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A Recyclable Acidic Ionic Liquid Gel Catalyst for Dehydration, Comparison with an Analogous SILP Catalyst.

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ABSTRACT: An acid-functionalized ionic liquid was entrapped within a silica gel to yield a recyclable liquid phase catalyst for the dehydration of *rac*-1-phenyl ethanol. Hot filtration tests showed that the activity was within the gel. Comparison with an analogous SILP system revealed fundamental differences in the properties and behavior of the materials.

The discovery of facile ionic-liquid silica gel formation,^{1,2} enabled the introduction of the first ionic liquid mediated sol-gel methods for the preparation of solid catalysts.³⁻⁵ There followed a period of relatively few publications, during which ionic liquid gels were seldom investigated as catalysts. Currently, in parallel with the development of new classes of ionic liquid, and an increase in interest in soft-matter, the area of ionic liquid gel catalysts has come back into focus, and new methods are emerging. This catalyst preparation methodology involves the entrapment of an ionic liquid within an inorganic oxide matrix by a gel method. At the same time a catalyst is co-entrapped,^{3,5-7} or, alternatively the catalytic center can be associated with the ionic liquid.⁴ The worked-up material is then used as a heterogeneous catalyst. Materials consisting of an ionic liquid within a porous oxide are often referred to as ionogels.⁸ These catalysts are a sub-set of the sol-gel prepared entrapped catalysts pioneered by Blum and Avnir.^{9,10} In contrast to the gel-based catalysts, the related SILP catalysts, in which a heterogeneous catalyst is prepared by layering an ionic liquid on a pre-existing oxide matrix, have elicited an explosion of interest in the last ten years. Several reviews and concept articles have been published covering the method.¹¹⁻¹⁷ Exemplars have been demonstrated in the gaseous phase,¹⁸ and using supercritical fluids,¹⁹⁻²¹ and the application of SILP technology is at an advanced stage. The simplicity of the system enables a wide variety of matrices, ionic liquids and dopants to be screened easily. In liquid phase reactions the ease of addition and removal of the ionic liquid is potentially detrimental, and leaching can be facile.

The development of supported nanoparticles catalysts by ionic-liquid assisted gel methods³ has been recently developed further by Han and co-workers.²² Catalysts with hierarchical pores were achievable by employing a metal salt (e.g. CaCl₂) initiated gelation. Doping with gold afforded a catalyst for esterification, and ruthenium catalyzed hydrogenation.

The introduction of functionalized ionic liquids that are ‘task specific’²³⁻²⁶ opens up many new possibilities for the application of ionic liquids to liquid phase reactions, not least the incorporation of Brønsted–Lowry Acidic/Basic sites. Acid functionalized ionic liquids have been demonstrated as robust catalysts for continuous esterification in a miniplant.²⁷ In order to improve separation and prevent corrosion caused by liquid phase acids, it would be fortuitous to develop a heterogenised system. The combination of functionalized ionic liquids and solid supports will give rise to a range of tunable solid acids and bases. Recently heterogeneous acid catalyzed esterification was demonstrated by Liu *et al*²⁸ using an acidic ionic liquid attached to a hydrophobic polymer. The result was an activity for biodiesel production that outstripped the homogeneous system. By analogy the combination of a hydrophobic acid functionalized ionic liquid and an inorganic oxide has great potential.

Solid acid catalysts created by sol-gel entrapment of ionic liquids have been known since pioneering work by Deng and co-workers.⁴ Guan and co-workers²⁹ developed a silica gel with a tethered propyl sulfonate ionic liquid and applied this to esterification of carboxylic acids. The catalyst gradually lost activity; this was attributed to loss of the ionic liquid. A modified tethering method produced a catalyst that performed the acetalization of aldehydes and alcohols and could recycled 10 times with minimal loss of activity.³⁰ Funabiki *et al*³¹ prepared a solid acid catalyst by the adsorption of the acidic ionic liquid 1,3-bis(3-sulfopropyl)-1H-imidazol-3-ium trifluoromethanesulfonate onto a commercial silica gel. The resulting SILP material could be reused 10 times for the esterification of bromoacetic acid with benzyl alcohol.

Here is reported a new method for the preparation of ionic liquid gels containing Brønsted–Lowry acidic groups. The procedure does not require tethering, nor synthetic modification of the silica. The addition of an additional catalyst for the gelation (such as HCl or formic acid) is not required, and therefore the characteristics of the material are dependent solely on the ionic liquid dopant. A gel catalyst prepared in this way has been applied as a heterogeneous catalyst in the liquid phase dehydration of *rac*-1-phenyl ethanol. The catalyst was recyclable, and leaching was negligible. The material was compared with the solid produced from the adsorption of the same ionic liquid onto commercial silica (SILP).

Dehydration of *rac*-1-phenyl ethanol is applied industrially to the synthesis of styrene.³²⁻⁴³ In this way 1-phenyl ethanol, a by-product of the Oxirane process (propylene oxide synthesis), can be effectively utilized. Poisoning is a major problem for the most active heterogeneous systems, and research is ongoing to develop new liquid phase catalysts.³³⁻⁴³ The serendipitous discovery of dehydration activity in toluene at low temperatures (100-120 °C) in the presence of acidic PEG gels,⁴⁴ led us to examine the dehydration activity and recycling of acidic ionic liquid gels, and compare this with the reaction catalyzed by the parent liquid and related SILP system.

Appending a sulfonyl group to the cation of an ionic liquid or solid is achieved relatively easy by nucleophilic attack on a sultone.²³ Utilizing 1,3-propanesultone, acidic ammonium or heterocyclic cations can be constructed with (CH₂)₃SO₃H groups appended. In this way triethylammonium propanesulfonic acid was prepared. Subsequent reaction with bistriflamidic acid yielded the ionic liquid triethylammonium propanesulfone bistriflamide, [TEAPS][NTf₂] (Scheme 1).

The ability of [TEAPS][NTf₂] to catalyze the liquid phase dehydration of *rac*-1-phenyl ethanol was evaluated. Applied as a liquid the IL catalyst was never fully miscible with the reaction mixture. Stirred to 300rpm and heated to 115 °C in toluene *rac*-1-phenyl ethanol was dehydrated to styrene, [1-(1-phenylethoxy)ethyl]benzene (ether) and [4-phenylbut-3-en-2-yl]benzene (Table 1). Activity was rapid leading to full conversion, build up of styrene, and the formation of dimeric products (heavy products HP). The proportion of ether, styrene or HP in the toluene product mixture was found to vary with the ratio of ionic liquid to substrate. The production of dimeric products of styrene indicates the possible formation of oligomers that are less soluble, or difficult to analyze, and therefore these results should not be viewed as overall selectivities, but as indicative of the composition of the toluene solution.

In liquid phase reactions the replacement of a liquid acid with a solid acid gives more process flexibility, enabling facile separation of the product solution for the catalyst, reducing contamination of the product, and facilitating the use of alternative reactors such as flow systems and trickle beds.⁴⁵ To this end [TEAPS][NTf₂] was supported to yield solid catalysts. Firstly the IL was deposited on commercial silica to yield a SILP catalyst. This was performed by dissolving [TEAPS][NTf₂] in a volatile solvent, stirring with silica, and removing the volatile solvent under vacuum. The catalytic activity of the SILP material was high, and high levels of styrene or heavy products were observed for liquid phase dehydration in toluene. In order to test the heterogeneity of the catalyst a hot filtration test^{46,47} was carried out (Chart 1). The test was carried out in three phases. In phase 1 the activity of the catalyst was tested normally. After a time period required to give partial conversion (shorter than a full catalyst run), the liquids were filtered from the catalyst, whilst maintaining reaction temperature, and the filtrate returned to the reactor for the second phase. In the third phase the solids and liquids were recombined. The SILP catalyst was found to fail the test, as the liquid phase was active for dehydration. Leaching was confirmed as [NTf₂]⁻ could be detected in the product mixture by ¹⁹F NMR.

Acidic ionic liquid gel (ion-gel) catalysts were prepared. The sol-gel reaction was used to entrap and thus heterogenize the ionic liquid, this process requires an acid catalyst to ensure reproducible gel formation. The majority of ionic liquid silica gels in publication were formed by employing the action of formic or hydrochloric acid on a solution containing tetraethoxy or tetramethoxy orthosilicate (TEOS or TMOS).^{1,4,5} The application of acidic ionic liquids to entrapment provides the opportunity to form an autocatalytic ionic gel.⁴⁸ In this way [TEAPS][NTf₂] was applied to TEOS to form acidic ionic liquid gels. Gel formation took several days and the gels were stiff. The gel was thoroughly extracted with refluxing ethanol to remove material that was not entrapped, and dried in air to form a solid catalyst. The gel was found to dehydrate *rac*-1-phenyl ethanol in toluene solution predominantly to styrene and HP. A yield of styrene in toluene solution of up to 92% was achieved (supplementary data). A hot filtration test was performed on the gel catalyst (Chart 2). During the second phase, when the reaction solution was not in contact with the gel, there was no significant change in the composition of the liquids. The recycling of the acidic gel catalyst was tested by sequentially removing reacted solutions and replacing them with fresh substrate solution. The ion-gel catalyst could be recycled repeatedly with little or no change in performance (Chart 3). These tests reveal that the gel of [TEAPS][NTf₂] acts as a recyclable solid acid catalyst for dehydration. No leaching of the ionic liquid was detected by ¹⁹F NMR. When run for 6 hours liquid sampling showed that the proportion of styrene, ether and heavy products (HP) altered with contact time, consistent with sequential dehydration to ester then styrene, followed by dimerization to form the HP (Chart S9). The activity reported here is significantly higher than that measured previously for PEG-based acid gels.⁴⁴

The high activity of the SILP compared to the ion-gel opened the possibility that extraction of the SILP could lead to a catalyst with performance similar to the ion-gel. The effect of extracting the SILP catalyst with ethanol, as required for the ion-gel synthesis, was investigated. The ethanol extracted [TEAPS][NTf₂] SILP was then tested for catalytic activity as before. Only substrate was detected in the product solution (by ¹H NMR and GCMS) consistent with a total absence of dehydration activity.

Solid state ²⁹Si NMR spectra of the SILP and ion-gel catalysts reveal significant differences in the matrix structure (Figure 1), particularly with respect to the relative intensities of Q³ and Q⁴ resonances. The spectra are long-recycle (30 s) direction excitation spectra and so the relative intensities are quantitative. The structures are clearly very different. The increased tri-substituted siloxane in the gel relative to the SILP (which presents a significantly larger Q⁴ signal), may provide additional hydrogen bonding.^{49,50} The interaction of the silanol groups of the matrix with the ionic liquid may help to anchor the ionic liquid inside the matrix and prevent leaching. TGA and BET measurements were also found to be significantly different for the two materials (supplementary data).

The heterogeneous dehydration of *rac*-1-phenylethanol can be affected by a silica gel containing functionalized acidic ionic liquid [TEAPS][NTf₂]. The acidic ion-gel is a recyclable catalyst for the liquid phase reaction. A SILP catalyst prepared from ultra-pure silica gel forms a less robust catalyst that is prone to leaching ionic liquid into the solvent. The ion-gel structure was found to have a larger proportion of tri-substituted siloxane in the matrix than the SILP catalyst.

Scheme 1. Synthetic route to [TEAPS][NTf₂].

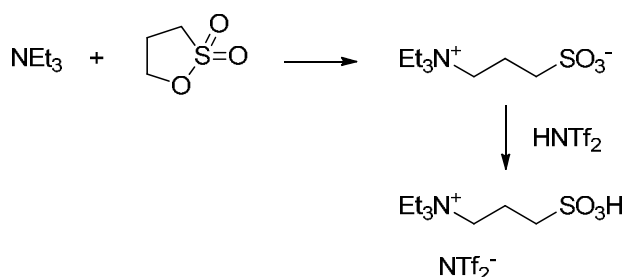
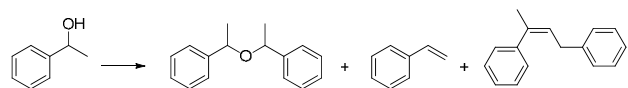


Table 1. [TEAPS][NTf₂] catalyzed dehydration of *rac*-1-phenyl ethanol.



	Catalyst:Substrate	Liquid Composition ^a /%		
		Ether	Styrene	HP
1	0.10	8	78	14
2	0.20	3	43	54
3	0.28	6	15	79

In toluene (8.6 mL), *rac*-1-phenyl ethanol (14.2 mmol), 115 °C, stir rate 300 rpm, time 2h, conversions were all >99% by ¹H NMR. ^a Liquid compositions in the toluene solution were calculated by ¹H NMR.

Chart 1. [TEAPS][NTf₂] SILP hot filtration, conversion and % liquid composition.

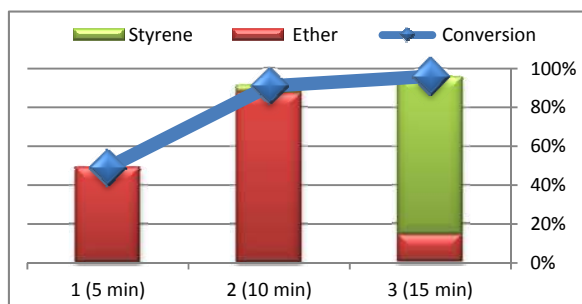


Chart 2. [TEAPS][NTf₂] ion-gel hot filtration, conversion and % liquid composition.

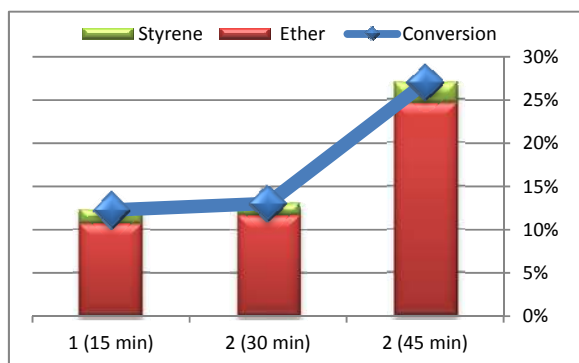
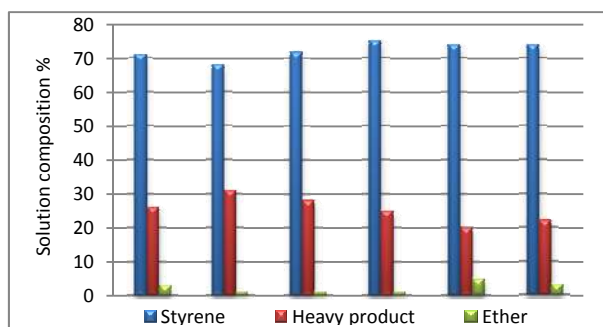


Chart 3. Recycle of [TEAPS][NTf₂] ion-gel catalyzed dehydration of *rac*-1-phenyl ethanol.



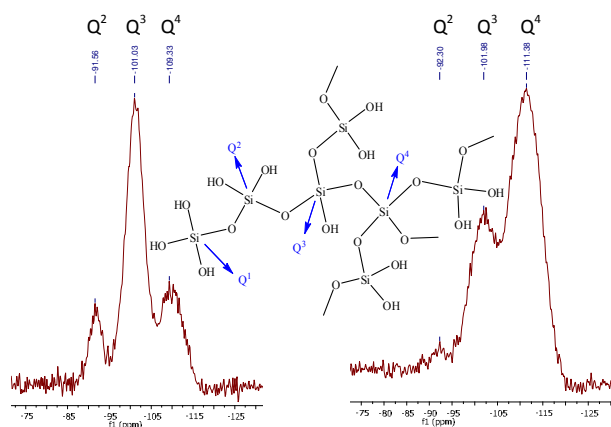


Figure 1. ^{29}Si ssNMR of ion-gel (LHS) and SILP (RHS).

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, NMR, ssNMR, TGA, BET, GCMS, mass spectrometry and microanalysis. Details of catalytic testing procedures, and further testing and recycling results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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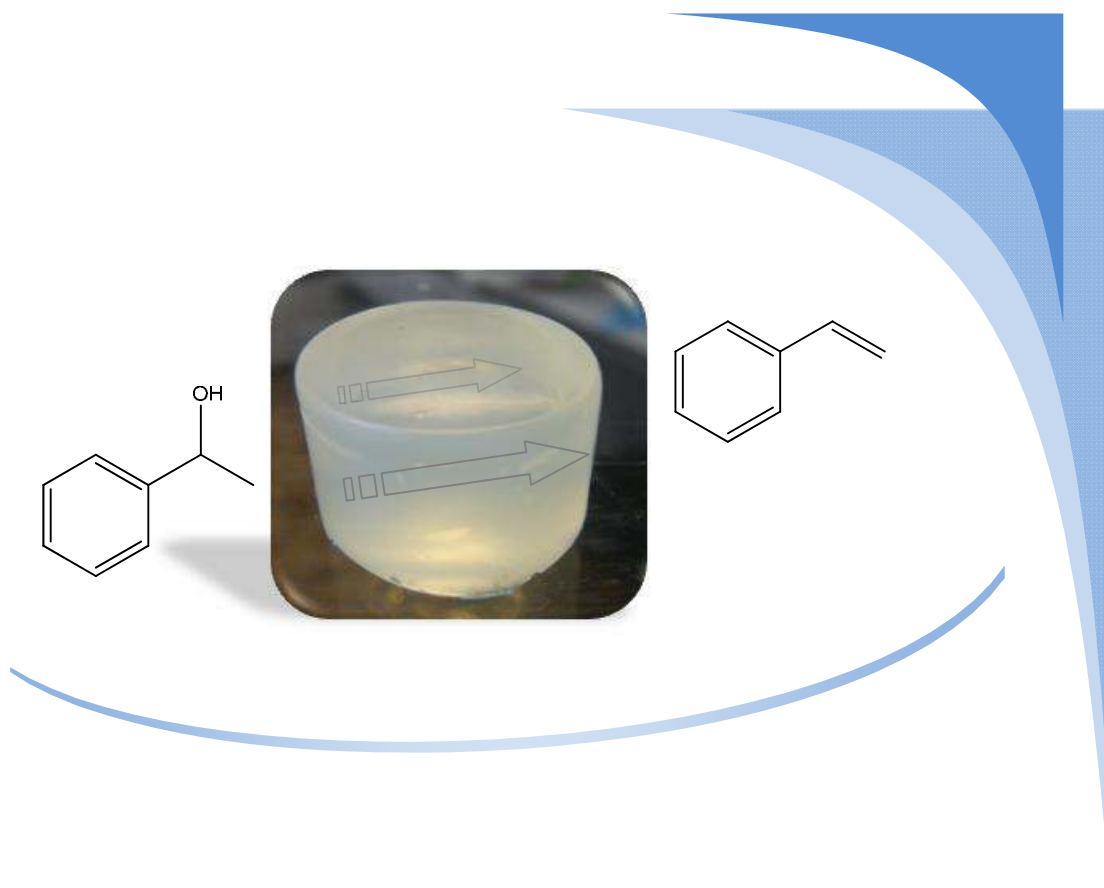
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A Recyclable Acidic Ionic Liquid Gel Catalyst for Dehydration, Comparison with an Analogous SILP Catalyst.

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Synopsis

An acid-functionalized ionic liquid entrapped within a silica gel formed a recyclable heterogeneous catalyst for the dehydration of *rac*-1-phenyl ethanol.
