Acidities and catalytic activities of persulfonated poly(styrene-*co*-divinylbenzene) ion-exchange resins

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A series of macroporous sulfonated poly(styrene-*co*-divinylbenzene) ion-exchange resins with varying levels of sulfonation have been prepared. The acidities of these resins have been measured calorimetrically by ammonia sorption. Catalytic activities have been measured in two liquid-phase reactions: the dehydration of 1-hexanol under flow conditions and the hydration of propene as a batch process. The molar enthalpies of ammonia sorption show that the strength of the acid sites increases as the level of sulfonation is increased; catalytic activities follow the same trend. The most active resins are those that have been sulfonated at levels above one sulfonic acid group per aromatic ring ("persulfonated"). These persulfonated resins also show higher thermal stabilities than conventional resins (sulfonated at just below one acid group per aromatic ring).

KEY WORDS: sulfonated polystyrene ion-exchange resins; acid catalysis; olefin hydration; alcohol dehydration; calorimetry; base adsorption; ammonia

1. Introduction

Sulfonated poly(styrene-*co*-divinylbenzene) resins are widely used as acid catalysts in liquid phase reactions [1,2]. Commercial acid resins are typically sulfonated to a level equivalent to just under one sulfonic acid group per aromatic ring (henceforth referred to as "normally" sulfonated). Compared to most inorganic solid acids, they exhibit high concentrations of acid sites. However, they cannot be used at temperatures significantly higher than 140–150 °C and, in general, the strengths of the acid groups are lower than those found on zeolitic and similar solid acids [3]. The work reported here is part of a programme to understand these limitations and to develop acidic ion-exchange resin catalysts with improved thermal stabilities and stronger acid sites.

One of the factors controlling the catalytic activities of the sulfonic acid groups in these materials is the water content. This varies from a maximum value in fully swollen resins of typically 50–60% w/w, depending on the degree of crosslinking, to the "fully dried" value (the limit to which the materials can be dehydrated) of typically 1–2% w/w residual moisture. Water content controls the acid "concentration" in the internal solution within the resin gel. In general, the activity of each sulfonic acid group increases as the water content per acid group is reduced. This can be illustrated with a typical normally sulfonated resin. If the resin is partially neutralised then it shows a reduced catalytic activity per remaining acid group, because those remaining acid groups are effectively in a more dilute solution in the gel [2,4]. The same reduced activity per acid group can be seen in resins which have been sulfonated to a lower degree than normal, again because the internal acid solution is more dilute than in a fully sulfonated resin [5,6]. In most catalytic applications, maximum activity is usually associated with minimum levels of acid group hydration. The most active sites are thought to be anhydrous, undissociated sulfonic acid groups, or their monohydrates [7].

Another factor, proposed to explain the relatively high specific activity of sulfonic acid groups in normally sulfonated resins, is related to interactions between neighbouring sulfonic acid groups. It has been suggested that some acid-catalysed reactions are facilitated by concerted participation of networks of sulfonic acid groups [8]. The extent to which such networks can exist clearly depends on the overall degree of sulfonation of the resin.

In summary, increasing the level of sulfonation of poly (styrene-*co*-divinylbenzene) resins increases the concentration of acid sites, their relative strengths, and their catalytic activities [2–8]. It is therefore of interest to examine the effect of excess sulfonation, preparing resins that contain more than one sulfonic acid group per aromatic ring. In the work reported here, new resins, prepared in this way (referred to as persulfonated resins), are compared with conventional, normally sulfonated, resins in terms of acidity, catalytic activity and thermal stability.

The work is focused on the so-called "macroporous" or "macroreticular" resins. This is partly because most catalytic applications require resins of this type, and partly because the acidities of these resins, unlike those of conventional gel resins, can be studied successfully by quantitative ammonia sorption microcalorimetry [3,9]. We have shown previously that ammonia is sorbed essentially stoichiomet-

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rically at 100 °C by acid sites on macroporous sulfonated poly(styrene-*co*-divinylbenzene) resins, and the catalytic activities of a series of resins in liquid-phase reactions correlate quite well with molar enthalpies of ammonia sorption [3,9].

Two relatively demanding model reactions have been used in this work to test catalytic activities. The first is the dehydration of 1-hexanol in a flow reactor. The second is the hydration of propene to 2-propanol in a batch process.

2. Experimental

2.1. Sulfonated poly(styrene-co-divinylbenzene) catalysts

The following macroporous resins were provided by Purolite International:

(i) CT-175, a standard, normally sulfonated material with a cation-exchange capacity (CEC) of 4.90 meq-H^+ g^{-1} (dry),

(ii) CT-275, a persulfonated version of CT-175, with a CEC of 5.40 meq-H^+ g^{-1} (dry),

(iii) CT-375, a further persulfonated resin with a CEC of 5.52 meq-H^+ g^{-1} (dry).

These resins were compared with Amberlyst 15 (Rohm and Haas Co.), one of the first broadly-applicable resin catalysts developed forty years ago [10]. Amberlyst 15 (CEC = 4.74 meq-H^+ g^{-1} (dry)) and CT-175 are roughly analogous.

All resins were used in their H^+ forms. All quoted data are based on the “dry weights” of the resins (containing 1–2% w/w residual water) which were determined by Purolite. The water contents of the fully swollen resins were also determined by Purolite and were all in the 50–60% w/w range.

2.2. Sorption 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, shown schematically in figure 1.

Resin 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. Using calibrated volumes, successive pulses of ammonia (ca. 0.06 mmol) were introduced to the sample. The amount of ammonia sorbed was measured for each pulse, using the recorded pressure of ammonia (typically ca. 25 Torr) in the dosing volume (ca. 40 cm^3) before exposure, and the pressure of ammonia in the combined cells/dosing volume (ca. 75 cm^3) on reaching equilibrium. Enthalpy changes associated with each dose were converted to molar enthalpies of sorption and expressed as functions of resin coverage.

The gas handling system was at room temperature. At this temperature, reversible ammonia adsorption on the glass walls is a possible source of error. This was accounted for in the experiments reported here by calibrating the system volumes using ammonia at a range of pressures. In fact, for resins, which have relatively high concentrations of acid sites and sorb high concentrations of ammonia, the error is relatively small anyway. However, in preparation for use with a wider range of materials, modifications are currently being made to heat the dosing system to eliminate the problem [11].

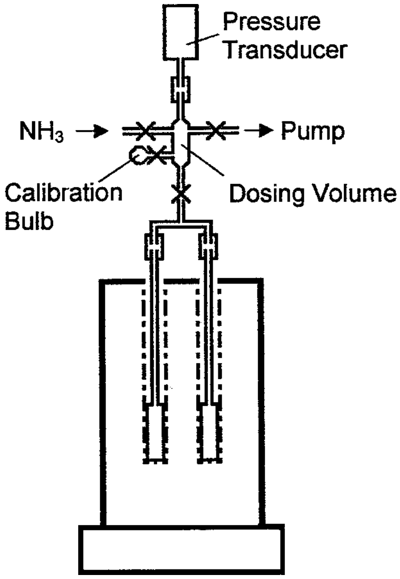

Figure 1. Combined gas handling system and differential microcalorimeter for measuring molar enthalpies of ammonia sorption.

A further point to note is that we are not reporting here the results of adsorption/desorption/adsorption cycles, which are conventionally performed to correct the first adsorption leg data for the effect of physisorption of ammonia occurring at the same time as chemisorption on acid sites [12]. The reason is that two-cycle experiments of this type were performed on selected resins and, unlike typical inorganic solid acids, they showed that almost no reversible ammonia adsorption (physisorption) occurs up to the point where all the acid sites are saturated. We are therefore confident in reporting the molar enthalpies of ammonia adsorption for a single adsorption leg, as representing the molar enthalpies of irreversible chemisorption on acid sites.

2.3. Catalytic activities

2.3.1. 1-hexanol dehydration

All the catalytic reactions were carried out at atmospheric pressure in a fixed-bed continuous-flow reactor at 140 °C. The resins were pre-soaked in 1-hexanol for three days. The swollen resins were ramped (10 °C min^{-1}) to 140 °C in dry He (25 cm^3 min^{-1}) and held at this temperature for 1 h. The resin was supported on a glass frit and a layer of glass beads above the catalyst bed served as a preheating zone, ensuring that the reactant reached reaction temperature before contacting the catalyst. The reactor temperature was monitored (constant to ±1 °C) with a thermocouple in the catalyst bed.

A microprocessor-controlled infusion pump was used to introduce 1-hexanol in a stream of dry helium at a W/Q ratio in the range 0.072–0.52 $\mathrm{g\,h\,cm^{-3}}$, where W represents the weight of catalyst and Q is the inlet liquid volumetric feed rate. The overall gas hourly space velocity (GHSV) was maintained at $2 \times 10^3\ \mathrm{h^{-1}}$. The product stream was collected in a liquid nitrogen trap and periodically analysed by gas chromatography (AI Cambridge GC94) using a DB-1 (50 m × 0.2 mm i.d.) 0.33 μm capillary column (J&W Scientific).

2.3.2. Propene hydration

The reaction was performed in a sealed copper-lined, high pressure, vessel of internal volume 240 $\mathrm{cm^3}$, fitted with a mechanical stirrer. This reactor was charged with 15 g resin (dry weight), 100 g water and 54 g of propene. The reaction mixture was stirred continuously at 300 rpm and heated to the reaction temperature of 140 °C. The pressure in the vessel was monitored continuously. The maximum pressure achieved was typically 300 bar. The progress of the reaction was followed using the pressure drop as propene was consumed, and a pseudo-first-order rate constant estimated. At the end of the run (typically 16 h) the autoclave was cooled to room temperature and excess propene vented. The reactor was then opened and the contents were transferred to a weighed sample container. A portion of the liquid product was analysed by capillary gas chromatography to determine propene conversion and selectivity to 2-propanol.

2.4. Resin thermal stability

The samples (1 g) were heated with 50 $\mathrm{cm^3}$ water at 200 °C for 8 h in a sealed 100 $\mathrm{cm^3}$ pressure vessel, under autogenous pressure. This temperature was chosen because it gave measurable degradation of resin acidity within a reasonable time, even though it was significantly higher than the target reaction temperatures. Resins were then thoroughly rinsed with water at 60 °C, prior to determination of the remaining acidity. This was measured by ammonia sorption calorimetry, as described above. The concentration of acid sites was also determined by thoroughly swelling the resins in water, exchanging with $\mathrm{Na^+}$ (1.5 $\mathrm{mol\,dm^{-3}}$ NaCl solution), and directly titrating with standard NaOH solution [13].

3. Results

3.1. Resin acidities

Representative plots showing the molar enthalpies of ammonia adsorption as a function of acid site coverages for the four resins are shown in figure 2(a). Note that, in each case, the profiles fall abruptly at coverages close to their cation-exchange capacities, showing that the interaction between these resins and ammonia is essentially stoichiometric. Molar adsorption enthalpies for each resin fall steadily with increasing coverage. For comparative purposes, it is convenient to plot the cumulative enthalpies against coverages and determine mean gradients up to saturation coverage (figure 2(b)). This gives average molar enthalpies of ammonia sorption for each catalyst.

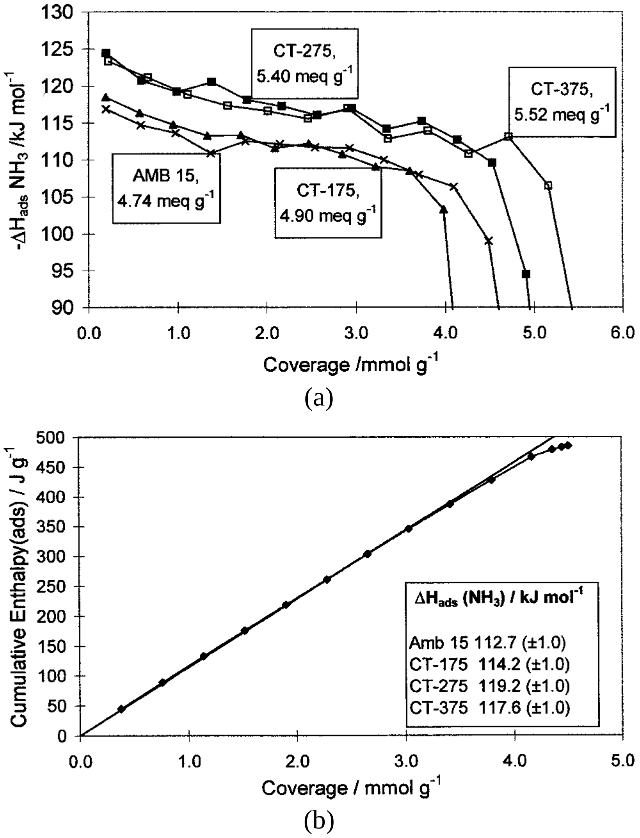

Figure 2. Enthalpies of adsorption of ammonia with coverage for CT-175, CT-275, CT-375 and Amberlyst 15: (a) differential plots and (b) an integral plot (CT-175) with mean gradients for the four resins.

On the assumption that enthalpies of adsorption do indeed reflect the strengths of the Brønsted acid sites, the two persulfonated resins show very similar acid strengths. The two normally sulfonated resins also exhibit very similar strengths to each other. However, the two persulfonated resins are significantly stronger acids than the normally sulfonated resins. This observation is consistent with our preliminary results on CT-175 and CT-275 [3,9].

Acidity measurements made before and after hydrothermal treatment at 200 °C are shown in figure 3. In addition to the calorimetric data, acid site concentrations measured on swollen resins by aqueous NaOH titration are also shown in the figure, together with the percentages of the original acid concentrations that these represent. The steep decreases seen in molar enthalpies of ammonia adsorption, which correspond to saturation of acid sites, occur at coverages which roughly coincide with the acid site concentrations measured by aqueous NaOH titration of the swollen resins. Given this broad agreement between the two methods of measuring acid site concentration, the results show clearly that the extent of desulfonation, in terms of the percentage of acid sites lost, is very much less for the persulfonated than for the normally sulfonated resins.

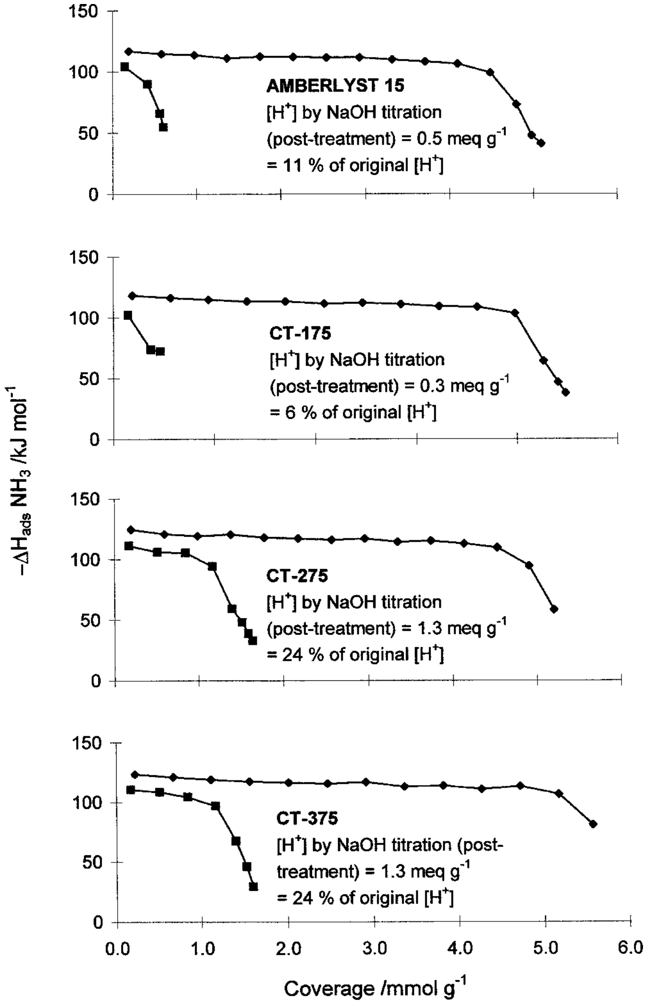

Figure 3. Enthalpies of adsorption of ammonia with coverage as differential plots, for Amberlyst 15, CT-175, CT-275 and CT-375, before (♦) and after (■) hydrothermal treatment at 200 °C for 8 h. Cation-exchange capacities of treated resins, determined by NaOH titration, are also shown.

3.2. Catalytic activities

The dehydration of 1-hexanol over all the activated resins gave primary and secondary hexenes, and dihexyl ether(s). The rate of dehydration of 1-hexanol over Amberlyst 15, CT-175 and CT-275, was measured over a range of inlet 1-hexanol volumetric flow rates (1.4–10.0 $cm^3\ h^{-1}$). At all flow rates the persulfonated resin (CT-275) delivered the highest conversions. Reaction rates and specific activities, incorporating corrections for the different concentrations of acid sites on each catalyst, are shown in table 1 for an intermediate inlet 1-hexanol flow rate. Molar ratios of hexene to ether at steady state are also shown. There is no obvious trend in terms of selectivity under these process conditions. It is worth noting that a higher selectivity in terms of alkene formation with the more active catalysts has been reported for other solid acids, such as acid-activated clays [14,15]. However, the reverse trend has also been observed [16,17], and a link between catalyst activity and selectivity in 1-hexanol dehydration has not been generally established.

Table 1

Reaction rates, specific activities and reaction selectivities at steady state for the dehydration of 1-hexanol under flow conditions at 140 °C over sulfonated poly(styrene-*co*-divinylbenzene) catalysts, at a 1-hexanol inlet flow rate of 6 $cm^3\ h^{-1}$.

Catalyst	Reaction rate (10^{-2} μmol converted $g^{-1}\ h^{-1}$)	Specific activity (10^{-3} μmol converted $mmol^{-1}$(–SO_3H) h^{-1})	Selectivity ([hexene]/[ether])
Amb15	2.5	5.3	1.4
CT-175	2.3	4.7	1.0
CT-275	7.6	14.1	1.4

Table 2

Pseudo-first-order rate constants (k) for the hydration of propene using sulfonated poly(styrene-*co*-divinylbenzene) catalysts in the batch mode at 140 °C.

Catalyst	k (h^{-1})	k (based on acid sites) (h^{-1})	Selectivity towards 2-propanol (6 h reaction) (mol%)
Amb15	2.7	0.57	92
CT-175	2.7	0.55	92
CT-275	5.7	1.06	95
CT-375	5.6	1.02	95

The pseudo-first-order rate constants for propene hydration are shown in table 2. Specific rate constants, corrected for the concentrations of acid groups on the resins, are also given. In all cases the major product was 2-propanol but small amounts of oligomers were also detected. Again, the persulfonated resins are more active than CT-175 and Amberlyst 15, and 2-propanol selectivity is slightly higher for the persulfonated resins.

4. Discussion

All the results support the view that persulfonation not only increases the concentration of acid sites on poly(styrene–divinylbenzene) resins but also increases the acid site strengths, and the catalytic activities towards hydration/dehydration reactions. At the same time, persulfonation significantly improves thermal stability.

It appears that the trends in catalytic activities previously observed [2,4–6] for fully and less than fully sulfonated resins are maintained when sulfonation is extended beyond the full or normal level. We suggest that the explanation may lie in both the varying water content per acid group in the resins, and structural characteristics associated with high levels of sulfonation.

4.1. Resin water content and internal acid solution

It is difficult to estimate the relative acid concentrations in the internal solutions in the gel regions of macroporous resins because it is not possible to fully differentiate between water in the resin and water in the macropores. This complication does not exist with the simpler gel resins, and there is direct evidence both in the literature and in our own work that the water content per sulfonic acid group in these materials does indeed decrease as the number of acid groups increases [18]. The polymeric matrix in a macroporous resin is essentially similar to that in a gel resin so the same trend is expected. This would explain, in part at least, the increase in acid strength, and hence catalytic activity, on going from normally sulfonated CT-175/Amberlyst 15 to the persulfonated CT-275/CT-375.

We appreciate that this explanation is based on the behaviour of hydrated, swollen resins. The catalytic activities were measured using reactions in which water was present either as a reactant or a product, so the explanation seems quite plausible for the differences in catalytic activities seen between resins. However, the acidity measurements shown in figure 2 were all made on almost dehydrated resins, containing only 1–2% w/w water. Relating catalytic activities to these measured acidities in terms of water content can therefore only be done on the assumption that the relative tendencies for the resins to retain water are similar when completely hydrated and after drying at 100 °C.

4.2. Structural effects of persulfonation

The theoretical cation-exchange capacity for a precisely mono-sulfonated resin of the types studied here is 5.2 meq g^{-1} (the value depends on the DVB content of the resin) [19]. The higher values exhibited by the persulfonated resins mean that some di-substitution (at least) must have occurred. A second sulfonic acid group on an aromatic ring should activate the first substituted group, increasing its acid strength. The effect of this would be to increase the overall molar enthalpies of ammonia adsorption, as seen in figure 2(a). It is worth pointing out that the presence of a fraction of stronger sites, as proposed here, would be unlikely to result in a discrete step in the acid strength distribution profile. This is because, firstly, it is unlikely that ammonia sorption would be under purely thermodynamic control at 100 °C, and, secondly, even if it were, the relatively small energy differences between the strong and weak sites would almost certainly mean that neutralisation of both types of site would occur simultaneously at all coverages [11].

Another possible consequence of vigorous sulfonation is the formation of sulfone, $-SO_2-$, bridges between neighbouring phenyl rings. These bridging sulfone groups should activate sulfonic acid groups on the same phenyl rings, increasing acid strength. Sulfone bridges could, in principle, be detected by IR spectroscopy and IR measurements will indeed be made on persulfonated resins. However, it is worth pointing out that IR studies of normally sulfonated resins have indicated that very few, if any, sulfone bridges are present in these materials [20] and, intuitively, it seems unlikely that their abundance will be increased dramatically on persulfonation.

An important consequence of di-substitution of the aromatic rings, and/or the presence of sulfone bridges between sulfonated rings, is a reduced susceptibility to electrophilic attack. This is important because the thermal degradation of sulfonated polystyrene resins is generally associated with an electrophilic, acid-catalysed desulfonation process [21,22]. The results of this work show that persulfonated resins are thermally more stable than normally sulfonated resins. This suggests that the effect of di-sulfonation in increasing thermal stability outweighs the tendency to reduce thermal stability that inevitably accompanies the higher acidity in the internal solution.

5. Conclusions

There are two possible consequences of persulfonating poly(styrene-*co*-divinylbenzene) resins. The first is an increase in acid concentration in the internal solution, and the second is an increase in the level of di-sulfonation. Both effects contribute to an increase in acid strength. However, while the former should also lead to reduced thermal stability as a result of higher acidity in the internal solution, it is necessary to invoke the presence of di-sulfonation to explain the increased thermal stabilities shown by persulfonated over normally sulfonated resins.

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