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Designing Materials for Aqueous Catalysis: Ionic Liquid Gel and Silica Sphere Entrapped Iron-TAML Catalysts for Oxidative Degradation of Dyes.[†]

Author Information

Peter McNeice,^{a,b} Andrew Reid,^a Hasan T. Imam,^{a,b} Carol McDonagh,^a Joel D. Walby,^a Terrence J. Collins,^c

Andrew C. Marr,^{*,a,b} Patricia C. Marr.^{*,a,b}

^a Affiliation: The School of Chemistry and Chemical Engineering, The Queen's University of Belfast, The David Keir Building, Stranmillis Road, Belfast, BT9 5AG, United Kingdom.

^b Affiliation: Queen's University Ionic Liquids Laboratories, The David Keir Building, Stranmillis Road, Belfast, BT9 5AG, United Kingdom.

^c Affiliation: Institute for Green Science, Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States of America.

Email: a.marr@qub.ac.uk

Email: p.marr@qub.ac.uk

Footnotes

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Abstract

Materials have been developed that encapsulate a homogeneous catalyst and enable it to operate as a heterogeneous catalyst in water. A hydrophobic ionic liquid within the material was used to dissolve Fe-TAML and keep it from leaching into the aqueous phase. One-pot processes were used to entrap Fe-TAML in basic ionic liquid gels, and ionic liquid gel spheres structured via a modified Stöber synthesis forming SiO₂ particles of uniform size. Catalytic activity was demonstrated via the oxidative degradation of dyes. Fe-TAML entrapped in a basic ionic liquid gel exhibited consistent activity in five recycles. This discovery of heterogenized H₂O₂ activators prepared by sol-gel and

Stöber processes opens new possibilities for the creation of engineered catalytic materials for water purification.

Keywords: Ionic liquid gel, Ionic liquid silica spheres, Stöber particles, Sol-gel, Fe-TAML, Water purification.

Table 1: Ionic liquids used in this study (top) and the structure of Fe-TAML (bottom).

G1	G2	Silica Spheres
<p>[P_{6,6,6,14}][OH]</p>	<p>[P_{6,6,6,14}][OⁱPr]</p>	<p>[N_{3,3,3,3}][OH]</p>
<p>[BMMIM][NTf₂]</p>	<p>[P_{6,6,6,14}][C₈SO₄]</p>	<p>[BMMIM][NTf₂]</p>
<p>Fe-TAML</p> <p>(TAML = tetraamidomacrocyclic ligand)</p>		

Introduction

Access to clean water is a human necessity.¹ Worldwide, 80 % of wastewater is released into the environment without treatment.² Water pollution is an increasing problem with, for example,

pharmaceuticals and illegal drugs detected in rivers.^{3,4} This is a concern for human and animal health.^{5,6} Oxidative degradation of organic pollutants can render water safer. This is broadly achieved biocatalytically,⁷ but with certain pollutants this is hindered by toxicity.^{8,9,10} Immobilization can help combat this, but can be difficult to achieve.¹¹ An alternative solution is to use synthetic biomimetic catalysts which can be more robust and promiscuous than their natural counterparts. Fe-TAML (TAML = tetraamidomacrocyclic ligand, Table 1) is a peroxidase mimic that effectively activates H₂O₂ to catalytically degrade persistent organic pollutants to non-toxic products,^{12,13,14,15,16} TAML catalysts have been shown to be nontoxic by low dose/concentration assays.^{15,17,18}

Our study focuses on removal of dyes from water. Dyes are not just a mimic for the pollutants mentioned above, but in drinking water can exhibit genotoxicity¹⁹ and mutagenicity.²⁰ Treatment of colored effluent contaminated with dyes decreases toxicity and increases water quality.¹¹ Fe-TAML has been successfully applied on a large scale to remove the colored impurities in a pilot plant at the Tasman Mill in New Zealand²¹ and has therefore been selected for this study.

Despite the high activity and negligible toxicity of Fe-TAML the operation of any catalyst dissolved in water means that ultimately the catalyst will also become a pollutant. Here we detail a method of heterogenizing a homogeneous catalyst that allows it to operate in water but avoids dissolving it in water. The Fe-TAML used here is the prototype, TAML design has recently advanced to New-TAMLS.¹⁷ The top performer is 100-1000 times more efficacious.

The development of a solid-supported heterogeneous Fe-TAML would increase the ease of use and in particular reuse. Previously Fe-TAML was covalently tethered to mesoporous silica.^{22,23} Here we report the entrapment of unmodified Fe-TAML in an ionic liquid gel and ionic liquid silica particles (Figure 1). These methods enable homogeneous operation of the catalyst, but as part of a material that is easy to separate, recycle and process. An important advantage of entrapment is that it doesn't require chemical modification of the catalyst, this enables use of the optimised catalyst.²⁴

Tuning the environment of a heterogeneous catalyst is a powerful way to improve the efficiency of the active site. Ionic liquids are ideal for this as they are known for their tuneable properties which can be selected by systematic alteration of the ionic liquid structure. Ionic liquids (ILs) have been shown to be viable and economical in industry. In PetroChina's "Ionikylation" process.^{25,26} and Chevron and Honeywell UOP's ISOALKYL process, ionic liquids replace HF and H₂SO₄.^{27,28} Evonik demonstrated that ionic liquids immobilized on silica are readily recycled.²⁹ Heterogeneous supported ionic liquids (SILPs) were economically evaluated for hydroformylation, and outperformed the homogeneous process.²⁹ The uses of ionic liquids described above suggest that ionic liquids could be economical for water purification on a large scale. Bulk ionic liquids have been used to absorb impurities from water^{30,31,32} but the separation of the ionic liquid from water was not facile. Supporting the ionic liquid on a solid enables easier separation. Ionic liquids form stable silica gels by sol-gel methods,^{33,34,35} which can be tuned by altering the ionic liquid structure. Species such as nanoparticles and metal complexes can be co-entrapped within the gels.^{36,37,38} Ionic liquid gels have been applied to a variety of catalytic applications,^{36,37,38} and can impart acidic³⁹ or basic^{40,41} properties. In some cases the catalyst is further activated by the gel environment.^{37,38} This may be the combination of confinement effects, high local concentrations of the catalyst and substrates in the gel, and ionic liquid specific effects. Ionic liquid gel materials have been reported in which no catalyst leaching is detected, and the catalyst could be reused with little or no decrease in activity.^{36,37,38,39,41} Cu-TEMPO entrapped in ionic liquid gels that are stable to oxidative conditions (at 50 °C) have been reported.⁴² These gels catalysed the selective oxidation of primary alcohols to aldehydes. The stability and activity of the gels was solvent dependent, this highlights the need for careful ionic liquid selection.

Figure 1: Schematic comparison of catalyst immobilization methods. **(A)** Tethering within the pores of a solid matrix; **(B)** Entrapment within an ionic liquid gel.

The reduction of extraneous materials is one of the principles of green chemistry and should be built into new catalyst syntheses.⁴³ Brønsted acidic or basic ionic liquids enable the ‘autocatalyzed’ sol-gel process, because the ionic liquid acts as the solvent and the catalyst for gel formation.^{39,40,41,44} This removes the need for additional acid or base. When considering the entrapment of Fe-TAML, the optimum ionic liquid to catalyse the sol-gel process was judged to be basic, as this catalyst works best in a basic environment.^{13,45} The base catalysed sol-gel process can lead to mechanically unstable gels⁴⁶ with low porosity due to the sol-gel process occurring too quickly.⁴⁷ However, the high viscosity of basic phosphonium hydroxide ionic liquids can be exploited to slow down the sol-gel process and allow the formation of stable basic gels with good porosity.⁴⁰ Combining a hydrophobic ionic liquid with a basic ionic liquid enhances the stability of the gels and prevents leaching.⁴¹ Long-chain phosphonium ionic liquids, such as tetradecyltriethylphosphonium octanesulfonate ([P_{6,6,6,14}][C₈SO₃], Table 1), have been found to be highly hydrophobic in nature and confer good phase behaviour as an immiscible phase with water.⁴⁸ These ionic liquids were chosen as components of our Fe-TAML entrapped basic ionic liquid gels.

An advantage of the sol-gel method is that it can be adapted to form layers and differently shaped particles, such as spheres. The Stöber synthesis of silica nanoparticles traditionally uses NH₃ to catalyse the sol-gel formation of silica spheres.^{49,50} Ionic liquid doped porous silica spheres were reported by Jacob *et. al.*, using HCl as a catalyst for silica formation.⁵¹ Ionic liquid silica nanomaterials

have since been prepared using surfactants with acids⁵² or bases.^{53,54} A mixture of non-ionic surfactant, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and benzene formed silica spheres without acid or base over three days; with two days of heating in an oven.⁵⁵ The preparation of ionic liquid entrapped in polystyrene spheres by evaporation of volatile solvent from an emulsion has been reported.⁵⁶ Here we report the formation of ionic liquid silica spheres from a basic ionic liquid by a modified Stöber synthesis.

Water remediation has been achieved using poly-ionic liquids,^{57,58,59} ionic liquid gels,^{60,61,62,63} ionic liquid grafted silica spheres,⁶⁴ and hollow carbon spheres,⁶⁵ which have been reported to remove dyes from water simply *via* absorption. Some of these systems can be recycled 15 times or more,^{60,61,62} however they have some drawbacks. They are often specific to certain dyes based on structure or charge. The materials also retain the dye in their structure, raising the possibility of contaminant leaching and requiring disposal of the contaminated material once it is saturated. This is illustrated by the recent report of a deep eutectic solvent gel made from naturally derived components.⁶⁶ The gel exhibited a high removal efficiency for a range of individual dyes over 10 cycles. When tested with a mixture of dyes the removal efficiency decreased after reuse as the dyes competed for the absorption sites.⁶⁶ A more powerful method of cleaning water would be to absorb then degrade the contaminant. Here we report a water bleaching process through a combination of dye absorption and catalytic degradation.

Results and Discussion

Catalyst preparation and characterisation

Ionic liquid gels

Fe-TAML binary ionic liquid gels (Tables 1, 2) were prepared in a one-pot method without the need for an additional acid or base catalyst (SI section 3). We have previously found that mixed ionic liquid silica gels have better mechanical and chemical stability than pure basic ionic liquid silica gels⁴¹ and

the right binary ionic liquid mixture facilitates sufficiently strong interactions with the matrix and negates leaching. The gel matrix has been reported to retard base catalysed decomposition of the ionic liquid cation.^{40,41} The ionic liquid combinations used were 1-butyl-2,3-dimethylimidazolium bistriflimide : trihexyltetradecylphosphonium hydroxide ([BMMIM][NTf₂]:[P_{6,6,6,14}][OH]) (for **G1**) and trihexyltetradecylphosphonium octanesulfonate : trihexyltetradecylphosphonium *i*-propoxide ([P_{6,6,6,14}][C₈SO₃]:[P_{6,6,6,14}][OⁱPr]) (for **G2**) (Tables 1, 2). **G1** and **G2** were formed as translucent orange gels whereas gels prepared without Fe-TAML were colorless (SI Figure S1).

The yield based on the mass of all added components was greater than 90 % (SI section 3.1). **G2** had a higher Fe-TAML content than **G1** (Table 2). This may result from better dissolution of the Fe-TAML in the [P_{6,6,6,14}][C₈SO₃]:[P_{6,6,6,14}][OⁱPr] solvent system. **G1** was found to have a larger surface area but a lower pore size than **G2** using Brunnauer-Emmett-Teller (BET) theory and Barrett-Joyner-Halenda (BJH) theory (Table 2). Both gels exhibited type IV BET isotherms characteristic of mesoporous materials (SI Figures S14, S17).⁶⁷ **G1** had an H2 hysteresis loop (SI Figure S14) making the pore shape difficult to determine. **G2** had an H3 hysteresis loop (SI Figure S17) which can indicate aggregates and slit like pores.⁶⁷ Differences in silica structure upon changing the ions are expected as the ionic liquid has a templating effect in addition to the catalytic effect of the basic anion. In ongoing work it will be instructive to study the relationship between gel morphology, rheology, and catalytic performance. By TGA (Table 2SI Figures S10, S11) **G2** exhibited a higher degradation temperature than **G1**. Binary alkoxide ionic liquids with a common cation have previously been reported to have similar thermal stability to each other regardless of the amount of basic anion they contained.⁶⁸ The higher thermal stability measured for **G2** is likely to result from the higher stability of [P_{6,6,6,14}][C₈SO₃]⁴⁸ compared to [BMMIM][NTf₂].⁶⁹ This good thermal stability should render basic gels of this type applicable to catalytic reactions at elevated temperatures and are therefore promising for the development of new oxidation catalysts for fine chemical synthesis, as observed for the basic ionic liquid gels used previously to promote hydrogen borrowing reactions at 150 °C.⁴¹

Table 2: Iron content, thermal stability, and structural properties of ionic liquid silica gels **G1** and **G2**.

Entry	Gel ^a	Basic IL	Hydrophobic IL	Iron Content (Wt %) ^b	TAML Anion Content (Wt %) ^c	TGA (°C) ^d	BET Surface Area (m ² /g)	BJH Pore Size (nm)
1	G1	[P _{6,6,6,14}][OH]	[BMMIM][NTf ₂]	0.03	0.24	325	373.2	7.2-8.3
2	G2	[P _{6,6,6,14}][O ⁱ Pr]	[P _{6,6,6,14}][C ₈ SO ₃]	0.16	1.27	349	308.1	8.7-10.9

^a Basic IL (0.5 mL), Hydrophobic IL (0.5 mL), TEOS (1 mL), Fe-TAML (6 mg). ^b Measured by ICP/OES. ^c

Calculated based on the molecular weight of Fe (55.84 gmol⁻¹) and the TAML anion (444.26 gmol⁻¹). ^d

Onset degradation temperature.

Ionic liquid silica spheres

Ionic liquid silica spheres (Figure 2) were prepared by modifying the method of Jacob *et. al.*,⁵¹ who used a hydrophobic ionic liquid ([BMIM][PF₆]) as the solvent and HCl as the catalyst. The catalyst and solvents used here were basic ionic liquid [N_{3,3,3,3}][OH] (Tetrapropylammonium hydroxide) and hydrophobic ionic liquid 1-butyl-2,3-methylimidazolium bistriflimide ([BMMIM][NTf₂]) (SI section 3.3). In addition to the silica precursor TEOS, (Aminopropyl)trimethoxysilane (APTMS) was added to improve the dispersibility of the spheres in water,⁷⁰ whilst triethoxymethylsilane (TEMS) was added to prevent aggregation.⁷¹

Figure 2: LHS, Optical microscope image (x10) of Fe-TAML entrapped ionic liquid silica spheres. RHS, SEM image (x1170) of a single Fe-TAML entrapped ionic liquid silica sphere.

ICP/OES indicated that the silica spheres contained 0.52 wt % Fe and therefore 4.14 wt % TAML anion, which was higher than gels **G1** and **G2** (0.24 and 1.27 wt % TAML anion, Table 2). As with ionic liquid gels **G1** and **G2**, the spheres provide a basic ionic liquid environment within the porous spheres⁷² to protect Fe-TAML. The spheres exhibited good thermal stability (296 °C, SI Figure S12), after an initial loss of water, but are 30-50 °C less stable than **G1** and **G2** (Table 2).

Aqueous dye degradation activity

The activity of Fe-TAML within the gels and spheres was screened by following the bleaching of aqueous solutions of dye by H₂O₂ in a similar manner to previous studies on homogeneous systems.⁷³ Degradation experiments were performed on indigo carmine under homogeneous conditions without buffer and similar tests were performed on brilliant blue and tartrazine (SI Figures S49, S50). This enabled a direct comparison with the heterogeneous system where the use of an engineered pH will reduce the effects of changes in the solution pH. The addition of peroxide to the indigo carmine solution lowered the pH from 7.0 (± 0.03) to 6.3 (± 0.16) (SI section 1). The results (Figure 3) showed that H₂O₂ and Fe-TAML have little to no activity when used independently. The homogeneous solution of the combined oxidant and promoter degraded the dye down to 20 % within 90 minutes under experimental conditions (Figure 3, SI section 4.2). The addition of basic

ionic liquid had a promoting effect, giving complete degradation in 60 minutes. Above the pK_a of H_2O_2 (11.5), strongly nucleophilic HO_2^- forms in a process called perhydrolysis and this leads to accelerated degradation.¹³ This highlights the importance of basic additives for homogeneous Fe-TAML activity and is the rationale behind our use of basic ionic liquids for the formation of Fe-TAML gel and spheres.

Figure 3: Homogeneous degradation reactions of indigo carmine (0.63×10^{-3} M) with and without Fe-TAML (10.7×10^{-6} M), H_2O_2 (0.16 M) and basic ionic liquid ($[P_{6,6,6,14}][OH]$ (1 mL solution in EtOH)).

Figure 4: Indigo carmine (0.63×10^{-3} M) degradation using H_2O_2 (0.16 M) and either homogeneous Fe-TAML (10.7×10^{-6} M), gel entrapped Fe-TAML (25 gL^{-1} gel) or silica sphere entrapped Fe-TAML (1.95 gL^{-1} spheres). The Fe-TAML/dye molar ratio was 0.02 (Homogeneous) 0.20 (**G1**), 1.0 (**G2**) and 0.003 (Spheres). No H_2O_2 was added for the blank gel run. **G** indicates an ionic liquid gel. Standard deviations are shown for reactions performed in triplicate.

After demonstrating that both H_2O_2 and Fe-TAML are necessary for the removal of dye we followed the degradation of indigo carmine by UV-visible spectrophotometry to compare the performance of **G1**, **G2**, the silica spheres and homogeneous Fe-TAML solutions (Figure 4, SI section 4). To make the process more environmentally friendly and applicable in the field, a buffer was not used. The pH at the start of the reaction was $6.3 (\pm 0.13)$. This is below the ideal pH for Fe-TAML^{13,73} but the engineered pH at the heterogeneous active centre should restore nearer-optimal activity to Fe-TAML. A gel that did not contain Fe-TAML did not promote dye removal. **G2** was more active towards the degradation of indigo carmine than **G1**. The difference in activity can be attributed to

the greater amount of Fe-TAML entrapped in **G2** and the larger pore size of this gel (Table 2), but the different ionic liquids in each gel (Table 1) may also play a role in determining the rate of bleaching. Different absorbances of chlorophenols and dyes have been observed by bulk ionic liquids^{30,31,32} and ionic liquid gels^{60,61,66} depending on the ionic liquids used.

The basic ionic liquid silica spheres degraded indigo carmine faster and to a greater extent than **G1**, **G2** or the homogeneous system (Figure 4, SI section 4). This is consistent with the higher wt % of entrapped Fe-TAML in the spheres compared to the gels (0.52 wt % compared to 0.03 and 0.16 wt %). There may also be a concentration effect of the catalyst and the substrate within the spheres due to confinement. This has previously been shown by gels and nanoparticles where the materials containing less catalyst were more active due to efficient interaction of reagents and catalysts in a confined environment,^{74,75} and by chiral organocatalysts entrapped in low molecular weight ionic liquid gels where the hydrogen bonding within the gels improved the reaction yield compared to the bulk ionic liquid.⁷⁶ The slower initial degradation compared to the homogeneous system suggests that initial diffusion of indigo carmine into the spheres slows the establishment of a steady state system. Unlike the other systems, bubbling was visible in the sphere reaction, indicating the fast decomposition of H₂O₂ to form O₂. After 45 minutes no individual absorbance was visible for indigo carmine, but the baseline was raised and this prevented the measurement to 100 % dye conversion (SI Figure S45).

G2 and homogeneous Fe-TAML were found to exhibit similar degradation behaviour for indigo carmine; the initial rate of homogeneous Fe-TAML was higher, but after 40 minutes, the two systems (homogeneous and **G2**) exhibited a very similar steady rate of bleaching. The slower initial rate in the gel system is consistent with the gel first having to absorb the dye before its degradation and supports the theory that the Fe-TAML is entrapped within the gel pores rather than simply absorbed to the surface.

The ionic liquid gels **G1** and **G2** were also used to catalyse the decomposition of brilliant blue (as a component of food coloring). Both gels catalysed the decomposition of brilliant blue more efficiently and to a greater extent than homogeneous Fe-TAML (SI Figure S51, S54). **G1** degraded brilliant blue to a similar extent to **G2** at a slower rate (SI Figures S51, S53), this is consistent with the results for indigo carmine bleaching. Degradation studies on tartrazine are detailed in the SI section 13.2.

Whilst homogeneous Fe-TAML would have increased activity at a higher pH,⁷³ we show that the engineered pH of the heterogeneous materials can support the activity of Fe-TAML in a low pH solution. Ionic liquids experience only a small slowing down of their dynamics when entrapped,⁷⁷ and we proposed that the homogeneous mechanism of Fe-TAML was maintained within the gel. The efficient dye degradation reported here shows that the basic ionic liquid materials provide a protective environment for the activity of Fe-TAML which facilitates activity and supports high rates of reaction.

Gels are known to absorb dyes^{60,61,62,66} so it could be argued that the dye is simply being absorbed by the gel and not degraded. It is likely that this is the first process in dye removal, and when the gel was removed early in the reaction it was colored, showing the dye had been absorbed. However, the color could be observed fading as the dye was degraded by the activity of entrapped Fe-TAML (Figure 5). A blank gel that did not contain Fe-TAML absorbed a negligible quantity of the dye (Figure 4), showing that absorption is not the sole method of dye removal in this system. Sulfonated gels, such as indigo carmine and brilliant blue, are known to have high water solubility and low absorbance onto solids.⁷⁸ The dyes did not become significantly darker as the reaction progressed which would occur if the gel continually absorbed the dye without degrading it. The presence of bubbles in the silica sphere catalysed degradation is further evidence for the co-operation between Fe-TAML and H₂O₂ to degrade the dye rather than simply remove it by absorption.

Figure 5: Left, an Fe-TAML gel stained by indigo carmine. Right, the same gel after the dye has degraded.

Catalyst stability and reuse

Following every heterogeneous degradation of dye, a liquid sample was removed and the Fe content was analysed by ICP/OES. A liquid sample from the sphere catalysed reaction was found to contain 1 ppm iron. This metal leaching accounts for the change in baseline position (SI Figure S45). Although they supported a high level of catalytic activity, the ionic liquid silica spheres prepared were not robust enough to survive the conditions of the reaction. Improvements to the spheres' stability may yield from increases in the percentage silica in order to form a thicker shell, and/or changes in the ionic liquids used, as the basic ammonium ionic liquid used may not be as stable as phosphonium analogues. The silica spheres were not found to recycle. After a bleaching experiment the spheres were collected *via* filtration and washed with a small amount of water. When the spheres were reused they showed relatively little degradation of indigo carmine in the second (18 %) and third use (10 %) (SI Figure S55). This is considerably lower than the first run (87 %) and is consistent with the leaching of Fe observed by ICP/OES.

The Fe content of every sample from the gel catalysed reactions was found to be less than 0.1 ppm, which indicates that the Fe-TAML leaching was minimal. Fe-TAML and H_2O_2 work best under basic conditions.¹³ In contrast Fe-TAML has been shown to leach metal under certain homogeneous acidic conditions.^{15,45} Entrapment of Fe-TAML within silica and the basic nature of **G1** and **G2** has prevented leaching during these dye degradation studies.

To compliment the ICP/OES results, further proof of the heterogeneity of the gel catalysts was provided by performing a filtration test⁷⁹ on **G2** in an aqueous solution of indigo carmine and H₂O₂ (Figure 6, SI section 4.4). After 45 minutes in solution the gel was removed and the solution monitored for a period without the gel. There was a significant decrease in the rate of bleaching from $2.2 \times 10^{-3} \text{ Mmin}^{-1}$ (0-45 minutes) to $1.0 \times 10^{-3} \text{ Mmin}^{-1}$ (45-60 minutes), and after a few minutes the bleaching ceased. The slight decrease in absorbance/concentration between T=45 and T=60 represents one data point, and this bleaching may have occurred during filtration. The gel was re-added to the reaction after 90 minutes and catalytic bleaching resumed. The rate of oxidation was found to be higher in the second period ($3.1 \times 10^{-3} \text{ Mmin}^{-1}$), this may be due to the presence of inhibitors in the first phase, and/or the formation of a more active form of the catalyst. During the period of separation any species absorbed within the gel will still be exposed to the action of Fe-TAML and H₂O₂. Similar tests were performed for the other dyes (SI Figures S30, S35, S46, S47) and for **G1** (SI Figures S42, S48). Brilliant blue gave similar trends, whereas low rates of bleaching for tartrazine rendered these results inconclusive.

The ionic liquid gel **G2** was recycled and reused five times (Figure 7). After the reaction the post-reaction gel was obtained from the reaction mixture by filtration and washed with a small amount of water. In each of the recycle experiments the degradation profile was similar, and the first bleaching test was consistent with the fifth. In contrast, the previously reported system of Cu-TEMPO entrapped in ionic liquid gels containing [BMIM][PF₆] was found to leach and become deactivated.⁴² This highlights the importance of the right catalyst, matrix and ionic liquid combination.

Figure 6: Graphs for a filtration test on **G2** (25 gL^{-1}) and indigo carmine ($0.63 \times 10^{-3} \text{ M}$) using H_2O_2 (0.16 M). Fe-TAML/dye molar ratio is 1.0. Left, UV-visible spectrum of the filtration test. Right, % dye remaining vs. time. Purple indicates the gel in the liquid mixture, red indicates the gel has been removed.

Figure 7: Reuse of **G2** (25 gL^{-1}) for the degradation of brilliant blue ($1.4 \% \text{ v/v}$ food coloring) using H_2O_2 (0.16 M).

Environmental Implications

Purification of water is necessary for human health. New methods for purification are needed as the current processes allow contaminants to remain in treated water.^{3,4} Fe-TAML is one-such efficient water treatment catalyst.^{12,13,14,15,16,17} We report the one-pot preparation of Fe-TAML entrapped in

basic ionic liquid silica gels and ionic liquid silica spheres with the ionic liquids chosen to maximise the activity and stability of the catalyst for water purification. To our knowledge this is the first report of the ionic liquid catalysed synthesis of ionic liquid silica spheres. The addition of peroxide to water lowers the pH and this is detrimental to Fe-TAML.^{15,45} Entrapping TAML within the basic gel environment allows Fe-TAML to be used in non-optimal conditions. The use of a heterogeneous catalyst with an engineered pH at the active centre removes any requirement to adjust the pH of the water, making the system much cleaner. Heterogeneous TAML does not cause metal pollution, as the metal complex is locked away in the gel. The ionic liquids used here have relatively low toxicity^{80,81} and the long chain phosphonium ionic liquids are particularly averse to water dissolution⁴⁸ and therefore ionic liquid leaching is unlikely.⁴¹ This is an important parameter to consider in case of an accidental release or gradual release over the mid to long term. Long term testing under field-like conditions should be performed to assess changes in the material which could indicate leaching has occurred.

The performance of Fe-TAML doped ionic liquid materials was very promising and, as the removal of colored impurities increases water quality and reduces its toxicity,¹¹ the Fe-TAML materials could be optimised for real-world systems. The gels could also be applied to the degradation of many organic compounds^{12,13,14,15,17} and pathogens,¹⁶ as previously demonstrated for Fe-TAML. Although the heterogeneous systems use more Fe-TAML, their ease of recovery and reuse prevents waste of the catalyst which occurs in the homogeneous system. It is anticipated that Fe-TAML entrapped in ionic liquid materials would be easier to apply to water purification in the field. The protective environment within the gel should make the catalytic system more resistant to poisoning and demetallation. Future generations of Fe-TAML catalysts (including New-TAML) could be incorporated with minimal changes to the synthesis methods.

The methods developed have the basic premise of providing a protective solvent environment for a catalyst that does not leach into water and can be readily separated and recycled. The system should

be applicable to different catalysts, and, we believe with modification, also to the entrapment of biocatalysts. The sol-gel process allows gels of different shapes to be formed by changing the processing method, as demonstrated for silica spheres. Gels could be processed in order to fit certain pipes or be incorporated into mixing tanks or hand-held devices. Beads could be prepared and then used to pack a pipe or held inside a mesh in a mixing tank. The formation of gel particles and silica spheres exemplifies the flexibility of ionic liquid mediated *chimie douce* methods. Many opportunities exist for the tuning of the morphology and physical properties of the resultant porous materials. The ionic liquid within the matrix provides a unique environment for the entrapment of active catalysts. This can in turn lead to the formation of many forms of heterogenized catalyst, giving flexibility of design in order to maximise performance.

Conflicts of interest

There are no conflicts to declare.

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TOC Image

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