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The influence of solvent on the acidity and activity of supported sulfonic acid catalysts

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The acid strengths and catalytic activities of sulfonic acids supported on polystyrene resins and ordered mesoporous HMS and SBA-15 silicas are compared. Acid strengths are measured by acid–base titration calorimetry in terms of the molar enthalpies of neutralisation with either NaOH or *n*-butylamine in water, acetonitrile and cyclohexane. Catalytic activities (turnover numbers) are reported in model reactions in water, 1,2-dichlorobenzene and anisole, and compared with acid strengths. In water, sulfonated resins are both stronger acids and more active catalysts than sulfonated silicas. Catalytic activities in water correlate well with these measured acid strengths. In acetonitrile the order of acid strengths is reversed and the sulfonated silicas are the stronger acids. Catalytic measurements in 1,2-dichlorobenzene, a similar dipolar aprotic solvent, show the same reversed order of activities. In the non-polar solvent cyclohexane (where only macroporous sulfonated resins show measurable acidity) the sulfonated silicas are again the stronger acids but by a larger margin. Catalytic activities in anisole, which is also only very weakly solvating towards sulfonic acid groups, show a similar trend. The results illustrate the role of the solvent in controlling the acid strength of solid acid catalysts, and the importance of taking this into account when designing acid catalysts for liquid phase processes.

KEY WORDS: acid catalysis; solid acid; ion-exchange resin; sulfonated silica; mesoporous molecular sieve; sulfonated polystyrene; titration calorimetry; enthalpy of neutralisation.

1. Introduction

Sulfonic acids supported on polymeric resins are well known acid catalysts, widely used in MTBE, TAME, bis-phenol A and other syntheses [1–3]. Analogous materials in which sulfonic acids are supported on inorganic rigid solids such as porous silicas have only been reported recently [4–6] and, as far as we know, have not yet been adopted for industrial application. A comparison between sulfonic acids on these two very different supports provides the opportunity to observe directly the effect of the support on the acidity and catalytic activity of the supported acid group.

In previous work we have shown how sulfonated polystyrene resin catalysts exhibit significantly higher acid strengths and specific catalytic activities (per acid group) than sulfonic acids supported on silica in the presence of water [7,8]. The implication of this result is that the way in which the solvent interacts with both the catalyst and the support might play an important role in controlling the catalytic properties of the acid groups. It therefore seemed important to examine the effects of other solvents on the relative acidities and activities of these two types of supported sulfonic acids. In the work reported here, we have extended the comparison to two non-aqueous solvents with different capacities to solvate the supported acid groups. In the case of sulfonated polystyrene resins this also affects the extent to which the resins swell in the presence of solvent, and so generate the "internal solutions" in the swollen gel in which catalysis occurs. The first is acetonitrile, a dipolar aprotic solvent which solvates polar groups reasonably well. It solvates supported sulfonic acid groups sufficiently strongly to swell sulfonated polystyrene beads, although not to the same extent as water. The second is the more weakly solvating cyclohexane. This solvent is unable to swell the sulfonated polystyrene matrix. It has been chosen as an inert solvent in the expectation that measured acidities might reflect the acid strengths of the catalysts in the absence of any solvent effects.

A range of sulfonated polystyrene resins has been used for the study. Some are of the gel type for which access to acid sites relies on solvation and swelling of the polymer beads, and others are of the macroporous type in which acid sites can be accessed in non-swelling solvents. Resins have been used with sulfonic acid loadings from 0.74 to 5.56 mmol g^{-1}. A level of 4.7–4.9 mmol g^{-1} is equivalent to about one acid group per styrene unit. Resins sulfonated at higher levels than this ("persulfonated") have previously been shown to exhibit disproportionately high acid strengths and catalytic activities compared to stoichiometrically sulfonated resins [7–14].

Silica supports for sulfonic acid have been based on ordered mesoporous molecular sieves. Two types have been used, the so-called HMS hexagonal mesoporous

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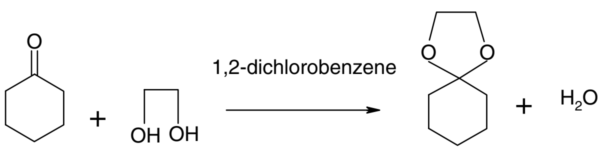
sieves [15] and the larger pore SBA-15 sieves [16]. These materials are prepared by sol gel synthesis using surfactant micelle templates, and in this work they have been co-condensed with propylthiol silanes which have been subsequently oxidised to give tethered propylsulfonic acids [4–6].

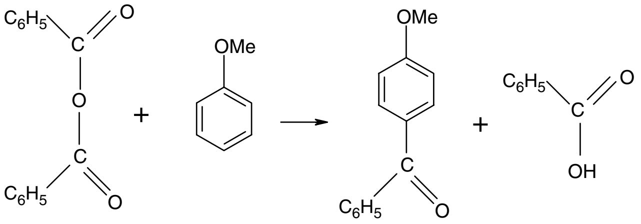
The objective has been to measure the strengths of the supported acid groups and their catalytic activities in the non-aqueous solvents, and to deduce how the solvent type influences these properties. Acid strengths have been measured by titration calorimetry, on the basis that, when using the same titrant base and the same solvent, enthalpies of neutralisation ($\Delta H^0_{\rm neut}$) are a relative measure of the strength of surface acid sites. This assumption requires justification. In fact, the measured enthalpy of neutralisation is made up from contributions from several sources: proton loss from the acid, proton gain by the base, changes in solvation as the acid and base are converted to the conjugate base and acid, and any enthalpy changes associated with ion pairs that form or break up during the neutralisation reaction. To assume that differences in measured $\Delta H^0_{\rm neut}$ values reflect differences in the acid strengths of solid acids requires that all contributions to $\Delta H^0_{\rm neut}$ other than the proton affinity of the acid are constant. We have taken the approach that this is a reasonable assumption only when comparing closely related solid acids, and we believe that the series of supported sulfonic acids used in this study are suitably similar to justify the use of this technique to compare their acid strengths. This approach to using titration calorimetry to study the strength of solid acids in the presence of solvents is in line with the work of others in the field [17–20].

Activities of some of the catalysts in water have already been reported, in the acid catalysed hydrolysis of ethyl ethanoate [7]. In the current work two additional Bronsted acid catalysed test reactions in non-aqueous solvents have been used. Ideally, we would have liked to measure activities in the same solvents as those in which acid strengths were measured. For practical reasons this was not possible, so the solvents used for catalytic testing were chosen to be as similar as possible, in terms if their capacities to solvate the supported acids, to those used for acid strength measurements.

The first new test reaction is the acetalisation of cyclohexanone with ethylene glycol in 1,2-dichlorobenzene solvent (Scheme 1). This is a dipolar aprotic solvent and able to swell sulfonated polystyrene resin beads to a limited extent. It was used because of its similarity to acetonitrile and catalytic activities measured in this 1,2-dichlorobenzene are compared with acid strengths measured in acetonitrile.



Scheme 1.



Scheme 2.

The second reaction is the acylation of anisole using benzoic anhydride, in anisole as the solvent (Scheme 2). Anisole is a solvent of low polarity and does not swell sulfonated resins to any measurable extent. It was chosen as a reactant/solvent on the basis that activity in this reaction would be comparable with acid strengths measured in cyclohexane.

2. Experimental

2.1. Catalysts

2.1.1. Sulfonated polystyrene resins

Sulfonated polystyrene resins were provided by Purolite International, except for Amberlyst 15 (Rohm and Haas co.). Three types of resin were used: (1) gel resins containing 4% w/w cross-linking divinylbenzene (DVB), (2) gel resins containing 10% w/w DVB, and (3) macroporous resins (with permanent porosity) which are believed to contain 15–18% w/w DVB (Purolite International 2000, personal communication). All resins 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 [21]. 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.

2.1.2. Sulfonated mesoporous silicas

Thiol-functionalised mesoporous silica molecular sieve HMS-SH was synthesised 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-synthesised HMS-SH with ethanol under reflux for 24 h [5].

The equivalent material based on the larger pore SBA-15 silica molecular sieve was prepared as follows. Pluronic 123 ($EO_{20}PO_{70}EO_{20}$, $M_{\rm av}$ 5800, Aldrich) (4 g) was dissolved 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-synthesised material per 400 ml of ethanol) [6].

Materials with immobilised mercaptopropyl groups were oxidised with H_2O_2 in a methanol-water mixture. Typically 2.04 g of aqueous 35% H_2O_2 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 H_2SO_4 solution for another 4 h. Finally, the material was rinsed with water and dried at 60 °C under vacuum [5,6].

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 based on the well-known Setaram C80, 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 catalyst was suspended in 2 cm^3 solvent in the sample cell, with the same volume of solvent in the reference cell. Experiments were performed at 30 °C. The titrant, 0.100 mol dm^{-3} NaOH in water, or 0.100 mol dm^{-3} *n*-butylamine in acetonitrile or cyclohexane, was added to the sample cell in 0.20 cm^3 aliquots at 1 h intervals until neutralisation was complete. Pure solvent was added to the reference cell in the same way. The heat output was measured for each addition and the cumulative heat plotted against amount of added base. 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 in kJ mol^{-1}.

Where possible, molar enthalpies of neutralisation in water, acetonitrile and cyclohexane were also measured for homogeneous solutions of HCl (0.1 mol kg^{-1}) and *p*-toluenesulfonic acid (*p*-TsOH) (1–5 mol kg^{-1}), using the same titrant solutions. In each case, enthalpies of dilution of the acid solutions were measured first (these were invariably small compared to enthalpies of neutralisation) and allowed for. The initial gradients of the corrected cumulative enthalpy versus added base plots were taken as the molar enthalpies of neutralisation at the initial acid concentrations. In fact, as is clear from the data, the graphs were essentially linear up to close to the end points, even for the most concentrated *p*-TsOH solutions.

2.3. *Catalytic activities*

The silica based catalysts were used as ground powders. The sulfonated polystyrene resins were used as conventional beads and were also examined following grinding to fine powder. In all cases higher rates were measured with the ground up beads and it is these rates that are reported. A systematic study of the dependence of reaction rate on particle size was not possible but crude attempts to grind the beads to different extents suggested that, when using them in the ground form, the reactions were not under external diffusion control.

Catalysts were activated before use at 110 °C for 18 h under flowing dry air. They were transferred to the reaction mixtures without exposure to the atmosphere.

Details of the ethyl ethanoate hydrolysis test reaction in water were given in a previous paper [7]. For the acetalisation of cyclohexanone, 11 mmol of ethylene glycol were dispersed in 30 g of 1,2-dichlorobenzene containing 320 mg catalyst [22,23]. The reaction medium was aged for 30 min at 60 °C. Cyclohexanone (11 mmol) was then added to start the reaction. The mixture was vigourously stirred. Samples (0.5 μL) were taken at regular intervals and analysed by GC, monitoring the acetal product peak and using the solvent peak as an internal standard.

For the acylation of anisole with benzoic anhydride, the reaction mixture (2.65 mmol benzoic anhydride, 12 ml anisole and 0.1 g tetradecane internal standard) was heated to 70 °C and stirred vigorously. Activated catalyst (200 mg) was added [24]. Reaction progress was followed with GC through the peak area of *p*-methoxyacetophenone measured against the tetradecane internal standard. For both reactions, initial reaction rates were determined and expressed as specific rates per mol of sulfonic acid groups on the catalyst.

3. Results and discussion

The sulfonated silica catalysts gave well resolved powder XRD patterns. For the HMS–SO_3H samples these 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-SO_3H patterns also showed intense reflections from 100 planes with a spacing of 9.4 nm. In both cases the patterns were similar to those reported in the literature [5,6].

From nitrogen adsorption data, the three HMS–SO_3H samples exhibited BET surface areas of 940 (HMS–SO_3H 1), 850 (HMS–SO_3H 2) and 750 m^2 g^{-1} (HMS–SO_3H 3), with pore volumes of 0.48, 0.34 and 0.31 cm^3 g^{-1}, respectively. All three showed maxima in the pore size distributions at diameters of approximately 2.0 nm. The SBA-15-SO_3H exhibited a surface area of 680 m^2 g^{-1} and a pore volume of 0.92 cm^3 g^{-1}, and showed a well-defined maximum in the pore size distribution around a diameter of 6.5 nm. These results are consistent with reported values [5,6].

The concentrations of acid sites on all catalysts measured by aqueous pH titration appear in the table 1. In figure 1a the molar enthalpies of neutralisation ($\Delta H^0_{\mathrm{neut}}$.) of the catalysts with aqueous NaOH solution are shown plotted against the acid group loading. In figure 1b these same $\Delta H^0_{\mathrm{neut}}$. values for the sulfonated resins are plotted against the effective concentrations of the internal acid solutions in the swollen resins. These concentrations are based on the known water contents of the fully hydrated resin beads. Most of the resins absorb approximately their own weight in water but the precise water uptake data used for the calculations were provided by the manufacturers. It is worth noting that for macroporous resins it is difficult to distinguish between water taken up in the swollen gel and water trapped in the permanent pores, and typical water uptake values include both. This means that calculated internal solution concentrations for macroporous resins are only lower limits for the actual solution in the gel regions. In the figure the data points for the macroporous resins are generally higher than those for the gel resins, consistent with an underestimation of concentrations in these resins. Also shown in the figure are $\Delta H^0_{\mathrm{neut}}$. values for homogeneous aqueous solutions of HCl and *p*-TsOH at concentrations similar to those of the internal solutions of the resins. In figure 1c the specific initial reaction rates for the ethyl ethanoate hydrolysis reaction, expressed as a turnover number per mole of catalyst acid, is again plotted against the acid group loading on the catalyst.

Table 1
Sulfonated polystyrene and sulfonated mesoporous silica catalysts

Catalyst	Acid Site Concentration/mmol g^{-1}
Polystyrene–SO_3H Resins	
Gel resins (4% w/w DVB)	
G(4)-1	1.31
G(4)-2	2.61
G(4)-3	3.45
G(4)-4	5.04
Gel Resins (10% w/w DVB)	
G(10)-1	0.80
G(10)-2	1.48
G(10)-3	1.98
G(10)-4	3.04
G(10)-5	5.00
G(10)-6	5.11
Macroporous resins	
M-1	0.74
M-2	1.82
M-3	2.97
M-4	3.28
M-5	4.18
M-6 (Amberlyst 15)	4.74
M-7 (CT-175)	4.9
M-8 (CT-275)	5.4
M-9 (CT-375)	5.56
Silica–SO_3H	
HMS–SO_3H 1	1.2
HMS–SO_3H 2	1.31
HMS–SO_3H 3	2.8
SBA-15-SO_3H	1.15

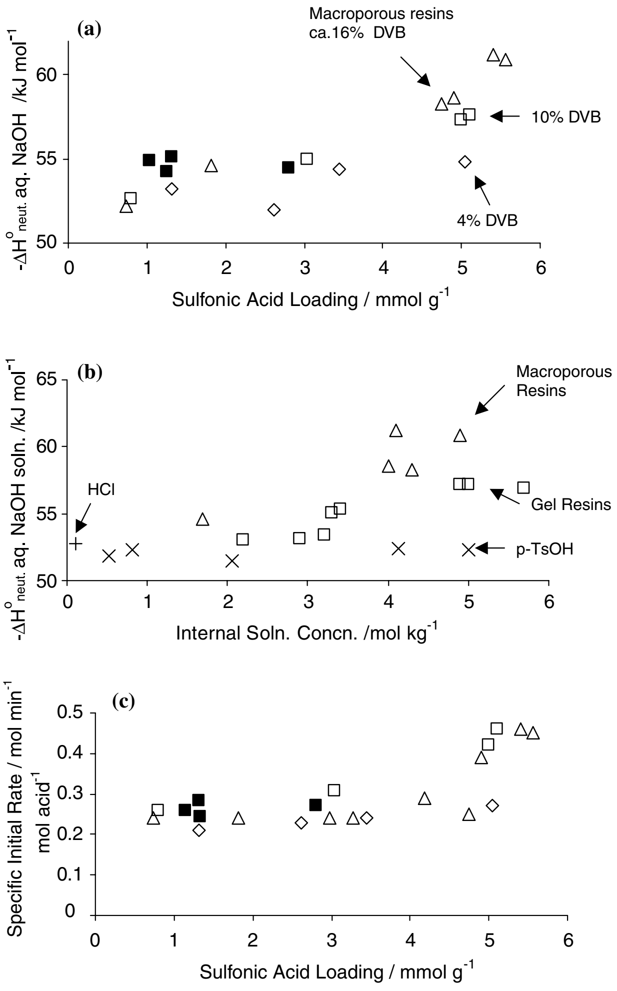


Figure 1. (a) $\Delta H^0_{\mathrm{neut}}$.(aq. NaOH) for sulfonated polystyrene and sulfonated silicas in water and dependence on the sulfonic acid loading. (b) $\Delta H^0_{\mathrm{neut}}$.(aq. NaOH) for sulfonated polystyrene in water and dependence on the concentration of the internal solution in the swollen resin. Data are also shown for aqueous solutions of *p*-TsOH and HCl against solution concentration. (c) Specific initial reaction rates (per mol acid sites) in the hydrolysis of ethylethanoate and dependence on sulfonic acid loading. Key: △, sulfonated macroporous polystyrene resins; □, sulfonated gel resins with 10% DVB; ◇, sulfonated gel resins with 4% DVB; ■, sulfonated silicas; ×, *p*-TsOH solutions; +, HCl solution.

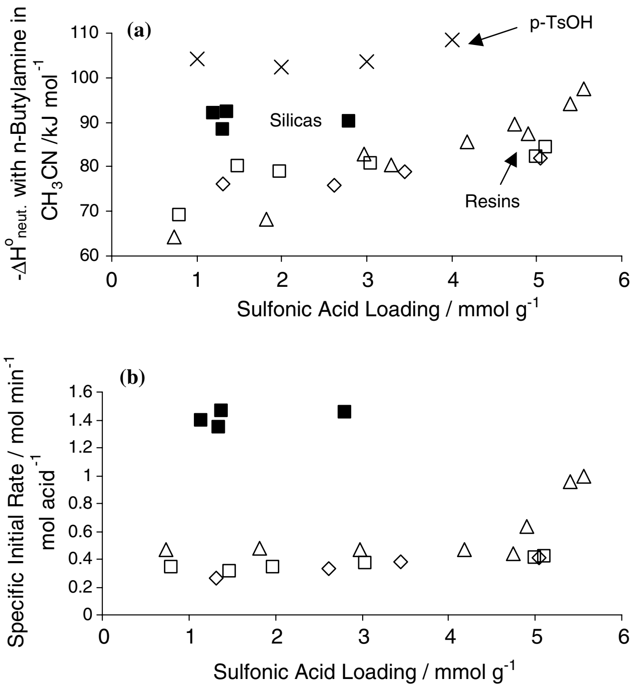


Figure 2. (a) $\Delta H^0_{\mathrm{neut}}$ (*n*-butylamine in CH_3CN) for sulfonated polystyrene and sulfonated silica catalysts and dependence on sulfonic acid loading. Data for solutions of *p*-TsOH are also shown against solution concentration. (b) Specific initial reaction rates (per mol acid sites) in the acetalisation of cyclohexanone with ethylene glycol in 1,2-dichlorobenzene and dependence on sulfonic acid loading. Key: △, sulfonated macroporous polystyrene resins; □, sulfonated gel resins with 10% DVB; ◇, sulfonated gel resins with 4% DVB; ■, sulfonated silicas; ×, *p*-TsOH solutions.

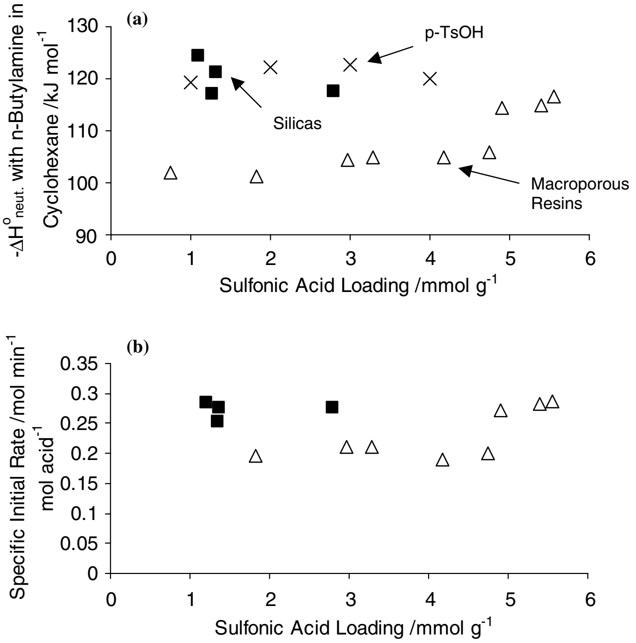


Figure 3. (a) $\Delta H^0_{\mathrm{neut}}$ (*n*-butylamine in C_6H_{12}) for sulfonated polystyrene and sulfonated silica catalysts and dependence on sulfonic acid loading. Data for solutions of *p*-TsOH are also shown against solution concentration. (b) Specific initial reaction rates (per mol acid sites) in the acylation of anisole with benzoic anhydride (solvent anisole) and dependence on sulfonic acid loading. Key: △, sulfonated macroporous polystyrene resins; ■, sulfonated silicas; ×, *p*-TsOH solutions.

Figure 2 gives the $\Delta H^0_{\mathrm{neut}}$ (*n*-butylamine) values in acetonitrile and catalytic data in 1,2-dichlorobenzene for sulfonated resins and sulfonated silicas, and acidity data for *p*-TsOH solutions. Figure 3 shows $\Delta H^0_{\mathrm{neut}}$ values for the catalysts and *p*-TsOH in cyclohexane, and catalytic data for the catalysts in anisole.

On the basis that an increase in the numerical value of $\Delta H^0_{\mathrm{neut}}$. is associated with an increase in the strength of the sulfonic acid sites, the following trends can be seen. Firstly, in the presence of water (figure 1), the strength of polystyrene supported sulfonic acids generally increases with the concentration of acid groups on the polymer. This is particularly noticeable at loadings above 4.5 mmol g^{-1}. Acid strength values for resins with high sulfonic acid group loadings also seem to depend on the level of polymer cross-linking, with higher acid strengths seen for the resins with higher DVB content (this is highlighted in the figure for three resins). Clearly, increasing sulfonation and increasing DVB content both tend to result in higher internal acid concentrations so these trends in acid strength suggest that there might be a relationship between acid strength and concentration of the internal solution in the swollen gel.

The plot of $\Delta H^0_{\mathrm{neut}}$. against internal acid concentration in the sulfonated resin beads (figure 1b) is included to illustrate this possibility and a reasonable correlation is seen. However, in the same Figure $\Delta H^0_{\mathrm{neut}}$. values for homogeneous *p*-TsOH solutions at equivalent concentrations are plotted, and these show that the acid strength of *p*-TsOH is essentially invariant over the same concentration range. On the basis that *p*-TsOH is a good monomeric analogue of sulfonated polystyrene, this suggests that it is not simply the high concentration of acid in solution in the swollen resin gel that is responsible for the elevated acid strengths. In an earlier paper we speculated on the possibility of networks of interacting sulfonic acid groups existing in hydrated resins and being responsible for the acid strength enhancement [8]. This was based on an earlier model proposed by Gates [25] and it remains our favoured explanation for the elevated acid strengths.

Turning attention to the silica supported sulfonic acid catalysts it can be seen from figure 1a that the acid strengths of these materials are similar to those of resins with low levels of sulfonation and homogeneous *p*-TsOH solutions, and significantly lower than those of the highly sulfonated resins. In other words, sulfonic acid groups on silica supports and on polystyrene at low loadings behave in water essentially like the strong mineral acid *p*-TsOH.

The catalytic activities in the hydrolysis of ethyl ethanoate are shown in figure 1c. There is a good correlation between acid strength ($\Delta H^0_{\mathrm{neut}}$.) in water (figure 1a) and specific rates in this reaction, with silica supported sulfonic acids and polystyrene supported sulfonic acids with low levels of sulfonation showing similar rates, and with rates increasing for resins with stoichiometric and higher levels of sulfonation.

In acetonitrile solvent a different pattern is seen. Acid strengths measured as the $\Delta H^0_{\mathrm{neut}}$ with *n*-butylamine are shown in figure 2a. The acid strengths of the resins increase as the level of sulfonation is increased, as they do in water. It is notable that gel and macroporous resins appear to behave in the same way, suggesting that acetonitrile swells the resins sufficiently to allow *n*-butylamine to access acid sites throughout the swollen resin. The major difference from the behaviour in water is seen in a comparison with the acid strengths of the sulfonated silicas. In acetonitrile these show higher acid strengths than nearly all the sulfonated resins. Another difference from the results in water is seen with the strengths of the homogeneous *p*-TsOH solutions. In this solvent the dissolved *p*-TsOH acid shows higher acid strengths than all the resins and the silicas.

Shown in figure 2b are catalytic activities for the acetylisation of cyclohexanone in 1,2-dichlorobenzene. As explained above, this solvent was thought to be similar to acetonitrile in terms of its capacity for solvating the supported sulfonic acid groups. The reaction rates in 1,2-dichlorobenzene correlate reasonably well with the acid strengths measured in acetonitrile. The specific activities of the resin catalysts increase with the level of sulfonation, in the same way the acid strengths increase in acetonitrile. And the catalytic activities of the sulfonated silicas are now higher than those of the resins, in line with the acid strengths in acetonitrile, and in complete contrast to their behaviour in water. Actually, if looked at in detail, the activities of the sulfonated silicas in 1,2-dichlorobenzene exceed those of the sulfonated resins by rather more than might have been predicted based on the acid strength differences in acetonitrile, but we suspect this simply means that the two solvents differ more than we anticipated in terms of their influence on the strength of the sulfonic acid groups.

The acid strength data in acetonitrile can be compared with data reported by Arnett and co-workers, who made a detailed study of sulfonated polystyrene resins in the same solvent, measuring enthalpies of neutralisation with a number of organic bases [17]. Like us, they compared the acid strengths of sulfonated polystyrene with those of homogeneous solutions of *p*-TsOH, and they reported that the homogeneous solutions exhibited higher acid strengths than the polymer supported sulfonic acids (by about 15 kJ mol^{-1} for stoichiometrically sulfonated resins). They explained this difference in terms of the formation of a complex between the sulfonate anion and undissociated sulfonic acid molecules in homogeneous solution, and they proposed that this complex is a stronger acid than an isolated sulfonic acid group. They suggested that this complex could not form when sulfonic acid groups were constrained by a polymer support, hence the lower acid strength of the supported acid. Our results for stoichiometrically sulfonated resins are in general agreement with Arnett's and support this model. In fact it appears that the model could also be consistent with the higher acid strengths seen for persulfonated resins, as it is conceivable that the interactions to form the complex described above between neighbouring groups might become increasingly feasible as the sulfonic acid loading on the polymer support is increased.

In the case of the sulfonic acids supported on HMS and SBA-15 silicas however, this model would at first seem unlikely to able to explain the high acid strengths of these materials in acetonitrile, since the level of sulfonation on these supports is relatively low. But it may not be entirely impossible to explain the high acid strengths of these materials using Arnett's model. it is possible for instance that functionalisation of the silica surface occurs unevenly on the silica surface, perhaps with acid groups clustered at the entrance to pores rather than within the pores, and this may facilitate interactions between neighbouring sulfonic acid groups. Furthermore, the *n*-propyl tethers for the sulfonic acid groups might reasonably be expected to be more flexible than the stryrene units on the polymer resins and this also may facilitate the interaction between neighbouring groups and possibly lead to the observed enhancements in acid strength.

The third type of solvent used in the study was less polar and essentially non-swelling towards sulfonated polystyrene resins. Acid strengths were measured in cyclohexane, again in terms of $\Delta H^0_{\mathrm{neut}}$ with *n*-butylamine, and are shown in figure 3a. In this solvent only the macroporous sulfonated resins, those with permanent porosity, are able to react measurably with the base. The trend amongst these resins is similar to that seen in acetonitrile and in water, with acid strength increasing with the level of sulfonation. A significant difference is seen again however when the acid strengths of the sulfonated silicas are compared with the sulfonated resins. In this solvent the sulfonated HMS and SBA-15 silicas show very much higher acid strengths than all the sulfonated resins, including the persulfonated resins, and are essentially of the same strength as homogeneous *p*-TsOH solutions.

An explanation for acidity variations in cyclohexane must take into account the fact that it would have little interaction with the sulfonic acid groups. There would be negligible dissociation to the sulfonate anion in this solvent so interactions such as those proposed in acetonitrile between anion and undissociated acid to enhance acid strength would not occur. In this solvent, acid strength would depend simply on the proton donating power of the sulfonic acid group. On this basis it is quite reasonable that the acid strengths of the sulfonated HMS and SBA-15 silicas are the same as those of homogeneous *p*-TsOH solutions. On the other hand it is not obvious why the sulfonated polystyrene resins should show very much lower acid strengths in this solvent. One speculative possibility is that a small amount of water retained in the resins is attenuating the acid strength and reducing $\Delta H^0_{\mathrm{neut}}$. It is well known that removal of the last 1–2% by weight of water from sulfonated polystyrene resins is extremely difficult [10,26]. It is possible therefore that some of the acid groups are partially hydrated, and that their acid strength reduced to that of H_3O^+ (although obviously not in a normal aqueous environment). A very rough calculation to illustrate the possible magnitude of the effect of this water suggests that 2% w/w water for a stoichiometrically sulfonated resin would yield one water molecule for 20% of the acid groups. If each of these sulfonic acid groups were converted to H_3O^+, and if these hydroxonium ions exhibited an estimated $\Delta H^0_{\mathrm{neut}}$ with *n*-butylamine of -60 kJ mol^{-1}, then the overall weighted average of $\Delta H^0_{\mathrm{neut}}$for all the–$SO_3H$ groups on the resins could quite conceivably be reduced from a value similar to that of *p*-TsOH (for a completely anhydrous resin) to one close to that observed in figure 3a for a resin containing this residual water. However, whatever the reason for the lower $\Delta H^0_{\mathrm{neut}}$ measured for the sulfonated resins, the important observation from the data shown in figure 3a is that the relative ordering of acid strengths of these closely related supported acids is dramatically different in cyclohexane to that in acetonitrile and to that in water.

The acid strengths of the supported sulfonic acids measured in cyclohexane can be compared with their catalytic activities in anisole solvent since, like cyclohexane, anisole exhibits low polarity and is incapable of swelling sulfonated polystyrene resins. In the test reaction, the acylation of ethanoic anhydride, the sulfonated resins (macroporous only) and the sulfonated silicas show specific activities that again correlate well with their acid strengths measured in cyclohexane (figure 3b), with the sulfonated silicas showing considerably higher specific activities than the sulfonated resins.

4. Conclusion

The overall conclusion of this work is that the nature of the solvent used with a solid acid catalyst can have a dramatic affect on the acid strength of the catalyst. Nominally similar catalysts, with the same functional acid group, can behave differently in different solvents. It seems that acid strength measurements made by titration calorimetry can be used reliably to predict catalytic properties, provided measurements are made in the same, or a similar, solvent to that in which the catalysed reaction is to be carried out.

The specific results from this study show that sulfonic acid groups supported on polystyrene show higher acid strength in water than similar acid groups supported on silica, but in acetonitrile, cyclohexane, and 1,2-dichlorobenzene and anisole, the order of acidities and activities is reversed. Polystyrene supported sulfonic acid catalysts are evidently particularly strong acids and active catalysts in the presence of water, and these materials may become increasingly important catalysts in the development of more benign solvent systems for fine chemical synthesis. In all the solvents tested, the acid strength of sulfonated polystyrene with high levels of sulfonic acid (persulfonated resins) are significantly higher than those of resins with stoichiometric or lower loadings of sulfonic acid. That this acid strength enhancement seems essentially independent of the type of solvent or the level of solvation of the resin may be of significance in designing new polymer supported catalysts, but the explanation for the increased strengths may not be easy to define, and earlier explanations in terms of networks of interacting sulfonic acid groups may be difficult to justify in the wide range of solvation conditions under which it is observed.

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