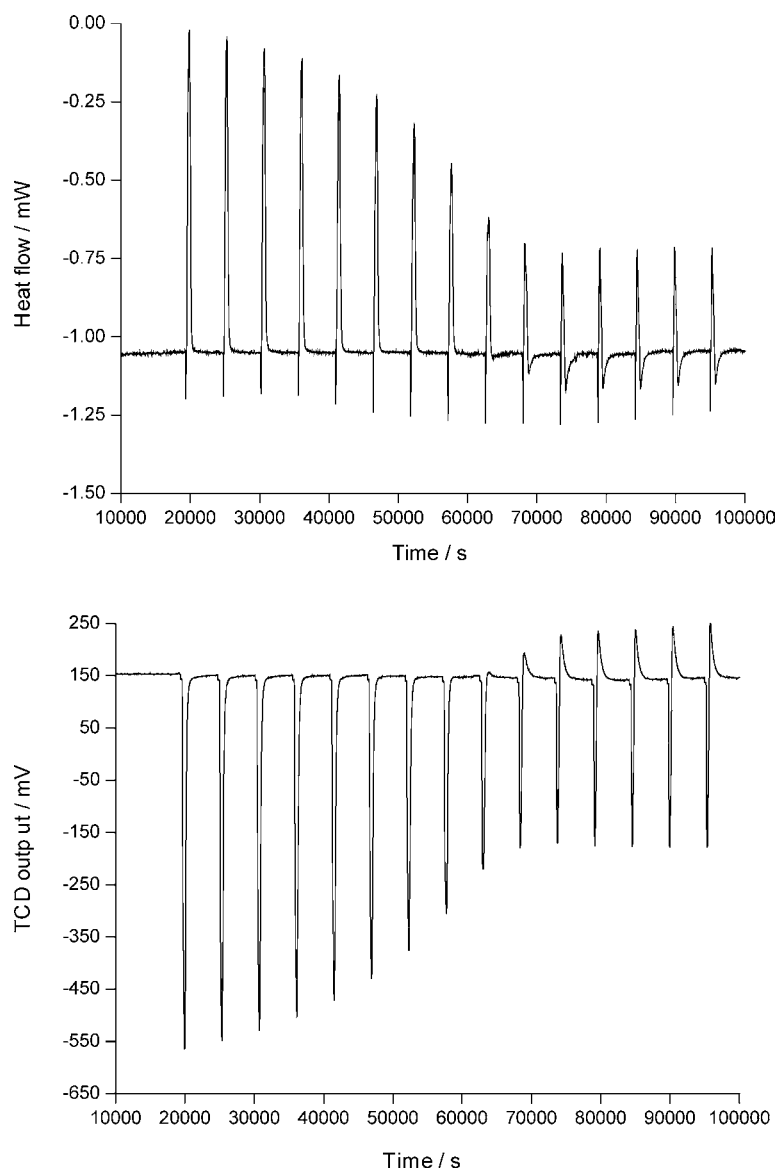Volume of each pulse of the probe gas (1% mixture of in He) was 10 ml.

Fig. 2. Typical pulse-FMC data for the ammonia adsorption on Amberlyst 15 at 100 °C and 2 ml min^{-1} flow rate. The TCD output was subtracted from a pulse of 10 ml of 1% NH$_3$/He mixture through the empty sample tube. So, peaks below baseline correspond to adsorption of ammonia and peaks above baseline correspond to desorption.

reversibly adsorbed ammonia and corresponding endothermic peaks were seen in the DSC thermal curves. From the 11th pulse onwards, all ammonia adsorption was essentially reversible. Throughout the experiment, the exothermic peak for ammonia adsorption during each pulse was preceded by a small endotherm in the pulse-FMC DSC thermal curve (Fig. 2). This is an artefact associated with a change in thermal conductivity, due to the introduction of ammonia to the sample tube [3]. A very small correction has been made to the integration of each exothermic peak to account for this artefact.

The ΔH°_{ads} measured during each pulse is plotted against the corresponding net amount of ammonia adsorbed for both Amberlyst 15 and Amberlyst 35 in Fig. 3. The corresponding data from the static adsorption method for both catalysts are also shown in the same figure. By assuming that one ammonia

molecule adsorbs on each acid site, and that the enthalpy of adsorption reflects the strength of the acid site, the plot can be considered as a surface acidity profile of the studied catalysts. It can be seen from Fig. 3 that the surface acidity profiles obtained from both pulse-FMC and pulse-SMC are quite comparable. The abrupt decreases in ΔH°_{ads} seen for both resins occur at values of surface coverage close to the known concentrations of sulfonic acid groups (Amberlyst 15 [4.2 mmol g^{-1}] and Amberlyst 35 [5.2 mmol g^{-1}]), showing fairly conclusively that strong adsorption occurs only at acid sites, that NH$_3$ does indeed adsorb stoichiometrically, and that adsorption on sites other than the sulfonic acid groups is relatively insignificant.

The data from the pulse flow experiments are additionally shown in a different way in Fig. 4, where cumulative
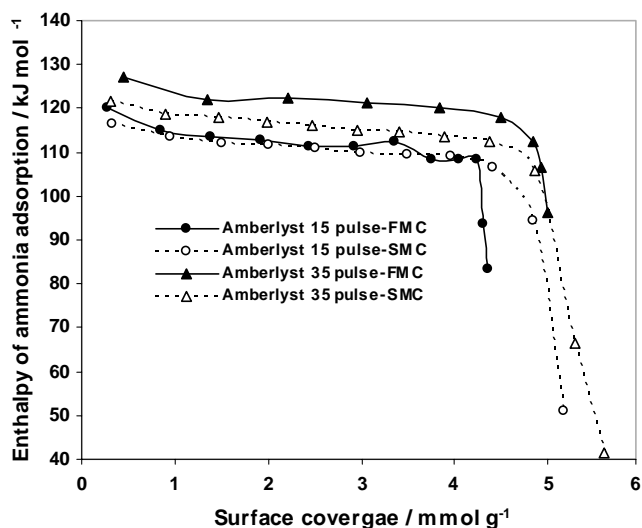
Fig. 3. Surface acid strength profiles of Amberlyst 15 and Amberlyst 35 obtained from pulse-FMC and pulse-SMC data. Experimental details are given in Table 1.
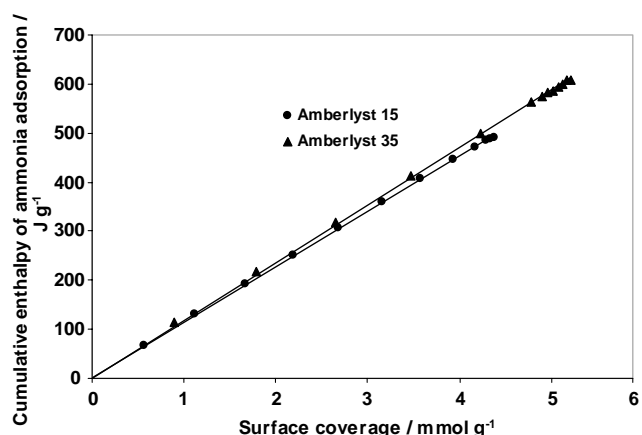

Fig. 4. Cumulative enthalpy of ammonia adsorption against surface coverage for Amberlyst 15 and Amberlyst 35.

enthalpy of ammonia adsorption on Amberlyst 15 and Amberlyst 35 are plotted against surface coverage. The gradient of this plot can be considered as an average of ΔH°_{ads} over all the acid sites and the corresponding values from both pulse-FMC and pulse-SMC are summarised in Table 2. Values of total surface coverage on Fig. 3 for which $-\Delta H^{\circ}_{ads}$ is greater
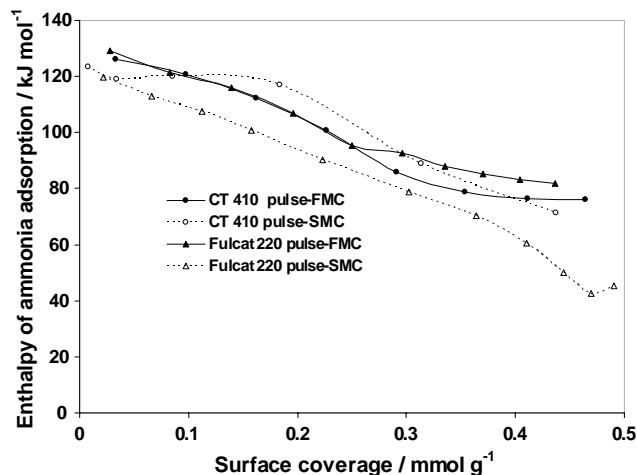

Fig. 5. Surface acid strength profiles of H⁺-ZSM-5 (CT-410) and acid clay (Fulcat 220) obtained from pulse-FMC and pulse-SMC data.

than 85 kJ mol^{-1} are also given in Table 2 (on the basis that adsorption enthalpies less than this are not associated with acid sites) along with known values of their acid site concentrations. As stated above, the results of our present study correspond reasonably well with the known [1,3,4] concentrations of sulfonic acid group on the two catalysts.

3.2. CT 410 and Fulcat 220

A plot of net ΔH°_{ads} for each pulse against the corresponding net adsorption in mmol g^{-1} are shown in Fig. 5. The corresponding data from pulse-SMC is also shown for comparison. For the zeolite catalyst, the data from pulse-FMC and pulse-SMC are comparable. The ΔH°_{ads} versus surface coverage plot for both these catalysts do not have a clear plateau region as observed for the resin catalysts. This is partly because there are fewer acid sites on these materials and also possibly because physisorption of ammonia occurs more readily on the high surface area solids than on the resins.

It is worth noting that since the data from the flow technique (pulse-FMC) corresponds solely to irreversibly adsorbed NH₃, but the static technique (pulse-SMC) gives data for the combined reversibly and irreversibly adsorbed NH₃, the similarities between the measured ΔH°_{ads} values and the similarities in the adsorption profiles generated by the two techniques suggest that the contribution to the measured ad-

Table 2
Pulse-FMC results and relevant physical constants for the studied catalysts

Property	Amberlyst 15	Amberlyst 35	H⁺-ZSM-5	Acid clay
Average $-\Delta H^{\circ}_{ads}$[a] (kJ mol^{-1})	113 ± 4 (110 ± 1)	117 ± 4 (114 ± 2)	114 ± 6 (119 ± 2)	111 ± 5 (103 ± 2)
Total coverage[b] (mmol g^{-1})	4.3 ± 0.4 (4.9 ± 0.2)	5.0 ± 0.4 (5.2 ± 0.2)	0.29 ± 0.06 (0.30 ± 0.05)	0.37 ± 0.06 (0.28 ± 0.05)
Acid site concentration (mmol g^{-1})	4.7[c]	5.2[c]	0.3[d]	–

Results from pulse-SMC are given in parentheses.

[a] Taken as the gradient of the plot of cumulative heat of adsorption against surface coverage.

[b] Coverage at which $-\Delta H^{\circ}_{ads}$ falls below 85 kJ mol^{-1}.

[c] Measured by aqueous titration.

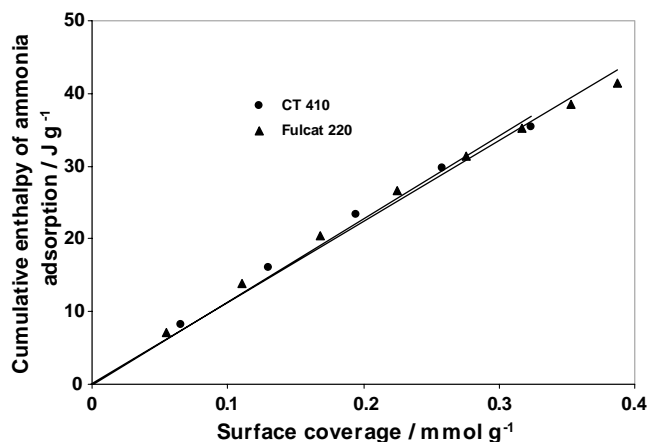[d] Concentration of Al^{3+} based on Si/Al ratio.

Fig. 6. Cumulative enthalpy of ammonia adsorption against surface coverage for H^+-ZSM-5 (CT 410) and acid clay (Fulcat 220).

sorption from the reversibly adsorbed NH_3 is relatively low, during the first few pulses anyway. The plot of cumulative enthalpy against cumulative coverage is shown in Fig. 6 and the gradient of this plot is given in Table 2 as an average value of ΔH°_{ads} for ammonia on CT410. The coverage at which $-\Delta H^{\circ}_{ads}$ falls below $85\,kJ\,mol^{-1}$ in Fig. 5 is also given in Table 2 and this value corresponds reasonably well with the estimated concentration of acid sites in the zeolite based on its Al content.

It can be seen from Fig. 5 that pulse-FMC gives slightly higher values for the enthalpy of ammonia adsorption on Fulcat 220 than those given by pulse-SMC, as might be expected, given that the FMC method responds only to chemisorbed NH_3. An average value of ΔH°_{ads} for Fulcat 220 was also calculated as for the other catalysts from the plot of cumulative enthalpy versus surface coverage (Fig. 6) and is given in Table 2 along with the surface coverage at which $-\Delta H^{\circ}_{ads}$ falls below $85\,kJ\,mol^{-1}$ from Fig. 5.

4. Discussion

The resin-type catalysts used in this study are macroporous polymer resins [11] and it is known that essentially all of their sites are accessible to ammonia [1,3,4]. It can be seen from Table 2 that these resins adsorb ammonia quantitatively even from a flowing gas stream in pulse-FMC to form 1:1 molar adsorption complexes. In addition to the similarities in average enthalpy values, the two techniques also yield very similar ΔH°_{ads} versus coverage profiles (Fig. 3). Similarly, ΔH°_{ads} versus coverage profiles obtained for the other two catalysts studied, acid treated clay (Fulcat 220) and H^+-ZSM-5 zeolite (CT 410), using ammonia adsorption from pulse-FMC and the conventional pulse-SMC are comparable. These observations, taken together, strongly suggest that the way ammonia distributes itself on acid sites of varying strength through the progressive dosing process is similar under the conditions prevalent in both the pulse-SMC and pulse-FMC techniques.

It is assumed that in the conventional ammonia adsorption experiments in the static system, where a sample is exposed to each dose of ammonia for a relatively long period, the distribution of ammonia amongst active sites of varying strength is under thermodynamic control, as far as it can be. A question which has arisen in the past with the flow techniques, in which the time of exposure of ammonia to the solid acids is relatively short, is whether adsorbed NH_3 is able to migrate on the surface to occupy the thermodynamically most favourable sites or whether the adsorption is effectively under kinetic control. The similarities in ΔH°_{ads} versus coverage profile referred to above suggest that the re-distribution of NH_3 on the surface is indeed possible, but to test this further we looked closely at the pulse-FMC data for Amberlyst 15 to see if there was evidence of NH_3 migration after initial adsorption. The DSC thermal curves and the corresponding TCD output for representative pulses are plotted with the same time scale in Fig. 7. The DSC thermal curves for pulses 8, 9 and 15 in the figure show a clear distinction between heat release during initial adsorption and the heat release during some subsequent process. Ammonia evidently adsorbs first
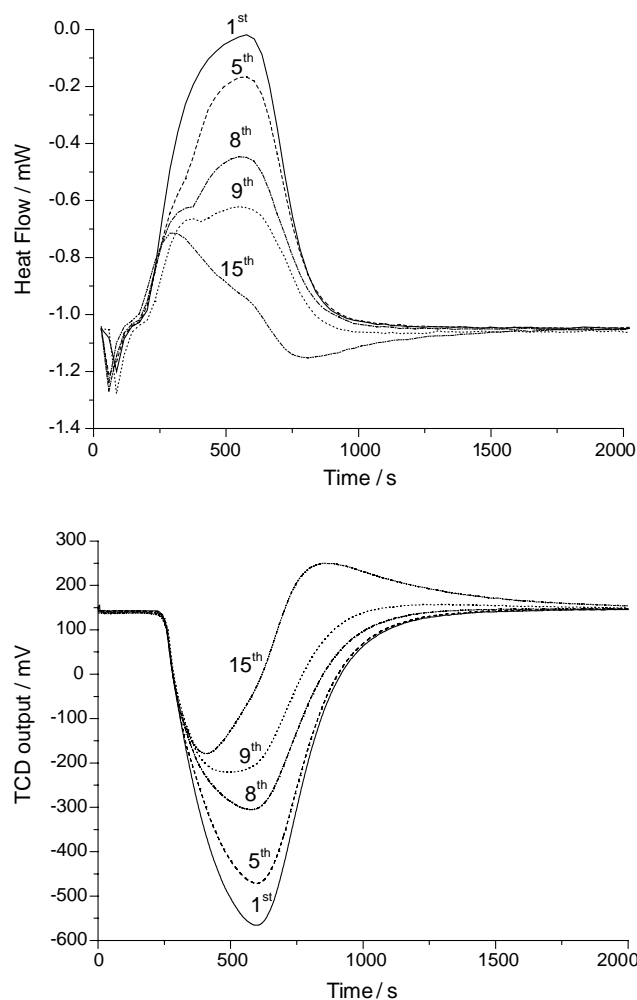

Fig. 7. An overlay of DSC and TCD outputs of some representative pulses of ammonia adsorption on Amberlyst 15.

on relatively weak sites. All the peaks shown in Fig. 7 and their shapes suggest migration to stronger and less accessible sites then occurs over the next few hundred seconds. In addition, there is desorption of physically adsorbed ammonia and this process occurs at the same time as this redistribution and even dominates for the later pulses (e.g., the 15th) shown.

Such an analysis for the acid activated clay and the H^+-ZSM-5 zeolite gave similar results. So in summary, ammonia adsorption from each pulse is shown by pulse-FMC data to be kinetically controlled in the first instance but the eventual distribution of adsorbed ammonia on acid sites appears to be under thermodynamic control. The equilibrium distribution of ammonia is achieved typically several hundreds of seconds after the pulse of probe gas has passed through the sample. We are confident that the control exerted on the distribution of adsorbed ammonia on acid sites in pulse-FMC is effectively the same as that in the static adsorption experiments.

5. Conclusions

For two very different types of catalysts, sulfonated polystyrene resins and porous inorganic materials, the pulse-FMC and pulse-SMC gave essentially the same differential enthalpy of ammonia adsorption versus coverage profiles. This means that the same factors control the progressive adsorption processes in the two techniques. As a result, we conclude that both these techniques may be used for characterising the surface acidity of solid acids. However, it is important to point out that pulse-FMC offers the following advantages over the conventional static microcalorimetric adsorption techniques. Firstly, in a single experiment the amount of both reversibly and irreversibly adsorbed probe compound can be measured. Secondly, the adsorption of probe compound is studied in a flowing gas environment and the composition of this gas can be altered to mimic the environment in which a catalyst might be used in practice. Thirdly, the technique is generally simpler to operate than the equilibrium technique.

Acknowledgements

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