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Taming the base catalysed sol-gel reaction. Basic ionic liquid gels of SiO₂ and TiO₂

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Keywords: Ionic liquid, basic ionic liquid, ion gel (ionogel), solid base.

Abstract

We describe the autocatalytic synthesis of SiO₂ and TiO₂ ionic liquid gels using a basic ionic liquid as the solvent, template and catalyst for the sol-gel reaction. Basic gels were synthesized using a two component mixture of the basic ionic liquid [P66614][OH] and either tetraethylorthosilicate (TEOS) or titanium isopropoxide (Ti(OiPr)4). The gels formed were clear glassy materials. The unstable basic ionic liquid was stabilised by the matrix and showed both increased thermal stability (by thermogravimetric analysis (TGA)) and chemical stability (by solid state NMR (SSNMR)) after over a year of storage.

Herein is reported the first autocatalytic synthesis of basic ionic liquid gels. Sol-gel reactions for the synthesis of technological materials are predominantly acid catalyzed. Among these materials the ionic liquid gels (sometimes called ‘ionogels’)[1,2] prepared by the sol-gel method, are overwhelmingly prepared in reactions catalyzed by the addition of either formic acid or HCl(aq).[3,4,5] More recently the autocatalytic synthesis of ionic liquid gels was introduced using an acidic ionic liquid.6 Occasionally ionic liquid gels have been synthesised using neutral ionic liquids, with an additional base as the catalyst,7 but these materials are reported to have low mechanical strength. Potential advantages of developing basic routes to ionic liquid gels are demonstrated by the application of basic ionic liquid SILPs (Supported Ionic Liquid Phases). SILC (Supported Ionic Liquid Catalyst) materials with basic ionic liquids have been shown to exhibit catalytic activity in a range of reactions, including the transesterification of glycerol trioleate, important in biodiesel production.8 Here we describe a two component method for producing SiO₂ and TiO₂ materials with potential in catalysis, electrochemistry, energy, electronics, and sensors from the simple combination of sol-gel precursors and a basic ionic liquid. The use of an ionic liquid as the solvent, catalyst and template will lead to facile coating methods of sol-gel derived SiO₂ and TiO₂ as the non-volatile nature of the ionic liquid allows for advances in the coating of surfaces and the processing of thin films9 (Figure 1 (c)). Compared to general methods this is a significant reduction in the number of reagents and processing steps required for the formation of materials of this type.

In traditional sol-gel processing the use of a basic catalyst often causes the reaction to proceed too quickly, creating larger sol particles and thus producing a cloudy opaque material with lower porosity, low mechanical stability and a more dense, ceramic like structure.10 Building on the understanding gained from our work on autocatalytic systems for acidic ionic liquid gels,6 our hypothesis was that the combination of a viscous ionic liquid with the right level of Brønsted basicity could slow down the sol-gel process, and allow a more controlled sol-gel reaction. We found that, by careful selection of Brønsted basic ionic liquid, we were able to tame the sol-gel reaction to form silica and titania ionic liquid gels on a slower time frame. The result is the synthesis of remarkably clear glassy materials (Figure 1).

Figure 1. (a) SiO₂ [P66614][OH] gel (b) TiO₂ [P66614][OH] gel (c) TiO₂ Film (cast).
This four dimensional control over the basic sol-gel route results in clear monoliths via a two-component sol-gel system (precursor + basic ionic liquid). These autocatalytic basic ionic liquid gels are remarkable in their stability and their ability to stabilize the entrapped basic ionic liquid. In its liquid form the parent ionic liquid [P66614][OH] is unstable in air and undergoes rapid degradation over 2-3 weeks at room temperature (as evidenced by $^{31}$P NMR, Fig 2). The gel materials were measured by SSNMR (solid state nuclear magnetic resonance) at 8 months and 1 year 5 months for SiO$_2$ gels and 5 months and 1 year 3 months for TiO$_2$ gels. SSNMR showed the suppression of the degradation of the basic ionic liquid, which is intact a year after gel formation (Figs 3,4). [P66614][OH] was synthesized as a pale yellow viscous liquid by anion exchange though an Amberlite resin column in a procedure adapted from literature methods (SI S1-S2).11,12 [P66614][Cl] was dissolved in ethanol and passed through an Amberlite (IRN78 hydroxide form) column, yielding a solution of [P66614][OH]. The excess ethanol was removed under reduced pressure and the isolated ionic liquid stored at 5°C. A halide test was carried out to ensure that all the chloride anions had been exchanged for hydroxide anions, as indicated by a lack of AgCl precipitate formed upon addition of AgNO$_3$ in nitric acid. [P66614][OH] was monitored by $^{31}$P{H}NMR over several weeks to follow its decomposition at room temperature; freshly synthesised [P66614][OH] gives a single resonance at δ34.0 (Fig. 2a), while after 3 weeks an additional resonance at δ50.8 was seen (Fig. 2b). This indicates that [P66614][OH] is not stable for long periods of time at room temperature. It has been previously reported that tetraalkylphosphonium cations can undergo decomposition to tertiary phosphine oxides and alkanes in the presence of base (equation 1).13,14

\[
[R_3P-CH_2-R']^+ + OH^- \rightarrow R_3P=O + CH_3-R' \quad (1)
\]

Equation 1 - decomposition of tetraalkylphosphonium cations

The peak at δ50.8 (Fig. 2b) is thought to be n-trihexylphosphonium oxide. While literature data for n-trihexylphosphonium oxide is not available, phosphonium oxides with similar chain lengths have $^{31}$P NMR resonances in a similar region (Trioctylphosphine oxide δ48.515 and Tributylphosphine oxide δ46.216).

Silica ionic liquid gels were synthesized from TEOS mixed with different ratios of [P66614][OH] at room temperature in order to find optimum gelling conditions (Table 1). The basic nature of the ionic liquid catalysed the gelation (SI S2). As the reagents were stirred together over several hours the sol became visibly more viscous, the results varied depending on the ratio of inorganic alkoxide to ionic liquid. Nine samples were prepared across different ratios of TEOS:[P66614][OH]. After aging for 4 weeks, it was observed that the ratio of TEOS:[P66614][OH] had affected the ionic liquid gel formation. With high ratios of IL to TEOS no gel formation was observed. Samples with a high ratio of TEOS to IL formed powdery, opaque, off white materials. Only ratios corresponding to samples Si1-4 (Table 1, entries 4-7) with ratios ranging from 1:1 to 1:0.25 of TEOS:[P66614][OH] formed transparent, pale yellow glass solid gels. After aging for 4 weeks, Si1-4 were broken into 3-4mm segments and washed in ethanol (50mL) under reflux at 80°C for 2 hours to remove any excess ionic liquid, followed by filtration and storage at room temperature. The $^{31}$P SSNMR of Si4 exhibited a single resonance at δ33.0, which remained the only resonance after 1 year 5 months storage, with none of the impurities from decomposition of the parent ionic liquid observed (Fig. 3).
Figure 3. a) $^{31}$P SSNMR of SiO$_2$ [P$_{66614}$][OH] Si4 (Table 1) at 8 months, b) $^{31}$P SSNMR of SiO$_2$ [P$_{66614}$][OH] Si4 at 1 year 5 months. (y-axis: frequency).

TGA analysis of the washed ionic liquid gel (table 1, Si1) showed thermal stability up to 283.9°C, while the ionic liquid on its own had significantly lower thermal stability 206.2°C. (SI S3.2 TGA). Both the TGA and SSNMR data analysis indicated that the silica matrix offers protection to the ionic liquid entrapped inside, allowing it to remain stable for significantly longer periods at room temperature and to withstand higher temperatures. Powder XRD analysis confirms the SiO$_2$ as amorphous (SI S3.4 XRD). BET analysis of Si1 the 1:1 ionic liquid silica gel gave a surface area of 87.97m$^2$/g with average pore size between 24.43-24.50 Å (SI S3.1 BET).

<table>
<thead>
<tr>
<th>[P$_{66614}$][OH] (mL)</th>
<th>Appearance after 4 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3, Viscous liquid</td>
</tr>
<tr>
<td>2</td>
<td>2, Viscous liquid</td>
</tr>
<tr>
<td>3</td>
<td>1.5, Viscous liquid</td>
</tr>
<tr>
<td>4</td>
<td>1, Transparent glass gel (Si1)</td>
</tr>
<tr>
<td>5</td>
<td>0.75, Transparent glass gel (Si2)</td>
</tr>
<tr>
<td>6</td>
<td>0.5, Transparent glass gel (Si3)</td>
</tr>
<tr>
<td>7</td>
<td>0.25, Transparent glass gel (Si4)</td>
</tr>
<tr>
<td>8</td>
<td>0.125, White powder</td>
</tr>
<tr>
<td>9</td>
<td>0.5, White powder</td>
</tr>
</tbody>
</table>

**Table 1** Samples prepared with different ratios of TEOS:[P$_{66614}$][OH] (in each entry TEOS =1mL)

<table>
<thead>
<tr>
<th>[P$_{66614}$][OH] (mL)</th>
<th>Appearance after 4 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, Pale yellow viscous liquid</td>
</tr>
<tr>
<td>2</td>
<td>0.9, Pale yellow viscous liquid</td>
</tr>
<tr>
<td>3</td>
<td>0.8, Pale yellow viscous liquid</td>
</tr>
<tr>
<td>4</td>
<td>0.7, Pale yellow viscous liquid</td>
</tr>
<tr>
<td>5</td>
<td>0.6, Pale yellow viscous liquid</td>
</tr>
<tr>
<td>6</td>
<td>0.5, Pale yellow soft gel</td>
</tr>
<tr>
<td>7</td>
<td>0.4, Pale yellow glass (Ti1)</td>
</tr>
<tr>
<td>8</td>
<td>0.3, Pale yellow glass (Ti2)</td>
</tr>
<tr>
<td>9</td>
<td>0.2, Pale yellow glass (Ti3)</td>
</tr>
<tr>
<td>10</td>
<td>0.1, White crystalline powder</td>
</tr>
</tbody>
</table>

**Table 2** Samples prepared with different ratios of Ti(OiPr)$_4$:[P$_{66614}$][OH] (in each entry Ti(OiPr)$_4$=1mL)
The same method was applied to the formation of titania ionic liquid gels. Different ratios of Ti(OiPr)₄ and [P₆₆₆₁₄][OH] were mixed together at room temperature in order to find the optimal gelling conditions (Table 2). As seen with the silica ionic liquid gels, the ratio of Ti(OiPr)₄ to [P₆₆₆₁₄][OH] affected the structure of the gel formed. Samples with a high IL:Ti(OiPr)₄ ratio did not gel and instead remained as viscous liquids, (Table 2, entries 1-5). The 1:0.5 Ti(OiPr)₄ to [P₆₆₆₁₄][OH] mixture (Table 2, entry 6) started to gel within 2-5 days and formed a transparent yellow gel which remained soft after 4 weeks. The mixture with the highest ratio of Ti(OiPr)₄:[P₆₆₆₁₄][OH] of 1:0.1 formed a white crystalline powder. Samples Ti1-3 (Table 2, entries 7-9), with ratios 1:0.4 to 1:0.2, formed TiO₂ glasses after 4 weeks. The TiO₂ gels could not be washed with ethanol by the same method as the SiO₂ gels as this was found to completely break apart and dissolve the Ti structure, as the alcohol is able to cleave the Ti-O-Ti linkages and reverse the condensation reaction,¹⁷ and therefore the characterization was carried out on the unwashed gels.

Figure 4. a) ³¹P SSNMR of TiO₂ [P₆₆₆₁₄][OH] Ti1 (Table 2) after 5 months, b) ³¹P SSNMR of TiO₂ [P₆₆₆₁₄][OH] Ti1 after 1 year 3 months (y-axis: frequency).

Ti1 (Table 2, 1:0.4 Ti(OiPr)₄:[P₆₆₆₁₄][OH]) was the most robust of the titania solid glass gels. The ³¹P SSNMR showed a single resonance at δ32.94 after 5 months storage at room temperature, indicating no decomposition of [P₆₆₆₁₄][OH]. However, after 1 year 3 months there were 2 additional, very small resonances present at δ95.44 and δ44.36, signifying that the entrapped [P₆₆₆₁₄][OH] has started to decompose (Fig. 4b). This indicates that the titania matrix offers less stability than the silica matrix, which exhibited stability of [P₆₆₆₁₄][OH] for up to 1 year and 5 months. Powder XRD analysis confirms the TiO₂ as amorphous (SI S3.4 XRD). TGA analysis suggested thermal stability up to 258.9°C, while the ionic liquid on its own was only stable to 206.2°C (SI S3.3 TGA). Both the TGA and SSNMR data analysis indicate that the titania matrix offers some protection to the ionic liquid trapped inside, allowing it to remain stable for longer periods of time at room temperature, and to withstand slightly higher temperatures than the parent liquid. BET data analysis Sample Ti1 showed a surface area of 0.13m²/g and an average pore size between 8.59-12.88Å (SI S3.3 TGA).

In conclusion stable clear silica and titania ionic liquid gels were successfully prepared with the basic ionic liquid [P₆₆₆₁₄][OH] as the solvent, template, liquid phase and catalyst, employing a sol-gel method from TEOS and Ti(OPri)₄ respectively. The basic ionic liquid gels were formed as clear glassy monolithic materials. SSNMRs taken after 1 year 5 months for SiO₂ [P₆₆₆₁₄][OH] gels and after 5 months for TiO₂ [P₆₆₆₁₄][OH] gels indicated that the matrices offered stability to the parent ionic liquid when compared to the parent ionic liquid in the liquid phase. The parent ionic liquid itself shows high thermal stability (206.2°C), the thermal stability of the gels of the ionic liquids is approx. 50 (TiO₂) and 80 (SiO₂) degrees higher. Tetraalkylphosphonium cations can undergo decomposition to tertiary phosphate oxides and alkanes in the presence of base (equation 1).¹³,¹⁴ However while in the silica/titania matrix the ionic liquid is entrapped physically (within the pores of the matrix) and by means of hydrogen bonding and non-bonding interactions within the matrix. Both factors must limit/kinetically restrict the reaction between the hydroxide anion and the phosphorous centre of the cation and so slow down or inhibit the rate of decomposition, compared to the rate in the ionic liquid on its own.

This discovery has potential in the storage and application of unstable ionic liquids. The non-volatile nature of the ionic liquid will facilitate alternative approaches to the formation of films of TiO₂ and SiO₂ for catalysis, photocatalysis, electrocatalysis, sensors, solar cells, batteries, and coatings.

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Dr. A. C. Marr (QUB) and Prof. P. G. Pringle (U. Bristol) for invaluable discussions and DEL (NI) for studentship funding (KMB).

Supporting information
Details of materials and methods, Synthesis, NMR, SSNMR, TGA, BET, XRD.

Notes and references
6 Wang, Y.; Ulrich, V.; Donnelly, G. F.; Lorenzini, F.; Marr, P.C.; Marr, A. C. A recyclable acidic ionic liquid gel catalyst for dehydrogenation comparison with an analogous SILP Catalyst. ACS Sustainable Chemistry & Engineering. 2015, 3, 792-796.
Taming the base catalysed sol-gel reaction. Basic ionic liquid gels of SiO$_2$ and TiO$_2$

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Synopsis
Optically clear basic ionic liquid gels suitable for catalytic and energy applications were prepared by low temperature autocatalytic two-component one-pot methods.