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Hypercrosslinked polystyrene sulfonic acid catalysts for the esterification of free fatty acids in biodiesel synthesis

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Abstract

New sulfonic acid catalysts supported on hypercrosslinked polystyrene have been studied in the esterification of oleic acid with methanol and in the rearrangement of α -pinene to camphene and limonenes. The catalysts have been characterised in terms of specific surface areas and porosities, affinities for water and for cyclohexane vapours, and both concentrations and strengths of acid sites. They have been compared with conventional macroporous polystyrene sulfonic acids (Amberlysts 15 and 35) and SAC-13, a composite between Nafion and silica. The results show that the hypercrosslinked polystyrene sulfonic acids, despite exhibiting relatively low concentrations of acid sites and acid site strengths below those of Amberlysts 15 and 35, are very much more catalytically active than conventional resins in reactions such as the esterification in which high acid site strengths are not required. It is thought that this is due to the highly accessible acid sites throughout the catalyst particles. Reusability studies are reported and it appears that the temperature at which the catalyst is used is important in controlling and minimising catalyst deactivation.

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1. Introduction

Biodiesel is usually produced by the transesterification of vegetable oil with methanol, converting the triglyceride in the oil to the fatty acid methyl ester (FAME), with glycerol as a by-product [1]. The reaction is conventionally carried out using sodium or potassium hydroxide homogeneous catalysts [2]. Problems arise when the raw materials are low grade oils or used cooking oils because they frequently contain relatively high concentrations of free fatty acids (FFA's). These can form intractable soaps with the catalyst, making subsequent separation of the fuel from the glycerol difficult [3,4]. To prevent this, a pre-esterification step with methanol under acid catalysis can be used to convert the FFA to FAME. Currently, sulfuric acid is often used for this step, but its use requires extensive washing to remove the catalyst [5]. The esterification of FFA, typically oleic acid, is a relative facile reaction and it is not unreasonable to assume that a solid acid catalyst could be used, removing the need for the expensive washing step.

Polystyrene-supported sulfonic acid catalysts have been extensively studied in the direct esterification of free fatty acids and similar reactions [6-12]. They are not amongst the strongest solid acids, but this is of less importance in this reaction than in some others [13]. Most studies of polystyrene sulfonic acid resins have been based on those with permanent macroporosity such as Amberlysts 15, 35 and 36 (sometimes referred to as "macroreticular" resins), although at least one report has shown, surprisingly, that some "gel" resins can exhibit slightly higher activities [6].

Sulfonic acid catalysts on a range of other supports have also been studied, including polyvinyl alcohol [14,15] and activated carbon [16]. Both amorphous and ordered porous silica has been studied extensively as supports for sulfonic acid but, in all cases, only relatively low concentrations of acid groups on the support surface have been achievable, limiting the catalytic activities of these materials [17,18]. Overall, the relatively high sulfonic acid loadings on polystyrene sulfonic acid resins combined with their ready availability makes these materials particularly attractive as esterification catalysts.

Conventional macroporous polystyrene resins rely on polymer cross-linking with divinylbenzene and the incorporation of an inert porogen compound at the polymerisation stage to impart permanent porosity. A variation on this theme is through the so-called "hypercrosslinked" polystyrene resins. These materials have been studied, mainly by Davankov [19], for many years. They are synthesised by carrying out a second crosslinking reaction on polystyrene/divinylbenzene using typically chlorodimethylether with a suitable Friedel-Crafts catalyst. Small angle X-ray diffraction studies have shown that this results in a three dimensional crosslinked polymer network with dramatically enhanced permanent porosity. In fact, if applied to polystyrene resins with existing permanent macroporosity, the additional crosslinking results in additional microporosity in a hierarchical pore

structure. These materials exhibit very high surface areas as measured by gas adsorption, of typically $1000 \text{ m}^2 \text{ g}^{-1}$.

Most of the reported studies have involved the use of these materials as adsorbents [20] and there is relatively little in the literature on their use as catalyst supports. However, they can be functionalised with sulfuric acid, although not to the same extent as conventional polystyrene/divinylbenzene (since functionalisation tends to be restricted to styrene residues not involved in cross linking). In the present work, two examples of sulfonated hypercrosslinked polystyrene have been studied as acid catalysts. These materials, D5081 and D5082, were made by Purolite International Ltd and are functionalised at the relatively low levels of nominally 1 mmol g^{-1} and 2 mmol g^{-1} . For comparison a standard sulfonated macroporous polystyrene/divinylbenzene resin, Amberlyst 15, has been used. The level of sulfonation is about 4.7 mmol g^{-1} , corresponding to approximately one sulfonic acid group per phenyl group in the resin. Amberlyst 35 is similar except that it has been “over-sulfonated” by 10-20%, and this is known to increase the average strength of the supported sulfonic acid groups, through the interaction and activating effects of neighbouring sulfonic acid groups [21]. Finally, Nafion SAC-13 has been used. This is a composite material, combining Nafion (sulfonic acid supported on a fluorinated polymer) and a porous silica. This material is known to exhibit relatively very strong acid sites [22-25].

Two reactions have been used to compare these catalysts. The first is the esterification of oleic acid with methanol to form methyl oleate (Scheme 1a), representative of the pre-esterification step that is necessary with low grade oils for biodiesel. The role of the catalyst is to protonate the methanol but it is essential that oleic acid is able to access the active sites as well as the methanol if esterification is to occur rather than dehydration of the methanol to form dimethylether.

The second reaction is the acid-catalysed rearrangement of α -pinene to camphene and limonenes (Scheme 1b). The driving force for this reaction is the alleviation of strain in the four-membered ring of α -pinene. This reaction is generally regarded as requiring relatively strong acid sites for effective catalysis [26]. It involves a non-polar reactant, and therefore places quite different requirements on catalysts in terms of their compatibilities with reaction media compared to the esterification reaction which is carried out in an excess of methanol.

Scheme 1

2. Experimental

2.1. Materials

D5082 and D5081 are sulfonated hypercrosslinked polystyrene resins and were supplied in bead form by Purolite Ltd. Amberlyst-15 and Amberlyst-35 were supplied by Rohm and Haas Ltd. In two

cases, the resins were also used as powders. To prepare powder samples the beads were cooled in liquid nitrogen and, while still cold, ground with a pestle and mortar. The fractions of particle size below 125 μm were used for catalytic testing. Nafion SAC-13 was obtained from Aldrich and is described as containing 13% w/w Nafion [23]. Oleic acid and methanol were obtained from Fluka and α -pinene from Aldrich.

2.2. Catalyst characterisation

Nitrogen adsorption experiments were conducted using a Micrometrics ASAP 2020. Adsorption and desorption isotherms were recorded at 77 K after degassing at 80 $^{\circ}\text{C}$. Surface areas were calculated from the adsorption isotherms using the BET method. Desorption isotherms were used to calculate pore volumes and mean pore diameters using the BJH method.

The surface morphology of the resins was investigated using a JEOL JSM 6600 scanning electron microscope. The images were taken with 20 mA emission current and 12 kV accelerator voltage. The resins were secured on brass stubs with carbon conductive tape, and coated with gold.

Catalyst acidity was characterised by ammonia adsorption calorimetry, under flow conditions, using a system based on a flow-through Setaram 111 differential scanning calorimeter and an automated gas flow and switching system, with a mass spectrometer (Hiden HPR20) connected via a heated capillary (at 175 $^{\circ}\text{C}$) for down-stream gas flow detection [27]. Resin catalysts were used in as-supplied bead form. SAC-13 was used as a powder.

In a typical experiment the sample (~ 50 mg) was activated under dry nitrogen (5 ml min^{-1}) for one hour at 100 $^{\circ}\text{C}$. Small pulses (typically 1 ml) of the probe gas (1% ammonia in nitrogen) were then injected into the carrier gas stream from a gas sampling valve at the same temperature, monitoring the concentration of ammonia (using $m/z - 15$) downstream of the sample. An important feature of the flow calorimetric technique is that net heat measurements relate only to ammonia bound irreversibly to the samples. Reversibly (weakly) bound ammonia 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 signals with a signal recorded during a control experiment through an empty sample tube. The molar enthalpy of ammonia adsorption ($\Delta H_{\text{ads}}^{\circ}$) was calculated for each pulse. Data is plotted as a profile of $\Delta H_{\text{ads}}^{\circ}(\text{NH}_3)$ vs. amount of ammonia irreversibly adsorbed.

The concentration of acid sites on each of the catalysts was determined by aqueous titration with 0.10 or 0.010 mol dm^{-3} NaOH solution following exchange with sodium ions from a 2.0 mol dm^{-3} sodium chloride solution.

Cyclohexane and water vapour adsorption isotherms were measured on the two hypercrosslinked resins and the two Amberlyst resins, all in bead form, and the SAC-13 in its as-supplied form, using a

Surface Measurement Systems Dynamic Vapor Sorption apparatus (Advantage™), using a method described by Hill *et al.* [28]. Adsorption isotherms were recorded at 25 °C, following activation of the catalysts at 100 °C.

2.3. Catalyst testing

Catalytic activity measurements were conducted in a 50 ml batch reactor equipped with a reflux condenser and magnetic stirrer. Stirrer speeds were set at 600 rpm, a speed at which the rates of reaction showed no stirrer speed dependence, verifying that they were not under mass transfer control. For the esterification reaction 4.0 g oleic acid and 20 g methanol were heated to the reaction temperature of 65 °C. Catalyst (0.20 g) was activated at 80 °C for one hour and then added to the reactant mixture. Aliquots were taken before addition of the catalyst and during the reaction. The FFA content was measured using a standard titration method with aqueous 0.25 M NaOH solution and phenolphthalein indicator, adding anhydrous ethanol to ensure miscibility (AOCS official method Cd 3d-63).

For the isomerisation of α -pinene 10.0 g α -pinene was charged to the reactor and heated to the reaction temperature of 120 °C [26]. Catalyst (0.20 g) was activated at 120 °C for one hour and then added to the reactant. Small aliquots were withdrawn periodically and analysed by GC using a 25 m BPI column at 2 ml min⁻¹ helium flow. The oven temperature was held at 60 °C for 15 min and then increased at 20 °C min⁻¹. The reaction was monitored in terms of the conversion of α -pinene, using n-decane as internal standard.

Further studies were carried out based on the esterification of oleic acid, to test for catalyst leaching and catalyst re-usability. The possibility of acid species leaching to the reactant solution was eliminated by removing catalyst (this test was performed using D5081 and D5082) from a partially converted reaction mixture and verifying that the reaction ceased.

Catalyst re-usability was tested for D5081 in the oleic acid esterification reaction. Used catalyst was washed in methanol, dried, re-activated and re-tested with fresh reactant mixture. Also, the activity of used catalyst after regeneration by stirring in 1.0 mol dm⁻³ H₂SO₄ solution overnight followed by washing, drying and re-activating was measured. The specific surface areas of the used and the regenerated catalysts were measured, along with the acid site concentrations by titration. Additional re-usability tests were carried out following the same reaction, but this time at the higher temperature of 85 °C, using a stirred (1000 rpm) Autoclave Engineers closed reactor, with the same reactant and catalyst concentrations. In these experiments, oleic acid conversion after one hour was measured, the catalyst was washed in methanol and dried, and, using fresh reactant mixture with used catalyst, the reaction was run again. The process was repeated four times.

3. Results

3.1. Catalyst characterization

Table 1 shows specific surface areas and pore volumes of the catalysts. The surface areas of the hypercrosslinked resins are very much higher than those of the simple macroporous resins. As mentioned above, the surface areas of the hypercrosslinked polymer before sulfonation, as measured by nitrogen adsorption, are even higher, approaching $1000 \text{ m}^2 \text{ g}^{-1}$. It is worth saying, however, that the idea of a conventional surface in an open polymer network of this type requires careful interpretation, and the link between the amount of nitrogen that can be adsorbed and a meaningful surface area is not as obvious as it might be [19]. Notwithstanding this reservation, the pore volumes and the mean pore diameters of the hypercrosslinked resins by nitrogen adsorption/desorption are similar to those of the Amberlyst resins. However, the pore size distributions for the hypercrosslinked resins, although not shown, are typically very different. They are usually bimodal, with one maximum in the macropore range and a second in the micropore range arising from the additional cross-linking [19,20].

The SEM images of cross-sectioned beads of Amberlyst 15 and of D5082 in Figure 1 illustrate the different surface textures of the conventional macroporous and the hypercrosslinked polystyrene resins. Even on the scale of the micrographs, some pores can be seen on the surface of the hypercrosslinked resin where none is visible on the conventional macroporous resin. This supports the notion of a much broader pore size distribution in the hypercrosslinked material, although it is somewhat surprising to see pores of quite such large diameters (100-300 nm) when conventional macroporous resins exhibit a relatively narrow distribution of pore size centred around 30-40 nm diameter.

The relative concentrations of acid sites on each of the catalysts are also shown, as measured by aqueous titration and by ammonia adsorption. The latter data is referred to later (section 3.4). There is broad agreement between concentrations determined in the two ways and the values are all close to the sulfonic acid concentrations quoted by the manufacturers. The acid concentrations vary from 5.40 mmol g^{-1} for the over-sulfonated Amberlyst 35 down to 0.15 mmol g^{-1} for the SAC-13 composite material, in line with the known acid site concentration on pure Nafion of 0.89 mmol g^{-1} and the Nafion loading in the composite of 13 % w/w [23]. These differences in acid site density have to be taken into account when considering catalytic activities which have initially been compared based on the weight of catalysts.

3.2. Catalyst testing

Figure 2 shows the rate plots for the two test reactions with the five catalysts. Initial turnover frequencies (TOF's) are given in the adjacent tables. These are based on the concentrations of active sites determined by aqueous titration. The important point to note is that the order of the catalysts in terms of activity is reversed in the two reactions. In the more demanding α -pinene reaction the two Amberlyst resins with relatively high concentrations of acid sites are the most active, with the over-sulfonated Amberlyst 35 more active than Amberlyst 15. The two hypercrosslinked materials are very much less active and show lower turnover frequencies. The catalyst with the highest turnover frequency is SAC-13, with a value six times higher than any of the others.

In the more facile esterification reaction, the highest activities are exhibited by the hypercrosslinked materials and, in terms of turnover frequencies, these show very much higher activities than the macroporous Amberlyst resins. D5081, with a lower concentration of acid sites, is the more active of the two. In this reaction even SAC-13 shows a turnover frequency only slightly higher than that of this hypercrosslinked resin.

In Figure 3 the effect of reducing the particle size of the resin catalysts on their activities in the esterification reaction is shown for hypercrosslinked D5081 and for macroporous Amberlyst 15, through comparisons between bead and powder forms of the catalysts. No dependence on particle size is seen for the hypercrosslinked resin, confirming the absence of reaction rate diffusion control, but a significant increase in rate is seen when the Amberlyst resin is used in powder form. This has been observed before for conventional macroporous resins. It is worth saying however that in bead form their catalytic properties are not generally found to be consistent with a diffusion controlled reaction rate, and this is thought to be because catalysis is dominated by acid sites close to the surface of the resins and, even though in bead form only a fraction of the sites are easily accessible in this way, the kinetics of reaction at this limited number of sites is not diffusion limited [13].

3.3. Catalyst re-usability

A summary of the results of the re-usability tests carried out on D5081 in the oleic acid esterification reaction appear in Figure 4. When the reaction is carried out at 65 °C, catalytic activity is substantially lost after one reaction. The used catalyst has a reduced surface area and reduced acid site concentration. Regeneration with H₂SO₄ solution results in the recovery of about 90% of the surface area and complete recovery of acid concentration, but catalytic activity remains substantially reduced. In remarkable contrast to this, if the reaction is carried out at the higher temperature of 85 °C, washing in methanol results in almost complete recovery of original activity, and, most importantly, the activity remains stable on repeated use (Figure 4b).

3.4. Vapour sorption

Figure 5 shows the adsorption isotherms for cyclohexane and for water vapours for the catalysts. Water uptake is generally higher than cyclohexane uptake, not surprisingly given the presence of hydrophilic sulfonate groups on all catalysts. But the important feature of this data is that the order of catalysts in terms of their adsorption capacities is reversed for the two solvent vapours. There is a broad correlation between the level of sulfonation and water uptake, and an inverse relationship with cyclohexane uptake suggesting, as expected, that the hydrophilicity/hydrophobicity of these resins is directly dependent on the degree of sulfonation.

3.5. Ammonia adsorption calorimetry

Figure 6 shows the molar enthalpy of ammonia adsorption plotted against the amount of adsorbed ammonia for all the catalysts. On the assumption that ammonia adsorbs stoichiometrically on acid sites and that only sites that adsorb with enthalpies greater than 80 kJ mol^{-1} are significantly acidic [29,30] the concentrations of acid sites can be determined. These values appear in Table 1 and can be compared with the acid site concentrations determined by aqueous titration. The values determined by the two methods are similar for the two Amberlyst resins and for Nafion SAC-13, justifying this assumption and confirming that if a Bronsted acid site is able to exchange with sodium ions from aqueous solution (as in the NaOH titration method), it is also accessible to ammonia adsorbed on a dry catalyst from the gas phase. This is not entirely expected for the macroporous Amberlyst 15 and 35 resins, for which most of the acid groups must be within the polymer matrix and not on the immediate surface. Evidently ammonia is able to diffuse into the polymer matrix, even in its anhydrous state, to react with all the acid sites. This is significant in reviewing these macroporous resins as catalysts in terms of the facility with which other reactant compounds might diffuse to acid sites within the polymer.

It is surprising that the acid site concentrations determined by ammonia adsorption for the two hypercrosslinked resins are, in contrast, significantly lower than the concentrations determined by aqueous titration, especially in view of the enhanced acid site accessibilities in these resins discussed later. It would have been reasonable to expect that ammonia could react with all acid sites. Indeed, it seems highly unlikely that reaction between acid sites and ammonia would be restricted in any way. A rather speculative explanation for these apparently low acid site concentrations for D5081 and D5082 is that some of the acid sites in these resins may be weaker than expected and, although they react with ammonia, the enthalpies of reaction fall below the 80 kJ mol^{-1} cut-off that we have used to define acid sites.

In terms of acid strength, it is assumed that the differential enthalpy of adsorption is a measure of acid site strength and that the profile of this value plotted against the amount of ammonia adsorbed is related to the acid site strength distribution for the catalyst. On this basis, Amberlyst 35 exhibits significantly stronger acid sites than Amberlyst 15. This has been observed before and has been put

down to close-neighbour sulfonic acid groups activating each other to a greater extent on the over-sulfonated resin than on the stoichiometrically sulfonated material. This results in enhanced activity for Amberlyst 35 in reactions requiring strong acid sites for catalysis. In contrast, the hypercrosslinked polystyrene sulfonic acid resins exhibit significantly weaker acid sites than the two Amberlyst resins, with D5081 showing weaker sites than D5082. This is consistent with the relatively large separations between acid groups in the hypercrosslinked resins and reduced interactions between neighbouring sulfonic acid groups. Similar observations have been made for sulfonic acids on other supports at high and low loadings [31]. The Nafion composite material exhibits a relatively low concentration of acid sites, as expected, but they are significantly stronger than those of the other catalysts, as a consequence of the electron withdrawing properties of the fluorinated polymer support.

4. Discussion

Comparing catalytic activities as turnover frequencies with acidity data shows that there is a broad correlation between activity and acid site strength for the α -pinene reaction, with the significantly stronger acid sites on Nafion resulting in dramatically higher activity than for any of the other catalysts. The two Amberlyst catalysts show similar activities in line with their intermediate acid strengths, and the sulfonated hypercrosslinked resins show the lowest turnover frequencies and the weakest acid sites.

It appears that the strength of acid sites is a major factor in controlling activity in this reaction. The other factor that might have been expected to be important is the hydrophobicity of the catalyst, since α -pinene is a completely non-polar hydrocarbon. But, on the basis that cyclohexane vapour adsorption is an indicator of hydrophobicity, it is clear that this is a less important factor than catalyst acid strength; indeed, the most active catalysts are the least hydrophobic.

For the esterification reaction the order is very different. Nafion SAC-13 again exhibits the highest turnover frequency, but only just. The surprising observation is that the hypercrosslinked resin catalysts are almost as active, with D5081 with the lower level of sulfonation showing the higher activity of this pair. The turnover frequencies for the hypercrosslinked catalysts are dramatically higher than those for the macroporous Amberlysts 15 and 35 and, even based on catalyst weight, D5081 and D5082 are much more active than the Amberlysts. There is no correlation between activity of the catalysts and their acid site strengths. The catalyst with the weakest acid sites shows the second highest activity, only slightly lower than that of SAC-13. It is striking that the turnover frequency for D5081 in this reaction is comparable with those of a series of cesium-exchanged silicotungstic heteropolyacids acid catalysts studied earlier for the esterification of palmitic acid [32]. These heteropolyacids are regarded as relatively strong solid acids but with relatively low concentrations of acid sites compared to the catalysts studied in this work.

The reaction is carried out in excess methanol and the catalytic step is the protonation of methanol, so it would not be unreasonable to expect a correlation between activity in the esterification reaction and catalyst hydrophilicity. However, based on the data in Figure 4b, there is no apparent relationship between these two. Furthermore, the pronounced particle size dependence of esterification activity for Amberlyst 15, one of the two most hydrophilic resins, suggests that the accessibility of its catalytic sites to methanol is not as might be expected from its affinity for water. Evidently Amberlyst 15 is not sufficiently hydrophilic to render all acid sites accessible to methanol, in bead form at least. In contrast, the activity of the most hydrophobic resin, hypercrosslinked D5081, shows no dependence on particle size, suggesting that, even in bead form, all the acid sites on this resin are accessible to methanol. Evidently the hypercrosslinked structure of D5081 (and D5082) results in significantly better accessibility for reactant molecules to sulfonic acid groups than exists in conventional sulfonated macroporous polystyrene (Amberlyst 15 and 35).

It appears that only a fraction of the sulfonic acid groups in Amberlyst resins are readily accessible to methanol, even when fully solvated. This fraction is increased when the material is used in powder rather than in bead form. Now, the initial esterification reaction rates in the presence of Amberlyst 15 in bead and in powder form can be estimated from Figure 3b and, roughly, the powder seems to be about ten times more active than the bead form. If this is the case then it means that ten times more acid sites are accessible in the powder form. It follows that a maximum of 10% of the acid sites on Amberlyst 15 are accessible to methanol when in bead form. Amberlyst 15 contains a total of 4.7 mmol g⁻¹ acid sites so this means that catalysis relies on a sulfonic acid concentration of, at most, only 0.47 mmol g⁻¹ when used in bead form. The behaviour of the hypercrosslinked polystyrene catalyst contrasts with this. If, as seems the case from the absence of any particle size dependence of the activity, all the acid sites are accessible, then it is obvious why the activity of these resins is higher than the Amberlysts, at least in reactions where the strength of acid sites is not a crucial factor. It is simply down to the accessibilities of all acid sites to reactant compounds, even when the catalyst is used in bead form.

A comparison between the two hypercrosslinked catalysts shows D5081 to exhibit a very much higher turnover frequency than D5082 in the esterification reaction, but a lower value in the α -pinene rearrangement. The TOF's in the α -pinene broadly correlate with the strengths of the acid sites as mentioned above. But in the esterification reaction, the much higher TOF for D5081 could be linked to the higher specific surface area of this catalyst, which is almost twice that of D5082. Based on these two materials, it appears that progressive functionalisation reduces the available surface area. This may be a result of acid groups, or solvated acid groups, blocking some of the network of micropores in the hypercrosslinked structure but, whatever the reason, it clearly points to the need for a careful balance between surface area and sulfonic acid loading if optimum catalytic activity is to be

achieved. The data for the two test reactions used here suggests that optimum loadings differ depending on the reaction to be catalysed and the reaction medium in which the catalyst is to be used.

Catalyst re-usability is addressed for D5081 in the oleic acid esterification reaction and we show that activity is significantly and irreversibly reduced after just one use when the reaction temperature is 65 °C, but activity is maintained when the higher reaction temperature of 85 °C is used. The reason for loss in activity is not certain but we speculate that it is related to the blockage of the fine pores in the hypercrosslinked resin by large fatty acid molecules, possibly even oligomerised forms of the acid. We suggest that at 65° C these molecules deposit in the pores. They are not effectively removed by methanol washing but prolonged washing with mineral acid does indeed have some effect. It is tempting to think that the reduction in measureable acidity in the resins after use is an indication of ion-exchange from the reactant mixture but the reactants used in this work were essentially free of contaminant cations so this possibility cannot explain the loss in acid concentration. It is more likely that the low measureable acidity in used resins is also a result of pore blockage and reduced accessibility of a proportion of the acid sites. Hoelderich *et al.* studied the deactivation of sulfonic acid ion-exchange resin catalysts for similar esterification reactions in some detail, but largely using natural vegetable oils spiked with additional fatty acids [6]. These workers proposed that it was ion-exchange of Na^+ , K^+ , Mg^{2+} and Ca^{2+} from the oils that was responsible for loss in activity but, even when using cation-free oils, some activity was lost, so this result is not inconsistent with our findings.

At the higher temperature of 85 °C, we suggest that pore blockage does not occur, or at least not to the same extent, and activity is retained for multiple cycles without the need for catalyst regeneration. It is possible that fatty acid diffusion is now fast enough to prevent deposition. We note that Banavali *et al.* reported the use of Amberlyst BD20 for the esterification of free fatty acids in oils with methanol at the same temperature of 85 °C [33]. Using temperatures above the boiling point of methanol adds complication to the process, so we wonder whether this too may be linked to possible deactivation of catalysts at lower temperatures.

For practical application of sulfonated hypercrosslinked polystyrene catalysts for the esterification of free fatty acids in biodiesel synthesis, reaction conditions must be set to avoid significant catalyst deactivation. We show here that running the reaction at elevated temperature is one solution. However, we observe that, in a single reaction, the oleic acid conversion vs time plot at the more practical reaction temperature of 65 °C (Figure 2) does not show that the catalyst is losing significant activity during the course of the reaction. And yet, on re-use, activity is massively diminished. It is possible that catalyst poisoning occurs when the reaction is stopped, the mixture cooled, and the catalyst removed. If this is the case, then using these new resin catalysts in a continuous flow reactor, rather than under batch conditions, may allow for better activity retention, without having to resort to elevated reaction temperatures.

5. Conclusion

Acid site accessibilities in sulfonated hypercrosslinked polystyrene resins appear to be significantly higher than for conventional polystyrene/divinylbenzene sulfonic acids, and facile diffusion to these sites is possible even for large reactant molecules such as oleic acid. The level to which these hypercrosslinked polymer supports can be functionalised with sulfonic acid is lower than for conventional cross-linked polystyrene, and the acid strengths are lower than those of typical conventional sulfonated polystyrene. But in acid-catalysed reactions where very high acid strengths are not required, the advantages of excellent acid site accessibility can result in higher activity than other typical solid acid catalysts. The high activity exhibited by these catalysts towards oleic acid esterification points to their possible use in many reactions, including the pre-treatment step in the synthesis of biodiesel from low grade oils with high free fatty acid contents.

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7. References

- [1] J.A. Melero, J. Iglesias, G. Morales, *Green Chem.* 11 (2009) 1285-1308.
- [2] F. Ma, M.A. Hanna, *Bioresource Technol.* 70 (1999) 1-15.
- [3] Y. Wang, S. Ou, P Liu, F. Xue, S. Tang, *J. Molec. Catal. A* 252 (2006) 107-112.
- [4] M. Canakci, J. Van Gerpen, *Trans. Am. Soc. Agric. Eng.* 44 (2001) 1429-1436.
- [5] Y. Zhang, M.A.Dube, D.D. McLean, M. Kates, *J. Bio. Tech.* 89 (2003) 1-16.
- [6] B.M.E. Russbuel, W.F. Hoelderich, *Appl. Catal. A* 362 (2009) 47-57.
- [7] N. Özbay, N. Oktar, N.A. Tapan, *Fuel* 87 (2008) 1789-1798.
- [8] J.M. Marchetti, V.U. Miguel, A.F. Errazu, *Fuel* 86 (2007) 906-910.
- [9] M.M.R. Talukder, J.C. Wu, S.K. Lau, L.C. Cui, G. Shimin, A. Lim, *Energy Fuels* 23 (2009) 1-4.
- [10] S. Pasiyas, N. Barakos, C. Alexopoulos, N. Papayannakos, *Chem. Eng. & Technol.* 29 (2006) 1365-1371.
- [11] M. Kouzu, T Kasuno, M. Tajika, Y. Sugimoto, J. Hidaka, *Fuel* 87 (2008) 2798-2806.
- [12] E. Lundquist, US Patent 5,426,199 (1999), Purolite International.
- [13] P.F. Siril, A.D. Davison, J.K. Randhawa, D.R. Brown, *J. Mol. Catal. A* 267 (2007) 72-78.

- [14] C.S. Caetano, L. Guerreiro, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Appl.Catal. A* 359 (2009) 41-46.
- [15] D.S Pito, I.M. Fonseca, J. Vital, J.E. Castanheiro, *Chem. Eng. J.* 147 (2009) 302-306.
- [16] X. Mo, E. Lotero, C. Lu, Y. Liu, J.G. Goodwin, *Catal. Lett.* 123 (2008) 1-6.
- [17] I.K. Mbaraka, K.J. McGuire, B.H. Shanks, *Ind. & Eng. Chem. Res.* 45 (2006) 3022-3028.
- [18] J.A. Melero, L.F. Bautista, G. Morales, J. Iglesias, R. Sanchez-Vazquez, *Chem. Eng. J.* 161 (2010) 323-331.
- [19] M.P. Tsyurupa, V.A. Davankov, *React. Funct. Polym.* 66 (2006) 768-779.
- [20] C-G. Oh, J-H. Ahn, S-K. Ihm, *React. Funct. Polym.* 57 (2003) 103-111.
- [21] P.F. Siril, H.E. Cross, D.R. Brown, *J. Molec. Catal. A* 279 (2008) 63-68.
- [22] P.F. Siril, N.R. Shiju, D.R. Brown, *Appl. Catal. A* 364 (2009) 95-100.
- [23] M.A. Harmer, W.E. Farneth, Q. Sun, *J. Am. Chem. Soc.* 118 (1996) 7708-7715.
- [24] M.A. Harmer W.E. Farneth, Q. Sun, *Adv. Mater.* 10 (1998) 1255-1257.
- [25] M A Harmer, Q Sun, A.J. Vega, W.E. Farneth, A. Heidekum, W.F. Hoelderich, *Green Chem.* 2 (2000) 7-14.
- [26] M.P. Hart, D.R. Brown, *J. Molec. Catal. A* 212 (2004) 315-321.
- [27] S.P. Felix, C. Savill-Jowitt, D.R. Brown, *Thermochim. Acta* 433 (2005) 59-67.
- [28] C.A.S Hill, A. Norton, G. Newman, *J. Appl. Polym. Sci.* 112 (2009) 1524-1537.
- [29] M.J. Meziani, J. Zajac, J.D. Jones, S. Partyka, J. Roziere, A. Auroux, *Langmuir* 16 (2000) 2262-2273.
- [30] A. Auroux, *Top. Catal.* 4 (1997) 71-93.
- [31] J-P Dacquin, H.E. Cross, D.R. Brown, T. Düren, J.J. Williams, A.F. Lee, K. Wilson, *Green Chem.* 12 (2010) 1383-1391.
- [32] L. Pesaresi, D.R. Brown, A.F. Lee, J.M. Montero, H. Williams, K. Wilson, *Appl. Catal. A* 360 (2009) 50-58.
- [33] R. Banavali, R.T. Hanlon, K. Jerabek, A.K. Schultz, in: M. Prunier (Ed), *Catalysis of Organic Reactions*, CRC Press, New York, 2009, pp. 279-289.

Hypercrosslinked polystyrene sulfonic acid catalysts for the esterification of free fatty acids in biodiesel synthesis

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Abstract

New sulfonic acid catalysts supported on hypercrosslinked polystyrene have been studied in the esterification of oleic acid with methanol and in the rearrangement of α -pinene to camphene and limonenes. The catalysts have been characterised in terms of specific surface areas and porosities, affinities for water and for cyclohexane vapours, and both concentrations and strengths of acid sites by ammonia adsorption microcalorimetry. These catalysts have been compared with conventional macroporous polystyrene sulfonic acids (Amberlysts 15 and 35) and SAC-13, a composite between Nafion, a fluorinated polymer-supported sulfonic acid and silica. The results show that the hypercrosslinked polystyrene sulfonic acids, despite exhibiting relatively low concentrations of acid sites and acid site strengths below those of Amberlysts 15 and 35, are very much more catalytically active than conventional resins in reactions such as the esterification in which high acid site strengths are not required. It is thought that this is due to the highly accessible acid sites throughout the catalyst particles.

1. Introduction

Biodiesel is usually produced by the transesterification of vegetable oil with methanol, converting the triglyceride in the oil to the fatty acid methyl ester (FAME), with glycerol as a by-product [1]. The reaction is conventionally carried out using sodium or potassium hydroxide homogeneous catalysts [2]. Problems arise when the raw materials are low grade oils or used cooking oils because they frequently contain relatively high concentrations of free fatty acids (FFA's). These can form intractable soaps with the catalyst, making subsequent separation of the fuel from the glycerol difficult [3,4]. To prevent this, a pre-esterification step with methanol under acid catalysis can be used to convert the FFA to FAME. Currently, sulfuric acid is often used for this step, but its use requires extensive washing to remove the catalyst [5]. The esterification of FFA, typically oleic acid, is a relative facile reaction and it is not unreasonable to assume that a solid acid catalyst could be used, removing the need for the expensive washing step.

Polystyrene-supported sulfonic acid catalysts have been extensively studied in the direct esterification of free fatty acids and similar reactions [6-12]. They are not amongst the strongest solid acids, but this is of less importance in this reaction than in some others [13]. Most studies of polystyrene sulfonic acid resins have been based on those with permanent macroporosity such as Amberlysts 15, 35 and 36 (sometimes referred to as "macroreticular" resins), although at least one report has shown, surprisingly, that some "gel" resins can exhibit slightly higher activities [6].

Sulfonic acid catalysts on a range of other supports have also been studied, including polyvinyl alcohol [14,15] and activated carbon [16]. Both amorphous and ordered porous silica has been studied extensively as supports for sulfonic acid but, in all cases, only relatively low concentrations of acid groups on the support surface have been achievable, limiting the catalytic activities of these materials [17,18]. Overall, the relatively high sulfonic acid loadings on polystyrene sulfonic acid resins combined with their ready availability makes these materials particularly attractive as esterification catalysts.

Conventional macroporous polystyrene resins rely on polymer cross-linking with divinylbenzene and the incorporation of an inert porogen compound at the polymerisation stage to impart permanent porosity. A variation on this theme is through the so-called "hypercrosslinked" polystyrene resins. These materials have been studied, mainly by Davankov [19], for many years. They are synthesised by carrying out a second crosslinking reaction on polystyrene/divinylbenzene using typically chlorodimethylether with a suitable Friedel-Crafts catalyst. Small angle X-ray diffraction studies have shown that this results in a three dimensional crosslinked polymer network with dramatically enhanced permanent porosity. In fact, if applied to polystyrene resins with existing permanent macroporosity, the additional crosslinking results in additional microporosity in a hierarchical pore

structure. These materials exhibit very high surface areas as measured by gas adsorption, of typically $1000 \text{ m}^2 \text{ g}^{-1}$.

Most of the reported studies have involved the use of these materials as adsorbents [20] and there is relatively little in the literature on their use as catalyst supports. However, they can be functionalised with sulfuric acid, although not to the same extent as conventional polystyrene/divinylbenzene (since functionalisation tends to be restricted to styrene residues not involved in cross linking). In the present work, two examples of sulfonated hypercrosslinked polystyrene have been studied as acid catalysts. These materials, D5081 and D5082, were made by Purolite International Ltd and are functionalised at the relatively low levels of nominally 1 mmol g^{-1} and 2 mmol g^{-1} . For comparison a standard sulfonated macroporous polystyrene/divinylbenzene resin, Amberlyst 15, has been used. The level of sulfonation is about 4.7 mmol g^{-1} , corresponding to approximately one sulfonic acid group per phenyl group in the resin. Amberlyst 35 is similar except that it has been “over-sulfonated” by 10-20%, and this is known to increase the average strength of the supported sulfonic acid groups, through the interaction and activating effects of neighbouring sulfonic acid groups [21]. Finally, Nafion SAC-13 has been used. This is a composite material, combining Nafion (sulfonic acid supported on a fluorinated polymer) and a porous silica. This material is known to exhibit relatively very strong acid sites [22-25].

Two reactions have been used to compare these catalysts. The first is the esterification of oleic acid with methanol to form methyl oleate (Scheme 1a), representative of the pre-esterification step that is necessary with low grade oils for biodiesel. The role of the catalyst is to protonate the methanol but it is essential that oleic acid is able to access the active sites as well as the methanol if esterification is to occur rather than dehydration of the methanol to form dimethylether.

The second reaction is the acid-catalysed rearrangement of α -pinene to camphene and limonenes (Scheme 1b). The driving force for this reaction is the alleviation of strain in the four-membered ring of α -pinene. This reaction is generally regarded as requiring relatively strong acid sites for effective catalysis [26]. It involves a non-polar reactant, and therefore places quite different requirements on catalysts in terms of their compatibilities with reaction media compared to the esterification reaction which is carried out in an excess of methanol.

Scheme 1

2. Experimental

2.1. Materials

D5082 and D5081 are sulfonated hypercrosslinked polystyrene resins and were supplied in bead form by Purolite Ltd. Amberlyst-15 and Amberlyst-35 were supplied by Rohm and Haas Ltd. In two

cases, the resins were also used as powders. To prepare powder samples the beads were cooled in liquid nitrogen and, while still cold, ground with a pestle and mortar. The fractions of particle size below 125 μm were used for catalytic testing. Nafion SAC-13 was obtained from Aldrich and is described as containing 13% w/w Nafion [23]. Oleic acid and methanol were obtained from Fluka and α -pinene from Aldrich.

2.2. Catalyst characterisation

Nitrogen adsorption experiments were conducted using a Micrometrics ASAP 2020. Adsorption and desorption isotherms were recorded at 77 K after degassing at 80 $^{\circ}\text{C}$. Surface areas were calculated from the adsorption isotherms using the BET method. Desorption isotherms were used to calculate pore volumes and mean pore diameters using the BJH method.

The surface morphology of the resins was investigated using a JEOL JSM 6600 scanning electron microscope. The images were taken with 20 mA emission current and 12 kV accelerator voltage. The resins were secured on brass stubs with carbon conductive tape, and coated with gold.

Catalyst acidity was characterised by ammonia adsorption calorimetry, under flow conditions, using a system based on a flow-through Setaram 111 differential scanning calorimeter and an automated gas flow and switching system, with a mass spectrometer (Hiden HPR20) connected via a heated capillary (at 175 $^{\circ}\text{C}$) for down-stream gas flow detection [27]. Resin catalysts were used in as-supplied bead form. SAC-13 was used as a powder.

In a typical experiment the sample (~ 50 mg) was activated under dry nitrogen (5 ml min^{-1}) for one hour at 100 $^{\circ}\text{C}$. Small pulses (typically 1 ml) of the probe gas (1% ammonia in nitrogen) were then injected into the carrier gas stream from a gas sampling valve at the same temperature, monitoring the concentration of ammonia (using $m/z - 15$) downstream of the sample. An important feature of the flow calorimetric technique is that net heat measurements relate only to ammonia bound irreversibly to the samples. Reversibly (weakly) bound ammonia 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 signals with a signal recorded during a control experiment through an empty sample tube. The molar enthalpy of ammonia adsorption ($\Delta H_{\text{ads}}^{\circ}$) was calculated for each pulse. Data is plotted as a profile of $\Delta H_{\text{ads}}^{\circ}(\text{NH}_3)$ vs. amount of ammonia irreversibly adsorbed.

The concentration of acid sites on each of the catalysts was determined by aqueous titration with 0.10 or 0.010 mol dm^{-3} NaOH solution following exchange with sodium ions from a 2.0 mol dm^{-3} sodium chloride solution.

Cyclohexane and water vapour adsorption isotherms were measured on the two hypercrosslinked resins and the two Amberlyst resins, all in bead form, and the SAC-13 in its as-supplied form, using a

Surface Measurement Systems Dynamic Vapor Sorption apparatus (AdvantageTM), using a method described by Hill *et al.* [28]. Adsorption isotherms were recorded at 25 °C, following activation of the catalysts at 100 °C.

2.3. Catalyst testing

Catalytic activity measurements were conducted in a 50 ml batch reactor equipped with a reflux condenser and magnetic stirrer. Stirrer speeds were set to ensure that reaction rates were not under mass transfer control. For the esterification reaction 4.0 g oleic acid and 20 g methanol were heated to the reaction temperature of 65 °C. Catalyst (0.20 g) was activated at 80 °C for one hour and then added to the reactant mixture. Aliquots were taken before addition of the catalyst and during the reaction. The FFA content was measured using a standard titration method with aqueous 0.25 M NaOH solution and phenolphthalein indicator, adding anhydrous ethanol to ensure miscibility (AOCS official method Cd 3d-63).

For the isomerisation of α -pinene 10.0 g α -pinene was charged to the reactor and heated to the reaction temperature of 120 °C [26]. Catalyst (0.20 g) was activated at 120 °C for one hour and then added to the reactant. Small aliquots were withdrawn periodically and analysed by GC using a 25 m BPI column at 2 ml min⁻¹ helium flow. The oven temperature was held at 60 °C for 15 min and then increased at 20 °C min⁻¹. The reaction was monitored in terms of the conversion of α -pinene, using n-decane as internal standard.

3. Results

3.1. Catalyst characterization

Table 1 shows specific surface areas and pore volumes of the catalysts. The surface areas of the hypercrosslinked resins are very much higher than those of the simple macroporous resins. As mentioned above, the surface areas of the hypercrosslinked polymer before sulfonation, as measured by nitrogen adsorption, are even higher, approaching 1000 m² g⁻¹. It is worth saying, however, that the idea of a conventional surface in an open polymer network of this type requires careful interpretation, and the link between the amount of nitrogen that can be adsorbed and a meaningful surface area is not as obvious as it might be [19]. Notwithstanding this reservation, the pore volumes and the mean pore diameters of the hypercrosslinked resins by nitrogen adsorption/desorption are similar to those of the Amberlyst resins. However, the pore size distributions for the hypercrosslinked resins, although not shown, are typically very different. They are usually bimodal, with one maximum in the macropore range and a second in the micropore range arising from the additional cross-linking [19,20].

The SEM images of cross-sectioned beads of Amberlyst 15 and of D5082 in Figure 1 illustrate the different surface textures of the conventional macroporous and the hypercrosslinked polystyrene resins. Even on the scale of the micrographs, some pores can be seen on the surface of the hypercrosslinked resin where none is visible on the conventional macroporous resin. This supports the notion of a much broader pore size distribution in the hypercrosslinked material, although it is somewhat surprising to see pores of quite such large diameters (100-300 nm) when conventional macroporous resins exhibit a relatively narrow distribution of pore size centred around 30-40 nm diameter.

The relative concentrations of acid sites on each of the catalysts are also shown, as measured by aqueous titration and by ammonia adsorption. The latter data is referred to later (section 3.4). There is broad agreement between concentrations determined in the two ways and the values are all close to the sulfonic acid concentrations quoted by the manufacturers. The acid concentrations vary from 5.40 mmol g⁻¹ for the over-sulfonated Amberlyst 35 down to 0.15 mmol g⁻¹ for the SAC-13 composite material, in line with the known acid site concentration on pure Nafion of 0.89 mmol g⁻¹ and the Nafion loading in the composite of 13 % w/w [23]. These differences in acid site density have to be taken into account when considering catalytic activities which have initially been compared based on the weight of catalysts.

3.2. Catalyst testing

Figure 2 shows the rate plots for the two test reactions with the five catalysts. Initial turnover frequencies (TOF's) are given in the adjacent tables. These are based on the concentrations of active sites determined by aqueous titration. The important point to note is that the order of the catalysts in terms of activity is reversed in the two reactions. In the more demanding α -pinene reaction the two Amberlyst resins with relatively high concentrations of acid sites are the most active, with the over-sulfonated Amberlyst 35 more active than Amberlyst 15. The two hypercrosslinked materials are very much less active and show lower turnover frequencies. The catalyst with the highest turnover frequency is SAC-13, with a value six times higher than any of the others.

In the more facile esterification reaction, the highest activities are exhibited by the hypercrosslinked materials and, in terms of turnover frequencies, these show very much higher activities than the macroporous Amberlyst resins. D5081, with a lower concentration of acid sites, is the more active of the two. In this reaction even SAC-13 shows a turnover frequency only slightly higher than that of this hypercrosslinked resin.

In Figure 3 the effect of reducing the particle size of the resin catalysts on their activities in the esterification reaction is shown for hypercrosslinked D5081 and for macroporous Amberlyst 15, through comparisons between bead and powder forms of the catalysts. No dependence on particle

size is seen for the hypercrosslinked resin, confirming the absence of reaction rate diffusion control, but a significant increase in rate is seen when the Amberlyst resin is used in powder form. This has been observed before for conventional macroporous resins. It is worth saying however that in bead form their catalytic properties are not generally found to be consistent with a diffusion controlled reaction rate, and this is thought to be because catalysis is dominated by acid sites close to the surface of the resins and, even though in bead form only a fraction of the sites are easily accessible in this way, the kinetics of reaction at this limited number of sites is not diffusion limited [13].

3.3. Vapour sorption

Figure 4 shows the adsorption isotherms for cyclohexane and for water vapours for the catalysts. Water uptake is generally higher than cyclohexane uptake, not surprisingly given the presence of hydrophilic sulfonate groups on all catalysts. But the important feature of this data is that the order of catalysts in terms of their adsorption capacities is reversed for the two solvent vapours. There is a broad correlation between the level of sulfonation and water uptake, and an inverse relationship with cyclohexane uptake suggesting, as expected, that the hydrophilicity/hydrophobicity of these resins is directly dependent on the degree of sulfonation.

3.4. Ammonia adsorption calorimetry

Figure 5 shows the molar enthalpy of ammonia adsorption plotted against the amount of adsorbed ammonia for all the catalysts. On the assumption that ammonia adsorbs stoichiometrically on acid sites and that only sites that adsorb with enthalpies greater than 80 kJ mol^{-1} are significantly acidic [29,30] the concentrations of acid sites can be determined. These values appear in Table 1 and can be compared with the acid site concentrations determined by aqueous titration. The values determined by the two methods are similar for the two Amberlyst resins and for Nafion SAC-13, justifying this assumption and confirming that if a Bronsted acid site is able to exchange with sodium ions from aqueous solution (as in the NaOH titration method), it is also accessible to ammonia adsorbed on a dry catalyst from the gas phase. This is not entirely expected for the macroporous Amberlyst 15 and 35 resins, for which most of the acid groups must be within the polymer matrix and not on the immediate surface. Evidently ammonia is able to diffuse into the polymer matrix, even in its anhydrous state, to react with all the acid sites. This is significant in reviewing these macroporous resins as catalysts in terms of the facility with which other reactant compounds might diffuse to acid sites within the polymer.

It is surprising that the acid site concentrations determined by ammonia adsorption for the two hypercrosslinked resins are, in contrast, significantly lower than the concentrations determined by aqueous titration, especially in view of the enhanced acid site accessibilities in these resins discussed later. It would have been reasonable to expect that ammonia could react with all acid sites. Indeed, it

seems highly unlikely that reaction between acid sites and ammonia would be restricted in any way. A rather speculative explanation for these apparently low acid site concentrations for D5081 and D5082 is that some of the acid sites in these resins may be weaker than expected and, although they react with ammonia, the enthalpies of reaction fall below the 80 kJ mol^{-1} cut-off that we have used to define acid sites.

In terms of acid strength, it is assumed that the differential enthalpy of adsorption is a measure of acid site strength and that the profile of this value plotted against the amount of ammonia adsorbed is related to the acid site strength distribution for the catalyst. On this basis, Amberlyst 35 exhibits significantly stronger acid sites than Amberlyst 15. This has been observed before and has been put down to close-neighbour sulfonic acid groups activating each other to a greater extent on the over-sulfonated resin than on the stoichiomerically sulfonated material. This results in enhanced activity for Amberlyst 35 in reactions requiring strong acid sites for catalysis. In contrast, the hypercrosslinked polystyrene sulfonic acid resins exhibit significantly weaker acid sites than the two Amberlyst resins, with D5081 showing weaker sites than D5082. This is consistent with the relatively large separations between acid groups in the hypercrosslinked resins and reduced interactions between neighbouring sulfonic acid groups. Similar observations have been made for sulfonic acids on other supports at high and low loadings [31]. The Nafion composite material exhibits a relatively low concentration of acid sites, as expected, but they are significantly stronger than those of the other catalysts, as a consequence of the electron withdrawing properties of the fluorinated polymer support.

4. Discussion

Comparing catalytic activities as turnover frequencies with acidity data shows that there is a broad correlation between activity and acid site strength for the α -pinene reaction, with the significantly stronger acid sites on Nafion resulting in dramatically higher activity than for any of the other catalysts. The two Amberlyst catalysts show similar activities in line with their intermediate acid strengths, and the sulfonated hypercrosslinked resins show the lowest turnover frequencies and the weakest acid sites.

It appears that the strength of acid sites is a major factor in controlling activity in this reaction. The other factor that might have been expected to be important is the hydrophobicity of the catalyst, since α -pinene is a completely non-polar hydrocarbon. But, on the basis that cyclohexane vapour adsorption is an indicator of hydrophobicity, it is clear that this is a less important factor than catalyst acid strength; indeed, the most active catalysts are the least hydrophobic.

For the esterification reaction the order is very different. Nafion SAC-13 again exhibits the highest turnover frequency, but only just. The surprising observation is that the hypercrosslinked resin catalysts are almost as active, with D5081 with the lower level of sulfonation showing the higher

activity of this pair. The turnover frequencies for the hypercrosslinked catalysts are dramatically higher than those for the macroporous Amberlysts 15 and 35 and, even based on catalyst weight, D5081 and D5082 are much more active than the Amberlysts. There is no correlation between activity of the catalysts and their acid site strengths. The catalyst with the weakest acid sites shows the second highest activity, only slightly lower than that of SAC-13. It is striking that the turnover frequency for D5081 in this reaction is comparable with those of a series of cesium-exchanged silicotungstic heteropolyacids acid catalysts studied earlier for the esterification of palmitic acid [32]. These heteropolyacids are regarded as relatively strong solid acids but with relatively low concentrations of acid sites compared to the catalysts studied in this work.

The reaction is carried out in excess methanol and the catalytic step is the protonation of methanol, so it would not be unreasonable to expect a correlation between activity in the esterification reaction and catalyst hydrophilicity. However, based on the data in Figure 4b, there is no apparent relationship between these two. Furthermore, the pronounced particle size dependence of esterification activity for Amberlyst 15, one of the two most hydrophilic resins, suggests that the accessibility of its catalytic sites to methanol is not as might be expected from its affinity for water. Evidently Amberlyst 15 is not sufficiently hydrophilic to render all acid sites accessible to methanol, in bead form at least. In contrast, the activity of the most hydrophobic resin, hypercrosslinked D5081, shows no dependence on particle size, suggesting that, even in bead form, all the acid sites on this resin are accessible to methanol. Evidently the hypercrosslinked structure of D5081 (and D5082) results in significantly better accessibility for reactant molecules to sulfonic acid groups than exists in conventional sulfonated macroporous polystyrene (Amberlyst 15 and 35).

It appears that only a fraction of the sulfonic acid groups in Amberlyst resins are readily accessible to methanol, even when fully solvated. This fraction is increased when the material is used in powder rather than in bead form. Now, the initial esterification reaction rates in the presence of Amberlyst 15 in bead and in powder form can be estimated from Figure 3b and, roughly, the powder seems to be about ten times more active than the bead form. If this is the case then it means that ten times more acid sites are accessible in the powder form. It follows that a maximum of 10% of the acid sites on Amberlyst 15 are accessible to methanol when in bead form. Amberlyst 15 contains a total of 4.7 mmol g⁻¹ acid sites so this means that catalysis relies on a sulfonic acid concentration of, at most, only 0.47 mmol g⁻¹ when used in bead form. The behaviour of the hypercrosslinked polystyrene catalyst contrasts with this. If, as seems the case from the absence of any particle size dependence of the activity, all the acid sites are accessible, then it is obvious why the activity of these resins is higher than the Amberlysts, at least in reactions where the strength of acid sites is not a crucial factor. It is simply down to the accessibilities of all acid sites to reactant compounds, even when the catalyst is used in bead form.

A comparison between the two hypercrosslinked catalysts shows D5081 to exhibit a very much higher turnover frequency than D5082 in the esterification reaction, but a lower value in the α -pinene rearrangement. The TOF's in the α -pinene broadly correlate with the strengths of the acid sites as mentioned above. But in the esterification reaction, the much higher TOF for D5081 could be linked to the higher specific surface area of this catalyst, which is almost twice that of D5082. Based on these two materials, it appears that progressive functionalisation reduces the available surface area. This may be a result of acid groups, or solvated acid groups, blocking some of the network of micropores in the hypercrosslinked structure but, whatever the reason, it clearly points to the need for a careful balance between surface area and sulfonic acid loading if optimum catalytic activity is to be achieved. The data for the two test reactions used here suggests that optimum loadings differ depending on the reaction to be catalysed and the reaction medium in which the catalyst is to be used.

5. Conclusion

Acid site accessibilities in sulfonated hypercrosslinked polystyrene resins appear to be significantly higher than for conventional polystyrene/divinylbenzene sulfonic acids, and facile diffusion to these sites is possible even for large reactant molecules such as oleic acid. The level to which these hypercrosslinked polymer supports can be functionalised with sulfonic acid is lower than for conventional cross-linked polystyrene, and the acid strengths are lower than those of typical conventional sulfonated polystyrene. But in acid-catalysed reactions where very high acid strengths are not required, the advantages of excellent acid site accessibility can result in higher activity than other typical solid acid catalysts. The high activity exhibited by these catalysts towards oleic acid esterification points to their possible use in many reactions, including the pre-treatment step in the synthesis of biodiesel from low grade oils with high free fatty acid contents.

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7. References

- [1] J.A. Melero, J. Iglesias, G. Morales, *Green Chem.* 11 (2009) 1285-1308.
- [2] F. Ma, M.A. Hanna, *Bioresource Technol.* 70 (1999) 1-15.
- [3] Y. Wang, S. Ou, P Liu, F. Xue, S. Tang, *J. Molec. Catal. A* 252 (2006) 107-112.
- [4] M. Canakci, J. Van Gerpen, *Trans. Am. Soc. Agric. Eng.* 44 (2001) 1429-1436.
- [5] Y. Zhang, M.A.Dube, D.D. McLean, M. Kates, *J. Bio. Tech.* 89 (2003) 1-16.
- [6] B.M.E. Russbuehl, W.F. Hoelderich, *Appl. Catal. A* 362 (2009) 47-57.

- [7] N. Özbay, N. Oktar, N.A. Tapan, *Fuel* 87 (2008) 1789-1798.
- [8] J.M. Marchetti, V.U. Miguel, A.F. Errazu, *Fuel* 86 (2007) 906-910.
- [9] M.M.R. Talukder, J.C. Wu, S.K. Lau, L.C. Cui, G. Shimin, A. Lim, *Energy Fuels* 23 (2009) 1-4.
- [10] S. Pasiás, N. Barakos, C. Alexopoulos, N. Papayannakos, *Chem. Eng. & Technol.* 29 (2006) 1365-1371.
- [11] M. Kouzu, T Kasuno, M. Tajika, Y. Sugimoto, J. Hidaka, *Fuel* 87 (2008) 2798-2806.
- [12] E. Lundquist, US Patent 5,426,199 (1999), Purolite International.
- [13] P.F. Siril, A.D. Davison, J.K. Randhawa, D.R. Brown, *J. Mol. Catal. A* 267 (2007) 72-78.
- [14] C.S. Caetano, L. Guerreiro, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Appl.Catal. A* 359 (2009) 41-46.
- [15] D.S Pito, I.M. Fonseca, J. Vital, J.E. Castanheiro, *Chem. Eng. J.* 147 (2009) 302-306.
- [16] X. Mo, E. Lotero, C. Lu, Y. Liu, J.G. Goodwin, *Catal. Lett.* 123 (2008) 1-6.
- [17] I.K. Mbaraka, K.J. McGuire, B.H. Shanks, *Ind. & Eng. Chem. Res.* 45 (2006) 3022-3028.
- [18] J.A. Melero, L.F. Bautista, G. Morales, J. Iglesias, R. Sanchez-Vazquez, *Chem. Eng. J.* 161 (2010) 323-331.
- [19] M.P. Tsyurupa, V.A. Davankov, *React. Funct. Polym.* 66 (2006) 768-779.
- [20] C-G. Oh, J-H. Ahn, S-K. Ihm, *React. Funct. Polym.* 57 (2003) 103-111.
- [21] P.F. Siril, H.E. Cross, D.R. Brown, *J. Molec. Catal. A* 279 (2008) 63-68.
- [22] P.F. Siril, N.R. Shiju, D.R. Brown, *Appl. Catal. A* 364 (2009) 95-100.
- [23] M.A. Harmer, W.E. Farneth, Q. Sun, *J. Am. Chem. Soc.* 118 (1996) 7708-7715.
- [24] M.A. Harmer W.E. Farneth, Q. Sun, *Adv. Mater.* 10 (1998) 1255-1257.
- [25] M A Harmer, Q Sun, A.J. Vega, W.E. Farneth, A. Heidekum, W.F. Hoelderich, *Green Chem.* 2 (2000) 7-14.
- [26] M.P. Hart, D.R. Brown, *J. Molec. Catal. A* 212 (2004) 315-321.
- [27] S.P. Felix, C. Savill-Jowitt, D.R. Brown, *Thermochim. Acta* 433 (2005) 59-67.
- [28] C.A.S Hill, A. Norton, G. Newman, *J. Appl. Polym. Sci.* 112 (2009) 1524-1537.
- [29] M.J. Meziani, J. Zajac, J.D. Jones, S. Partyka, J. Roziere, A. Auroux, *Langmuir* 16 (2000) 2262-2273.
- [30] A. Auroux, *Top. Catal.* 4 (1997) 71-93.
- [31] J-P Dacquin, H.E. Cross, D.R. Brown, T. Düren, J.J. Williams, A.F. Lee, K. Wilson, *Green Chem.* 12 (2010) 1383-1391.
- [32] L. Pesaresi, D.R. Brown, A.F. Lee, J.M. Montero, H. Williams, K. Wilson, *Appl. Catal. A* 360 (2009) 50-58.

Table 1. Characteristics of supported sulfonic acid catalysts.

Catalyst	Specific surface area /m ² g ⁻¹	Pore volume /cm ³ g ⁻¹	Average pore diameter /nm	Acid site concentration (by titration) /mmol g ⁻¹	NH ₃ adsorbed with $-\Delta H_{\text{ads}}^{\circ} \geq 80 \text{ kJ mol}^{-1}$ /mmol g ⁻¹
Amberlyst 15	53	0.40	30	4.7	4.9
Amberlyst 35	50	0.35	30	5.4	5.5
Nafion SAC-13	196	0.60	10	0.15	0.12
Purolite D5082	381	0.34	27	2.0	1.2
Purolite D5081	701	0.39	19	1.0	0.8

Scheme 1:



b)

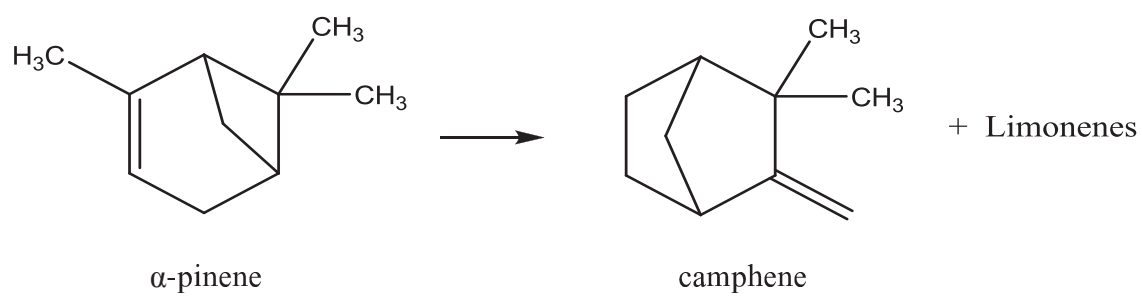
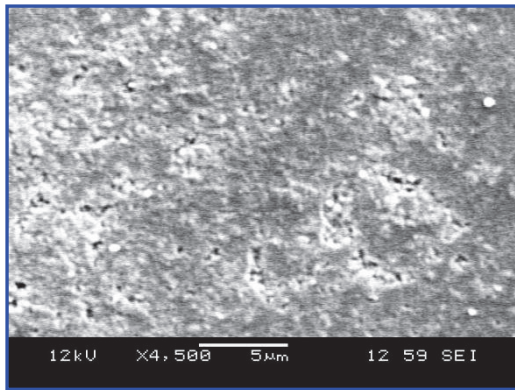


Figure 1.

a)



b)

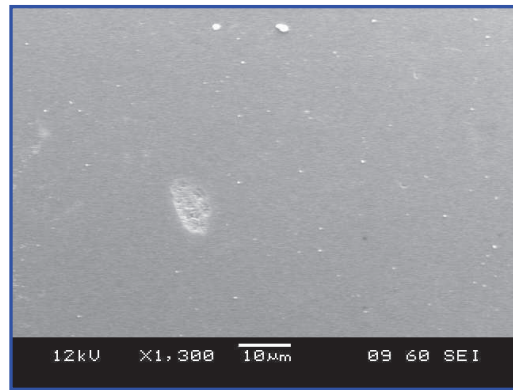
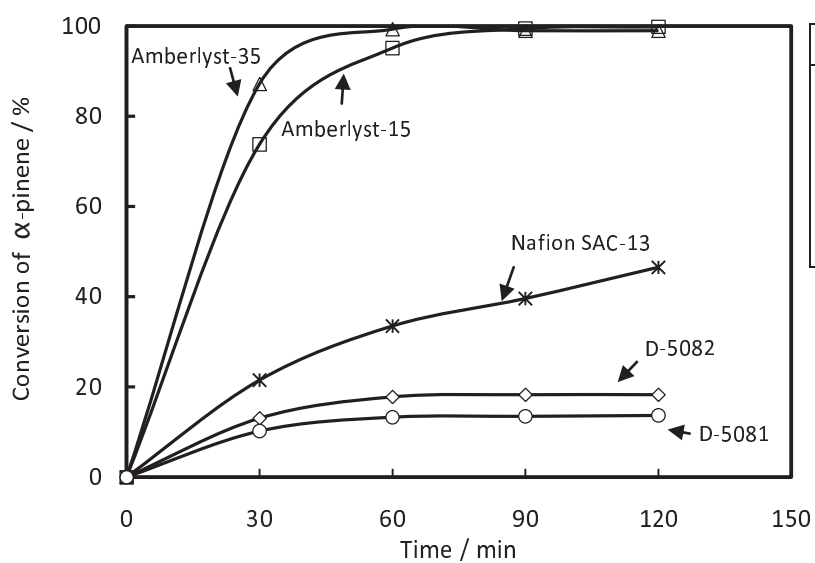


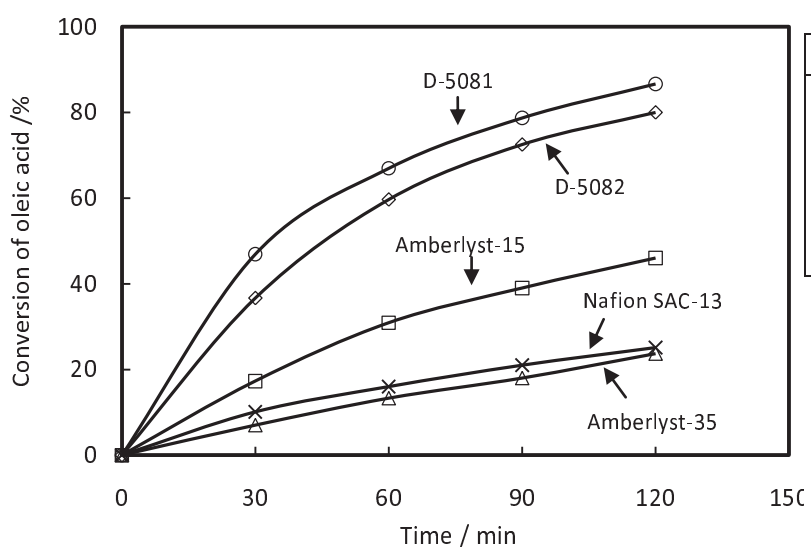
Figure 2.

a)



Catalyst	TOF (h ⁻¹)
Nafion SAC-13	740
Amberlyst-35	118
Amberlyst-15	113
D-5082	52
D-5081	37

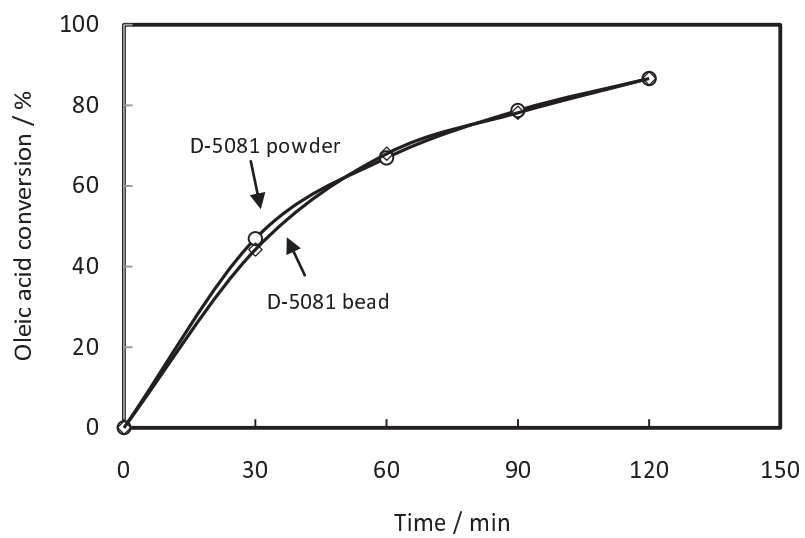
b)



Catalyst	TOF (h ⁻¹)
Nafion SAC-13	80
D-5081	65
D-5082	26
Amberlyst-15	4.8
Amberlyst-35	2.4

Figure 3.

a)



b)

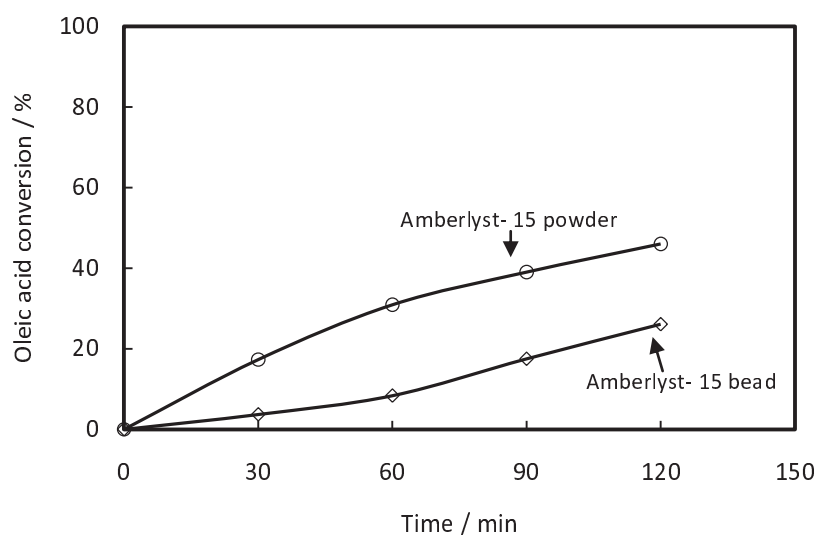
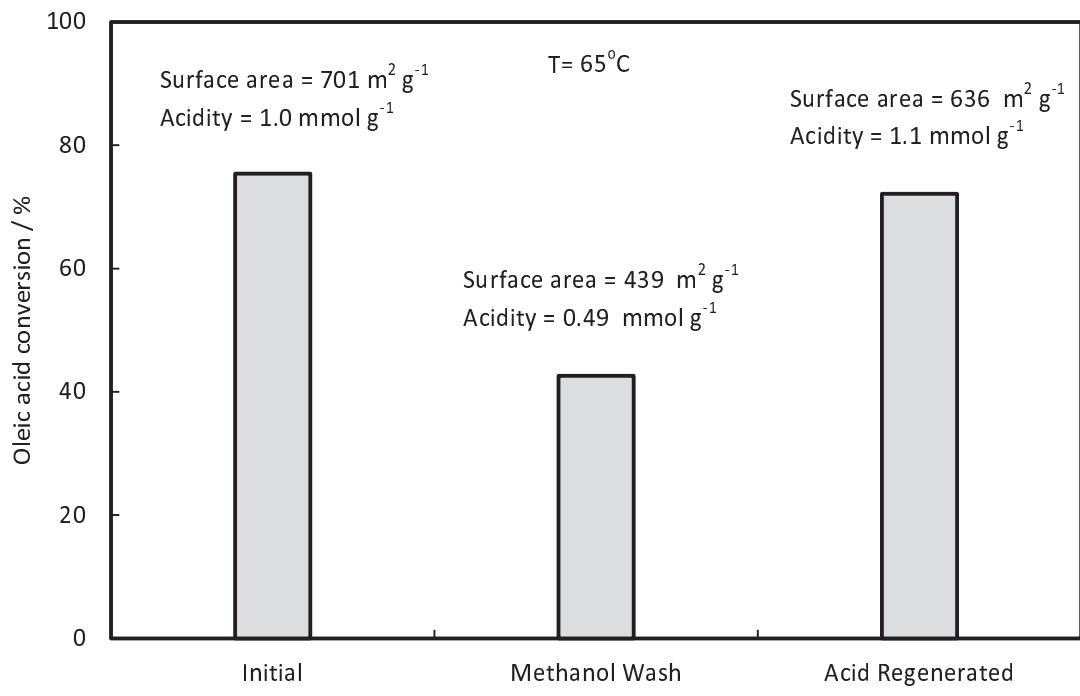


Figure 4.

a)



b)

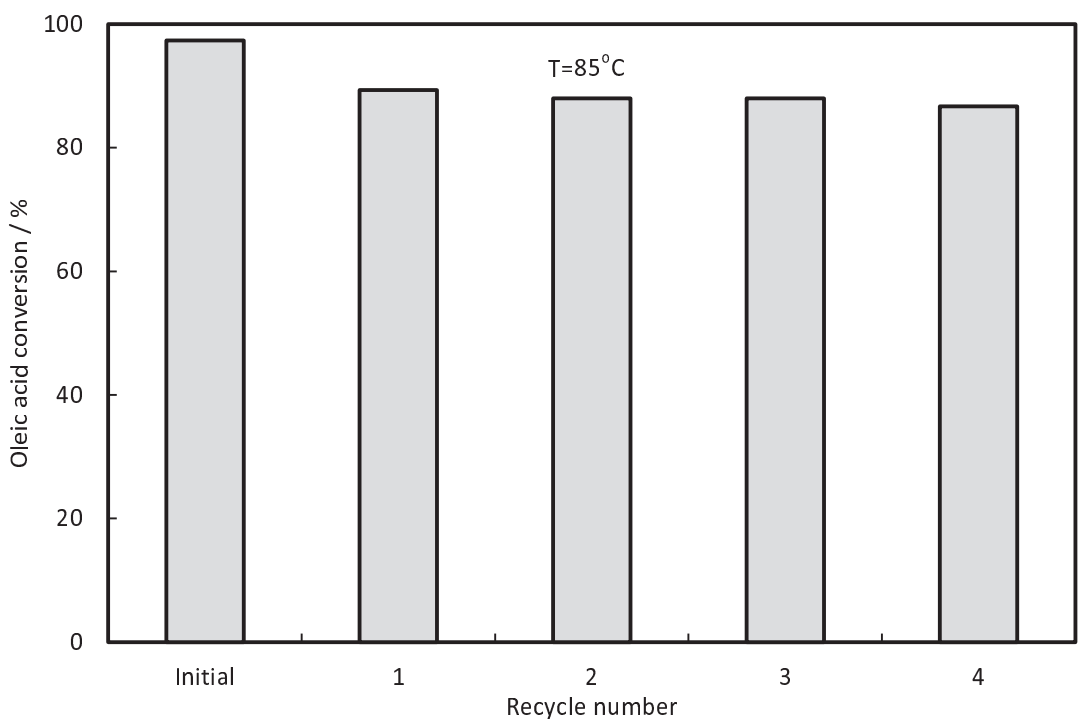
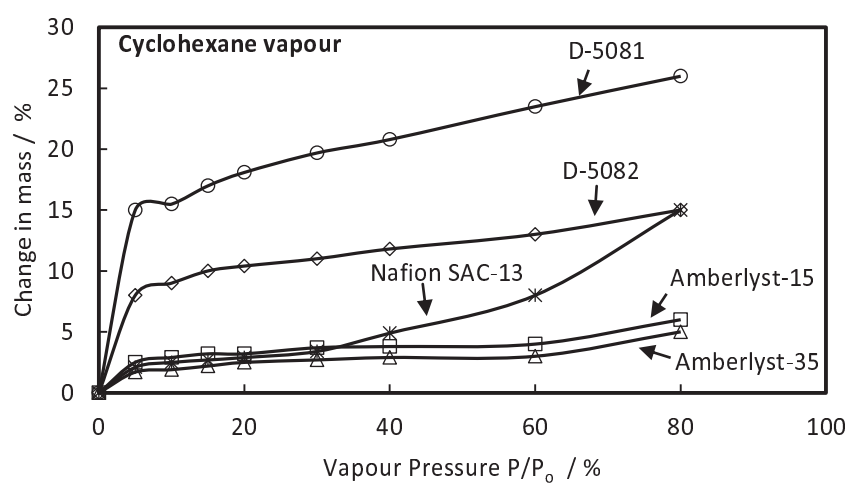


Figure 5.

a)



b)

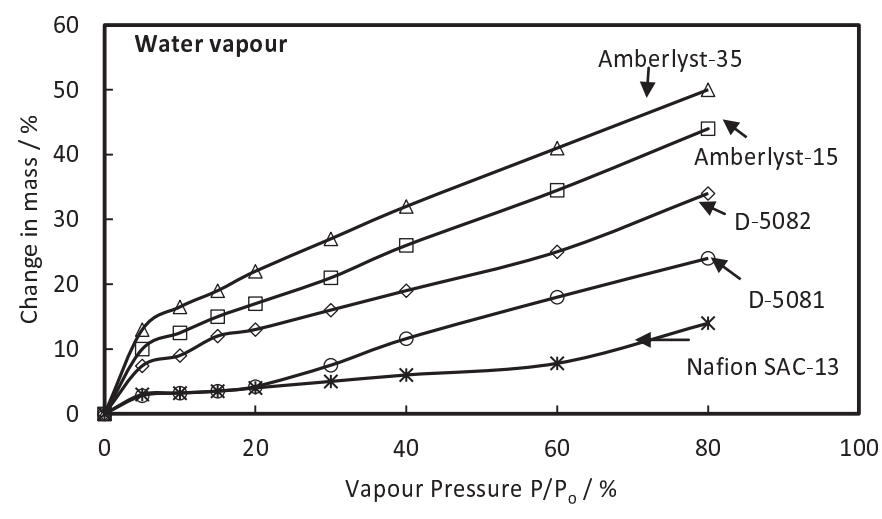


Figure 6.

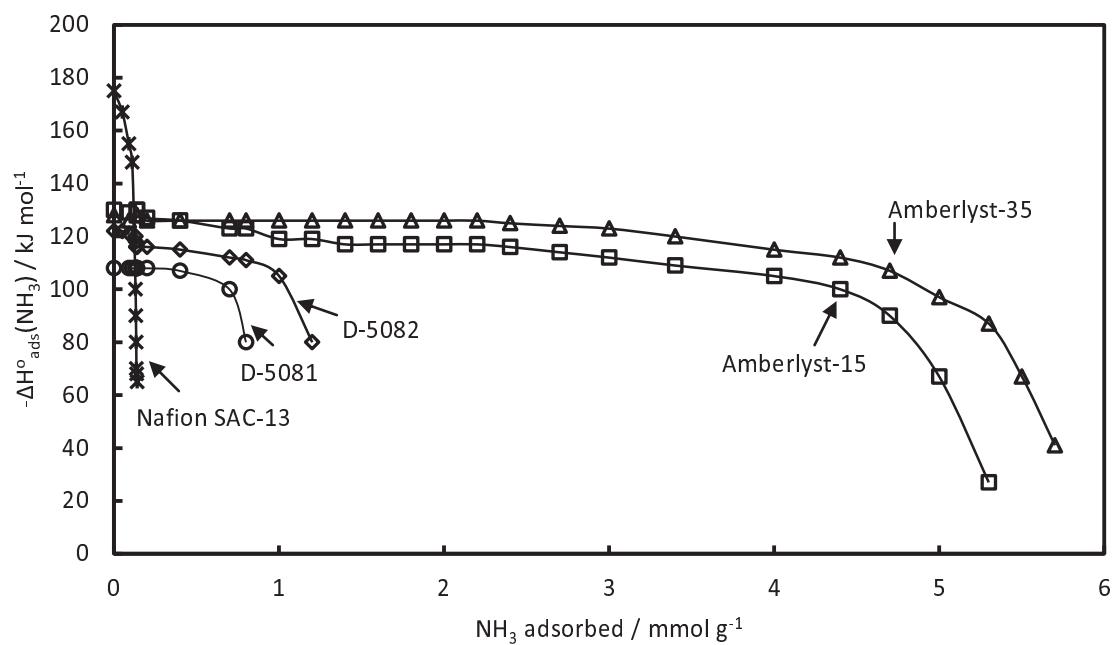
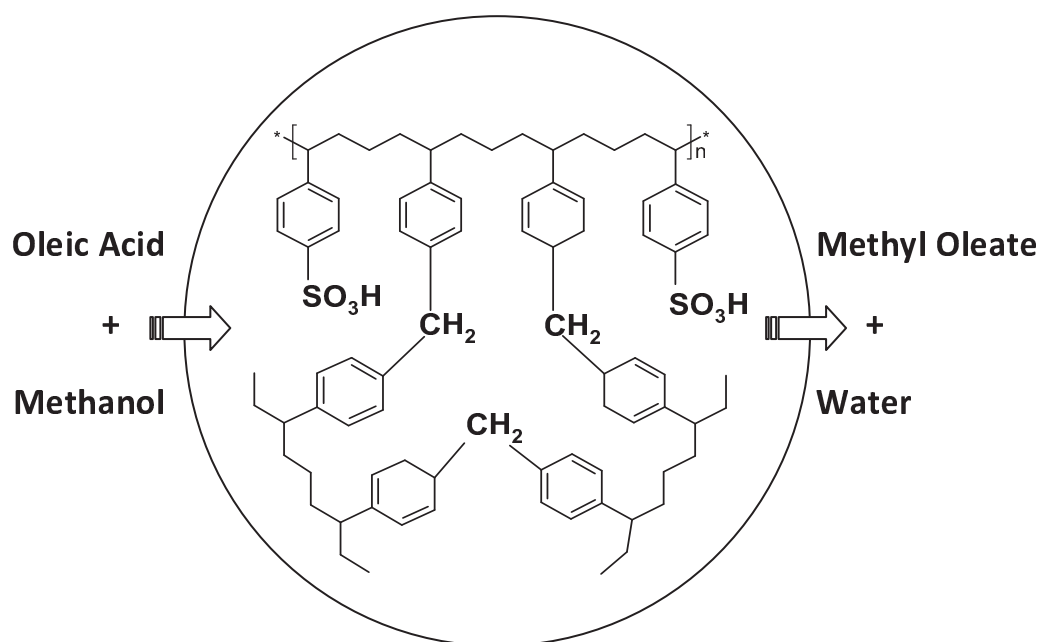


Figure Captions

- Scheme 1. a) esterification of oleic acid, and b) α -pinene isomerisation.
- Figure 1. Scanning electron microscope images of: a) D-5082 (hypercrosslinked resin) and b) Amberlyst-35 (macroporous resin).
- Figure 2. Catalytic activity of the catalysts in: a) α -pinene isomerisation and b) oleic acid esterification.
- Figure 3. Effect of particle size on activity towards the esterification of oleic acid, for: a) hypercrosslinked D-5081 and b) Amberlyst-15.
- Figure 4. Catalytic activity of hypercrosslinked D-5081 on re-use, a) reaction temperature 65 °C and b) reaction temperature 85 °C (catalyst methanol washed between runs).
- Figure 5. Cyclohexane and water vapour adsorption isotherms for catalysts studied, at 25 °C.
- Figure 6. Molar enthalpies of ammonia adsorption vs. amount adsorbed for catalysts studied, at 100 °C.



□ hypercrosslinked polystyrene sulfonic acid catalysts for the esterification of free fatty acids in biodiesel synthesis.

□ Andriānto, □ A Dawson and D. □ Brown

Highlights

- 1 □ hypercrosslinked polystyrene sulfonic acid resins are active solid acid catalysts
- 2 □ highly accessible acid sites on hypercrosslinked polystyrene sulfonic acid resins
- □ few solid acid catalysts for free fatty acid esterification in biodiesel synthesis