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Exploring Opportunities for Platinum Nanoparticles Encapsulated in Porous Liquids as Hydrogenation Catalysts

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Abstract

The unusual combination of characteristics observed for porous liquids, which are typically associated with either porous solids or liquids, has led to considerable interest in this new class of materials. However, these porous liquids have so far only been investigated for their ability to separate and store gases. Herein, we explore the catalytic capability of Pt nanoparticles encapsulated within a Type I porous liquid (Pt@HS-SiO_2 PL) for the hydrogenation of several alkenes and nitroarenes under mild conditions (T = 40 °C, P_{H_2} = 1 atm). To understand the effect of each component of the porous liquid on the catalysis, the different intermediates in the porous liquid synthesis (*i.e.* the initial Pt@HS-SiO_2, the organosilane-functionalised intermediate and final porous liquid) were employed as catalysts. For the hydrogenation of 1-decene, the Pt@HS-SiO_2 PL catalyst in ethanol had the fastest reaction rate when normalised with respect to the concentration of Pt. The reaction rate slowed when the reaction was completed in a “neat” porous liquid system, which was most likely due to the high viscosity of the system. These systems may find application in cascade reactions, in particular, those with mutually incompatible catalysts.

Introduction

The idea that well-defined permanent porosity could, through careful design, be introduced into a liquid was first suggested in 2007 by O’Reilly *et al.*[1] They proposed three possible categories of porous liquids: neat porous liquids composed of discrete molecular hosts (Type I), discrete molecular hosts dissolved in a bulky solvent (Type II), and liquids comprising porous frameworks dispersed in a sterically hindered solvent (Type III).[1-2] Porosity is a characteristic typically associated with solid materials and so it was hypothesised that these porous liquids could potentially possess unique combinations of properties, such as the size-selective sorption properties of a porous solid and the fluidity of a liquid.[1-2] However, it was not until 2015 that these systems became a reality with the first reports of the successful synthesis of liquids containing permanent pores.[3-4] Since then examples of porous liquids of all three classes have been reported.[5-9] Despite the advancements made within this field, to date these systems have been reported in the literature only with respect to their ability to capture, separate and store gases.[3-6, 8, 10] Conversley, the unique combinations of properties means that the potential applications for these systems are extremely broad.[2, 11-12]

Recently, we reported the first successful encapsulation of metal nanoparticles within a Type I porous liquid.[13] This porous liquid consists of hollow silica spheres (diameter *ca* 16 nm) that are functionalised with a large corona-canopy (Figure 1).[4] The corona-canopy consists of a positively charged organosilane corona moiety ionically bound to a negatively charged poly(ethylene glycol)-based canopy (PEGS). The 2 nm pores that permeate through the silica shell prevent the movement of either the corona or the canopy into the cavity, thus, maintaining the intrinsic porosity.[4] Our method for encapsulating Pt nanoparticles within the porous liquid, involved first encapsulating the Pt nanoparticles (*ca* 1.2 nm) in thiol-functionalised hollow silica spheres (HS-SiO_2) before corona-canopy functionalisation.[13] The presence of the thiol functional groups was found to be crucial to the successful encapsulation and then retention of the nanoparticles during corona-canopy functionalisation.[13] The present work was undertaken to explore the possible application of these systems as catalysts, with the intention of understanding the underlying principles behind catalysis in porous liquids.

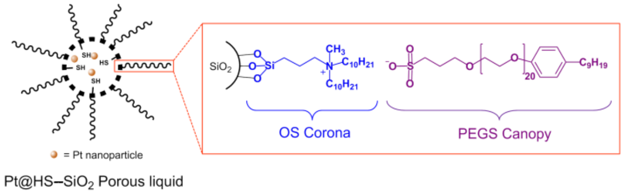


Figure 1. Schematic of Pt nanoparticles encapsulated in a Type I porous liquid.

Previous research has firmly established the enhanced capacity of these liquids to dissolve/absorb gas, inherently enabled by the presence of cavities, which become enriched with gas.[3-4, 10] This cavity enrichment should lead to an increased concentration of gas around the catalyst and, hence, might in some cases improve the rates of reactions for the porous liquid as compared to a conventional, molecular one.[11] Therefore, it is expected that the application of porous liquids as catalysts will be most advantageous when applied to reactions involving gaseous reagents. As porous liquids have not previously been employed as catalysts, a simple catalytic reaction, preferably with at least one gaseous reagent, was required in order to advance our understanding of the catalytic capability of these systems. Hydrogenation reactions are one of the most studied and most important synthetic transformations at both the laboratory and industrial scales.[14-15] These reactions have been reported with an extensive range of both heterogeneous and homogeneous transition metal-based catalysts using a variety of hydrogen donors, including hydrogen gas.[16] Herein, we report on our investigation of the catalytic applicability of Pt nanoparticles encapsulated in a Type I porous liquid for hydrogenation reactions under mild conditions.

Results and Discussion

Hydrogenation of 1-decene

The hydrogenation of 1-decene to decane was selected as the initial reaction to study the catalytic activity of the porous liquid system due to its simplicity. This test reaction was completed under benign batch reaction conditions (T = 40 °C, P_{H_2} = 1 atm). As porous liquids have not previously been studied as catalysts, we first needed to understand how each component of the shell-corona-canopy influences the catalytic activity of this Type I porous liquid. This was investigated by testing the catalytic activity of the three stages of the porous liquid synthesis: the initial Pt nanoparticles encapsulated in hollow silica sphere (Pt@HS–SiO_2), the organosilane-functionalised intermediate (OS–(Pt@HS–SiO_2)), and the resulting porous liquid (Pt@HS–SiO_2 PL). The amounts of each catalyst used were standardised, from the TGA traces (Figure S1), to the mass of inorganics (e.g. Pt@SiO_2) present in each sample rather than the amount of Pt. This ensured that comparable numbers of hollow silica spheres were present in each reaction.

The Pt@HS–SiO_2 PL is liquid-like. However, as both Pt@HS–SiO_2 and OS–(Pt@HS–SiO_2) are solids they require a solvent. To enable direct comparison of reactivity between all catalysts, all three catalysts were studied using ethanol as the solvent. However, as ethanol is small enough to diffuse through the pores in the silica shell and fill the cavities, in this system the reactants must diffuse through pores that are (at least partially) occupied by solvent. But it is this intrinsic porosity that provides the unique properties of these systems. So in addition to reactions in ethanol, the Pt@HS–SiO_2 PL catalyst was also studied using poly(ethylene glycol) sulfonate-based potassium salt (KPEGS) as a non-conventional solvent, in which the pores and cavity of the functionalised SiO_2 spheres are free of solvent. As the PEGS anion forms the canopy, and thus is the main component of the porous liquid, the addition of KPEGS will not affect the porosity of the system. Moreover, due to the small scale of the reaction with the porous liquid catalyst, an additional solvent was required in this case to ensure efficient mixing. Since the addition of KPEGS does not affect the intrinsic porosity, this system could be considered as comparable to a "neat" porous liquid. Figure 2 shows the reaction profiles for the conversions of 1-decene for the four catalytic systems.

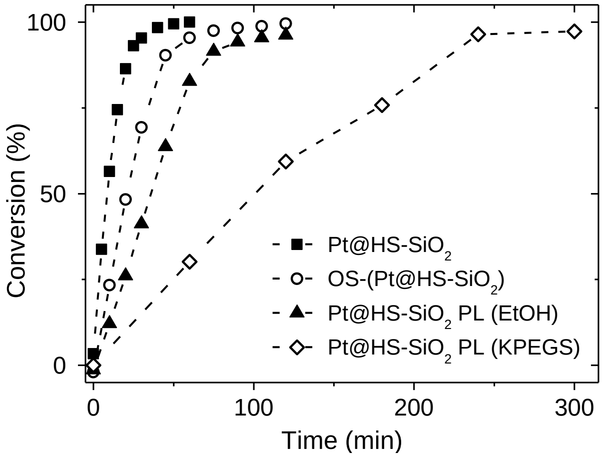


Figure 2. Conversion of 1-decene for Pt@HS–SiO$_2$ (■), OS–(Pt@HS–SiO$_2$) (○), Pt@HS–SiO$_2$ PL(EtOH, ▲) and Pt@HS–SiO$_2$ PL(KPEGS, ◇) at 40 °C and 1 atm H$_2$.

From the reaction profiles (Figure 2) it can be seen that the rates of reaction for each catalytic system decreased in the order Pt@HS–SiO$_2$ > OS–(Pt@HS–SiO$_2$) > Pt@HS–SiO$_2$ PL(EtOH) ≥ Pt@HS–SiO$_2$ PL(KPEGS). For the Pt@HS–SiO$_2$ catalyst, a strong linear correlation was observed when ln(decene) was plotted as a function of time (Figure S2), indicating that for this catalyst the kinetics of this reaction are first order with respect to decene. However, hydrogenation reactions catalysed by supported metal nanoparticles typically follow zero order kinetics with respect to the substrate.[17-19] The first order kinetics observed for Pt@HS–SiO$_2$ suggest that under these conditions the hydrogenation of decene is diffusion controlled.[20] The permeability of the shell in core-shell nanoreactors is known to significantly influence the kinetics of a reaction, impacting on the diffusion of reagents and products into and out of the cavity and, hence, to and from the active catalyst.[21-22] Conversely, the reaction profiles (Figure 2) for the OS–(Pt@HS–SiO_2), Pt@HS–SiO_2 PL(EtOH) and Pt@HS–SiO_2 PL(KPEGS) catalytic systems all initially display a linear correlation for the conversion of decene as a function of time, signifying zero order kinetics with respect to decene for these systems. At high decene conversions (>80 %) the kinetics change so that the decene conversion as a function of time is well reproduced by assuming kinetics that are first order with respect to decene (Figure S2). The initial zero order kinetics can be attributed to the saturation of the catalytic surface by the reagents and implies that for these systems the initial rate was not affected by the mass transfer of decene to the catalyst.[18] However, as the concentration of decene decreases over the course of the reaction, the reaction eventually becomes diffusion controlled, leading to a shift in the kinetics from zero order to first order with respect to decene.[23] The change in the kinetics of the reactions, with respect to decene, from first order for Pt@HS-SiO_2 to zero order upon functionalisation with the corona-canopy, is unlikely to be due to an improvement in the diffusion of the reagents to the catalyst as it is expected that functionalisation will slow the rate of diffusion into the cavity. Rather it is more probable that the difference in the kinetics of the catalytic systems is due to a change in the structure of the metal nanoparticles themselves. During the functionalisation of the silica spheres by the corona-canopy the Pt nanoparticles were found to agglomerate, increasing from approximately 0.84 to 1.2 nm.[13] It has been well established that the shape/morphology, size and environment can have a considerable effect on the catalytic reactivity of metal nanoparticles.[24-25] Therefore, it is probable that the change in the kinetics is due to a combination of factors, which would require further in-depth study beyond the scope of the current paper.

The initial pseudo zero order rate constants (k_{0th}) for the OS–(Pt@HS–SiO_2), Pt@HS–SiO_2 PL(EtOH) and Pt@HS–SiO_2 PL(KPEGS) catalytic systems were calculated from the reaction profiles (Figure 2). The pseudo first order rate constants (k_{1st}) for each catalytic system were calculated by modelling the data from Figure 2, assuming pseudo-first order kinetics (Table 1). However, these rate constants are calculated independently of the Pt concentration and, thus, do not take into account the different amounts of Pt in each catalyst. This is significant because, as previously stated, the amount of each catalyst used was normalised to the mass of silica not Pt. From ICP-OES analysis the Pt@HS–SiO_2 PL sample had considerably lower concentrations of Pt than either Pt@HS–SiO_2 or OS–(Pt@HS–SiO_2) (Table S1). Therefore, the rate constants cannot be used to compare the catalytic activities of the different catalytic systems.

Table 1. Catalytic activity of the different catalyst systems for the hydrogenation of 1-decene.

Entry	Catalyst	Solvent[a]	k_{0th} (mmol min^{-1})[b]	k_{1st} (min^{-1})[c]	TOF_{app} (h^{-1})[d]
1	Pt@HS–SiO_2	EtOH	—	0.0896	2006
2	OS–(Pt@HS–SiO_2)	EtOH	0.0120	0.0682	930
3	Pt@HS–SiO_2 PL	EtOH	0.0071	0.0431	2062
4	Pt@HS–SiO_2 PL	KPEGS	0.0025	0.0087	768

[a] Conditions: 5 mg Pt@HS-SiO_2 (or equiv.), 1-decene (0.5 mmol), 40 °C, 1 atm H_2.

[b] Approximated from the initial linear sections of the reaction profiles in Figure 2

[c] Approximated by modelling decene consumption with DynaFit4 assuming pseudo-first order reaction kinetics (*i.e.* $-d[\text{decene}]/dt = k[\text{decene}]$).[26]

[d] Apparent turnover frequency; $mol_{decene}\ mol_{Pt}^{-1}\ h^{-1}$, calculated at roughly 25–30% conversion.

A common method used to compare the catalytic activity of different catalysts is the turnover frequency (TOF). However, the TOF assumes zero order kinetics with respect to the reactants and varies with changing reaction conditions.[27-28] Despite the ambiguity of this term in this instance it does provide a means to compare the different catalytic systems. Here, the apparent turnover frequency (TOF$_{app}$) is defined as the number or moles of decene converted per mole of Pt per hour, calculated at a decene conversion of about 90%. From the TOF$_{app}$ the order of reactivity follows the trend Pt@HS–SiO$_2$ PL(EtOH) > Pt@HS–SiO$_2$ > OS–(Pt@HS–SiO$_2$) > Pt@HS–SiO$_2$ PL(KPEGS) (Table 1). The TOF$_{app}$ for Pt@HS–SiO$_2$ was 2006 h^{-1} (Table 1, entry 1). This decreased to 930 h^{-1} when the silica spheres were functionalised with the organosilane (Table 1, entry 2). The catalytic activities of polymer-supported catalysts are known to be adversely affected when diffusional processes hinder the movement of reagents to the catalyst thus resulting in a reduction in the rate of reaction.[29] Therefore, this decrease is not unexpected as the reagents have to diffuse across the large charged corona-layer (~2 nm) to reach the active catalyst. Furthermore, it could reasonably be expected that the addition of the canopy to form the porous liquid would result in a further decrease in the rate of reaction. Conversely, the opposite occurred with the TOF$_{app}$ actually increasing upon the addition of the canopy to 2062 h^{-1} (Table 1, entry 3). This could possibly be attributed to the improved dispersion of the porous liquid in ethanol compared to the Pt@HS–SiO$_2$ and OS–(Pt@HS–SiO$_2$). From the transmission electron microscopy (TEM) images (Figure S3) the porous liquid exists as discrete spheres, while the silica spheres in both Pt@HS–SiO$_2$ and OS–(Pt@HS–SiO$_2$) typically aggregate forming large clusters of spheres. It is expected that it would be difficult for reagents to diffuse into the cavities of the spheres in the middle of the clusters if similar behaviour occurs in solution. Conversely, when the catalytic system exists as discrete spheres, the reagents can diffuse into the cavities from all directions, making the Pt nanoparticles more accessible and, hence, improving the rate of reaction.

When the reaction is completed in ethanol the solvent facilitates the diffusion of reagents into the cavities. We hypothesised that, for the “neat” porous liquid, when a liquid with molecules small enough to diffuse through the pores of the silica shells is added, the molecules will preferentially diffuse into the cavities as it is easier to displace gas than to dissolve in the corona-canopy, where it would need to break interactions between the chains. This could be expected to lead to an increase in the concentration of reactants around the catalyst and, hence, increase the rate of reaction. However, the TOF_{app} was found to decrease by more than three-fifths to 768 h^{-1} (Table 1, entry 4) for the Pt@HS–SiO_2 PL catalyst when KPEGS was employed as the solvent instead of ethanol. This decrease in the TOF_{app} is likely (at least partly) due to the high viscosity of the KPEGS-based system. This phenomenon is known to occur for reactions in viscous media, with the rate of reaction becoming diffusion dependent.[30-31] Additionally, it has previously been shown that the dipolarity/polarizability (π^*) of the solvent used has a significant effect on the kinetics of hydrogenation reactions, with solvents with higher π^* improving the adsorption of non-polar reagents on to the catalytic surface leading to faster rates of reactions.[32] For the “neat” porous liquid catalytic system the cavities are most likely to be occupied by decene and decane rather than the solvent molecules, KPEGS, which is too large to diffuse into the cavities. Therefore, the rate of reaction observed for this system is not influenced by the π^* of the solvent as the species around the catalyst are non-polar and, hence, a slower reaction rate is observed when compared to the reactions completed in ethanol ($\pi^* = 0.51$), where the solvent can diffuse into the cavities, interact with the Pt nanoparticles and alter the rate of reaction.[32] While the expected increases in catalytic activity in the “neat” porous liquid was not observed, this may be due to the mild conditions employed. It possible that under more forcing conditions, for example higher temperatures and H_2 pressures, a more significant improvement of the catalytic activity would be observed for the neat porous liquid, because of a decrease in viscosity.[33-35]

Another important factor in the application of a catalyst, particularly industrially, is its recyclability. In this regard, a number of properties of this Type I porous liquid, including its non-volatility and thermal stability, means that this system could potentially be recycled by a simple distillation of the products. To test this hypothesis, the Pt@HS–SiO_2 PL(KPEGS) system was recycled, for the hydrogenation of 1-decene, by drying the reaction mixture under vacuum at 40 °C overnight between each reaction. It was found that this catalytic system could be used at least three times with no loss in the catalytic activity (Table 2).

Table 2. Recyclability of the Pt@HS–SiO_2 PL(KPEGS) system for the hydrogenation of 1-decene.[a]

Cycle	1st	2nd	3rd
Conversion of 1-decene (%)[b]	97.8	99.3	98.4

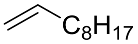
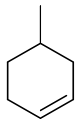
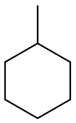
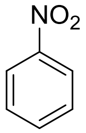
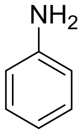
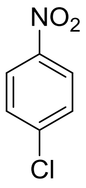
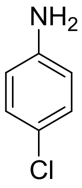
[a] Conditions: 5 mg Pt@HS–SiO_2 (or equiv.), 1-decene (0.5 mmol), 40 °C, 1 atm H_2 for 5 h.

[b] Conversion were determined by GC.

Hydrogenation of other substrates

The reaction protocol was further extended to include other substrates to explore the scope of these catalytic systems for hydrogenation reactions (Table 3). For all substrates studied, the activity of the different catalytic systems followed the general trend observed for 1-decene, with the slowest rate occurring for the Pt@HS–SiO_2 PL(KPEGS) system. There was complete selectivity to the desired hydrogenation product for 1-decene and 4-methylcyclohexene with the four catalytic systems (Table 3, entries 1–8). However, for the hydrogenation of nitrobenzene, side products were detected, to varying degrees, for all catalytic systems except for Pt@HS–SiO_2 (Table 3, entries 10–12). This was most significant for the Pt@HS–SiO_2 PL(KPEGS) system where, despite a conversion of 46%, the selectivity towards aniline, the desired product, was only 51% (Table 3, entry 12). These side products included *N*-phenylhydroxylamine, nitrosobenzene and azoxybenzene, all of which are known intermediates of the hydrogenation of nitroarenes.[36] The presence of these intermediates is therefore, a result of the slower reaction rates observed for the OS–(Pt@HS–SiO_2) and Pt@HS–SiO_2 PL catalysts.

Table 3. Hydrogenation of various substrates by the different catalytic systems.[a]

Entry	Substrate	Catalyst	Solvent	Time (h)	Product	Yield (%)[b] (Selectivity, %)[c]
1		Pt@HS–SiO_2	EtOH	0.5	$C_{10}H_{22}$	90.4
2		OS–(Pt@HS–SiO_2)	EtOH	1.5		94.2
3		Pt@HS–SiO_2 PL	EtOH	1.5		90.8
4		Pt@HS–SiO_2 PL	KPEGS	5.0		88.4
5		Pt@HS–SiO_2	EtOH	1.0		94.9
6		OS–(Pt@HS–SiO_2)	EtOH	7.0		94.2
7		Pt@HS–SiO_2 PL	EtOH	7.0		85.9
8		Pt@HS–SiO_2 PL	KPEGS	24		81.6
9		Pt@HS–SiO_2	EtOH	3.0		89.7
10		OS–(Pt@HS–SiO_2)	EtOH	24		87.4 (88)
11		Pt@HS–SiO_2 PL	EtOH	24		95.9 (93)
12		Pt@HS–SiO_2 PL	KPEGS	24		23.7 (51)
13		Pt@HS–SiO_2	EtOH	3.0		92.7
14		Pt@HS–SiO_2 PL	EtOH	24		26.2 (52)
15		Pt@HS–SiO_2 PL	KPEGS	24		8.5

[a] Conditions: 5 mg Pt@HS–SiO_2 (or equiv.), 1-decene (0.5 mmol), 40 °C, 1 atm H_2.

[b] Yields were determined by GC.

[c] Selectivity relative to converted substrate quoted towards the product illustrated, calculated when additional products were detected by GC. In all other instances, the selectivity was 100%.

One of the major difficulties often encountered during the hydrogenation of halonitrobenzenes is a poor selectivity towards the reduction of the nitro-group, with dehalogenation often occurring as an undesirable side reaction.[36-37] For the reduction of 4-chloronitrobenzene, both the Pt@HS–SiO_2 and Pt@HS–SiO_2 PL showed complete selectivity towards reduction of the nitro-group, with no dehalogenation products observed (Table 3, entries 13–15). When this reaction was completed by the Pt@HS–SiO_2 PL catalyst in ethanol, however, the selectivity towards 4-chloroaniline was only 52%, with two additional products detected (See supporting information). The formation of these side products is most likely due to a reaction between an intermediate and ethanol.[38] Significantly, when the Pt@HS–SiO_2 PL(KPEGS) system was utilised for the same reaction no side products were detected (Table 3, entry 15). Therefore, completing this reaction in a "neat" porous liquid system improved the selectivity as there was no ethanol with which the intermediates could react. Additionally, all hydrogenation reactions were completed at 40 °C, which is well below the melting point of 4-chloronitrobenzene (*ca* 84 °C). Despite the higher melting point and absence of a conventional solvent, the Pt@HS–SiO_2 PL(KPEGS) system was still capable of catalysing the hydrogenation of 4-chloronitrobenzene. The PEGS-based canopy was capable of dissolving 4-chloronitrobenzene, enabling the diffusion of the reagent to the catalyst.

The application of a "neat" porous liquid system could therefore, enable a range of catalytic reactions to be completed at lower temperatures without the addition of a conventional solvent, potentially reducing undesirable side reactions and improving selectivity. While the Type I porous liquids reported so far have all been based around a hollow silica sphere, the conceivable scope of these systems is vast, particularly with respect to potential catalysts.[4-5] These systems could be readily tailored in terms of the catalyst, shell material and corona-canopy and so it should be possible to design systems for specific reactions. Clearly also, although beyond the scope of the present paper, different porous liquids could be easily combined to catalyse sequential reactions, perhaps even combining otherwise incompatible catalysts.[39-40] We have operated only at moderate pressures. However, given the enhanced solubility of gases in porous liquids, additional scope exists for reactions with gaseous reagents.[3-4, 10]

Conclusions

In summary, we have demonstrated for the first time the applicability of porous liquids as catalysts. In this study we investigated the hydrogenation of several different reagents under mild conditions. The Pt@HS-SiO_2 PL catalyst in ethanol was found to be most active, with respect to the concentration of platinum, for the hydrogenation of 1-decene compared to Pt@HS–SiO_2 and OS–(Pt@HS–SiO_2). However, the reaction rate slowed when completed in a “neat” porous liquid system due to the high viscosity of the system. For the hydrogenation of 4-chloronitrobenzene, the “neat” porous liquid system was found to have complete selectivity towards 4-chloroaniline, which was a significant improvement compared to the 52% selectivity for the same reaction completed in ethanol. Additionally, it was found that the “neat” porous liquid system could be recycled at least twice with no loss in catalytic activity for the hydrogenation of 1-decene.

This study provides the first step to improving our understanding of the utilisation of porous liquids for a range of applications. However, further research is required to fully explore the catalytic applicability of these systems.

Experimental

Materials

Dodecane, mesitylene, nitrobenzene (all Merck), poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt (KPEGS), 4-methylcyclohexene (both Sigma Aldrich), Celite 545, *n*-heptane (both VWR), 4-chloronitrobenzene (Fluka), 1-decene (Alfa Aesar), ethanol (UChem) and hydrogen gas (High purity, BOC) were used as received.

Preparation of Pt-based catalysts

The Pt-based catalysts were prepared and characterised as previously reported.[13]

General procedure for the catalytic hydrogenation reactions

Typically, a mixture of the catalyst (5 mg Pt@HS–SiO_2, 6 mg OS–(Pt@HS–SiO_2) or 50 mg Pt@HS–SiO_2 PL) in ethanol (5 mL) was flushed with H_2 and then stirred under an atmosphere of H_2 at 40 °C for 1 hour to activate the catalysts prior to the reaction. The substrate (0.5 mmol) and internal standard (20 µL) were added and the mixture was stirred at 40 °C under an atmosphere of H_2 (balloon) for the desired length of time. The workup was conducted in air. For the solid catalysts (Pt@HS–SiO_2 and OS–(Pt@HS–SiO_2)) the reaction mixture was centrifuged to remove the catalyst. For the reactions utilising Pt@HS–SiO_2 PL as the catalyst, the reaction mixture was passed through a plug of Celite to remove the porous liquid.

For reactions completed in the "neat" porous liquid, a mixture of Pt@HS–SiO_2 PL (50 mg) in KPEGS (0.45 g) was dried under vacuum at 40 °C overnight before backfilling with H_2. The catalyst was activated by stirring the solution at 40 °C under an atmosphere of H_2 for 1 hour prior to use. The substrate (0.5 mmol) and standard (20 µL) were added and the solution was stirred at 40 °C under an atmosphere of H_2 (balloon) for the desired length of time. The reaction mixture was then dispersed in ethanol (~5 mL) in air and a sample was passed through a plug of Celite to remove the catalyst. An external standard was used for reactions involving 1-decene and 4-chloronitrobenzene.

The reaction mixtures were analysed by either Gas Chromatography-Flame Ionisation Detector (GC-FID, Shimadzu GC 2010 Plus Gas Chromatograph) or Gas Chromatography-Mass Spectrometry (GC-MS, Shimadzu GCMS-QP2010 Gas Chromatograph). The standards used were as follows; mesitylene for 1-decene, *n*-heptane for 4-methylcyclohexene, and dodecane for both nitrobenzene and 4-chloronitrobenzene.

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References

[1] N. O'Reilly, N. Giri, S. L. James, *Chem. - Eur. J.* **2007**, *13*, 3020-3025.
[2] S. L. James, *Adv. Mater.* **2016**, *28*, 5712-5716.
[3] N. Giri, M. G. Del Popolo, G. Melaugh, R. L. Greenaway, K. Ratzke, T. Koschine, L. Pison, M. F. C. Gomes, A. I. Cooper, S. L. James, *Nature* **2015**, *527*, 216-221.
[4] J. S. Zhang, S. H. Chai, Z. A. Qiao, S. M. Mahurin, J. H. Chen, Y. X. Fang, S. Wan, K. Nelson, P. F. Zhang, S. Dai, *Angew. Chem., Int. Ed.* **2015**, *54*, 932-936.
[5] T. Shi, Y. Zheng, T. Wang, P. Li, Y. Wang, D. Yao, *ChemPhysChem* **2018**, *19*, 130-137.
[6] W. Shan, P. F. Fulvio, L. Kong, J. A. Schott, C.-L. Do-Thanh, T. Tian, X. Hu, S. M. Mahurin, H. Xing, S. Dai, *ACS Appl. Mater. Interfaces* **2018**, *10*, 32-36.
[7] M. Costa Gomes, L. Pison, C. Červinka, A. Padua, *Angew. Chem., Int. Ed.* **2018**, *57*, 11909-11912.

[8] S. Liu, J. Liu, X. Hou, T. Xu, J. Tong, J. Zhang, B. Ye, B. Liu, *Langmuir* **2018**, *34*, 3654-3660.

[9] P. Li, H. Chen, J. A. Schott, B. Li, Y. Zheng, S. M. Mahurin, D.-e. Jiang, G. Cui, X. Hu, Y. Wang, L. Li, S. Dai, *Nanoscale* **2019**, *11*, 1515-1519.

[10] F. Zhang, F. Yang, J. Huang, B. G. Sumpter, R. Qiao, *J. Phys. Chem. B* **2016**, *120*, 7195-7200.

[11] A. I. Cooper, *ACS Central Science* **2017**, *3*, 544-553.

[12] A. Bavykina, A. Cadiau, J. Gascon, *Coordination Chemistry Reviews* **2019**, *386*, 85-95.

[13] E. B. Hemming, A. F. Masters, T. Maschmeyer, *Chem. Commun.* **2019**, *55*, 11179-11182.

[14] H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103-151.

[15] J. G. deVries, C. J. Elsevier, *The Handbook of Homogeneous Hydrogenation*, WILEY-VCH, Weinheim, **2006**.

[16] D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621-6686.

[17] E. E. Gonzo, M. Boudart, *J. Catal.* **1978**, *52*, 462-471.

[18] H.-B. Pan, C. M. Wai, *New J. Chem.* **2011**, *35*, 1649-1660.

[19] D. Li, J. R. Dunlap, B. Zhao, *Langmuir* **2008**, *24*, 5911-5918.

[20] S. Kidambi, M. L. Bruening, *Chem. Mater.* **2005**, *17*, 301-307.

[21] R. Roa, W. K. Kim, M. Kanduč, J. Dzubiella, S. Angioletti-Uberti, *ACS Catal.* **2017**, *7*, 5604-5611.

[22] J.-F. Zhu, G.-H. Tao, H.-Y. Liu, L. He, Q.-H. Sun, H.-C. Liu, *Green Chem.* **2014**, *16*, 2664-2669.

[23] R. J. Madon, J. P. O'Connell, M. Boudart, *AIChE J.* **1978**, *24*, 904-911.

[24] M. A. Mahmoud, R. Narayanan, M. A. El-Sayed, *Acc. Chem. Res.* **2013**, *46*, 1795-1805.

[25] T. S. Rodrigues, A. G. M. da Silva, P. H. C. Camargo, *J. Mater. Chem. A* **2019**, *7*, 5857-5874.

[26] P. Kuzmič, *Anal. Biochem.* **1996**, *237*, 260-273.

[27] M. Boudart, *Chem. Rev.* **1995**, *95*, 661-666.

[28] S. Kozuch, J. M. L. Martin, *ACS Catal.* **2012**, *2*, 2787-2794.

[29] W. T. Ford, J. Lee, M. Tomoi, *Macromolecules* **1982**, *15*, 1246-1251.

[30] I. Mita, K. Horie, *J. Macromol. Sci., Part C* **1987**, *27*, 91-169.

[31] D. Behar, P. Neta, C. Schultheisz, *J. Phys. Chem. A* **2002**, *106*, 3139-3147.

[32] M. Khodadadi-Moghaddam, A. Habibi-Yangjeh, M. R. Gholami, *Appl. Catal., A* **2008**, *341*, 58-64.

[33] Y. Mei, Y. Lu, F. Polzer, M. Ballauff, M. Drechsler, *Chem. Mater.* **2007**, *19*, 1062-1069.

[34] P.-T. Huang, Y.-N. Chen, K.-C. Chen, S.-H. Wu, C.-P. Liu, *J. Mater. Chem. A* **2019**, *7*, 20919-20925.

[35] Y. Stetsyshyn, K. Awsiuk, V. Kusnezh, J. Raczkowska, B. R. Jany, A. Kostruba, K. Harhay, H. Ohar, O. Lishchynskyi, Y. Shymborska, Y. Kryvenchuk, F. Krok, A. Budkowski, *Applied Surface Science* **2019**, *463*, 1124-1133.

[36] P. Lara, K. Philippot, *Catal. Sci. Technol.* **2014**, *4*, 2445-2465.

[37] G. Fan, W. Huang, C. Wang, *Nanoscale* **2013**, *5*, 6819-6825.

[38] D. He, X. Jiao, P. Jiang, J. Wang, B.-Q. Xu, *Green Chem.* **2012**, *14*, 111-116.

[39] A. F. Fois, A. Yap, A. F. Masters, T. Maschmeyer, *Top. Catal.* **2008**, *48*, 153-157.

[40] A. Yap, A. F. Masters, T. Maschmeyer, in *Handbook of Green Chemistry, Green Processes, Green Nanoscience, Vol. 8* (Ed.: P. T. Anastas), Wiley-VCH Weinheim, Germany, **2012**, pp. 137-163.

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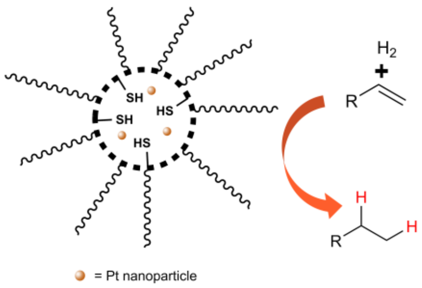

Neat Pt@HS-SiO_2 Porous liquid

Porous liquids for catalysts: Platinum nanoparticles encapsulated within a Type I porous liquid were successfully employed for the first time as hydrogenation catalysts. In addition, this work explored the effect of each component of the corona-canopy on the catalytic activity.

Keywords: Heterogeneous catalysis, Hydrogenation, Mesoporous material, Platinum, Porous liquids