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A new technique for measuring surface acidity by ammonia adsorption[1]

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Abstract

A new method for measuring the surface acidity of solid acid catalysts is described. A Stanton Redcroft combined TG-DSC instrument has been modified to allow the introduction of a series of controlled pulses of ammonia into the helium stream passing over the sample. The weight of ammonia adsorbed by the sample and the enthalpy of adsorption are interpreted in terms of the abundance and strength of the surface acid sites. Surface acidity measurements made on three acid-activated clays and an acidic sulphonated ion-exchange resin are compared with catalytic activity data in two model reactions. © 1997 Elsevier Science B.V.

Keywords: DSC; TG; Surface acidity; Ammonia; Catalyst; Clay; Ion-exchange resin

1. Introduction

Thermal methods are often used to characterise solid acid catalysts [1–3]. The determination of surface acidity, for instance, is most often performed by the temperature programmed desorption (TDP) of a pre-adsorbed base, in which the rate of desorption of the base is monitored as a function of temperature [4,5]. The resulting profile is then interpreted in terms of the number and strength of acid sites.

However, this method cannot be used with thermally sensitive solid acids, such as ion-exchange resins and clay minerals, where the solid may decompose at temperatures required to desorb the base. In these cases it is preferable to monitor the *adsorption* of the base, which of course can be performed at a lower temperature. For gaseous bases, this can be most accurately achieved with a gas burette delivering the base to the catalyst held in a microcalorimeter. However, the instrumentation for this is expensive and not always readily available. In this paper we describe a relatively inexpensive alternative to the traditional combination of a microcalorimeter and gas burette for measuring base adsorption, which has recently been developed in our laboratory.

In this technique, ammonia adsorption by a catalyst is monitored using a combination of thermogravimetry (TG) and differential scanning calorimetry (DSC). The gas supply for a commercial TG-DSC instrument is controlled to expose the sample to a series of small pulses of ammonia. The sample weight increases and associated enthalpy changes are interpreted in terms of the abundance and strength of surface acid sites.

Since the usefulness of acidity measurements on solid acid catalysts depends on their ability to predict catalytic activity, the acidity measurements made in this work have been compared with catalytic data. A range of commercial acid catalysts have been used, and catalytic activities have been compared in two Brönsted catalysed reactions. The first is the transes-

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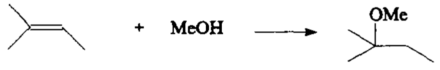
Scheme 1.



Scheme 2.

terification reaction between isopropenyl acetate and ethanol which yields ethyl acetate and acetone, shown in Scheme 1.

The second is the addition of methanol to isoamylene to produce *tert*-amyl methyl ether (TAME) shown in Scheme 2.

The reactions were chosen to differentiate catalysts on the basis of acid strength. The production of TAME from methanol and isoamylene is known to be catalysed by weak acid sites [6] while the transesterification is rather more demanding and requires stronger acid sites. The objective of the current work was to examine the correlation between measured surface acidities and catalytic activities in these two reactions.

2. Experimental

2.1. Ammonia adsorption measurements

A Stanton Redcroft STA 625 TG-DSC instrument was used in this study. This instrument permits simultaneous monitoring of both heat and mass changes. It incorporates a null deflection thermobalance capable of weighing sub-milligram quantities and a chromel-alumel heat flux DSC head. The small internal volume of the furnace makes it ideal for rapid gas switching. The instrument was used without further modification except that a gas handling unit was incorporated into the carrier gas supply. This unit contained a pneumatically operated 3-way valve which permitted switching between 100% helium and a blend of 5% ammonia in helium. The sample was dosed with ammonia in a controlled stepwise fashion by repeatedly switching between pure helium and the ammonia in helium mixture. In this way, the entire range of acid sites present on the sample, progressing from strong through to weak, could be dosed with ammonia.

The sequenced switching action was controlled by a digital electronic timer. It was important to maintain a constant and steady flow of gas over the sample to avoid disturbing the thermobalance, particularly during the course of the gas switching operation, and this was achieved by means of a Brooks TR8550 mass flow controller located immediately after the valve. In addition to the switching valve and mass flow controller, the gas handling unit also housed the necessary pressure regulators for the two gas supplies and an electronic module for adjusting and monitoring the carrier gas flow rate. A schematic diagram of the apparatus is shown in Fig. 1.

The DSC was first calibrated by measuring the heat of fusion of a sample of indium. In a typical acidity

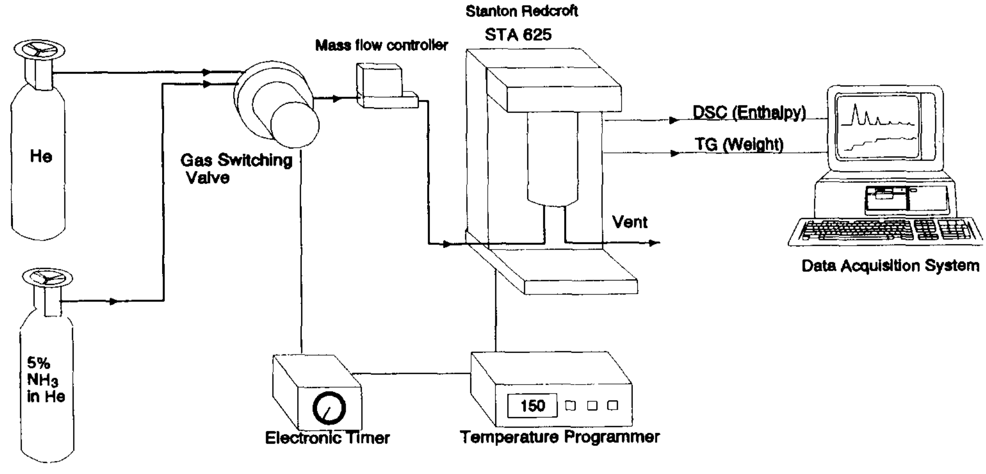


Fig. 1. Schematic diagram of ammonia adsorption instrumentation.

determination, a catalyst sample (~10 mg) was thermally activated at an appropriate activation temperature under helium (flow rate=20 $cm^3 min^{-1}$) for ≈20 min. The furnace was then set to the dosing temperature, chosen to allow chemisorption of ammonia but avoid physisorption.

In the reported experiments the activation and the dosing temperatures were both 100°C. The suitability of this temperature for dosing ammonia was established using a non-acidic silica sample which showed almost zero ammonia adsorption at 100°C. Furthermore, parallel studies on less thermally sensitive catalysts showed similar levels of ammonia adsorption, from 100°C up to 180°C, suggesting that chemisorption occurs almost quantitatively throughout this temperature range.

After allowing the catalysts to reach equilibrium at the dosing temperature, the carrier gas switching sequence was started, in which pulses of 5% ammonia in helium, each lasting two minutes, were switched into the carrier gas stream, returning to 100% helium for six minutes between each pulse. The DSC signal and the sample mass were recorded continuously. When no further adsorption of ammonia could be detected, the run was continued for six or seven additional pulses and then stopped. The sample weight gain and the exothermic peaks recorded on the DSC were collected and processed using Stanton Redcroft data acquisition software.

The net overall weight gain incurred during ammonia adsorption was converted to give the number of moles of ammonia taken up by the sample and hence the total number of acids sites, assuming that one acid site adsorbs one ammonia molecule. In this work the cumulative area under the sequence of exotherm peaks was recorded and expressed as the average enthalpy of adsorption per mole of ammonia and hence used as a measure of acid site strength. Surface acidity measurements were made on duplicate samples of each catalyst. Confidence limits (95%) were estimated and based on variations observed in previous sets of repetitive measurements made on a commercial acid-treated clay catalyst.

It is worth pointing out that, while the average enthalpy of adsorption (and hence average acid site strength) is adequate for characterising most solid acid catalysts, an acid strength distribution profile is useful in some cases. In the technique described here, the use of a series of discrete pulses of ammonia, and the ability to analyse the weight and enthalpy changes associated with each pulse separately, can provide at least a partial acid site distribution profile, when required.

2.2. *Measurement of catalytic activity*

The catalysts used in this study were as follows: a macroporous sulphonated polystyrene ion-exchange resin in the acid form, CT 175 (kindly supplied by Purolite International), three acid-treated clays, K10 and KSF (kindly supplied by Sud Chemie), and Fulcat 22A (kindly supplied by Laporte Inorganics). It is worth noting that the temperature of polystyrene-based ion-exchange resins cannot be raised significantly above the activation and dosing temperature of 100°C without degrading the polymer, emphasising the value of this technique with such heat-sensitive materials.

Prior to catalytic testing the catalysts were activated at 100° in a forced air oven for 24 h. The transesterification reaction between isopropenyl acetate and ethanol was performed in a stirred batch reactor at 80°C. A reaction mixture consisting of 0.5 mol of ethanol and 0.1 mol of isopropenyl acetate was submitted to a reaction with 100 mg of activated catalyst. The extent of reaction was measured by analysing the amount of unreacted isopropenyl acetate present in the reactor after various times using GLC.

The addition of methanol to isoamylene was performed in a stirred batch reactor at 80°C. A mixture consisting of 1.0 mol of methanol and 0.1 mol of isoamylene was added to 100 mg of activated catalyst. The progress of the reaction was monitored by periodically taking samples from the reactor and analysing their composition by GLC.

3. Results and discussion

A TG-DSC trace for ammonia adsorption on CT175 is shown in Fig. 2. The activation period can be seen, followed by the introduction of ammonia pulses. The weight increases in steps with the first four pulses and then levels off when the catalyst is saturated with ammonia. Further small but reversible, weight rises can be seen with subsequent pulses. These are asso-

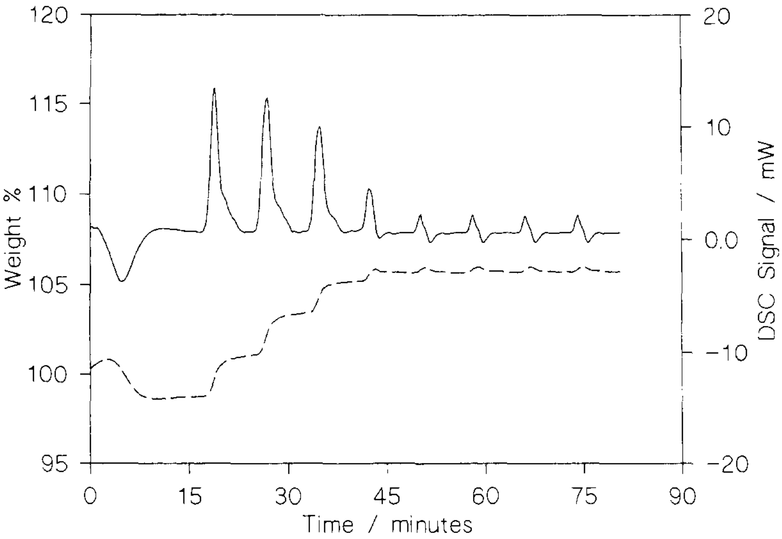


Fig. 2. Thermal analysis trace produced by thermal activation followed by adsorption of ammonia on ion-exchange resin CT175 (- - - represents TG signal, — represents DSC signal).

ciated with physisorption occurring when ammonia is in the gas stream, which is reversed when the gas reverts to pure helium.

The DSC trace displays intense exotherms associated with the first four pulses. When chemisorption is complete, each subsequent ammonia pulse results in a small exotherm followed by an endotherm of similar magnitude. These features, which are mainly associated with ammonia adsorption and desorption on the saturated catalyst, are reproducible, but the small exo- and endotherms do not quite cancel each other, as might be expected. This is almost certainly an artefact associated with the change in thermal conductivity of the carrier gas as ammonia is introduced, and the features are still apparent when an inert material with no acid sites, such as silica, is analysed using the technique. In order to allow for this in practice, pulses are continued beyond saturation so that the net area associated with this artefact can be established. This net area is then subtracted as a small correction from each of the exothermic peaks recorded during the earlier phase of the experiment.

The number of acid sites per gram is calculated from the weight of ammonia adsorbed, and the average acid strength of these sites is calculated from the integrated, corrected, enthalpies of adsorption over the whole run, expressed as enthalpy of adsorption per mole of adsorbed ammonia.

Table 1 shows the acidity results obtained for the four catalysts. It is evident that the three acid-treated clays, K10, KSF and Fulcat 22A, exhibit strong acid sites with average heats of ammonia adsorption ranging from 122 to 151 kJ mol^{-1}. These values contrast with the much lower acid strength of the ion-exchange resin at 46 kJ mol^{-1}. In terms of acid site abundance, however, the position is reversed. The data shows that the ion-exchange resin has about ten times as many acid sites per gram as Fulcat 22A and K10, and nearly twice as many as KSF.

The Table also shows the rate constants for the two test reactions using the four catalysts. The most active catalysts towards the transesterification reaction are the acid-treated clays. This reaction is known to be relatively demanding and it seems clear that the dominant factor in determining activity is the strength of the surface acid sites, and the relatively small number of strong sites on the clays are more active than the much larger number of weaker sites on the ion-exchange resin. The KSF clay, not unexpectedly, shows the highest activity of all in this reaction. Ammonia adsorption measurements show that the surface acid sites on this catalyst are of similar strength to the other two clays but they are present in much greater number.

The catalytic activities towards the synthesis of TAME show a very different trend. This reaction is

Table 1
Surface acidities and catalytic activities of ion-exchange resin CT175 and acid-treated clays KSF, Fulcat 22A and K10

Catalyst	Number of surface acid sites/(mmol g^{-1}) (±0.1)	Average strength of acid sites/kJ (mol NH_3)$^{-1}$ (±3)	Rate constant: transesterification/($\times 10^{-5} s^{-1}$) (±0.3)	Rate constant: TAME/($\times 10^{-5} s^{-1}$) (±0.1)
CT175	4.0	46	6.2	5.0
KSF	2.0	126	16.6	3.1
Fulcat 22A	0.50	122	9.0	1.93
K10	0.20	151	11.4	1.47

much more facile than transesterification and it is reasonable to assume that it would be catalysed by weaker surface acid sites. The catalytic activities towards this reaction seem to reflect the relative abundance of acid sites on the catalysts, and the order of activities is the same as the order of acid site concentrations: CT175 > KSF > 22A > K10. The relative strengths of the surface acid sites appear to have little influence on catalytic activity in this reaction, under the conditions used.

By comparing the surface acidity data with catalytic data we conclude that surface acidity measurements on solid acid catalysts, made using the ammonia adsorption technique described in this study, can be used as reliable predictors of catalytic activity. The technique is a useful alternative to a microcalorimeter and gas burette for monitoring base adsorption. It is, however, restricted to smaller samples than can generally be used in a microcalorimeter, and this means that the sensitivity and precision of the TG-DSC method are considerably lower. On the other hand, it offers advantages of a lower cost, simplicity, and speed of operation.

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