Hiden Reference: AP0326
Hiden Product: HPR-20 QIC Real time Gas Analyser

Calorimetric Adsorption for Catalyst Characterisation

The development of new solid acid and base catalysts depends on the availability of suitable catalyst characterisation techniques. One of the accepted methods for characterising surface acidity and surface basicity is adsorption calorimetry, using probe compounds to study the concentration and strength of active sites. For solid acids a basic probe such as NH_3 is used, and for solid bases acidic probes such as SO_2 or CO_2 are used.

In our system, a catalyst sample is held in a flow-through differential calorimeter and the probe gas is introduced as a series of pulses injected into a steady flow of carrier gas, normally nitrogen. The outflow from the calorimeter cell is sampled by a low-flow capillary interface linked to a Hiden HPR-20 Quadrupole Mass Spectrometer.

Once calibrated with the probe gas, the mass spectrometer signal (using an m/z unique to the probe gas) provides a measure of the amount breaking through the sample from each pulse and therefore allows the amount adsorbed from each pulse by the sample to be calculated. The output from the differential calorimeter, combined with that from the mass spectrometer, is presented as a profile of $\Delta H_{ads}°$(probe) against the amount adsorbed, which can be broadly interpreted as an active site strength distribution profile for the catalyst.
The system is shown in Figure 1 and example data from an experiment in which NH_3 is introduced to a solid acid catalyst is shown in Figure 2.

Figure 1:
Flow adsorption calorimetry instrumentation. The flow-through Setaram DSC111 differential calorimeter is visible on the extreme left. The sample tube is held vertically in the stainless steel furnace. The automated gas sampling valve is held on the platform. The low-flow capillary interface to the Hiden HPR-20 Mass Spectrometer can be seen under the valve platform. The tube furnace alongside the calorimeter is for catalyst activation.

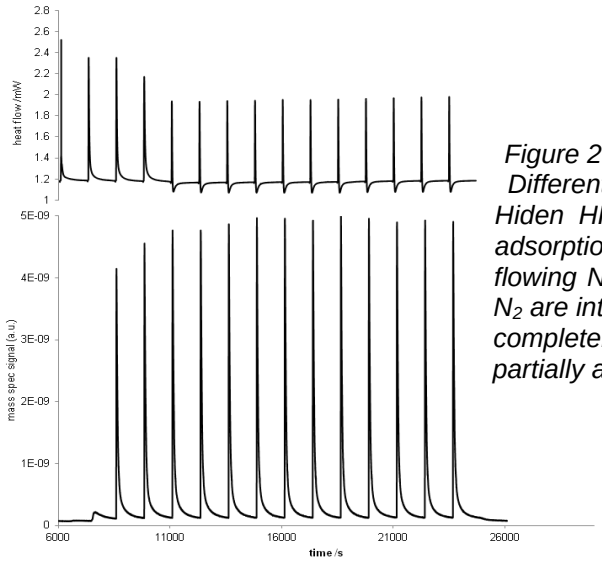

Figure 2:
Differential calorimeter output (top trace), and downstream Hiden HPR-20 output for m/z = 15 (lower trace) for NH_3 adsorption on an acid catalyst (50 mg), held at 120 °C, under flowing N_2 (5 ml min^{-1}) into which 1 ml pulses of 1% NH_3 in N_2 are introduced. In this experiment, the first two pulses are completely adsorbed by the sample. Pulses three to eight are partially adsorbed.

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The usefulness of this data in characterising solid acid catalysts is illustrated in Figure 3, where profiles of $-\Delta H_{ads}°(NH_3)$ vs amount of NH_3 adsorbed are shown for a series of polymer-supported sulfonic acid catalysts. The objective of this study was to investigate the relationship between catalyst structure and the concentration and strength of the surface acid sites. The catalysts range from Nafion SAC-13 with 0.1 -0.2 mmol g^{-1} of acid sites of high strength, to Amberlyst 35 with over 5 mmol g^{-1} of medium strength sites, to D-5081/2 with approximately 1 mmol g^{-1} of lower strength sites. This information can be related to the catalytic activities of these materials and can be used in a synthetic programme of catalyst optimisation.

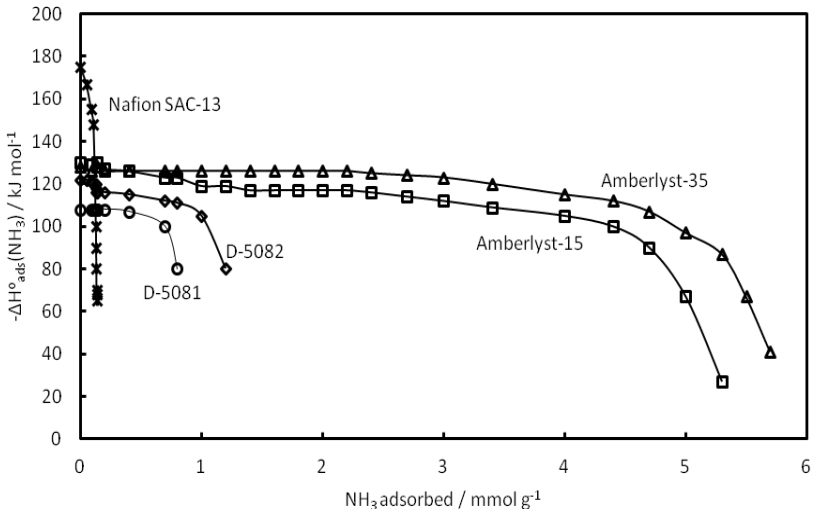

Figure 3: $-\Delta H_{ads}°$ (NH_3) vs. amount adsorbed for catalysts studied, at 120 °C.

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Paper Reference:
E. Andrijanto, E. A. Dawson, D. R. Brown (2012) "Hypercrosslinked polystyrene sulphonic acid catalysts for the esterification of free fatty acids in biodiesel synthesis" *Applied Catalysis B: Environmental* **115-116**, Pages 261-268

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