Hydrogensulfate and tetrakis(hydrogensulfato)borate ionic liquids: synthesis and catalytic application in highly Brønsted-acidic systems for Friedel–Crafts alkylation

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Hydrogensulfate and tetrakis(hydrogensulfato)borate ionic liquids have been synthesised and characterised. These ionic liquids are halogen-free, available from cheap raw materials and easy to prepare. They have been used as additives to sulfuric acid in the Friedel–Crafts-alkylation of benzene with 1-decene. The results clearly demonstrate an interplay of acidity and solubility effects caused by the ionic liquid additive. In some cases, low amounts of ionic liquid additive result in a dramatic improvement of product yield.

Introduction

Transformations catalysed by highly acidic and superacidic (stronger Brønsted-acidic than 100% sulfuric acid) catalysts are among the most important reactions in industrial chemistry. Refinery alkylation, alkane isomerisation and functionalisation reactions of aromatic compounds (alkylation, carbonylation, acylation, isomerisation) are typical examples.

However, many of these reactions using mineral acids or classical superacidic systems cannot be regarded as environmentally benign. Often, hazardous, volatile acids are involved (e.g. HF). In other cases, the acid has to be used in stoichiometric or even in over-stoichiometric ratio to the feedstock. Hereby, a lot of waste is produced e.g. during the hydrolysis for product isolation. Other restrictions originate from the physico-chemical properties of the commonly used acidic systems. Especially, insufficient solubility of the substrates in the liquid acid is a common limitation.

Ionic liquids are low melting (< 100 °C) salts which represent a new class of non-molecular, ionic solvents.1–3 High Brønsted acidic ionic liquids have been known since 1989 when Smith et al. described ionic liquids obtained from the reaction of an acidic chloroaluminate melt and HCl to be superacidic. For example, Smith et al. determined quantitatively the acidity of the system 1-ethyl-3-methylimidazolium ([EMIM])Cl/AlCl3/HCl (see eqn. (1)).4

\[
\text{HCl} + \text{AlCl}_3^- \rightarrow [\text{H}^+]_{\text{non-solvated}} + 2 \text{AlCl}_4^- \quad (1)
\]

In general, there are many good reasons to study ionic liquids as alternative Brønsted-acids in acid catalysed reactions. Besides the engineering advantage of their non-volatile nature, the investigation of new biphasic reactions with an ionic catalyst phase is of special interest. Here, the possibility to adjust solubility properties by different cation/anion combinations allows a systematic optimisation of the biphasic reaction, e.g. with regard to product selectivity. Attractive options to improve selectivity in multiphase reactions derive from the preferential solubility of only one reactant in the catalyst solvent or from the in situ extraction of reaction intermediates out of the catalyst layer. Finally, the ionic liquid may be in some applications a superior solvent for the acidic species. In these cases, significant enhancement of catalyst activity and stability should be possible.

Acidic ionic liquids were used as reaction media for Friedel–Crafts reactions as early as 1976.5 Systematic investigations into Friedel–Crafts alkylation of benzene with short–chain alkyl halides were published in 1986 by Wilkes and coworkers.6 The alkylation of benzene with alkenes in acidic imidazolium chloroaluminate melts is the subject of a patent from BP Chemicals from 1994.7 As advantages over the reaction with...
aluminum trichloride in organic solvents, claims are made regarding the easy isolation of the product, the practically total reusability of the liquid catalyst and the better selectivity to the alkylated products. Later, Akzo Nobel claimed that acidic chloroaluminate melts with trialkylammonium ions can be applied in the same manner as much cheaper alternatives to the imidazolium based systems.8 In more recent times Hölderich and coworkers described Friedel–Crafts alkylation reactions with acidic chloroaluminate systems that have been immobilised on different supports.9 Finally, a Brønsted super-acid medium obtained by reaction of an acidic chloroaluminate melt with HCl was used as catalyst for the alkylation of benzene with dodecene by Qiao and Deng.10

However, highly acidic systems based on chloroaluminate ionic liquids have some serious limitations. They are extremely oxophilic thus forming adducts with C–O functionalities and reacting irreversibly with traces of water to form HCl and Al-oxides. Therefore, our aim was to develop highly acidic, non-chloroaluminate systems.

In the present paper, we report the synthesis of hydrogensulfate and tetrakis(hydrogensulfato)borate ionic liquids. Moreover, we describe the first catalytic application of these melts in highly Brønsted acidic systems. For the catalytic evaluation, the Friedel–Crafts alkylation of benzene with 1-decene (see eqn. (2)) was chosen as model reaction for several reasons. (a) The reaction is of significant technical interest since monoaalkylenes with alkyl chains of 10–14 C-atoms are important intermediates for the production of alkylbenzenesulfonates. These are widely used as biodegradable, anionic detergents in commercial washing powder. Sulfuric acid is one of the technically used catalysts for this reaction; (b) the reaction is an ideal starting point for future investigations of Friedel–Crafts alkylations with functionalised aromatic compounds. Obviously, this future goal makes the application of non-chloroaluminate systems particularly interesting. (c) The reaction proceeds in biphasic reaction mode with all ionic liquid systems under investigation thus offering a simple way for catalyst recovery and recycling.

Synthesis of the acidic ionic liquid systems

The synthesis of ionic liquids of general type [cation][HSO4] has been first described in the patent literature.13

1-Butyl-3-methylimidazolium sulfate [bmim][SO4]2, [bmim][SO4]2 was prepared from [bmim][Cl]14 by anion exchange over the ion exchange resin Amberlyst A27 (sulfate form) in water. The aqueous [bmim][SO4]2 solution was evaporated and the wet residue was dissolved in acetonitrile. The acetonitrile solution was dried by azotropic removal of water at the rotatory evaporator. This procedure was repeated three times until the residue showed no solubility in acetonitrile. The reaction mixture was filtered under argon and washed twice with acetonitrile. The white, chloride free crystalline powder was dried from traces of water by evaporation in high vacuum at 50 °C over night (80% yield, mp.185–190 °C). δH(D2O) 0.91 (t, J 7.5 Hz, 3H), 1.24–1.37 (m, 2H), 1.79–1.89 (m, 2H), 3.89 (s, 3H), 4.19 (t, J 6.9 Hz, 2H), 7.43 (m, 1H), 7.47 (m, 1H), 8.72 (s, 1H); δC(D2O) 13.8, 20.5, 33.2, 36.5, 50.5, 123.4, 124.9, 137.9.

1-Butyl-3-methylimidazolium hydrogensulfate [bmim][H2SO4]13. A stoichiometric amount of neat sulfuric acid was added to 1-butyl-3-methylimidazolium sulfate and stirred for at least 2 h at 50 °C to obtain an almost colourless, viscous melt which crystallised after few hours (mp 29–32 °C). δH(CD3CN) 0.91 (t, J 7.3 Hz, 3H), 1.25–1.37 (m, 2H), 1.76–1.86 (m, 2H), 3.88 (s, 3H), 4.18 (t, J 7.3 Hz, 2H), 7.45 (m, 1H), 7.47 (m, 1H), 8.94 (s, 1H), 10.09 (s, 1H); δC(D3CN) 13.8, 20.0, 32.7, 36.8, 50.1, 123.2, 124.6, 137.8.

1-Octyl-3-methylimidazolium hydrogensulfate [omim][H2SO4]15. 1.0 eq [omim][CF3SO2N]2 were prepared in analogy to a method described by Grätzel and coworkers15 and 0.95 equiv. [NBu4][HSO4] were dissolved in water (mass ratio water/salts = 2) and extracted twice with the same amount of dichloromethane. Again 0.05 equiv. [omim][CF3SO2N]2 were added. The solution was vigorously shaken and again extracted twice with dichloromethane. The aqueous phase was evaporated at the rotatory evaporator. The residue was diluted three times with dichloromethane and evaporated for azetropic removal of water. The yellow, highly viscous liquid was dried from traces of water in high vacuum at 50 °C over night. It crystallised very slowly overnight (95% yield, mp 38–39 °C). δH(CD3CN) 0.85 (t, J 6.6 Hz, 3H), 1.17–1.34 (m, 10 H), 1.75–1.90 (m, 2H), 3.98 (s, 3H), 4.23 (t, J 7.4 Hz, 2H), 7.35 (s, 1H), 7.54 (s, 1H), 9.22 (s, 1H), 10.24 (s, 1H); δC(CD3CN) 14.1, 22.6, 26.3, 29.0, 29.1, 30.2, 31.7, 36.4, 49.9, 137.2, 121.9, 123.9.

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonato)amide [bmim][(CF3SO2)2N]15. To a solution of [bmim][Cl]14 in water lithium bis(trifluoromethanesulfonato)amide was added in small excess. The solution was extracted with dichloromethane and the layers were separated. The organic layer was washed three times with water, dried over molecular sieve and evaporated in high vacuum. [bmim][Tf2N] was obtained as a colourless liquid of low viscosity in 95% yield, δH(CD3CN) 0.95 (t, J 7.3 Hz, 3H), 1.30–1.43 (m, 2H), 1.80–1.90 (m, 2H), 3.92 (s, 3H), 4.17 (t, J 7.3 Hz, 2H), 7.36 (m, 1H), 7.38 (m, 1H), 8.64 (s, 1H); δC(CD3CN) 13.2, 19.4, 32.0, 36.3, 50.0, 120.0 (q, J 321.1 Hz), 122.6, 123.9, 135.9; δC(CD3CN) −79.8.

1-Octyl-3-methylimidazolium bis(trifluoromethanesulfonato)amide [omim][(CF3SO2)2N]. The synthesis of 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonato)amide was in analogy to the preparation of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonato)amide according to Grätzel


135

Experimental

General remarks

All reactions were carried out under argon unless otherwise noted. Benzene and 1-decene were distilled from sodium. Octane and tetradecane were dried over molecular sieves 4Å. Sulfuric acid, 100%, was purchased from Merck. Other solvents were dried according to common methods and distilled under argon.12 Gas chromatography was carried out on a Siemens Sichromat 3 with a 50 m Pona HP-FS column, equipped with a Hewlett Packard 3359 integrator. Octane and tetradecane were used as internal standards.

NMR spectra were recorded on a 300 MHz Bruker spectrometer in CDCl3 or CD3CN and calibrated with tetramethylsilane (TMS) as the internal reference.

1

\[
\begin{align*}
\text{H}^+ & \quad + \quad \text{1-decene} \\
\text{CH}_3 & \quad \text{H}_2\text{C}_6 \text{H}_5 \\
\text{H}_2\text{C}_6 \text{H}_5 & \quad \text{H}_2\text{C}_6 \text{H}_5 \\
\text{H}_2\text{C}_6 \text{H}_5 & \quad \text{H}_2\text{C}_6 \text{H}_5 \\
\text{H}_2\text{C}_6 \text{H}_5 & \quad \text{H}_2\text{C}_6 \text{H}_5 \\
\text{H}_2\text{C}_6 \text{H}_5 & \quad \text{H}_2\text{C}_6 \text{H}_5 \\
\text{H}_2\text{C}_6 \text{H}_5 & \quad \text{H}_2\text{C}_6 \text{H}_5
\end{align*}
\]

2-phenyldodecane 3-phenyldodecane 4-phenyldodecane 5-phenyldodecane
and coworkers\textsuperscript{15} Instead of [bmim][Cl] 1-octyl-3-methylimidazolium ([omim]) chloride\textsuperscript{16} was used to obtain a yellow liquid of low viscosity (96% yield). $\delta_d$(CDC$_3$)$_3$ 0.87 (t, J 6.6 Hz, 3H), 1.20–1.36 (m, 10H), 1.78–1.92 (m, 2H), 3.93 (s, 3H), 4.15 (t, J 7.3 Hz, 2H), 7.32–7.36 (m, 2H), 8.70 (s, 1H); $\delta_d$(CDCl$_3$) 14.0, 22.6, 26.1, 28.8, 28.9, 30.1, 31.6, 36.3, 50.2, 119.8 (q, J 321.1 Hz), 122.3, 123.8, 135.9; $\delta_d$(CDCl$_3$) –79.6.

Boron trihydrgensulfate B(HSO$_4$)$_3$\textsuperscript{17}. SO$_3$ was condensed into a glass autoclave at $-78$ °C. The boron acid B(OH)$_3$ was added in stoichiometric amount at one time and the autoclave was closed immediately. The mixture was allowed to warm up and after a violent reaction a clear, colourless liquid was obtained. A few minutes later the solution became viscous and was stirred 15 h at 100 °C. The B(HSO$_4$)$_3$ has the consistency of wax and hardens after a few days.

1-Butyl-3-methylimidazolium tetrakis(hydrogensulfato)borate [bmim][B(HSO$_4$)$_4$]. [bmim]$_2$[SO$_4$], sulfuric acid and boron trihydrgensulfate were added in the same stoichiometric amounts and stirred for 3 h at 50 °C to yield a slightly yellow liquid of high viscosity. $\delta_d$(neat substance, C$_6$D$_6$, coaxial NMR tube) 0.82 (br, 3H), 1.25 (br, 2H), 1.76 (br, 2H), 3.81 (br, 3H), 4.07 (br, 2H), 7.24 (br, 1H), 7.26 (br, 1H), 8.23 (br, 1H), 10.70 (br, 4H); $\delta_d$(neat substance, C$_6$D$_6$, coaxial NMR tube) 13.0, 19.1, 31.6, 36.0, 49.7, 122.5, 123.9, 135.3.

1-Octyl-3-methylimidazolium tetrakis(hydrogensulfato)borate [omim][B(HSO$_4$)$_4$]. [omim][B(HSO$_4$)$_4$] was prepared by adding a stoichiometric amount of [omim][HSO$_4$] to B(HSO$_4$)$_3$. The very viscous, reddish-brown liquid was used for the catalysis in an in situ system without further characterisation.

Catalytic experiments

All alkylation experiments were carried out in Schlenk tubes under argon with 15 mm PTFE stirring bars. The liquid was stirred for 10 min with sulfuric acid at room temperature before the organic solution was added to give a biphasic reaction mixture. The molar ratio of benzene to 1-decene was 5:1. The amount of the standards octane and tetradecane were 8 mass% each. The standard alkylation reactions were carried out at 50 °C for 1 h with a mass ratio of 1-decene to sulfuric acid of 2:1. The reaction was stopped after 1 h by stirring the solution for 2 min in an ice-bath. After a further 2 min during which the solution separated into two phases, a sample of the organic layer was taken. The sample was neutralised over dried Amberlyst A21 (weakly basic anion exchange resin, free base form) by shaking for 30 min in the same amount of acetic acid. The remainder of the reaction solution was quenched with a 1:1 mixture of water and acetonitrile and stirred vigorously for 1 min. The organic layer was dried over molecular sieves 4Å. Both samples were analysed by gas chromatography.

The standard reaction conditions were selected to obtain with neat sulfuric acid as catalyst (without ionic liquid additive) a monoalkylbenzene yield of 40.8%. This allowed to determine both activating and deactivating effects caused by the added ionic liquids.

Results and discussion

Benzene alkylation using Brønsted acidic ionic liquids of general type $\text{H}_2\text{SO}_4/\text{cation}[[\text{HSO}_4]$.

In a first set of experiments ionic liquids of the general type [cation][HSO$_4$] were tested as additives to sulfuric acid for the catalytic benzyne alkylation with 1-decene. The biphasic reactions were carried out under standard conditions. The results with two different cations and different amounts of added ionic liquid are illustrated in Fig. 1.

The experiments reveal a significant dependence of the catalytic reactivity on the cation of the ionic liquid. With added [bmim][HSO$_4$] a continuous drop in catalytic activity is observed. In contrast, added [omim][HSO$_4$] results at low concentration (<12 mol%) in a clear enhancement of activity. These results can be interpreted taking into account both acidity and solubility effects of the ionic liquid additive.

From the autoprotolysis equilibrium of pure sulfuric acid, it is clear that the addition of a hydrogensulfate salt to 100% sulfuric acid should reduce the concentration of the most acidic species $\text{H}_2\text{SO}_4$. For this reason the overall acidity of the $\text{H}_2\text{SO}_4/\text{cation}[[\text{HSO}_4$ mixture is lower then the acidity of 100% sulfuric acid alone. Interestingly, in the case of [omim][HSO$_4$] this effect is overcompensated at low ion liquid concentration by a phase-transfer effect of the added liquid acid. Very probably the higher 1-decene solubility of the ionic liquid modified catalyst layer accounts for this effect. In this context it is noteworthy that the selectivity to monoalkylbenzene was found to be higher than 97% in all cases.

These first experiments already demonstrate two general features of a hydrogensulfate ionic liquid additive to a sulfuric acid catalyst: on the one hand, the chance to moderate in a defined manner the catalyst’s acidity by proper choice of the sulfuric acid to hydrogensulfate ionic liquid ratio; on the other, the possibility to adjust the solubility of the feedstock in the acidic layer by variation of the cation of the ionic liquid and again by choice of the sulfuric acid to hydrogensulfate ionic liquid ratio.

Brønsted acidic ionic liquids of general type $\text{H}_2\text{SO}_4/\text{cation}[[\text{HSO}_4$.

Encouraged by these interesting results we dedicated a second set of experiments to investigate the influence of the anion of the ionic liquid. Here we pursued the concept to test anions which should combine the following properties: (a) very low basicity in order to maintain or even enhance the acidity of the acidic mixture with sulfuric acid; (b) high tolerance towards substrates with e.g. hydroxy or carbonyl functions in order to use the developed system in future work for the alkylation of functionalised aromatic compounds.

In this context we synthesized, for the first time, ionic liquids with the anion $[\text{B}(\text{HSO}_4)\text{a}]^-$. The idea that ionic liquids with this anion could generate highly acidic systems came to our
minds when we recognised a certain analogy with the well-known chloroaluminate ionic liquids. In the latter case, the Lewis acid AlCl₃ is added to a chloride melt to create the less coordinating, less basic anion [AlCl₄]⁻. In a comparable way the anion [B(HSO₄)₄]⁻ can be regarded as the product of a reaction between [HSO₄]⁻ and the Lewis-acid [B(HSO₄)₃]. Ionic liquids with the [B(HSO₄)₄]⁻ anion are very easily obtained by mixing a hydrogensulfate ionic liquid with boron acid and SO₃ in the correct stoichiometry or by reaction of equimolar amounts of an sulfate ionic liquid with sulfuric acid and [B(HSO₄)₃].

As shown in Fig. 2, [bmim][B(HSO₄)₄] proved to be a very suitable ionic liquid additive to sulfuric acid for the alkylation of benzene. While ionic liquids with identical cation and [HSO₄]⁻ and [(CF₃SO₂)₂N]⁺ showed a continuous drop in catalytic activity with increasing molar amount of added ionic liquid, the catalytic mixtures with [bmim][B(HSO₄)₄] displayed even higher catalytic activity at ionic liquid addition of up to 30 mol%! Again, the selectivity to monoalkylbenzene was > 97% in all cases.

In order to take maximum advantage of the ionic liquid additive we tried to combine, in a third set of experiments, the observed cation and anion effects. For this purpose, we synthesised [omim][B(HSO₄)₄] which should combine low basicity with enhanced solubility for the 1-decene feedstock in the catalytic layer. In fact, using this ionic liquid as an additive to sulfuric acid, excellent yields of monoalkylbenzene were obtained. With an addition of only 2.2 mol% of [omim][B(HSO₄)₄] we could increase the catalytic activity of the acidic layer by almost 90% (in comparison to neat sulfuric acid) The catalytic results are presented in Fig. 3. As in the experiments before the selectivity to monoalkylbenzene was > 97% in all cases with added ionic liquid (the monoalkylbenzene selectivity was found to be only around 95% with the [B(HSO₄)₃] additive).

Again, the influence of the different additives is related to an interplay of acidity and solubility effects. The lower product yield with added [bmim][B(HSO₄)₄] cf. added [omim][B(HSO₄)₄] can be understood as result of the higher 1-decene solubility in the catalytic layer in the latter case. Since the acidity of the catalytic protons is believed to be mainly dependent on the basicity of the anions of the melt, no major acidity change is expected upon variation of the cation. Interestingly, the acidic layer obtained by adding low amounts of [omim][B(HSO₄)₄] yields even more monoalkylbenzene than the same molar addition of the Lewis-acid [B(HSO₄)₃]. The latter should have a significant effect on the Brønsted-acidity of the catalytic mixture due to complexation of [HSO₄]⁻ to [B(HSO₄)₃]⁻. This clearly demonstrates that the effect of added [omim][B(HSO₄)₄] can not uniquely be explained by enhanced proton acidity.

**Regioselectivity of the alkylation reaction**

In benzene alkylation with 1-decene several regioisomers are produced (as already shown in eqn. (2)). While 1-phenyldecane is scarcely detectable for mechanistic reasons, 2-phenylnadecane is the alkylation product of benzene with 1-decene. However, 3-, 4- and 5-phenyldecane are obtained to a significant extent due to the fast isomerisation of 1-decene to the internal decenes by the acidic catalyst system. Hence, the regioselectivity obtained with different catalysts can be regarded as an indicator for the rate of catalytic 1-decene isomerisation vs. rate of aromatic alkylation.

In Table 1, the selectivity to 2-phenylnadecane is presented for different acidic catalysts described above. In order to allow a proper comparison, only the regioselectivity of those reactions that showed very similar yields of monoalkylbenzene are compared. Obviously, the use of different sulfuric acid + additive mixtures can significantly influence the distribution of regioisomers depending on the nature of the additive and depending on the acid/additive ratio (comparison of entries a and b, c and d, e and f).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive (mol%)</th>
<th>Yield of monoalkylbenzene (%)</th>
<th>Selectivity (1,8-product) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>B(HSO₄)₃ (20.2)</td>
<td>65.7</td>
<td>37</td>
</tr>
<tr>
<td>b</td>
<td>[omim][B(HSO₄)₄] (16.72)</td>
<td>66.8</td>
<td>40</td>
</tr>
<tr>
<td>c</td>
<td>[bmim][B(HSO₄)₄] (9.16)</td>
<td>51.3</td>
<td>35</td>
</tr>
<tr>
<td>d</td>
<td>[omim][HSO₄] (9.07)</td>
<td>51.7</td>
<td>41</td>
</tr>
<tr>
<td>e</td>
<td>[bmim][HSO₄] (25.80)</td>
<td>3.5</td>
<td>5</td>
</tr>
<tr>
<td>f</td>
<td>[bmim][(CF₃SO₂)₂N] (19.87)</td>
<td>3.4</td>
<td>57</td>
</tr>
</tbody>
</table>

**Table 1** Regioselectivity of benzene alkylation with sulfuric acid + additive; formation of 2-phenylnadecane (2-PD) as a function of added ionic liquid or Lewis-acid at comparable monoalkylbenzene yields.
phenyldecanes. By use of the developed ionic liquid additives it is therefore possible to create catalytic systems which combine lower isomerisation activity with higher alkylation activity (at least in comparison to neat sulfuric acid). Consequently, higher yields of the technically desired 2-phenylalkyl product would be possible in a potential technical application of the ionic liquid modified sulfuric acid catalyst.

**Conclusion**

The use of ionic liquids in highly Brønsted-acidic catalysts has so far been limited to chloroaluminate systems. However, chloroaluminate ionic liquids have a number of serious limitations, namely their irreversible destruction by moisture and their lack of tolerance to functionalities in the substrates. From the results of this publication we conclude that hydrogensulfate and tetrakis(hydrogensulfato)borate ionic liquids are highly interesting additives to mineral acids to form new, highly Brønsted-acidic catalysts. These ionic liquids are halogen-free, available from cheap raw materials and easy to prepare.

The first catalytic application of these systems in the biphasic alkylation of benzene with 1-decene revealed a number of very interesting features. For example, we found that e.g. mixtures of sulfuric acid with only 2.2 mol% of [omim][B(HSO₄)₄] ionic liquid yielded 90% more monoalkylbenzene product than the neat sulfuric acid catalyst under identical reaction conditions. This and related results are explained by an interplay of solubility and acidity effects caused by the ionic liquid additive. The acidity of the catalyst can be fine-tuned by choice of the amount of ionic liquid additive and by choice of its anion. In the same way the solubility properties of the catalytic layer for the substrates can be adjusted by a suitable choice of the ions of the ionic liquid and again by the amount of added ionic liquid. Finally, the use of the ionic liquid additives provides a very general tool to optimise the biphasic reaction system. For example, modification of the density of liquid acidic catalysts should be possible by ionic liquid additives, so enabling faster phase separation and easier recovery of the acidic catalyst layer.

In future work, we will investigate the alkylation of functionalised aromatic compounds and other proton catalysed reactions where tuneable acidity, tuneable solubility and reduced volatility of the acidic catalyst may be of interest.

**References**