Taming the Base Catalyzed Sol–Gel Reaction: Basic Ionic Liquid Gels of SiO2 and TiO2

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Taming the base catalysed sol-gel reaction. Basic ionic liquid gels of SiO$_2$ and TiO$_2$

Kyra M. Bothwell and Patricia C. Marr*

School of Chemistry and Chemical Engineering, The Queen's University of Belfast,

The David Keir Building, Stranmillis Road, Belfast, BT9 5AG, United Kingdom.

Tel:+44 (0) 28 90 974740.

Email: p.marr@qub.ac.uk.

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Abstract

We describe the autocatalytic synthesis of SiO$_2$ and TiO$_2$ 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 [P$_{66614}$][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 SiO$_2$ and TiO$_2$ 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 the template will lead to facile coating methods of sol-gel derived SiO$_2$ and TiO$_2$ as the non-volatile nature of the ionic liquid allows for advances in the coating of surfaces and the processing of thin films[9] (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) SiO$_2$ [P$_{66614}$][OH] gel (b) TiO$_2$ [P$_{66614}$][OH] gel (c) TiO$_2$ 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 [P_{66614}][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). [P_{66614}][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] [P_{66614}][Cl] was dissolved in ethanol and passed through an Amberlite (IRN78 hydroxide form) column, yielding a solution of [P_{66614}][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. [P_{66614}][OH] was monitored by ^{31}P{H}NMR over several weeks to follow its decomposition at room temperature; freshly synthesised [P_{66614}][OH] gives a single resonance at $\delta 34.0$ (Fig. 2a), while after 3 weeks an additional resonance at $\delta 50.8$ was seen (Fig. 2b). This indicates that [P_{66614}][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]

$$[R_3P\text{-}CH_2\text{-}R']^+ \ + \ OH^- \longrightarrow R_3P\text{=}O \ + \ CH_3\text{-}R' \quad (1)$$
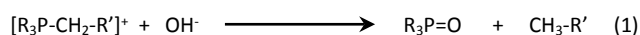
Equation 1 - decomposition of tetraalkylphosphonium cations

The peak at $\delta 50.8$ (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 $\delta 48.5$[15] and Tributylphosphine oxide $\delta 46.2$[16]).
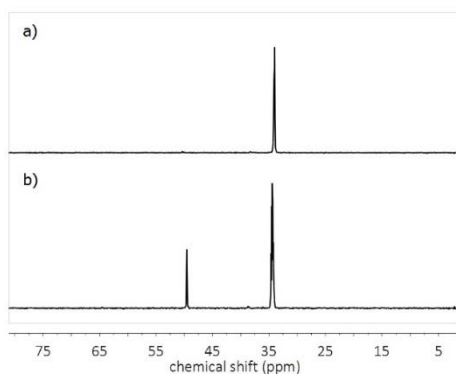

Figure 2. a) ^{31}P{H} NMR of [P_{66614}][OH] - Day 7 at room temperature, b) ^{31}P{H} NMR of partially decomposed [P_{66614}][OH] - day 22 at room temperature

Silica ionic liquid gels were synthesized from TEOS mixed with different ratios of [P_{66614}][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:[P_{66614}][OH]. After aging for 4 weeks, it was observed that the ratio of TEOS:[P_{66614}][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:[P_{66614}][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 $\delta 33.0$, 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).
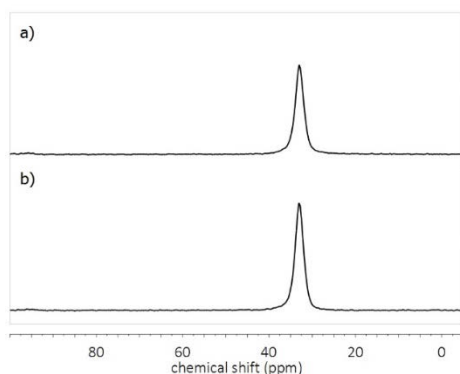
Figure 3. a) ^{31}P SSNMR of SiO_2 [P_{66614}][OH] **Si4 (Table 1)** at 8 months, b) ^{31}P SSNMR of SiO_2 [P_{66614}][OH] **Si4** at 1 year 5 months. (y-axis:frequency).

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 87.97m²/g with average pore size between 24.43-24.50 Å (SI S3.1 BET).

	[P_{66614}][OH] (mL)	Appearance after 4 weeks
1	3	Viscous liquid
2	2	Viscous liquid
3	1.5	Viscous liquid
4	1	Transparent glass gel (**Si1**)
5	0.75	Transparent glass gel (**Si2**)
6	0.5	Transparent glass gel (**Si3**)
7	0.25	Transparent glass gel (**Si4**)
8	0.125	White powder
9	0.5	White powder

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

	[P_{66614}][OH] (mL)	Appearance after 4 weeks
1	1	Pale yellow viscous liquid
2	0.9	Pale yellow viscous liquid
3	0.8	Pale yellow viscous liquid
4	0.7	Pale yellow viscous liquid
5	0.6	Pale yellow viscous liquid
6	0.5	Pale yellow soft gel
7	0.4	Pale yellow glass (**Ti1**)
8	0.3	Pale yellow glass (**Ti2**)
9	0.2	Pale yellow glass (**Ti3**)
10	0.1	White crystalline powder

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 [P$_{66614}$][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 [P$_{66614}$][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 [P$_{66614}$][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)$_4$:[P$_{66614}$][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 TiO$_2$ glasses after 4 weeks. The TiO$_2$ gels could not be washed with ethanol by the same method as the SiO$_2$ 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.
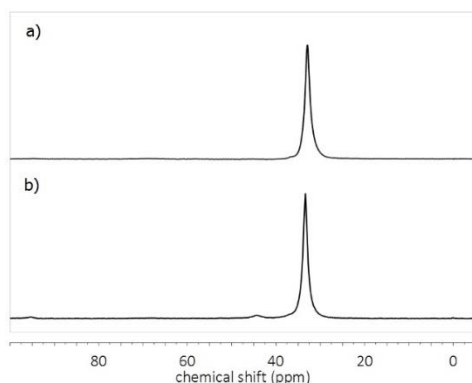

Figure 4. a) ^{31}P SSNMR of TiO$_2$ [P$_{66614}$][OH] **Ti1** (Table 2) after 5 months , b) ^{31}P SSNMR of TiO$_2$ [P$_{66614}$][OH] **Ti1** after 1 year 3 months (y-axis:frequency).

Ti1 (Table 2, 1:0.4 Ti(OiPr)$_4$:[P$_{66614}$][OH]) was the most robust of the titania solid glass gels. The ^{31}P SSNMR showed a single resonance at δ32.94 after 5 months storage at room temperature, indicating no decomposition of [P$_{66614}$][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 [P$_{66614}$][OH] has started to decompose (Fig. 4b). This indicates that the titania matrix offers less stability than the silica matrix, which exhibited stability of [P$_{66614}$][OH] for up to 1 year and 5 months. Powder XRD analysis confirms the TiO$_2$ 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 0.13m^2/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 [P$_{66614}$][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 SiO$_2$ [P$_{66614}$][OH] gels and after 5 months for TiO$_2$ [P$_{66614}$][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 (TiO$_2$), and 80 (SiO$_2$) degrees higher. Tetraalkylphosphonium cations can undergo decomposition to tertiary phosphine 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 TiO$_2$ and SiO$_2$ for catalysis, photocatalysis, electrocatalysis, sensors, solar cells, batteries, and coatings.

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

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Kyra M. Bothwell and Patricia C. Marr*

Synopsis

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