

Acid strengths and catalytic activities of sulfonic acid on polymeric and silica supports

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Abstract

The acidic and catalytic properties of sulfonic acids supported on polystyrene, on silica (via propyl and phenyl tethers) and on a fluorinated hydrocarbon polymer (Nafion) are compared. Surface acidities are characterised using ammonia adsorption calorimetry under flow conditions in which pulses of ammonia are introduced to the sample from a flowing carrier stream. The extent of adsorption and molar enthalpies of ammonia adsorption ($\Delta H_{\text{ads}}^\circ$) are interpreted in terms of the abundance, accessibility and strength of surface acid sites. Catalytic activities are measured for the isomerisation of α -pinene. The Nafion catalysts show the highest $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ and the highest catalytic activities. Although both silica-supported and polystyrene-supported sulfonic acids show lower specific activities and lower $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ values, the correlation between activity and $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ is relatively poor for these supported forms of the acid. It appears that while $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ is certainly sensitive to the strength of acid groups on which ammonia is adsorbed, it can only be used to compare acid strengths in a meaningful way for structurally similar catalysts. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Sulfonic acid groups can be bound to the surface of inert support materials to form solid acid catalysts. The first objective of this work has been to investigate the effect of the support material, and the way in which sulfonic acid groups are tethered, on the acidities and the catalytic activities of the acid groups. The second objective has been to assess the usefulness and limitations of ammonia adsorption calorimetry as a technique for characterising supported sulfonic acid catalysts on a range of supports.

In previous work, we have shown that the catalytic activities of a series of polystyrene supported sulfonic acid catalysts can be correlated to the strengths of their acid sites measured using ammonia adsorption calorimetric techniques [1–4]. In the work reported here, we have extended this to sulfonic acid on other polymeric and porous silica supports, in which acid groups are tethered by short alkyl or aryl groups.

Polystyrene supported sulfonic acids are widely applied industrially [5–11] in, for example, MTBE, TAME and bisphenol A syntheses. They are convenient to use and invariably exhibit high concentrations of acid sites. However, compared to many acid catalysts, they exhibit relatively low thermal stabilities and comparatively low acid strengths [1–4].

The fluorinated polymer-supported sulfonic acid, Nafion, is widely believed to be of high acid strength, even superacidic, on account of the fluorine atoms close to the sulfonic acid groups [9,12–16]. In its pure form it is essentially non-porous and somewhat resistant to solvation in commonly used solvents, limiting catalytic applications. However, it can be obtained as a composite material with silica gel (known as SAC-13) with a higher surface area and more accessible sulfonic acid groups [14–16].

Sulfonic acids supported on porous silica have been widely studied, in part because they offer an alternative, and generally superior, way of imparting surface acidity to mesoporous molecular sieve materials such as MCM-41 and SBA-15 to those methods that rely on isomorphous lattice substitution to generate intrinsic acidity [17,18]. The usual ways in which silica-supported sulfonic acids are synthesised are either via co-condensation during silica gel formation or through post-synthesis grafting on the silica walls, in both cases with a suitable

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sulfur-containing silane compound such as trialkoxysilane-propylthiol [19–22]. Condensation of the alkoxy with silanol groups binds the tether to the silica support and the acid is then generated by oxidation of the thiol to sulfonic acid. A disadvantage of these materials is that, compared to polystyrene supported sulfonic acid, the concentrations of supported sulfonic acid groups tend to be low. An advantage is that the nature of the tether can be manipulated to control acid strength, even to the extent of using a perfluorinated hydrocarbon tether [23].

Many spectroscopic and thermochemical methods can be used to characterise the surface acidity of solid acid catalysts [7,24] but there is no single method that is accepted as being the most suitable for providing data that is useful in predicting catalytic properties. However, base adsorption calorimetry is generally regarded as a technique that can reasonably be used to compare the acid strengths of related solid acids, and it is this technique that has been used in the work reported here, with ammonia as the basic probe compound [7,24,25]. Most commonly, base adsorption calorimetry involves exposure of the sample to a series of small doses of the probe base compound, under conditions where adsorption from the gas phase is allowed to reach equilibrium after each addition. The molar enthalpy of adsorption, measured for each addition, is then plotted against the total uptake of ammonia per unit mass (surface coverage) of the solid acid. On the assumptions that (i) ammonia adsorbs stoichiometrically on acid sites, (ii) the enthalpy of adsorption is an indicator of the strength of the acid sites, and that (iii) acid sites react in order of decreasing strength (constrained by the Boltzmann distribution governing the relative populations of sites of different strengths), the resultant $\Delta H_{\text{ads}}^\circ/\text{coverage}$ profile is interpreted in terms of the abundance, strength and strength distribution of the surface acid sites [1–4].

In the work reported here, we have used base adsorption calorimetry under flow conditions. In this technique ammonia adsorption takes place from small pulses of ammonia which are introduced to a flowing carrier gas which passes over the sample in the calorimeter. An important difference between this flow technique and the conventional equilibrium technique is that ammonia that adsorbs weakly and reversibly on the catalyst surface from each ammonia pulse desorbs back into the carrier after the pulse has passed. This ensures that the ammonia which remains bound, and the measured enthalpies of adsorption, are associated only with irreversibly and strongly adsorbed ammonia—presumably that which is chemisorbed on acid sites. This pulse-by-pulse discrimination between probe compound adsorbed on strongly binding acid sites and that adsorbed on weakly binding non-acidic sites cannot be obtained with the conventional equilibrium base adsorption calorimetric experiment.

2. Experimental

2.1. Materials

Three commercially available sulfonated poly(styrene-*co*-divinylbenzene) resins were used: Amberlyst 15, Amberlyst 35 (Rohm and Haas) and C100H (Purolite). The first two are macro-

porous (sometimes called “macroreticular”) and the third is a gel resin with no permanent porosity. All were supplied as spherical beads and ground to fine powders (facilitated by cooling) of size $\leq 125 \mu\text{m}$ for our experiments. Nafion NR50 was from Dupont and silica-supported Nafion, SAC-13 (Nafion loading, 13% (w/w)) from Sigma–Aldrich. Both Nafion NR50 and SAC-13 were also ground to powders of size $\leq 125 \mu\text{m}$. Dried helium and 1% ammonia in helium mixture were from BOC gases.

Silica-gel supported sulfonic acids were prepared as follows. A mesoporous silica gel (EP116) was supplied by Ineos Silicas. The silica (1.5 g) was dispersed in 50 ml toluene. 3-Mercaptopropyltrimethoxysilane or 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (3.6 g) was added and the mixture refluxed for 12 h at 383 K. The solid was collected by filtration, washed with hot toluene followed by methanol and water, and air-dried. In the case of the mercapto- synthesis the resulting solid was stirred at room temperature for 2 h with excess 33% (v/v) H_2O_2 solution, filtered, washed with water. All samples were dispersed in excess 0.1 M H_2SO_4 solution and stirred overnight. The resultant solids were filtered, washed with water and dried at 333 K [26–29]. The concentrations of acid sites were measured by exchange in 1.0 M NaCl solution followed by titration with 0.1 M NaOH solution. Elemental analysis (Medac) for C and S clearly established from the C/S ratios that the surface grafting was achieved, on average, by the condensation of two out of three ethoxy or methoxy groups with surface silanol groups for both types of tether compound.

2.2. Methods

Nitrogen adsorption isotherms were recorded at 77 K. Surface areas calculated by the BET method are given in Table 1. Desorption isotherms were used to calculate pore size distributions using the BJH method.

Ammonia adsorption calorimetry under flow conditions was performed on the catalysts using the system described earlier based on a flow-through Setaram 111 differential scanning calorimeter (DSC) and an automated gas flow and switching system [30,31], modified through the use of a mass spectrometer detector for the down-stream gas flow (Hiden HPR20) connected via a heated capillary (at 175 °C) instead of the previously used thermal conductivity detector. In a typical experiment, the catalyst (5–30 mg) was activated at 150 °C under dried helium flow at 5 ml min⁻¹. Following activation, and maintaining the sample temperature at 150 °C, small (typically 1.0 ml but from 0.2 to 5.0 ml) pulses of the probe gas (1% ammonia in helium) at atmospheric pressure were injected at regular intervals into the carrier gas stream from a gas-sampling valve. The concentration of ammonia downstream of the sample was monitored continuously with the mass spectrometer. The interval between pulses was chosen to ensure that the ammonia concentration in the carrier gas (including that adsorbed and then desorbed after the pulse had passed) returned to zero, and to allow the DSC baseline to re-establish itself.

The net amount of ammonia irreversibly adsorbed from each pulse was determined by comparing the MS signal during each pulse with a signal recorded during a control experiment through

Table 1
Characterisation, acidity and catalytic activity data for supported sulfonic acid catalysts

Catalyst	N ₂ adsorption data			Average $\Delta H_{\text{ads}}^{\circ}(\text{NH}_3)^{\text{a}}$ (kJ mol ⁻¹)	Saturation NH ₃ coverage ^b (mmol g ⁻¹)	Turnover frequency per acid site (h ⁻¹)	Molar selectivity to camphene (%)
	Surface area (m ² g ⁻¹)	Pore volume (ml g ⁻¹)	Average pore diameter (nm)				
Amberlyst 15	53 ^c	0.4 ^c	30 ^c	-110 ± 4	4.7 ± 0.2 (4.7)	47	22
C100H	–	–	–	-110 ± 4	4.6 ± 0.2 (4.7)	9	20
Amberlyst 35	50 ^c	0.35 ^c	30 ^c	-116 ± 4	5.3 ± 0.2 (≥5.2)	112	40
Nafion NR50 pellets	–	–	–	-158 ± 5	0.76 ± 0.06 (≥0.8)	102	50
Nafion NR50 powder ≤125 μm	–	–	–	-161 ± 5	0.85 ± 0.06 (≥0.8)	1325	55
Nafion SAC-13	196	0.6	10	-162 ± 5	0.12 ± 0.04 (0.11)	1709	50
SiO ₂ (EP116)	270	1.6	20.1	–	–	–	–
SiO ₂ -propylSO ₃ H	260	1.4	17.1	-128 ± 5	1.10 ± 0.10	11	8
SiO ₂ -phenylSO ₃ H	190	0.95	15.5	-126 ± 5	0.68 ± 0.08	13	10

^a Average value of $\Delta H_{\text{ads}}^{\circ}(\text{NH}_3)$ for ammonia adsorbing up to saturation coverage.

^b Saturation NH₃ coverage defined as total NH₃ uptake with $\Delta H_{\text{ads}}^{\circ}$ numerically greater than -80 kJ mol⁻¹.

^c Value supplied by manufacturer.

a blank sample tube. Net heat released for each pulse, corresponding to irreversible adsorption of ammonia, was calculated from the DSC thermal curve. From this the molar enthalpy of adsorption of ammonia ($\Delta H_{\text{ads}}^{\circ}$) was obtained for the ammonia adsorbed from each successive pulse. The $\Delta H_{\text{ads}}^{\circ}$ values were then plotted against the amount of (irreversibly) adsorbed ammonia per gram of the catalyst, to give a $\Delta H_{\text{ads}}^{\circ}$ /coverage profile for each catalyst.

Activities of the catalysts in the isomerisation of α -pinene were tested at 100 °C. Catalyst (of various weights, see later) was activated at 150 °C in a glass reactor under flowing dry air for 3 h. The reactor was cooled to 100 °C and a pre-heated mixture of 0.05 mol α -pinene and 0.01 mol decane (internal GC standard) was injected and reaction initiated. The reaction mixture was stirred fast enough to avoid external mass transfer constraints. Small aliquots were withdrawn at regular intervals and analysed with GC, using a 25 m BP1 column with 5 ml min⁻¹ helium flow and at a constant oven temperature of 75 °C.

3. Results and discussion

Physical characterisation data for the catalysts, a summary of calorimetric adsorption and catalytic activity data are shown in Table 1. More detailed results from the calorimetric adsorption experiments are shown in the form of $\Delta H_{\text{ads}}^{\circ}$ versus surface coverage profiles for the catalysts in Figs. 1–3. Conversion versus time plots for the α -pinene reaction appear in Fig. 4.

3.1. Acidity data

The $\Delta H_{\text{ads}}^{\circ}$ versus surface coverage profiles for the polystyrene sulfonic acid resin catalysts are shown in Fig. 1. These data are similar to those reported previously for the same catalysts where ammonia adsorption was carried out in a static system and allowed to reach equilibrium after each pulse [30,31]. The similarity between results obtained by the flow and the static method is almost certainly linked to the very small surface area of these materials – the acid sites are distributed throughout

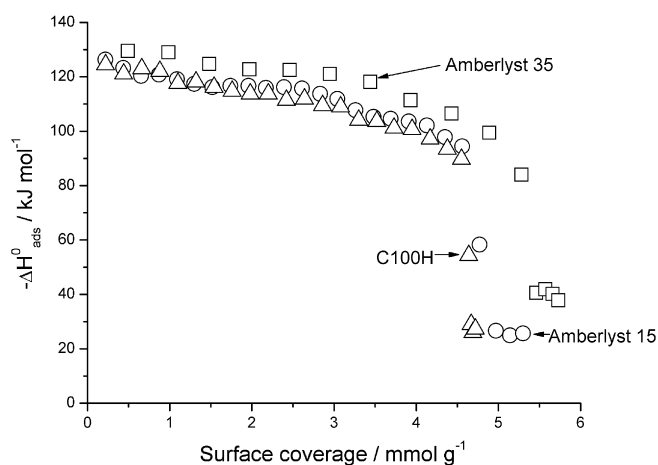


Fig. 1. Molar enthalpy of ammonia (irreversible) adsorption vs. surface coverage for powdered polystyrene sulfonic acid resins, Amberlyst 15 and Amberlyst 35 (macroporous), and Purolite C100H (gel-type). Catalysts were activated at 150 °C and adsorption carried out at the same temperature.

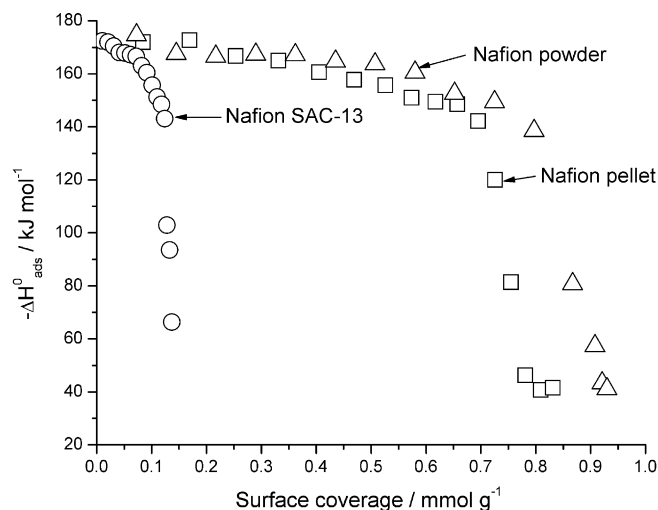


Fig. 2. Molar enthalpy of ammonia (irreversible) adsorption vs. surface coverage for pure Nafion (beads and powder) and Nafion/silica composite SAC-13. Catalysts were activated at 150 °C and adsorption carried out at the same temperature.

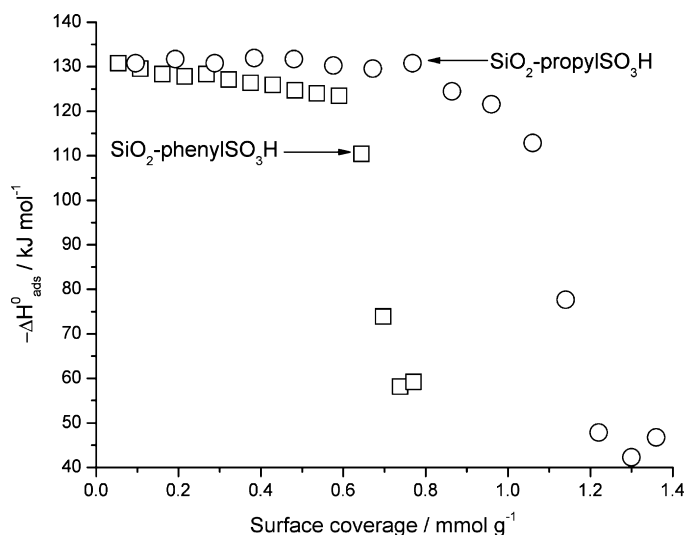


Fig. 3. Molar enthalpy of ammonia (irreversible) adsorption vs. surface coverage for powdered sulfonated silicas, silicapropylsulfonic acid and silicaphenylsulfonic acid. Catalysts were activated at 150 °C and adsorption carried out at the same temperature.

the bulk of the polymer particles – and the fact that very little reversible ammonia adsorption would occur on these materials under any conditions.

The data in Fig. 1 shows the following. Firstly, if it is assumed that the point at which $\Delta H_{\text{ads}}^\circ$ drops steeply corresponds to saturation of acid sites, and more specifically that only ammonia adsorption at enthalpies of numerically more than -80 kJ mol^{-1} correspond to adsorption on acid sites of significant strength [17,32], then it appears that total ammonia adsorption (saturation NH_3 coverage) corresponds closely to one to one stoichiometric adsorption on all acid sites. Amberlyst 15 is reportedly sulfonated at 4.7 mmol g^{-1} [1] corresponding approximately to one sulfonic acid group per styrene monomer unit. Amberlyst 35 is known to be sulfonated at a level of about 5.2 mmol g^{-1} ,

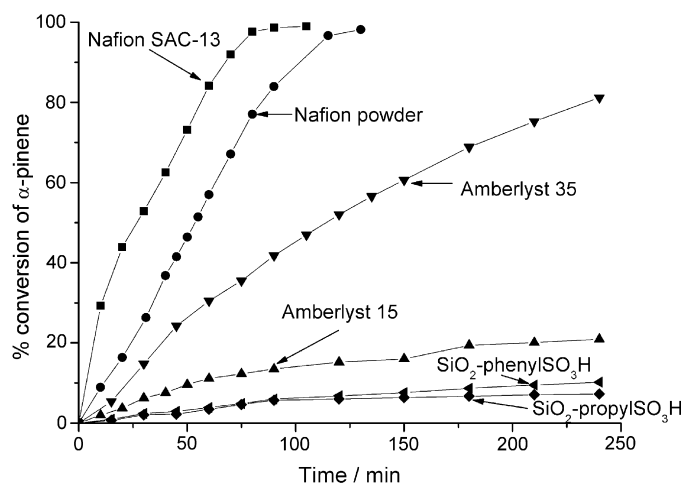


Fig. 4. Catalytic activity data for supported sulfonic acid catalysts. Conversion of α -pinene as a function of time. Conditions—catalyst: Nafion and polystyrenesulfonic acids, 25 mg; SAC-13, 195 mg; silicapropylsulfonic acid, 125 mg; silicaphenylsulfonic acid, 200 mg; α -pinene, 0.05 mol, 100 °C.

corresponding to more than one acid group per styrene unit (persulfonated).

Secondly, the molar enthalpies of ammonia adsorption of the persulfonated resin, Amberlyst 35, are significantly higher than those of the normally sulfonated resin, Amberlyst 15. This has been observed before, and is generally explained in terms of the enhanced acid strength of sulfonic acid groups on phenyl rings on some of which there is a second (electron withdrawing) sulfonic acid group. The enhanced acid strength of Amberlyst 35 is consistent with the very much higher catalytic activities that have been observed with persulfonated resins [1].

Amberlyst 15 and 35 are macroporous resins (sometimes referred to as “macroreticular”). A degree of permanent porosity is built into the resin beads to ensure that a high proportion of the acid sites, although distributed through the bulk of the resin, are accessible to non-swelling solvents and reactants. The resin C100H on the other hand is a gel resin, with no permanent porosity. The nominal surface area of this material is very small and it is generally assumed that access to all but a very few of the acid sites require significant diffusion through the resin gel. The resin C100H is sulfonated at a similar level to the porous Amberlyst 15 resin. The data in Fig. 1 for C100H in powder form shows that in this form the resin adsorbs ammonia from a flowing gas stream in an almost identical way to the porous Amberlyst 15, generating an almost identical $\Delta H_{\text{ads}}^\circ/\text{coverage}$ profile. Average values for $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ and saturation coverage shown in Table 1 confirm this. It appears that ammonia is quite effective at diffusing into the dry polymer matrix, at least in powder form. This facility with which ammonia diffuses through polystyrene sulfonic acid resins is mentioned here partly because similar behaviour is seen with Nafion resin (described below), and partly because, since typical reactant molecules are unlikely to diffuse into these sulfonated resins in precisely the same way as ammonia, it highlights possible difficulties in correlating acidity measurements made with adsorbed ammonia with activities in typical acid catalysed organic reactions.

The $\Delta H_{\text{ads}}^\circ$ versus surface coverage profiles for Nafion as cylindrical pellets (diameter 1–2 mm), as powder ($<125 \mu\text{m}$) ground from the pellets, and as the silica composite, Nafion SAC-13, also as a powder, are shown in Fig. 2. If, again, it is assumed that adsorption on sites with significant acid strength occurs only with enthalpies numerically greater than -80 kJ mol^{-1} then NH_3 appears to probe about 0.12 mmol g^{-1} acid sites on SAC-13, 0.76 mmol g^{-1} on Nafion in pellet form, and 0.85 mmol g^{-1} in powder form. The total acid site concentrations for these three materials are given in Table 1 as saturation NH_3 coverages and these figures taken from Fig. 2 represent reaction with almost all the acid sites on the catalysts. Nafion has no permanent porosity and, compared to sulfonated polystyrene, swells slowly and relatively little in most polar solvents. The fact that such a large proportion of the acid sites on even pelleted Nafion is accessible to NH_3 was at first surprising. However, Nafion is known to be particularly permeable to NH_3 . Nafion membrane has a very high ammonia permeability (of the order of 10^4 barrer), and shows selectivity over other gases such as hydrogen (500:1 at room temperature) and nitrogen [33,34]. In fact, Nafion membrane has been explored as a selective membrane for separation

of ammonia from other product gases for the Haber process [34].

In terms of enthalpies of ammonia adsorption and acid strengths, the three forms of Nafion show very similar values and relative homogeneity of acid strength up to saturation. They seem to be very much stronger acids than the polystyrene supported sulfonic acids. Nafion is frequently cited as a superacid catalyst, on the basis of a Hammett acidity function (H_0) of -11 to -13 [35], and the high $\Delta H_{\text{ads}}^\circ$ values recorded here are not inconsistent with this. It is worth mentioning that the $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ for Nafion is one of the highest measured for a solid Bronsted acid using ammonia adsorption calorimetric techniques [31,32].

The $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ versus surface coverage profile for the silica-supported sulfonic acids appear in Fig. 3. Clear delineation between irreversibly adsorbed NH_3 and reversibly adsorbed NH_3 on the high surface area supports is apparent. A very different and less well resolved profile would have been observed had the equilibrium adsorption technique been used.

The concentrations of acid sites on these sulfonic acid functionalised silica samples were determined separately in water, by exchanging with excess Na^+ (from NaCl) followed by titration with standard NaOH solution. Values essentially the same as the ammonia saturation coverage figures appearing in Table 1 were found. However, the concentrations of sulfur in these materials, measured by direct elemental analysis, were somewhat higher (typically 30–40%) than predicted from acid site concentrations. It is concluded from this that, when using both the mercaptopropyl- and the chlorosulfonylphenyl- precursors to tether sulfonic acids, a significant percentage of the precursor resists conversion to the acid form.

The aqueous titration and calorimetric adsorption data suggest that ammonia, at 150°C , can access essentially all the acid sites on these functionalised silicas, perhaps unsurprisingly given their relatively large pores and high surface areas. The concentrations of acid sites on these two catalysts are, however, relatively low. Acid strengths (enthalpies of ammonia adsorption) are reasonably uniform and are slightly higher than on polystyrene, but well below those of the fluorinated Nafion catalysts. Enthalpies of adsorption with propyl and phenyl tethers for the acid groups are not significantly different, despite the expectation that the electron withdrawing aryl group might have increased the sulfonic acid strength compared to the propyl tether.

The reason for the difference in apparent acid strengths between polystyrene and silica supported sulfonic acids is not absolutely clear. The tether on polystyrene is a phenyl group, so is essentially similar to one of the tethers on silica. We have already shown how the strength depends on the degree of sulfonation of the phenyl groups. Only in the case of sulfonated polystyrene is disulfonation possible (because of the high overall level of sulfonation), so a reasonable expectation might have been that the sulfonated polystyrenes would have shown higher average acid strengths than the sulfonated silicas. That the reverse is actually observed may be linked to the fact that removal of water from sulfonated polystyrene resins is difficult, and even nominally dehydrated resins are known to hold at least

one water molecule per acid group [36], meaning that the measured acidity is in fact that of the H_3O^+ ion (albeit in a rather unusual environment). Another, alternative, factor which may influence the difference between $\Delta H_{\text{ads}}^\circ(\text{NH}_3)$ on sulfonated silica and sulfonated polystyrene is the enthalpy associated with adsorption and chelation of ammonia molecules in silica pores, the “confinement” effect [37–39]. The contribution from this would be larger for the silica support than for the hydrophobic polystyrene support.

The acid strength data for silica- and polystyrene-supported sulfonic acids based on ammonia adsorption contrasts with that found by Stucky and co-worker [40], who compared the acid strengths of propylsulfonic acid and phenylsulfonic acid on silica with Amberlyst 15 polystyrene sulfonic acid, based on the ^{31}P NMR shift for adsorbed triethylphosphine oxide. They reported that Amberlyst 15 was the strongest of the three, followed by the silica arylsulfonic acid and the silica propylsulfonic acid, somewhat in line with our own expectations. This certainly puts into question the relative acid strengths based on enthalpies of ammonia adsorption, and may even support the possibility that the higher enthalpies observed for the silica-supported sulfonic acids in this work are not in fact due to higher acid strength but the additional heats of ammonia confinement in silica pores referred to in the last paragraph.

3.2. Catalytic activity

Catalytic activities are shown as reactant conversion over 4 h reaction periods in Fig. 4. The weights of catalyst used were 25 mg for polystyrene sulfonic acids, 125 mg for silicaproylsulfonic acid and 200 mg for silicaphenylsulfonic acid, to give approximately the same number of acid groups for each catalyst. For the very much more active Nafion catalysts, 25 mg of Nafion was used and 195 mg of SAC-13, so that the Nafion content was the same in the two experiments. The kinetic data is shown in Table 1 as turnover numbers per hour (TONs). Molar product selectivity to camphene is also given.

Of the polystyrene supported sulfonic acids, the non-porous C100H powder showed almost immeasurably low activity, as shown in Table 1. Macroporous Amberlyst 15 and Amberlyst 35 powders showed very much higher activities. The higher TON for Amberlyst 35 over Amberlyst 15 reflects the higher acid site strength on this resin.

Nafion powder and Nafion SAC-13 both exhibited TONs ten times higher than the Amberlyst sulfonic acids. Nafion pellets were less effective, consistent with the inaccessibility of most of the acid sites. Note that, even though all or most of the acid sites in Nafion pellets and indeed C100H powder were accessible to ammonia in the calorimetric adsorption experiments, the majority of the acid sites are still buried inside the polymer matrix and are evidently not accessible to a bulky, non-swelling reactant such as α -pinene.

The high TONs of sulfonic acid in powdered Nafion and Nafion SAC-13 catalysts reflect the high acid strengths of Nafion. As the measured strengths of acid sites are similar for Nafion powder and Nafion SAC-13, it seems likely that the higher activity and TON of Nafion SAC-13 is due to better

accessibility of acid sites. It is reported that Nafion in SAC-13 is dispersed “on a nanometre scale” [16] and this would certainly be consistent with the very high specific activity of Nafion on this support.

Both silica-supported sulfonic acids show comparatively low activities with low TONs. The very low activities mean it is not possible to say with any certainty whether changing the tether from a propyl to a phenyl group has any effect. The porosity data from nitrogen adsorption suggests that the functionalisation of this mesoporous silica has neither blocked the pores nor reduced the surface areas significantly, so accessibility to acid sites would be expected to be good.

Given that the strengths of the silica-supported sulfonic acid groups (based both on ammonia adsorption and on ^{31}P NMR of adsorbed triethylphosphineoxide) are at least comparable to the strength of sulfonic acid on polystyrene, the low activity of these groups is surprising. A possible explanation is that the hydrophilicity of the support hinders surface reaction with the hydrophobic reactant α -pinene. Indeed, in other reactions involving more polar reactants, silica-supported sulfonic acid has been reported to be as active as polystyrene sulfonic acid [29] and even, in the very polar methanol/ethanoic acid esterification reaction medium, more active than Nafion [28]. It is clear that the relative activities of supported sulfonic acids are extremely sensitive to the nature of the reaction, and the compatibility of catalyst surface with the reaction medium. It is well documented that the activity of silica-supported sulfonic acid towards non-polar reactants can be enhanced by tuning the surface hydrophobicity of silica-supported sulfonic acids with additional grafted alkyl or aryl groups [41,42].

The catalysts tested show quite different selectivities towards camphene over limonenes and other products as shown in Table 1. Both Nafion and Nafion SAC-13 show the highest selectivities to camphene. Of the polystyrene sulfonic acids, Amberlyst 35 shows the higher selectivity to camphene. These trends possibly suggest that the degree of selectivity to camphene follows the general trend in overall activity towards α -pinene conversion, but it is worth pointing out that there is no consensus in the literature over the conditions or catalytic features that favour camphene formation [43–46], so no attempt is made here to link trends in product selectivity to acid properties of the catalysts.

4. Conclusions

The results reported here show that the acid strength of sulfonic acid on polymeric and on silica supports are similar. On the fluorinated support used in Nafion the acid strength of the sulfonic acid is significantly higher. Nafion catalysts show very much higher specific activities in α -pinene conversion than the other supported sulfonic acids, in line with this. In comparing Amberlyst 35 (persulfonated) and Amberlyst 15, again the higher catalytic activity of the former can only be explained in terms of its higher acid strength as predicted from differences in $\Delta H_{\text{ads}}^{\circ}(\text{NH}_3)$. However, other comparisons, particularly involving the silica sulfonic acid catalysts, do not reveal a simple relationship between acid strength, as measured by calorimetric

ammonia adsorption, and catalytic activity. It seems likely that two factors are responsible. Firstly, the molar enthalpy of ammonia adsorption on sulfonic acid, while certainly sensitive to the strength of the sulfonic acid group, also appears to be sensitive to environment of the sulfonic acid. Using these enthalpies of adsorption to compare acid strengths of sulfonic acid groups on similar polymer supports (Amberlyst 15 versus Amberlyst 35) or on silica supports (silicapropylsulfonic acid versus silicaphenylsulfonic acid) is quite likely justified, and trends in catalytic activity tend to be consistent with trends in $\Delta H_{\text{ads}}^{\circ}(\text{NH}_3)$, but comparisons between the two types of supported acids based on this calorimetric data are subject to question because there may be additional events with significant associated enthalpies occurring on one type of support and not on the other. Secondly, in trying to predict catalytic behaviour from enthalpies of ammonia adsorption, differences in the way the ammonia probe and the reactant might interact with the surface have to be taken into account. Again, comparisons between members of a set of similar catalysts (e.g. Amberlyst 15 and Amberlyst 35) may provide reliable predictions of difference in catalytic performance, but comparisons between different types of catalyst, even if they contain the same functional groups, yield less reliable and less strong correlations between adsorption enthalpies and catalytic activities.

Despite this, the work has demonstrated the usefulness of flow calorimetric adsorption studies for characterising surface acidity in terms of acid site abundance, strength and acid site strength distribution. The ability to discriminate between irreversibly and reversibly adsorbed probe compound over the range of surface coverage makes the technique particularly powerful in this regard. It has however highlighted the vital fact that differences between the ways an experimental probe compound and a reactant molecule might interact with catalyst acid sites and the catalyst surface in general, have to be taken into account. The overall conclusion is that acidity characterisation techniques that rely on the calorimetric measurements of the adsorption (or even desorption) of probe compounds can only be safely used to predict catalytic activities for closely related catalysts.

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