

Calorimetric base adsorption and neutralisation studies of supported sulfonic acids

S. Koujout, D.R. Brown*

Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield HD13DH, UK

Received 25 August 2004; received in revised form 29 November 2004; accepted 30 December 2004

Available online 3 February 2005

Abstract

Base adsorption calorimetry (from the gas phase) and acid–base neutralisation titration calorimetry (in the liquid phase) have been used to characterise a series of solid sulfonic acids supported on porous silicas and polystyrene resins. The results illustrate the limitations of using calorimetric techniques for relative acidity measurements and the assumptions that must be made if molar enthalpies of adsorption or molar enthalpies of neutralisation are to be used to compare the strengths of solid acids. They also show how the relative acid strengths of nominally similar acids can be highly dependent on whether measurements are made in the presence or absence of a solvent, and, if the former, on the type of solvent.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid acid; Sulfonic acid; Calorimetry; Adsorption; Neutralisation

1. Introduction

Base adsorption calorimetry and base neutralisation calorimetry can both be used to study the relative strengths of acid sites on solid acid materials [1–5]. In this work we have used these techniques to study sulfonic acids supported on polystyrene and silica solids (Fig. 1) and shown how the relative acid strengths of these two very similar types of supported acid depend markedly on whether a solvent is present and, if so, the nature of the solvent. The results also illustrate some of the limitations of using these techniques for comparative acid strength measurements.

The relative strengths of acid sites on a solid acid can be measured as the molar enthalpy of adsorption ($\Delta H_{\text{ads}}^{\circ}$) of a probe base compound. One of the most common probes is gaseous ammonia. The ammonia is typically adsorbed on a solid acid at 100–200 °C in an otherwise evacuated system as a series of successive small doses. Under these conditions, provided one probe molecule reacts with one acid site

and provided the chemisorption of ammonia on acid sites can be distinguished from physisorption on other sites, it is reasonable to assume that the value of $\Delta H_{\text{ads}}^{\circ}$ reflects the relative strength of the adsorbing acid site. In fact, the adsorption process can be broken down into three processes: proton loss by the acid, proton gain by the base, and the formation of an ion pair between the conjugate acid and base. When comparing solid acids it has to be assumed that the last two contributions to the measured $\Delta H_{\text{ads}}^{\circ}$ are the same for the solid acids being compared and that the only variable is the proton affinity of the solid acid. When comparing related solid acid materials with a common base probe compound this is usually taken as a reasonable assumption [2,3]. An additional aspect of these measurements is that, by adsorbing at relatively high temperature, the adsorption process is largely under thermodynamic control and, in principle, the strongest acid sites are populated first. However, the distribution of adsorbed ammonia on adsorption sites of different energies is always governed by the Boltzmann distribution law. So, although a differential plot of $\Delta H_{\text{ads}}^{\circ}$ against acid site coverage gives an indication of the distribution of acid site strengths on the surface, it is effectively smoothed by the

* Corresponding author. Tel.: +44 1484 473397; fax: +44 1484 472182.
E-mail address: d.r.brown@hud.ac.uk (D.R. Brown).

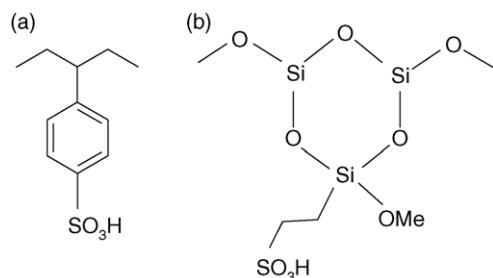


Fig. 1. (a) Sulfonated polystyrene. No divinylbenzene cross-linking is shown nor any styrene units which may have been di- or even trisulfonated; (b) sulfonated silica, prepared from 3-mercaptopropyltrimethoxysilane, followed by oxidation to sulfonic acid. Elemental analysis (C, S) verified that binding to silica is predominantly through condensation of two of the three methoxy groups.

effect of the distribution of sites populated by each dose of ammonia [3].

Similar experiments can also be performed in the liquid phase, titrating a solution of the probe base into a suspension of the solid acid material. The molar enthalpy of neutralisation ($\Delta H_{\text{neut.}}^{\circ}$) is measured throughout the titration. Using this technique, more assumptions have to be made if $\Delta H_{\text{neut.}}^{\circ}$ values are to be used as measures of relative acid strengths. This is because, again, the measured enthalpy of neutralisation is made up from contributions from several sources: proton loss from the acid and proton gain by the base as in the case of gaseous base adsorption, but, in addition, changes in solvation as the acid and base are converted to the conjugate base and acid, plus any enthalpy changes associated with ion pairs that form or break up during the neutralisation reaction. To assume that differences in measured $\Delta H_{\text{neut.}}^{\circ}$ values reflect differences in the acid strengths of solid acids again requires that all contributions to $\Delta H_{\text{neut.}}^{\circ}$ other than the proton affinity of the acid are constant. As before, this can only be taken as a reasonable assumption when comparing closely related solid acids [4–7], such as the members of the series of supported sulfonic acids studied here. Another point is that titration calorimetric experiments of this type are usually performed at temperatures close to room temperature so the progressive neutralisation process is likely to be kinetically controlled. This means that a single mean value for $\Delta H_{\text{neut.}}^{\circ}$ is generally obtained for each sample, and information about any distribution of acid site strengths on an individual sample is not available.

Obviously an important aspect of this titration calorimetric method is the facility to change solvent and investigate the influence of solvent on acid strength. In this work we have used water and cyclohexane. Water was chosen because it is representative of strongly solvating solvents and it is a “green” solvent for synthetic chemistry; the acid properties of potential solid acid catalysts in water are important. We expected that the levelling effect of water would result in all the supported sulfonic acids in water behaving simply like strong mineral acids. The fact that they do not behave in this way as will be described later suggests that the chemistry

of sulfonic acid groups in the internal solutions in hydrated sulfonated polystyrene resins may be more complex than expected. Cyclohexane was chosen as an example of a very weakly solvating solvent, in many ways at the other end of the scale to water. In principle, acid strength measurements in this solvent should show differences in acid strength that would be otherwise levelled in water. Measurements in cyclohexane might be expected to reflect acid strengths in all similar non-polar solvents, and even the acid strengths in the complete absence of any solvent.

2. Experimental

2.1. Supported sulfonic acids

Sulfonated poly(styrene-co-divinylbenzene) resins were provided by Purolite International Ltd. All resins were of the macroporous type, estimated to contain 15–17% cross-linking agent divinylbenzene. The series of resins were functionalised with sulfonic acid at levels ranging from 0.74 to 5.6 mmol g⁻¹. They were used in their H⁺ forms. The sulfonic acid group concentrations were measured using a standard procedure of ion-exchange with Na⁺ followed by aqueous titration with standard NaOH solution [8]. Water contents of the fully hydrated resins were determined by the manufacturers and, in some cases, confirmed by drying fully hydrated resins to constant weight at 90 °C. For brevity the resins are referred to simply as sulfonated polystyrene from here on.

Three of the silica supported sulfonic acids were based on silica hexagonal mesoporous sieves (HMS) [9,10]. Thiol-functionalised HMS silica (HMS-SH) was synthesized at room temperature from a gel containing 0.8 mol tetraethoxysilane (TEOS), 0.2 mol 3-mercaptopropyltrimethoxysilane (MPTS), 0.275 mol *n*-dodecylamine, 8.9 mol ethanol and 29.4 mol water. The amine was first dissolved in the alcohol–water mixture. The TEOS–MPTS mixture was added and stirred for 24 h. The amine template was finally extracted from the as-synthesized HMS-SH with ethanol under reflux for 24 h [10].

The equivalent material based on the larger pore SBA-15 silica molecular sieve [11] was prepared by first dissolving Pluronic 123 (EO₂₀PO₇₀EO₂₀, M_{av} 5800, Aldrich) (4 g) with stirring in 125 g of 1.9 M HCl solution at room temperature. The solution was heated to 40 °C before adding 32.8 mmol TEOS. After 1 h, 8.2 mmol thiol precursor MPTS was added to the mixture. The resultant solution was stirred for 20 h at 40 °C, and then aged at 100 °C for 24 h without stirring. The solid product was recovered by filtration and air-dried. The template was extracted with excess ethanol under reflux for 24 h (1.5 g of as-synthesized material per 400 ml of ethanol) [11].

Materials with immobilised mercaptopropyl groups were oxidised to sulfonic acids with H₂O₂ in a methanol–water mixture. Typically 2.04 g of aqueous 35% H₂O₂ dissolved in three parts of methanol was used per gram of material

and the mixture stirred for 24 h. The mixture was filtered and washed with water and ethanol. The wet material was then re-suspended in 0.1 M H₂SO₄ solution for another 4 h. Finally, the material was rinsed with water and dried at 60 °C under vacuum [10,11].

The resultant materials were characterised by powder X-ray diffraction (XRD) and by nitrogen adsorption at 77 K, using the adsorption isotherm to calculate BET surface area, and the desorption isotherm and BJH method to determine the pore size distribution. The concentrations of acid sites were measured by pH titration with standard NaOH solution, following exchange with excess NaCl solution. Water contents were measured by heating to constant weight at 110 °C.

2.2. Titration microcalorimetry

A Setaram “Titrys” microcalorimeter was used for these experiments. This instrument is a Calvet differential heat flow microcalorimeter modified to allow continuous stirring of liquid samples. The pre-heated titrant is added to both sample and reference cells simultaneously using a programmable twin syringe pump.

In a typical experiment, 50 mg (dry weight) solid acid was suspended in 2 cm³ solvent in the sample cell, with the same volume of solvent in the reference cell. Experiments were performed at 30 °C. Solid acid samples were dried at 70 °C and then fully solvated in cyclohexane before titration in this solvent. The titrant, 0.100 mol dm⁻³ NaOH in water, or 0.100 mol dm⁻³ *n*-butylamine in cyclohexane, was added to the sample cell in 0.20 cm³ aliquots at one hour intervals until neutralisation was complete. Pure solvent was added to the reference cell in the same way. Blank runs with no solid acid present were run to establish whether correction was necessary due to an enthalpy of dilution of the base as titrant is added. This was found to be negligible in all cases.

The heat output was measured for each addition and the cumulative heat plotted against amount of added base. A typical plot of cumulative heat against amount of added base is shown in Fig. 2. The gradient (which was essentially constant up to close to complete neutralisation in all cases) was calculated and is reported as the molar enthalpy of neutralisation ($\Delta H_{\text{neut.}}^{\circ}$) in kJ mol⁻¹. The assumption in this is that,

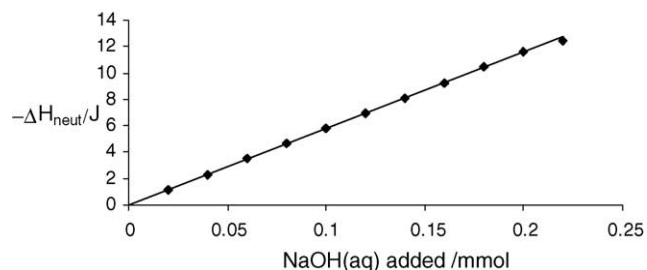


Fig. 2. Cumulative heat vs. amount of added base for a titration of aqueous 0.10 mol dm⁻³ NaOH solution against hydrated sulfonated polystyrene resin M-4 (CT-175). The gradient gives $\Delta H_{\text{neut.}}^{\circ} : -58.0 \text{ kJ mol}^{-1}$.

up to the equivalence point, each aliquot of added base reacts completely with the solid acid, leaving no unreacted base in the supernatant solution with the solid acid. We verified that this was the case in both NaOH/H₂O and cyclohexane/*n*-butylamine titrations by carrying out parallel titrations outside the calorimeter. After each addition of base to the solid acid suspension a portion of the supernatant was removed and titrated with HCl solution. When cyclohexane was used, an aqueous extraction was performed first. We found that, in all cases, the amount of unreacted base was negligible until the titration was within one aliquot (of typically 10 required to reach equivalence) of the equivalence point.

2.3. Ammonia adsorption microcalorimetry

A Setaram C80 differential microcalorimeter, operating on the Calvet principle, was used to measure the enthalpies of ammonia sorption. Custom-made glass cells were attached to an evacuable glass gas-handling system or gas burette, comprising a dosing volume of approximately 17 cm³ attached directly via a tap to the cells (volume approximately 50 cm³). The pressure in the dosing volume was recorded using a Baratron pressure transducer (range to 100 Torr) and in the cells with a similar pressure transducer (range to 10 Torr). Both pressures were logged continuously. The volumes were calibrated precisely before each experiment, based on an ancillary calibration bulb of known volume, using helium. The temperature of the gas burette outside the calorimeter was maintained at 22(±1) °C. Solid acid samples (150 mg dry weight) were conditioned in the calorimeter sample cell at 100 °C under vacuum for 2 h. The reference cell was empty. Ammonia sorption was carried out at 100 °C. The method used for introducing ammonia to the sample was developed to minimise errors due to the adsorption of ammonia on the glass walls. To introduce a dose of ammonia, a suitable amount of the gas was allowed to reach pressure equilibrium in the dosing volume. The tap was then opened to allow this gas to expand into the cells, and then closed immediately, and the new pressure in the dosing volume recorded. The amount of ammonia introduced was calculated from the difference between the two pressure readings, on the basis that there would not be significant adsorption of ammonia on, or desorption from, the walls of the dosing volume in the very short time between the two readings. The pressure in the cells was then monitored as adsorption took place. The final amount of ammonia adsorbed from the dose was calculated from the final pressure reached. Typically, 10–15 successive doses of ammonia (of ca. 0.05–0.10 mmol) were introduced to each sample using this technique. Enthalpy changes associated with each dose were converted to molar enthalpies of sorption and expressed as functions of resin coverage, as reported previously [12].

It is worth noting that we experimented with an alternative way of correcting measurements with the gas burette for ammonia adsorption on the glass walls, by simply calibrating the volumes of the dosing section and the cells using ammonia (rather than helium). We concluded that this was not a

satisfactory method as it was very difficult to introduce the ammonia to the volumes in a way that mimicked the way it is introduced in the adsorption experiment itself.

3. Results and discussion

The powder XRD patterns for the HMS-SO₃H samples were dominated by the 100 reflections corresponding to *d*₁₀₀ spacings of about 3.6 nm in each of the three samples. The SBA-15-SO₃H patterns also showed intense reflections from 100 planes with a spacing of 9.4 nm. From nitrogen adsorption data, the three HMS-SO₃H samples exhibited BET surface areas of 940 m² g⁻¹ (HMS-SO₃H-1), 850 m² g⁻¹ (HMS-SO₃H-2) and 750 m² g⁻¹ (HMS-SO₃H-3), with pore volumes of 0.48, 0.34 and 0.31 cm³ g⁻¹, respectively. All three showed maxima in the pore size distributions at diameters of approximately 2.0 nm. The SBA-15-SO₃H exhibited a surface area of 680 m² g⁻¹ and a pore volume of 0.92 cm³ g⁻¹, with a well-defined maximum in the pore size distribution around a diameter of 6.5 nm. These results are all consistent with those reported in the literature [10,11].

The concentrations of acid sites on all solids were measured by aqueous pH titration and appear in Table 1. In Fig. 3a the molar enthalpies of neutralisation ($\Delta H_{\text{neut.}}^{\circ}$) of the supported sulfonic acids with aqueous NaOH solution are shown plotted against the acid group loading. (Note that the loading is given in terms of mmol of acid per gram of catalyst. The alternative way of expressing the loading, relative to the surface area of the catalyst, is not appropriate in the case of the sulfonated polystyrene resins since the sulfonic acid groups are distributed throughout the bulk of the resins and not simply on the surface.)

The first point to note is that the $\Delta H_{\text{neut.}}^{\circ}$ values for the sulfonated resins with relatively low sulfonic acid loadings (M-1 and M-2) and for the sulfonated silicas are quite similar and in the range -52 to -55 kJ mol⁻¹. In previous work we have shown how these $\Delta H_{\text{neut.}}^{\circ}$ values are very similar to those exhibited by homogeneous aqueous solutions of *p*-toluene sulfonic acid (a monomeric analogue of sulfonated

Table 1

Polystyrene- and mesoporous silica-supported sulfonic acids

Supported sulfonic acid	Acid site concentration (mmol g ⁻¹)
Macroporous polystyrene-SO ₃ H resins	
M-1	0.7
M-2	1.8
M-3	4.8
M-4 (CT-175)	4.9
M-5 (CT-275)	5.4
M-6	5.6
Mesoporous silica-SO ₃ H	
HMS-SO ₃ H-1	1.2
HMS-SO ₃ H-2	1.3
HMS-SO ₃ H-3	2.8
SBA-15-SO ₃ H	1.2

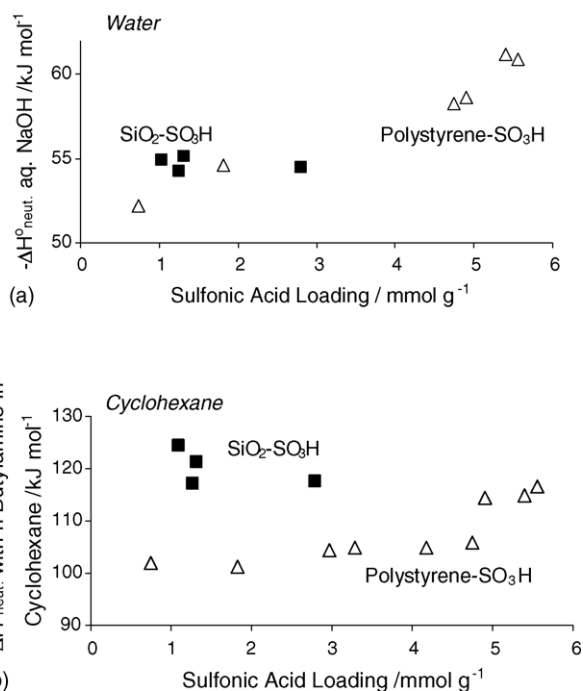


Fig. 3. (a) $\Delta H_{\text{neut.}}^{\circ}$ (aq. NaOH) for sulfonated polystyrene and sulfonated silicas in water and dependence on the sulfonic acid loading ($\Delta H_{\text{neut.}}^{\circ}$: ± 1 kJ mol⁻¹). (b) $\Delta H_{\text{neut.}}^{\circ}$ (*n*-butylamine in C₆H₁₂) for sulfonated polystyrene and sulfonated silicas and dependence on sulfonic acid loading ($\Delta H_{\text{neut.}}^{\circ}$: ± 5 kJ mol⁻¹). Sulfonated macroporous polystyrene resins (Δ) and sulfonated silicas (\blacksquare).

polystyrene) and solutions of HCl [13,14]. In this respect, the sulfonated silicas and sulfonated polystyrene with low levels of sulfonation behave in the same way as typical strong mineral acid solutions. This is as expected. In contrast, the four sulfonated polystyrene resins (M-3, M-4, M-5 and M-6) with levels of sulfonation of 4.8 mmol g⁻¹ (equivalent to roughly one sulfonic acid group per styrene unit) or greater show significantly higher $\Delta H_{\text{neut.}}^{\circ}$ values than both the other solid acids and the homogeneous solutions of strong mineral acids. In related work, in which we studied the catalytic activities of these supported sulfonic acids, we showed that these elevated enthalpies of neutralisation are associated with significantly enhanced specific activities in typical Bronsted acid catalysed reactions, suggesting that, for these materials, high $\Delta H_{\text{neut.}}^{\circ}$ values can be interpreted in terms of increased acid strengths [12–16]. Furthermore, we have used FT-Raman spectroscopy to characterise the sulfonic acid groups in these highly sulfonated polystyrene resins in the presence of water and we have shown that these acid groups are largely undissociated. It seems that the undissociated form of the acid is stronger than the hydroxonium ion which normally dominates in aqueous sulfonic acid systems [14]. The reason why the acid groups remain undissociated is not clear. At first we thought that restricted dissociation of the acid groups might be related to the high acid concentration in the internal solution (in the swollen hydrated gel) in resins with high levels of sulfonation. However, measurements made on aqueous solutions of

p-toluene sulfonic acid at concentrations equivalent to those in the internal solutions suggested that this is not the case [14]. As a result we proposed that there might be networks of interacting sulfonic acid groups, brought into alignment by the polymer backbone in the hydrated resins, which in some way favour the undissociated state. The existence of networks of interacting sulfonic acid groups has been invoked before to explain the enhanced acid strength of essentially dry, highly sulfonated resins [17]. We admit that the idea that similar networks can exist in water in the very different environment of swollen, hydrated resins is not an intuitively satisfactory model, and this can only be treated as speculation at the moment.

In Fig. 3b the molar enthalpies of neutralisation for the same supported sulfonic acids in cyclohexane with *n*-butylamine are shown. In this solvent, the sulfonated polystyrene resins show the same trend as in water in that $\Delta H_{\text{neut.}}^{\circ}$ increases with the level of sulfonation. But, in contrast to the behaviour in water, the sulfonated silicas show numerically higher $\Delta H_{\text{neut.}}^{\circ}$ values than all the sulfonated resins. The implication is that the acid strengths of the sulfonated silicas are higher than those of the sulfonated polystyrene resins in cyclohexane, a reversal of the order of acid strengths to that seen in water. This has been borne out by catalytic measurements [13]. Homogeneous solutions of the analogous *p*-toluene sulfonic acid in cyclohexane have shown $\Delta H_{\text{neut.}}^{\circ}$ values similar to those of the sulfonated silicas of $-120 \pm 5 \text{ kJ mol}^{-1}$. These are significantly higher than values for the sulfonated polystyrene resins [13]. This suggests that, in this solvent, the sulfonated silicas exhibit the same acid strengths as the equivalent homogeneous solutions of analogous acids, whereas the sulfonated resins show lower acid strengths than these equivalent solutions. It is not clear why the strength of sulfonic acid groups on polystyrene supports should be depressed relative to *p*-toluene sulfonic acid (especially since the reverse is seen in water). Of course, cyclohexane is a non-swelling solvent and access of the base probe to the acid sites requires diffusion through the polymer matrix. While this is facile in the hydrated swollen resin, in the collapsed resin there may be significant resistance and it may be this factor which somehow reduces the effective acid strength of the embedded sulfonic acid groups.

Turning now to the acid strength measurements in the absence of solvent, Fig. 4 shows the molar enthalpy of NH_3 adsorption ($\Delta H_{\text{ads.}}^{\circ}$) as a function of surface coverage for the two types of supported sulfonic acid at 100°C . (Note that the data for the NH_3 adsorption experiments in this figure are presented in a very different way to that for liquid titrations in Fig. 3 where only one $\Delta H_{\text{neut.}}^{\circ}$ value is shown for each solid acid.)

In Fig. 4a the data is shown for the sulfonated polystyrene resins. A number of aspects are worth noting. The first is that relatively strong adsorption occurs up to a coverage equivalent to close to one NH_3 molecule per acid site (the concentration of acid sites on the resins is given in brackets), followed by an abrupt fall in adsorption enthalpy when this

is exceeded. This suggests that stoichiometric chemisorption on all acid sites in the resin occurs and that this is accompanied by relatively little physisorption on other sites. (This is not surprising since the resin beads have very small conventional surface areas and rely on diffusion through the polymer gel to access acid sites.) So, evidently with these particular solid acids, NH_3 adsorption at 100°C is an effective technique for selectively characterising Bronsted acid sites. The second point is that the $\Delta H_{\text{ads.}}^{\circ}$ values for each resin vary relatively little as the acid sites are progressively populated. This suggests that the acid sites on an individual resin are of an almost constant strength. Although this cannot be concluded unambiguously because, as was mentioned in Section 1, NH_3 molecules in each dose will occupy sites with a range of energies governed by a Boltzmann distribution, and not simply the strongest vacant sites, the variations in $\Delta H_{\text{ads.}}^{\circ}$ seen in Fig. 4a up to saturation are rather similar to those seen by others in similar experiments with well-characterised zeolitic materials where the acid sites are known to be of uniform type [18]. We conclude, therefore, that the acid sites on the sulfonated polystyrene resins are indeed most probably of fairly uniform strength on individual resins.

The final point to note from Fig. 4a is that, for the four sulfonated resins illustrated, the mean molar enthalpies of NH_3 adsorption on acid sites, as judged from the relatively flat parts of the profiles, increase with the level of sulfonation, implying that the strength of the sulfonic acid sites increases as the level of sulfonation is increased. This trend is the same as that observed in the two solvents tested, water and cyclohexane, and has been reported previously by us [13–16]

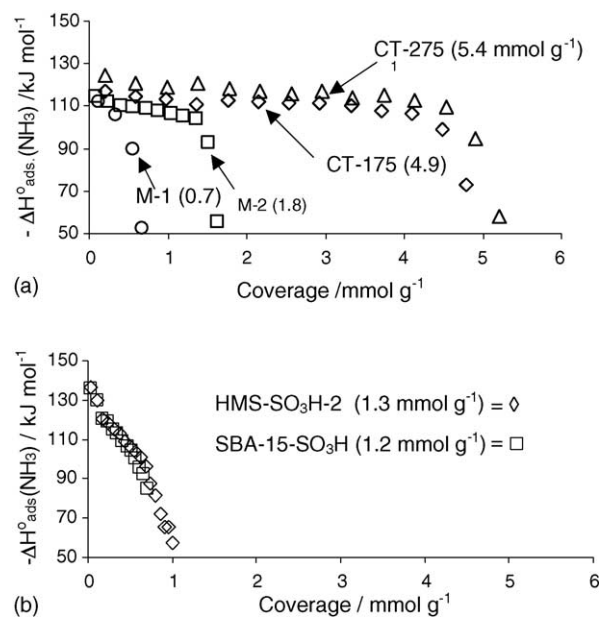


Fig. 4. (a) $\Delta H_{\text{ads.}}^{\circ}(\text{NH}_3)$ at 100°C with coverage for macroporous M-1, M-2, M-3 and M-4 sulfonated polystyrene resins ($\Delta H_{\text{ads.}}^{\circ} : \pm 3 \text{ kJ mol}^{-1}$). The concentration of acid sites on each resin is given in brackets; (b) $\Delta H_{\text{ads.}}^{\circ}(\text{NH}_3)$ at 100°C with coverage for sulfonated mesoporous silica molecular sieves SBA-15- SO_3H and HMS- SO_3H -2 ($\Delta H_{\text{ads.}}^{\circ} : \pm 3 \text{ kJ mol}^{-1}$).

and other workers in dehydrated resins [19–22]. We referred above to the possible difficulties in explaining this trend when the resins are fully hydrated. In the absence of solvent, or in the presence of cyclohexane, it is easier to find an explanation for why highly sulfonated resins might exhibit enhanced acid strengths. Quite simply, the presence of disulfonated styrene rings on the polystyrene polymer, and the presence of sulfone bridges between aromatic rings, both of which would be more abundant in highly sulfonated resins, would result in activation of sulfonic acid groups and higher acid strengths than would be seen for isolated mono-sulfonated rings. It has to be said, however, that although this is an attractive and simple model, the fact that a similar trend in the acid strengths of highly sulfonated resins occurs under the very different conditions of full hydration casts some doubt on its veracity.

In Fig. 4b $\Delta H_{\text{ads.}}^{\circ}(\text{NH}_3)/\text{coverage}$ profiles at 100 °C are shown for two of the sulfonated silicas, one of the HMS-SO₃H samples and the SBA-15-SO₃H. These are representative of the series and the other two HMS-SO₃H solid acids both show very similar profiles (slightly surprising in the case of HMS-SO₃H-3 in view of its higher level of sulfonation). Points to note about these results are as follows. Firstly, the concentrations of acid sites on these materials are very much lower than on the sulfonated resins. Secondly, more physisorption of NH₃ on these solids might be expected because of their very much higher surface areas. This would occur simultaneously with chemisorption and would result in a reduction in the overall measured $\Delta H_{\text{ads.}}^{\circ}(\text{NH}_3)$ throughout the adsorption process. This is clearly seen in both cases, as the profiles fall steadily as coverage increases, falling below -80 kJ mol^{-1} (a value taken by many workers to represent the lower limit of adsorption enthalpy for NH₃ on acid sites [2]) at coverages corresponding to less than the known concentrations of surface acid sites. These factors make a comparison with the adsorption data for the sulfonated resins difficult. For instance, at the very lowest coverages, achieved with the first pulses of NH₃, the sulfonated silicas show enthalpies of adsorption similar to the sulfonated resins. On the face of it, this implies that the strengths of the strongest sites on the two solids are similar. However, the values recorded for the sulfonated silicas are, as described above, probably reduced because of simultaneous physisorption on these solids, so it is quite possible that, in fact, the strongest sites on the silica are significantly stronger than those on the resins. In principle it would be possible to separate the two types of adsorption by carrying out an adsorption–desorption–adsorption experiment, so that reversibly adsorbed (physisorbed) NH₃ is removed and re-adsorbed in the second and third legs of the experiment. However, in our experience, while this sort of experiment can give an overall mean value for $\Delta H_{\text{ads.}}^{\circ}(\text{NH}_3)$ (chemisorption only) by subtracting the data for physisorption from that for the combined physisorption and chemisorption measured in the first leg, it involves too many experimental uncertainties to yield more than a mean value for $\Delta H_{\text{ads.}}^{\circ}(\text{NH}_3)$, and cannot readily be used to extract information on the distribution of acid

site strengths or, by extension, values for the strengths of the strongest acid sites.

4. Conclusion

For a comparable series of solid acids such as the supported sulfonic acids studied here, base adsorption or base neutralisation calorimetry can be used to measure the relative acid strengths of the members of the series. The results of this work show how these relative acid strengths vary as the medium in which the acidity measured is changed. Interestingly, for the sulfonated polystyrene resins, the acid strengths of the highly sulfonated (above the stoichiometric level) resins are greater than for those sulfonated at lower levels in both of the solvents studied and in the absence of solvent. It is surprising that the mechanism responsible for the acidity enhancement in the highly sulfonated materials is able to operate under such widely differing conditions, of full hydration, in the presence of a non-swelling solvent, and in the complete absence of solvent. The fact that the orientations of neighbouring sulfonic acid groups is likely to be very different under these different sets of conditions suggests that the enhancement of acid strength in highly sulfonated resins may perhaps be less to do with interactions between neighbouring sulfonic acid groups and more to do with the primary structure of the sulfonated polymer, which is unaffected by solvation.

In contrast to this, a comparison between all the sulfonated resins and the sulfonated silicas shows that their relative acidities are reversed when going from water to cyclohexane. The sulfonated polystyrene resins, particularly those with greater than stoichiometric levels of sulfonation, show enhanced acid strength in water compared to conventional strong acids (and we have discussed possible reasons for this elsewhere) whereas the sulfonated silicas behave very much like conventional strong mineral acids. In cyclohexane, the sulfonated silicas behave again like homogeneous solutions of strong acids, but now the sulfonated resins show significantly *lower* acid strength. The reasons for this are unclear, but the point being illustrated here is simply the dramatic affect of the solvent on relative acidities.

Comparing these results to those obtained by NH₃ adsorption at 100 °C, it is clear that these progressive adsorption experiments under vacuum conditions are very difficult to interpret because of the unknown contribution to the overall adsorption process from simultaneous physisorption on non-acidic sites. One way to reduce the effect of physisorption is to carry out the adsorption at higher temperature, and, as mentioned above, the contribution from physisorption can, in principle, be subtracted by performing an adsorption–desorption–adsorption experiment. Nevertheless, to use these data to reliably compare solid acids, it is necessary for the solid matrix to be at least similar through the series of materials studied and, in this way, to ensure that the variable contribution from physisorption to the overall

adsorption process is not overwhelming. This is a very different requirement to that imposed on solid acids if liquid phase acid–base titrations are to be used to measure and compare acid strengths, where solvation effects and ion pair formation are the factors that restrict comparisons. Despite this, where physisorption can be controlled, the advantage of these relatively high temperature adsorption experiments is that they can, under the right circumstances, give an indication of the acid strength distribution profile. It is reasonable to expect that if a solid acid exhibits say a small number of quite strong sites alongside the bulk of weaker sites, this would not be seen in a liquid phase titration at 30 °C but possibly would be detected using high temperature adsorption from the gas phase.

Overall, the work illustrates that different aspects of the acidic character of solid acids can be probed using different adsorption/neutralisation experiments. It also shows how the nature of the solvent used for liquid phase titrations can have a dramatic affect on measured acid strength. It also illustrates the requirement that, should measurements such as these be used for predicting catalytic properties, it is essential that the acidity measurements be made in solvents similar to those in which the catalysts are ultimately to be used.

References

- [1] A. Auroux, *Topics Catal.* 4 (1997) 71.
[2] R.J. Gorte, *Catal. Lett.* 62 (1999) 1.
[3] D.J. Parillo, R.J. Gorte, *Thermochim. Acta* 312 (1998) 125.
[4] R.S. Drago, N. Kob, *J. Phys. Chem. B* 101 (1997) 3360.
[5] C. Chronister, R.S. Drago, *J. Am. Chem. Soc.* 115 (1993) 4793.
[6] E.M. Arnett, R.A. Haaksma, B. Chawla, M.H. Healy, *J. Am. Chem. Soc.* 108 (1986) 4888.
[7] E.M. Arnett, T. Absan, K. Amarnath, *J. Am. Chem. Soc.* 113 (1991) 6858.
[8] C.E. Harland, *Ion Exchange: Theory and Practice*, 2nd ed., Royal Society of Chemistry Monograph, London, 1994.
[9] W.M. Van Rhijn, D.E. DeVos, B.F. Sels, W.D. Bossaert, P.A. Jacos, *J. Chem. Soc., Chem. Commun.* (1998) 317.
[10] W.D. Bossaert, D.E. DeVos, W.M. Van Rhijn, J. Bullen, P.J. Grobet, P.A. Jacobs, *J. Catal.* 182 (1999) 156.
[11] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, *Chem. Mater.* 12 (2000) 2448.
[12] M. Hart, G. Fuller, D.R. Brown, C. Park, M.A. Keane, J.A. Dale, C.M. Fougret, R.W. Cockman, *Catal. Lett.* 72 (2001) 135.
[13] S. Koujout, D.R. Brown, *Catal. Lett.* 98 (2004) 195.
[14] S. Koujout, B.M. Kiernan, D.R. Brown, H.G.M. Edwards, J.A. Dale, S. Plant, *Catal. Lett.* 85 (2003) 33.
[15] M. Hart, G. Fuller, D.R. Brown, J.A. Dale, S. Plant, *J. Mol. Catal. A: Chem.* 182–183 (2002) 439.
[16] S. Koujout, D.R. Brown, in: S.D. Jackson, J.S.J. Hargreaves, D. Lennon (Eds.), *Catalysis in Application*, Royal Society of Chemistry, London, 2003, pp. 178–185.
[17] R. Thornton, B.C. Gates, *J. Catal.* 34 (1974) 275.
[18] D.J. Parrillo, R.J. Gorte, *J. Phys. Chem.* 97 (1993) 8786.
[19] C. Buttersack, H. Widdeske, J. Klein, *React. Polym.* 5 (1987) 181.
[20] F. Ancillotti, M.M. Mauri, E. Pescaraollo, *J. Catal.* 46 (1977) 49.
[21] K. Jerabek, K. Setinek, *J. Mol. Catal.* 39 (1987) 161.
[22] J.H. Ahn, S.K. Ihn, K.S. Park, *J. Catal.* 113 (1988) 434.