

# New polystyrene sulfonic acid resin catalysts with enhanced acidic and catalytic properties

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## Abstract

The effects of halogenation of polystyrene sulfonic acid resins on acidic and catalytic properties have been evaluated. Four polystyrene-*co*-divinylbenzene sulfonic acid resins from Rohm and Haas (Amberlyst 70, Amberlyst 15, Amberlyst 35 and Amberlyst 36) have been characterised in terms of their acidities (both strength and acid site concentrations) by ammonia adsorption flow microcalorimetry, their thermal and hydrothermal stabilities, and their catalytic activities in two test reactions, the isomerisation of  $\alpha$ -pinene and the benzylation of toluene using benzyl alcohol. Amberlysts 35 and 36 are “over-sulfonated” and exhibit stronger acid sites than the conventional sulfonated resin Amberlyst 15. These acid properties explain differences in catalytic activities, although differences between the porosities of Amberlysts 35 and 36 have a profound affect on catalytic performance in non-polar reaction media. Amberlyst 70, which is reported to be halogenated and is claimed to exhibit better thermal stability than the other three resins, shows acid site strengths similar to those of the over-sulfonated Amberlysts 35 and 36, and shows significantly better thermal and hydrothermal stability. It exhibits a relatively low pore volume, however, constraining its catalytic activity in non-swelling solvents.

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## 1. Introduction

Polystyrene sulfonic acid resins are useful catalysts for olefin hydration and etherification, alcohol dehydration, the alkylation of phenols, ester hydrolysis and other acid catalysed reactions [1–4]. They are attractive catalysts because, compared to most other solid acids, they exhibit high concentrations of acid sites and the nature of the acid sites tends to be highly uniform. Disadvantages are their poor thermal stability which restricts their use to typically 150 °C, and their relatively low acid strengths.

In principle both the acid strength of the supported sulfonic acid groups and the resistance to thermal de-sulfonation can be enhanced by the substitution of additional electron withdrawing groups on the sulfonated phenyl groups [5]. Recently, sulfonated

resins have been developed in which the aromatic rings and/or the polymer backbone are halogenated. Amberlyst 70 is claimed to be stable up to 190 °C [6] and has been shown to be so in the dehydration of 1-pentanol [7]. In the work reported in the present paper Amberlyst 70 is compared with sulfonated polystyrene resins Amberlysts 15, 35 and 36 in terms of acidity, catalytic activity and thermal stability.

Acidity is measured by ammonia adsorption microcalorimetry, operating under flow conditions so that the sample is exposed to a series of small pulses of ammonia introduced into an inert carrier gas stream [8–10]. We have already used this technique to characterise the acidities of conventional sulfonated polystyrene resins [9,10], zeolites [11] and supported heteropolyacid catalysts [12,13].

The catalytic activity of sulfonated polystyrene depends on the accessibility of acid sites via diffusion through the polymer matrix. This depends on the extent to which the resins solvate and swell in the solvent used and on the pore structure, if any, of the materials. All four resins studied here have been synthesised with some permanent porosity but this is highly variable will be shown.

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Catalytic activities are measured in two Bronsted acid catalysed test reactions: the skeletal isomerisation of  $\alpha$ -pinene [10], using the reagent as solvent, and the benzylation of toluene with benzyl alcohol [14,15]. In the former, the rate-determining step is the protonation of  $\alpha$ -pinene. Products are either camphene or a range of limonenes. There is no consensus in the literature over the conditions or catalytic features that favour one or other product [16–19] so in this work we monitor simply pinene conversion. The reagent (solvent) is non-swelling towards sulfonated polystyrene so access to acid sites will be dependent on resin surface area and porosity. In the benzylation of toluene with benzyl alcohol, the first step is the protonation of the alcohol. Aliphatic and aromatic alcohols are known to swell sulfonated polystyrene resins and diffuse through the swollen polymer gel to bulk acid sites [7,14,15] so porosity will be less important here in controlling activity. By carrying out the reaction in excess toluene, benzyltoluene is the dominant product.

## 2. Experimental

Amberlyst 70, Amberlyst 15, Amberlyst 35 and Amberlyst 36 were kindly supplied by Rohm and Haas as wet beads and were dried in an oven at 100 °C. These materials were used as dried powders ( $\leq 125 \mu\text{m}$ ), prepared by grinding the beads (at low temperature to render them brittle).

Helium and ammonia/helium mixture were from BOC gases. Helium was dried by passing through molecular sieve. Reagents  $\alpha$ -pinene, toluene, benzyl alcohol and *n*-decane were from Aldrich and were used as received.

Nitrogen porosimetry experiments were conducted on the powdered samples using a Micrometrics ASAP 2020. Adsorption isotherms were recorded at 77 K after degassing at 100 °C. Surface areas were calculated by the BET method. Desorption isotherms were used to calculate pore volumes and mean pore diameters using the BJH method. X-ray fluorescence measurements were made directly on resin beads with a Spectro X-lab 2000.

Ammonia adsorption calorimetry under flow conditions was performed using an indigenously developed system based on a flow-through Setaram 111 differential scanning calorimeter (DSC) and an automated gas flow and switching system, with a mass spectrometer detector for the down-stream gas flow (Hiden HPR20) connected via a heated capillary (at 175 °C) [8–10]. In a typical experiment the sample ( $\sim 5 \text{ mg}$ ) was activated under dried helium ( $5 \text{ ml min}^{-1}$ ) for 2 h at 100 °C. Small pulses (typically 5 ml but can be varied from 0.2 to 10.0 ml) of the probe gas (1% ammonia in helium) were then injected at regular intervals into the carrier gas stream from a gas-sampling valve. The concentration of ammonia ( $m/z$ , 15) downstream of the sample was monitored 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 has passed) returned to zero and the DSC baseline re-established itself. An important feature of the flow calorimetric technique is that net heat measurements relate only to ammonia bound irreversibly to the samples. Weakly bound (physisorbed) ammo-

nia desorbs immediately the gas flow reverts to the carrier gas.

The net amount of ammonia irreversibly adsorbed from each pulse was determined by comparing the mass spectrometer signal during each pulse with a signal recorded during a control experiment through a blank sample tube. Net heat released for each pulse was calculated from the DSC thermal curve. From this the molar enthalpy of ammonia adsorption ( $\Delta H_{\text{ads}}^0$ ) was obtained for the ammonia adsorbed from each pulse. Each sample was analysed in triplicate under the same experimental conditions. Data was plotted as a profile of  $\Delta H_{\text{ads}}^0$  vs. amount of ammonia irreversibly adsorbed.

Thermal stability tests were carried out (i) by varying the activation temperature of the resin in the DSC before ammonia adsorption experiments and (ii) by heating the resin beads in excess water in a sealed Parr pressure vessel for set times (data for 6 h shown). After this hydrothermal treatment, beads were thoroughly washed in hot water until neutral pH was measured in the wash water, and the remaining acid concentration in the beads was determined by suspending in a concentrated aqueous NaCl solution and titrating with  $0.10 \text{ mol dm}^{-3}$  NaOH solution.

Catalytic activity measurements for the isomerisation of  $\alpha$ -pinene were performed in a batch reactor with reflux condenser and magnetic stirrer. Catalyst (50 mg) was activated at 120 °C under flowing nitrogen ( $10 \text{ ml min}^{-1}$ ) for 3 h. For some experiments, the catalysts were activated at higher temperatures. A pre-heated mixture of 10 ml  $\alpha$ -pinene and 0.1 ml *n*-decane (internal GC standard) was charged to the reactor at 120 °C and reaction initiated. A stirrer speed of 800 rpm was used, after establishing that this speed was sufficient to remove external mass transfer constraints. Rate comparisons between resin catalysts in powder and bead form showed dependence on particle size. Powders ground more finely than the  $125 \mu\text{m}$  fractions showed no enhancements in activity so this fraction was used throughout for all kinetic measurements. Through the reaction small aliquots were withdrawn periodically and analysed by GC, using a 25 m BP1 column at  $2 \text{ ml min}^{-1}$  helium flow. The oven temperature was held at 60 °C for 15 min and then increased at  $20 \text{ °C min}^{-1}$ . The reaction was monitored in terms of the conversion of  $\alpha$ -pinene.

For the benzylation of toluene with benzyl alcohol, catalyst (100 mg) was activated at 80 °C in a batch reactor under nitrogen flow of  $10 \text{ ml min}^{-1}$  for 3 h. The reaction was initiated by charging a pre-heated (80 °C) mixture of 10 ml toluene, 1.0 ml benzyl alcohol and 0.1 ml *n*-decane. The reaction mixture was stirred at 800 rpm. Small aliquots were withdrawn at regular intervals and analysed by GC as above, with the oven temperature linearly programmed from 50 to 300 °C in 30 min. The reaction rate was monitored as conversion of benzyl alcohol.

## 3. Results

Cation exchange capacities and data from nitrogen adsorption experiments for the four resins appear in Table 1. Cation exchange capacities are a measure of the sulfonic acid loading on the resins. Amberlyst 15 is a well-known macroporous (sometimes called “macroreticular”) resin based on polystyrene,

Table 1  
Physical characteristics of Amberlyst resin powders (particle size  $\leq 125 \mu\text{m}$ )

Sulfonated resin	Cation exchange capacity <sup>a</sup> (mmol g <sup>-1</sup> )	Surface area <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume <sup>c</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
Amberlyst 70	2.55	1.0	0.002	29.3
Amberlyst 15	4.7	37.3	0.203	24.0
Amberlyst 35	5.2	40.7	0.218	24.2
Amberlyst 36	5.4	10.4	0.060	27.6

<sup>a</sup> Rohm and Haas data.

<sup>b</sup> BET adsorption isotherm using N<sub>2</sub>.

<sup>c</sup> Total volume of pores with diameters 1.7–300 nm (BJH).

cross-linked with divinylbenzene (DVB) and sulfonated at a level equivalent to one sulfonic acid group per styrene/DVB unit. Amberlysts 35 and 36 are sulfonated at a higher level and are referred to as over-sulfonated. Amberlyst 70 exhibits a lower cation exchange capacity by weight presumably because of the halogenation of the polymer support. Amberlyst 35 is very similar to Amberlyst 15 in terms of surface area and porosity. The sample of Amberlyst 36 used here has a much lower pore volume. Amberlyst 70 exhibits a very low surface area and low pore volume compared to the other three. Our surface area and porosity data is generally consistent with that reported by others for these resins, except for Amberlyst 36, our sample of which seems to have a lower pore volume than is usual [7].

### 3.1. Flow adsorption calorimetry

The results of the flow ammonia adsorption calorimetry experiments are shown as  $\Delta H_{\text{ads}}^0$ /amount adsorbed profiles for the powdered samples of Amberlysts 15, 35 and 36 in Fig. 1. Data for Amberlyst 70 is not shown because, using the same sample size (5 mg), saturation occurs too quickly to give a meaningful profile. The results from similar experiments where 20 mg samples of all four resins were used (three of which do not reach acid site saturation using this sample mass) appear in Fig. 2. It is worth noting that the experiments are sensitive to sample mass. In comparing the profiles in Figs. 1 and 2 slightly lower values

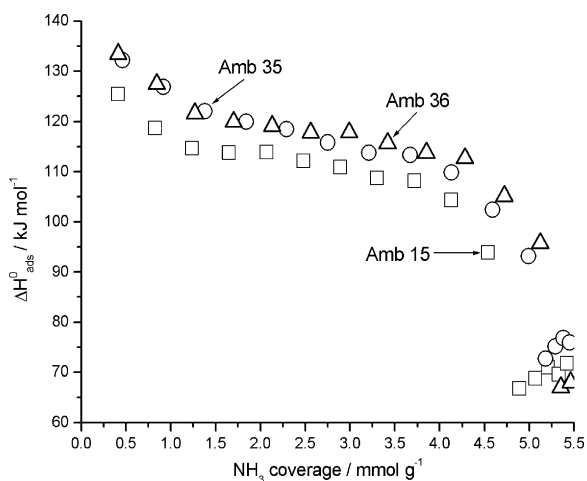


Fig. 1.  $-\Delta H_{\text{ads}}^0$ /adsorbed NH<sub>3</sub> profiles for Amberlyst resins (5 mg) at 100 °C by flow adsorption calorimetry.

for  $\Delta H_{\text{ads}}^0$  are observed in Fig. 2. This is probably due to less efficient heat conduction through the larger samples.

We have quantified these profiles in the following way. Firstly, the concentration of acid sites is taken as the concentration of ammonia adsorbed with  $\Delta H_{\text{ads}}^0$  numerically greater than  $-80 \text{ kJ mol}^{-1}$ , on the assumption that only one ammonia molecule is adsorbed by each acid site and only those sites that adsorb with this enthalpy or more are significantly acidic [20,21]. Secondly, an average value for  $\Delta H_{\text{ads}}^0$  for all pulses which adsorb on acid sites for each resin is calculated. We take this single  $\Delta H_{\text{ads}}^0$  value to be a relative measure of the acid strength of each resin. This data appears in Table 2.

A comparison between the concentration of acid sites measured by ammonia adsorption and the known acid site concentrations based on the cation exchange capacities shows that, for Amberlysts 15, 35 and 36, ammonia appears to be able to access essentially all acid sites but for Amberlyst 70 only about 60% of sites are able to react with ammonia. This surprising result contrasts with our previous findings, especially those with a conventional sulfonated polystyrene gel resin, Purolite C100H. This gel resin has no permanent porosity and a surface area too low to measure using conventional nitrogen adsorption techniques and yet 100% of acid sites were found to be accessible to ammonia when the resin was ground to a powder with similar particle size to those used in this work [10]. Evidently, in the dry state at least, the presence of halogen atoms in Amberlyst 70 severely restricts diffusion of ammonia in the polymer lattice.

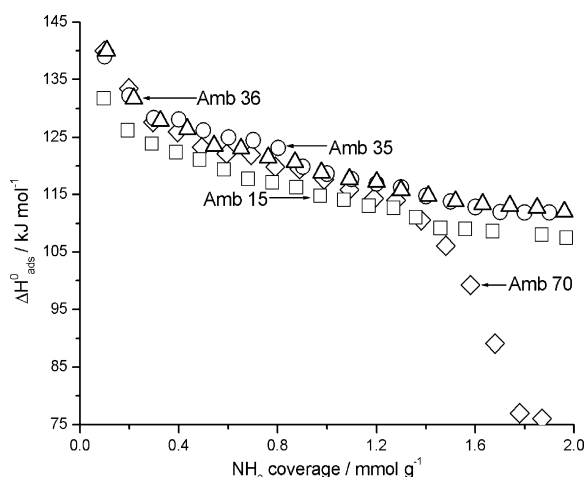


Fig. 2.  $-\Delta H_{\text{ads}}^0$ /adsorbed NH<sub>3</sub> profiles for Amberlyst resins (20 mg) at 100 °C.

Table 2  
Acidity data on Amberlyst resin powders (>125  $\mu\text{m}$ ) by flow adsorption calorimetry at 100 °C

Sulfonated resin	Average $-\Delta H_{\text{ads}}^0$ <sup>a</sup> (kJ mol <sup>-1</sup> )	Total NH <sub>3</sub> adsorbed <sup>b</sup> (mmol g <sup>-1</sup> )	Cation exchange capacity <sup>c</sup> (mmol g <sup>-1</sup> )
Amberlyst 70	117 $\pm$ 2	1.65 $\pm$ 0.05	2.55
Amberlyst 15	111 $\pm$ 2	4.70 $\pm$ 0.10	4.7
Amberlyst 35	117 $\pm$ 2	5.20 $\pm$ 0.10	5.2
Amberlyst 36	117 $\pm$ 2	5.30 $\pm$ 0.10	5.4

<sup>a</sup> Average up to coverage where  $\Delta H_{\text{ads}}^0$  falls below  $-80$  kJ mol<sup>-1</sup>.

<sup>b</sup> Where  $\Delta H_{\text{ads}}^0$  falls below  $-80$  kJ mol<sup>-1</sup>.

<sup>c</sup> Rohm and Haas data.

It can be seen that Amberlysts 35 and 36 have stronger acid sites than Amberlyst 15. This has been observed in our previous studies using both the flow technique [9,10] and equilibrium ammonia adsorption calorimetry [15] and has been explained in terms of the over-sulfonation of Amberlysts 35 and 36 and the consequent activation of sulfonic acid groups by having more than one acid group on at least some of the benzene rings in the polymer. The strength of acid sites on Amberlyst 70 is also higher than Amberlyst 15, presumably as a result of activating halogen substitution on the benzene rings.

### 3.2. Thermal stability

It is generally assumed that the thermal stability of sulfonated polystyrene is limited by the tendency of the materials to desulfonate. We observed this to be the case when temperature programmed desorption experiments were carried out in our flow calorimeter. In all cases we detected SO<sub>2</sub> evolution at the degradation temperatures. This suggests rupture of the aromatic carbon to sulfur bond. It is quite reasonable, therefore, that the presence of additional electron withdrawing groups on the benzene ring would strengthen this bond and so contribute to improved thermal stability.

Fig. 3 shows the  $\Delta H_{\text{ads}}^0$ /amount adsorbed profiles for Amberlyst 35 (representative of non-halogenated resins) and Amberlyst 70 following activation under flowing helium at the elevated temperatures of 150, 190 (Amberlyst 70), 200 and 250 °C for 2 h. Firstly, note that the profiles for both resins are very similar after activation at 150 °C as after activation at 100 °C. On treatment at 200 °C, Amberlyst 70 loses about 10% and Amberlyst 35 about 15% of measurable acid sites. Both resins lose 70–75% of acid sites at 250 °C. It is worth noting that Amberlyst 70 does not lose significant acidity on treatment at 190 °C, in line with the manufacturer's finding [6].

We expected to see less acid loss for Amberlyst 70 than for Amberlyst 35 in these experiments, but did not. However, interpreting the apparent similarity in acid loss by Amberlysts 35 and 70 requires caution because, while ammonia probes all acid sites on Amberlyst 35, it reacts with only 60% of acid sites on Amberlyst 70, presumably those closest to the surface. These may not be representative of the whole and may be more susceptible to thermal degradation.

The results of the hydrothermal stability tests appear in Table 3. In these experiments all acid sites on both resins are accessed in the aqueous titration with NaOH solution and it is

clear that Amberlyst 70 retains very much more acidity than both Amberlyst 35 and Amberlyst 15. For example, at 200 °C Amberlyst 70 loses only 20% of acid functionality compared to 43 and 42% respectively for the other two.

We carried out X-ray fluorescence measurements on Amberlyst 35 and 70 beads after this hydrothermal treatment and, when compared with untreated beads, the sulfur signal was reduced by about 75% for both materials. This compares to the total acidity losses of 43 and 20% for the two resins. Since XRF is a surface or at best a shallow depth technique, this supports

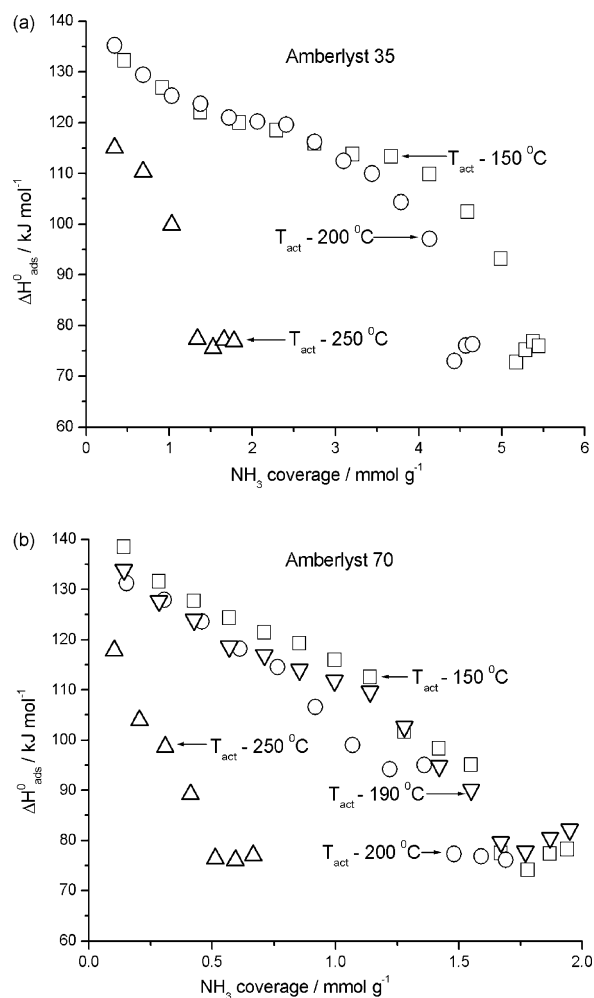


Fig. 3.  $-\Delta H_{\text{ads}}^0$ /adsorbed NH<sub>3</sub> profiles for (a) Amberlyst 35 (5 mg) and (b) Amberlyst 70 (20 mg) activated at elevated temperature for 2 h prior to adsorption at 150 °C.

Table 3  
Acid site concentrations in Amberlyst resin beads following hydrothermal treatment for 6 h in pressure vessel

Sample	Temperature (°C)	Acid concentration by aq. NaOH titration (mmol g <sup>-1</sup> ) (dry wt.)	Acid sites lost (%)
Amberlyst 70	35	2.20	0
	180	2.01	9
	200	1.75	20
	220	1.6	27
Amberlyst 15	35	4.73	0
	180	3.95	16
	200	2.72	42
	220	2.70	43
Amberlyst 35	35	5.08	0
	180	4.06	20
	200	2.89	43
	220	2.78	46

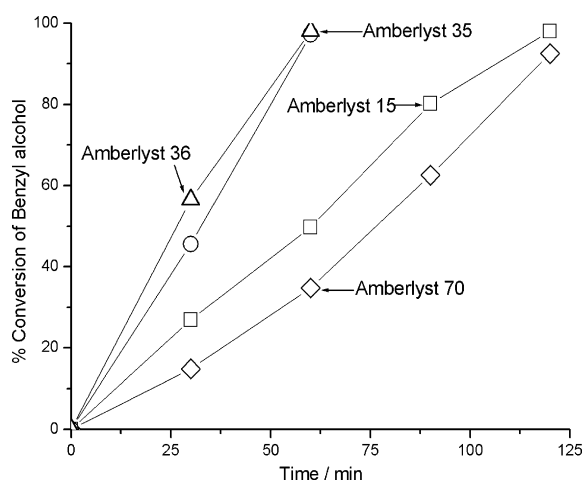


Fig. 4. Conversion of  $\alpha$ -pinene/time at 120 °C with Amberlyst catalysts (50 mg).

our view that thermal de-sulfonation does indeed take place preferentially near the outside of the resin particles.

### 3.3. Catalytic activity

In Fig. 4, the kinetic data for the isomerisation of  $\alpha$ -pinene is shown. In Table 4, the initial rates (of reactant conversion) for both the  $\alpha$ -pinene isomerisation reaction and the benzylation of toluene with benzyl alcohol with the four resin catalysts are shown.

Table 4  
Reaction rate data for test reactions

Catalyst	Isomerisation of $\alpha$ -pinene (conversion) at 120 °C		Benzylation of toluene (conversion of benzyl alcohol) at 80 °C			
	Initial rate constant (min <sup>-1</sup> )		Initial rate constant (80 °C act.) (min <sup>-1</sup> )	TOF (min <sup>-1</sup> )	Initial rate constant (200 °C act.) (min <sup>-1</sup> )	Activity lost at 200 °C (%)
Amberlyst 70	0.001		0.007	0.28	0.006	24
Amberlyst 15	0.004		0.009	0.19		
Amberlyst 35	0.025		0.016	0.31	0.010	38
Amberlyst 36	0.004		0.018	0.33		

In the first reaction, in which the reagent  $\alpha$ -pinene is also the solvent, wide differences in activity are seen. Particularly, telling is the difference between Amberlysts 35 and 36, with the former showing very much higher activity than the latter. These catalysts are similar in terms of acid site concentration and acid strength but differ in their degree of permanent porosity and surface area. It seems likely that the relatively low surface area and pore volume of Amberlyst 36 are responsible for its low catalytic activity in the non-swelling  $\alpha$ -pinene. The low activity of Amberlyst 15 on the other hand, which exhibits a similar and apparently favourable porosity to Amberlyst 35, is almost certainly due to its lower acid site concentration and strength than Amberlysts 35 and 36. By the same logic it seems that the very low activity of Amberlyst 70 is mainly a consequence of the very low pore volume and surface area for this material.

The relative activities in the benzylation of toluene are different. Even though the reaction is run in excess toluene, the polar benzyl alcohol is evidently able to swell the resin catalysts and access acid sites through the bulk of the particles. The activities of Amberlysts 35 and 36 are now similar, suggesting that it is their acidity characteristics that control catalytic performance, and differences in pore volume and surface area are not important. Amberlyst 15 is considerably less active, again in line with its lower acid site concentration and strength. In earlier work, we observed similar differences in activity between normally sulfonated and over-sulfonated polystyrene resin catalysts in reactions in swelling media [22].

In the benzylation reaction Amberlyst 70 shows activity comparable to the other resins. Although its activity on a weight basis is a little lower than the others in this reaction, in terms of specific activity or turn over frequency it is almost as active as Amberlysts 35 and 36. Tejero and co-workers found very similar relative activities for Amberlyst 70 and Amberlyst 36 at 140–150 °C in the dehydration of *n*-pentanol [7]. Overall, these kinetic results seem to be reasonably consistent with acid site concentrations and strengths although, even here, it seems possible that the low porosity of Amberlyst 70 may be restricting its catalytic performance somewhat.

The effect of activating Amberlyst 35 and 70 at 200 °C (instead of 80 °C) on the benzylation rate constants is also shown in Table 4. Amberlyst 70 loses much less activity than Amberlyst 35, consistent with the acidity loss measurements reported above, certainly under hydrothermal conditions. Again, however, it is worth noting that for Amberlyst 70 with its low porosity, acid groups close to the outside of the polymer particle might be disproportionately active in this reaction, possibly

making the material more thermally sensitive than it would be were acid groups throughout the bulk of the particles equally important in imparting activity.

#### 4. Discussion

It appears that the acid site strength of Amberlyst 70 is similar to the over-sulfonated Amberlysts 35 and 36. This is not unreasonable as, in both, the supported sulfonic acid groups are subject to activation from neighbouring substituents on the benzene rings. The enhancement in acid strength for the three stronger acid resins over Amberlyst 15 corresponds to a  $\Delta H_{\text{ads}}^0$  of  $-117$  compared to  $-111 \text{ kJ mol}^{-1}$ . It is interesting to compare this with the enhancement in sulfonic acid strength brought about by a perfluorinated polymer support (Nafion) for which the equivalent average value for  $\Delta H_{\text{ads}}^0$  is  $-160 \text{ kJ mol}^{-1}$  [10]. Nafion shows very much higher catalytic activity than the Amberlyst resins in line with this. It is reasonable that the incorporation of considerably fewer (and less strongly activating) electronegative substituents in the Amberlysts than in Nafion should lead to the much more modest increase in acid strength seen in this work.

The catalytic activity measurements illustrate the importance of resin porosity as well as acidity. This is evidently vital in reactions in non-swelling solvents like  $\alpha$ -pinene. The quite different relative activities of the catalysts towards the benzylation of toluene with benzyl alcohol must be linked to the fact that benzyl alcohol is able to at least partially swell the resin catalysts. These observations are in line with more general studies on the dependence of swelling and internal site accessibility on solvent type for functionalised polymers [23–25].

#### 5. Conclusions

In summary, we have convincing evidence of the higher thermal stability and resistance to de-sulfonation of Amberlyst 70 over conventional sulfonated polystyrene resins. It also appears to exhibit acid site strengths as high as those of the over-sulfonated resins Amberlyst 35 and 36. However, the relatively low concentration of acid sites on a weight basis is a disadvantage in catalytic applications, and its very low level of permanent porosity means that it is only likely to be a viable acid catalyst in liquid systems that are able to significantly swell the resin to facilitate diffusion of reactant to active sites.

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