Hydrogenation in Ionic Liquids

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1. Introduction

One of the principal present-day challenges facing the field of transition metal catalysis is the efficient recycling and reuse of catalysts and ligands. The use of ILs is rapidly advancing in this discipline. Due to their tunable physico-chemical properties, which differ markedly from those of conventional organic and aqueous media, ILs can provide a means of catalyst immobilization. The non-nucleophilic and weakly co-ordinating nature of many classes of ionic liquid provides an inert reaction medium that can extend the lifetime of a catalyst. Recyclability of the catalyst system is a key attribute of IL media and it is this enhancement of catalyst performance that is driving research in this field. Low-polarity compounds, for example diethyl ether and *n*-hexane, are poorly soluble in common ILs, providing a suitable accompanying solvent for biphasic catalysis. The positive aspects of homogeneous and heterogeneous catalysis are combined using a biphasic system, in which the catalyst resides in the IL, but the substrates/products are retained in the alternate phase. Thus, the biphasic system provides a cost-effective way to successfully separate the desired product by simple decantation, leaving the catalyst immobilised in the IL and ready for reuse. Product isolation is often simplified even in monophasic catalysis if the substrate is soluble in the IL medium, but the product can be separated by simple extraction or distillation, due to the low vapour pressure of the IL. The reduced polarity of the hydrogenated products in comparison with the substrate can also be exploited for separation from the IL/catalyst phase. Increasing the difference in polarity between the IL and the hydrogenated product can also render the product insoluble in the IL, thus allowing facile decantation of the product from the IL, leaving the IL/catalyst phase ready for the next reaction.

Research into catalytic hydrogenations in ILs began in 1995 with the almost simultaneous work of Chauvin[1] and Dupont.[2] Since then this field has been extended from conventional hydrogenation using transition metal catalysts to transfer hydrogenation and the effect of nanoparticles on hydrogenation reactions in ILs. Supported ionic liquid catalysis (SILC) is also a relatively new field. Using this method, the added benefit of selectivity provided by the homogeneous catalyst can be combined with the attributes of heterogeneous biphasic catalysis. The homogeneous catalyst is, in effect, immobilised on a heterogeneous support. One of the first investigations in this area was carried out by Mehnert *et al.*[3] in 2002, with a flurry of papers ensuing from 2007-2009.

It is intended that this chapter should cover recent progress in hydrogenation reactions carried out in ILs. Wasserscheid and Schulz[4] contributed a chapter in 'The Handbook of Homogeneous Hydrogenation' covering homogeneous hydrogenation in ILs which covers

advances up to 2005. More recent summaries of hydrogenation in ILs can be found in 'Ionic Liquids in Synthesis' as part of the chapter on Transition Metal Catalysis in Ionic Liquids[5] and within several reviews covering the wider area of IL catalysis.[6, 7, 8] Moreover, outside the scope of this chapter is the concept of tailored ILs used in hydrogenation reactions, which was covered in 2008 by Sebesta *et al*.[9] For each hydrogenation reaction reviewed in this chapter, the catalyst and IL are noted, together with the genre of substrate. Particular consideration is paid to conversion and turnover numbers obtained using ILs as alternatives to commonly used volatile organic solvents. A section describing kinetic and thermodynamic studies of reactions in ILs is also presented. ILs are not always the preferred choice of solvent, and cases where the IL was found to be less effective than a conventional molecular solvent are included. Throughout this chapter abbreviations used are as follows:

[emim]: 1-ethyl-3-methylimidazolium, [bmim]: 1-*n*-butyl-3-methylimidazolium, [omim]: 1-*n*-octyl-3-methylimidazolium, [dmim]: 1-*n*-decyl-3-methylimidazolium, [dodecylmim]: 1-*n*-dodecyl-3-methylimidazolium, [bdmim]: 1-*n*-butyl-2,3-dimethylimidazolium, [TEA]: tetraethylammonium, [TBA]: tetrabutylammonium, [mbpy]: 4-methyl-*N*-butyl-pyridinium, [DAMI]: 1,3-di(*N*,*N*-dimethylaminoethyl)-2-methylimidazolium, [C$_8$Py]: *N*-octylpyridinium, [BMPL]: *N*-butyl-*N*-methylpyrrolidinium, [B3MPYR]: *n*-butyl-3-methylpyridinium, [bmmim]: 1-*n*-butyl-2,3-dimethylimidazoliium, [bmimOH]: hydroxyl-functionalized butyl-3-methylimidazolium, [BF$_4$]: tetrafluoroborate, [PF$_6$]: hexafluorophosphate, [NTf$_2$]: trifluoromethanesulfonimide, [OTf]: triflate, [N(CN)$_2$]: dicyanamide, [NO$_3$]: nitrate, [HSO$_4$]: hydrogen sulphate, [EtOSO$_3$]: ethyl sulphate, [BuOSO$_3$]: butyl sulphate, [HexOSO$_3$]: hexyl sulphate, [OctOSO$_3$]: octyl sulphate, TOF: turn over frequency, TON: turn over number, BINAP: 2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl, COD: 1,5-cyclo-octadiene, ee: enantiomeric excess, CIL: chiral ionic liquid, scCO$_2$: supercritical carbon dioxide, IPA: isopropanol, SILC: supported ionic liquid catalysts, SILP: supported ionic liquid phase, SSILP: structured supported ionic liquid-phase, SCILL: solid catalyst with ionic liquid layer, CTH: catalytic transfer hydrogenation, OSN: organic solvent nanofiltration, TSIL: task-specific ionic liquid, COE: cyclooctene, COA: cyclooctane, PVP: poly(*N*-vinyl-2-pyrrolidone), [N$_{6222}$]: triethylhexylammonium, [N$_{22212}$]: triethyldodecylammonium, [N$_{22214}$]: triethyltetradecylammonium, MAA: methyl acetoacetate, Ts-DPEN: *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine, [P$_{14,6,6,6}$]: trihexyltetradecylphosphonium, [P$_{4,4,4,4}$]: tetrabutylphosphonium, [P1,*i*4,*i*4,*i*4]: tri-*iso*-butylmethylphosphonium, ECOENG 500™: Peg-5 cocomonium methosulfate.

2. Kinetic and Thermodynamic properties:

 A major advantage of ionic liquids as the solvent in hydrogenation reactions is the ability to fine tune the properties of the solvent by altering the structure. Hence it becomes very important for a chemist to investigate the kinetic and thermodynamic aspects of the reactions. Although only few detailed studies of the kinetics of hydrogenation reactions in ionic liquids have been reported, from available results it can be shown that the reaction kinetics, product selctivity, reaction yields, TOFs of catalysts are greatly influenced by the cations and anions of ionic liquids and their concentration in the reaction system.

It is also important to compare the trends of H$_2$ gas solubilities in ionic liquids and molecular solvents, while studying reaction kinetics. Table 1 summarizes the H$_2$ solubilities in various solvents, along with densities and viscosities. [10]

Solvent	Henry's Constant, k_H/MPa[a]	10^3[H$_2$] (M)	Density (g/Ml)	Viscosity (cP)	Ref.
Water[b]	6.8×10^3	0.81	0.9982[11]	0.89[c,12]	[13]
Methanol[b]	6.6×10^2	3.75	0.7914[11]	0.55[c,12]	[14]
Ethanol[b]	5.9×10^2	2.98	0.7893[11]	1.06[c,12]	[14]
Toluene[b]	2.69×10^2	3.50	1.4961[11]	0.45[b,12]	[14]
Benzene[b]	4.47×10^2 (4.39×10^2)	2.54 (2.57)	0.878[11]	0.60[c,12]	[10,13]
Cyclohexane[b]	2.57×10^2 (2.55×10^2)	3.63 (3.66)	0.777[11]	1.62[b,12]	[10,13]
[bmim][BF$_4$][b]	5.8×10^2 (1.63×10^2)	0.86[d] (3.0)	1.12[15]	219[c,15]	[10,16]
[bmim][PF$_6$][b,c]	6.6×10^2 (5.38×10^2)	0.73[d] (0.88)	1.363[15]	450[c,15]	[10,16]
[bmim]Tf$_2$N][c]	4.5×10^2	0.77[d]	1.433	69[c,15]	[10]
[bm$_2$im][Tf$_2$N][c,e]	3.8×10^2	0.86[d]	1.421	97.1[c,17]	[10]
[bupy][Tf$_2$N][c,f]	3.9×10^2	0.89[d]	1.449	57[c,18]	[10]
[bmpy][Tf$_2$N][c,g]	3.7×10^2	0.90[d]	1.387	85[c,19]	[10]
[bmim][SbF$_6$][c]	4.9×10^2	0.93[d]	1.699	95	[10]
[bmim][CF$_3$CO$_2$][c]	4.9×10^2	0.98[d]	1.198	73[b,20]	[10]
[hmim][BF$_4$][c,h]	5.7×10^2	0.79[d]	1.14[21]	314.0[b,22]	[10]
[omim][BF$_4$][c]	6.4×10^2	0.62[d]	1.106	135.0[b,22]	[10]
[bmim][CF$_3$SO$_3$][c]	4.6×10^2	0.97[d]	1.290[20]	90[b,20]	[10]
[P(C$_6$H$_{13}$)$_3$(C$_{14}$H$_{29}$)] [PF$_3$(C$_2$F$_5$)$_3$][c]	0.7×10^2	1.84[d]	1.196	498[b,21]	[10]

[a] $k_H = P_{H_2}/X_{H_2}$, where the partial pressure of hydrogen is expressed in MPa. [b] 293 K.

[c] 298 K. [d] Calculated from the solubility under 10.1 MPa, supposing that it changes linearly with the partial pressure. [e] [bm$_2$im]$^+$ = 1,2-Dimethyl-3-butylimidazolium.

[f] [bupy]$^+$ = N-Butylpyridinium. [g] [bmpy]$^+$ = N-Butyl-N-methylpyrrolidinium.

[h] [hmim]$^+$ = 1-Hexyl-3-methylimidazolium.

Table 1. Solubility of H$_2$ in water, organic solvents and ionic liquids, at 0.101 MPa (1 atm)

Table 1 shows that H$_2$ solubility in ionic liquids is typically much lower than in molecular solvents, which can lead to low reaction rates. Mass transfer effects associated with low gas solubility play a key role in hydrogenation, and may be critical when processes such as catalytic asymmetric hydrogenation are carried out in ionic liquids. Blackmond and co-workers[23] described in detail the key kinetic parameters affecting enantioselectivity in asymmetric hydrogenations, namely the concentration of molecular H$_2$ in the liquid phase, itself related to the pressure of the system, the rate of mass transfer and the intrinsic kinetics of competing reactions. Blackmond also determined that in cases where the enantioselectivity decreases with increasing H$_2$ pressure, the system can benefit from H$_2$-starved conditions. In other words a diffusion-limited regime could be beneficial because the rate of consumption of H$_2$ by the reaction would be higher than the rate of diffusion of H$_2$ in the liquid phase. For other reactions requiring high H$_2$ concentrations, low solubility problems can be solved by carrying out reactions at elevated pressures, which raises the H$_2$ solubility.[16] Interestingly in many cases product selectivities are achieved due to solubility

differences between the intermediate and fully hydrogenated products.[24] For example, in the partial hydrogenation of 1,3-butadiene using Pd(0) nanoparticles in [bmim][BF₄], it was observed that 1,3-butadiene is at least three times as soluble in the ionic liquid as the intermediate butenes, inhibiting further hydrogenation and leading to product selectivity.[25]

  The high viscosity of ionic liquids can also be a limitation for in hydrogenation reactions as diffusion of reactants through the medium is restricted. Temperature also plays an important role in hydrogenation, following the usual trend that at higher temperatures a high reaction rate is observed. However, the viscosity of the ionic liquid also decreases as temperature increases, facilitating mass transport of the reactants.

The choice of the anion is another crucial aspect of selecting an ionic liquid for hydrogenation studies. For example, in heterogeneous catalytic hydrogenations, the reaction occurs at the surface of the catalyst and the solvent cannot directly affect the energy of the activated complex. Nevertheless, solvent polarity (which varies from one anion to another) still plays an important role because polar solvents facilitate the adsorption of nonpolar substrates on the catalyst, while non-polar solvents have the opposite effect.[26] Gas solubility *(vide infra)* also varies with the anion, and it can be seen from Table 1 that ionic liquids with ditriflimide $[NTf_2^-]$ as the counter anion have greater H_2 solubility than ILs with tetrafluoroborate $[BF_4^-]$. Anions can also have more specific interactions with the catalyst, which can control the conversion and enantiomeric excess of the product.[27]

Kinetic studies into the heterogeneous catalytic hydrogenation of cyclohexene in ionic liquid-alcohol mixtures have also been carried out by Khodadadi-Moghaddam *et al.*[28] with a Pt/Al_2O_3 catalyst in the IL, 2-hydroxy ammonium formate and the alcohols, methanol, ethanol or propan-2-ol at 25 °C. Mass transfer limitation effects of H_2 solubility and solvent polarity on reaction rates were studied. The rotation speed of the reaction mass was used to determine the mass transfer barriers as the hydrogen transfers from gas phase to liquid phase. It was found that there is a linear relationship between observed rate constant and rotation speed up to 700 rpm, after which the rate constant becomes independent of the rotation speed up to 1250 rpm, which suggests that the reaction is under kinetic control and takes place without external mass transfer limitations. The H_2 solubility was measured for the IL-alcohol mixtures which shows that increase in mole fraction of the IL increases the solubility and ultimately in pure IL the solubility was maximum (0.01 mL of H_2 gas in 20 g IL at 25 °C and 1 atm). A rate expression was derived considering the RDS as dissociative adsorption of hydrogen on catalyst as follows,

$$K_{obs} = K_{app} \left(\frac{H_{H_2}}{H_T} \right) C_{H_2}$$

Where k_{obs} = observed rate constant

k_{app} = apparent rate constant (incudes other concentrations and parameters)

H_{H_2} = Henry's law constant for H_2 in the solvent.

H_T = Henry's law constant for the transition state.

C_{H_2} = Concentration of H_2 in liquid phase.

Based on this equation the rate constant was found to be proportional to H_2 concentration in liquid phase and the reaction was first order with respect to H_2. (Figure 1)
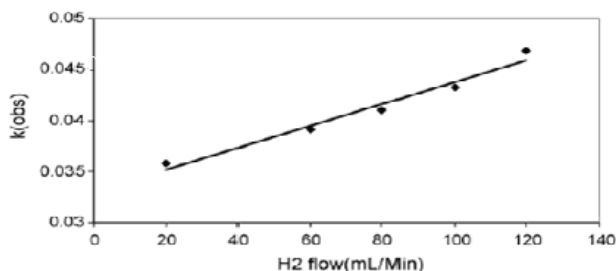
Fig. 1. Dependence of k_{obs} on hydrogen flow in ionic liquid at 25 °C (solvent 20 g, cyclohexene 0.1 g, rotation speed 1250 rpm and catalyst 0.02 g).

Furthermore the rate constants were calculated for three mixtures of IL-alcohol with increasing mole fractions of the IL (Table 2). The results indicated that with increasing mole fraction of IL, π* (dipolarity/polarizability) increases, leading to an increase in rate constant. In heterogeneous catalysis the reaction occurs on the catalyst surface, and polar solvents facilitate non-polar substrate adsorption on the catalyst.[26] Hence, Kishida linked the increase in rate constants to increased solvent polarity.

X_{IL}	IL-methanol mixture					IL-ethanol mixture					IL-propan-2-ol mixture				
	$k \times 10^{-2}$ $s^{-1} g^{-1}$	E^N	Π^*	β	α	$k \times 10^{-2}$ $s^{-1} g^{-1}$	E^N	Π^*	β	α	$k \times 10^{-2}$ $s^{-1} g^{-1}$	E^N	Π^*	β	α
0.0	0.80	0.76	0.57	0.81	1.16	1.03	0.65	0.51	0.91	0.97	0.26	0.54	0.49	1.07	0.74
0.1	1.20	0.88	0.71	0.82	1.31	1.17	0.84	0.63	0.91	1.27	0.35	0.80	0.56	1.04	1.23
0.2	2.43	0.89	0.80	0.80	1.25	1.29	0.85	0.68	0.93	1.27	0.50	0.81	0.60	1.02	1.24
0.3	2.97	0.89	0.87	0.78	1.20	2.41	0.85	0.72	0.91	1.22	0.62	0.82	0.66	0.98	1.21
0.4	3.31	0.89	0.88	0.77	1.20	3.17	0.85	0.79	0.87	1.18	0.97	0.82	0.71	0.95	1.18
0.5	3.60	0.89	0.95	0.74	1.15	3.24	0.86	0.81	0.89	1.18	1.32	0.83	0.76	0.91	1.16
0.6	4.03	0.89	1.01	0.67	1.10	3.24	0.85	0.89	0.81	1.12	1.59	0.84	0.80	0.89	1.15
0.7	4.23	0.89	1.04	0.66	1.09	3.12	0.87	0.94	0.79	1.11	3.00	0.84	0.87	0.83	1.11
0.8	4.62	0.90	1.05	0.67	1.11	3.30	0.87	1.01	0.72	1.07	5.73	0.86	0.95	0.76	1.09
0.9	5.19	0.90	1.03	0.71	1.11	3.31	0.89	1.04	0.71	1.08	6.59	0.88	0.98	0.74	1.10
1.0	7.25	0.89	1.15	0.59	1.01	7.25	0.89	1.15	0.59	1.01	7.25	0.89	1.15	0.59	1.01

K = Rate constant, E^N = Normalized polarity parameter, Π^* = Dipolarity/polarizability,
β = Hydrogen-bond acceptor basicity, α = Hydrogen-bond donor acidity.

Table 2. First-order rate constant of the reaction in the RTIL mixed with methanol, ethanol or propan-2-ol, together with solvatochromic parameters for the media

Similarly Fonseca et al.[29] carried out hydrogenation of 1-decene on Ir(0) nanoparticles in [bmim][PF$_6$] at 75 °C with varying pressures of H$_2$. They observed an increase in initial reaction rates with increase in H$_2$ pressures upto 4 atm, which was expected. However, above 4 atm the reaction rate is independent of the H$_2$ pressure, which can be ascribed to the surface saturation of the Ir(0) nanoparticles with H$_2$ gas. Thus at elevated pressures, (> 4

atm), a monomolecular mechanism is proposed (Figure 2) for hydrogenation occurring at the surface of catalytic nanoparticles within the IL.
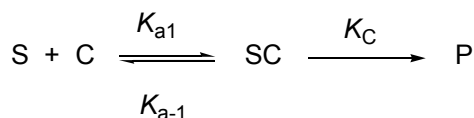
$$S + C \; \underset{K_{a-1}}{\overset{K_{a1}}{\rightleftharpoons}} \; SC \; \overset{K_C}{\longrightarrow} \; P$$

Fig. 2. Monomolecular mechanism

Where S = substrate, C = activated catalyst, P = final product, K_a = adsorption rate constant, K_{a-1} = desorption rate constant and K_c = catalytic rate constant.

When K_c was calculated at various pressures, it was found that for pressures ≥ 4 atm, K_c is almost identical (0.45 ± 0.06 min^{-1}) and at low pressures (2 atm) reaction rates decreased significantly, indicating that below 4 atm the hydrogenation is controlled by a mass transfer process.

In the case of fibre-supported Rh catalysts the rate of homogeneous hydrogenation was found to be dependent on the ligand to metal ratio and acid to IL ratio. Ruta *et al.*[30] when carried out gas phase hydrogenation of 1,3-butadiene using SMF$_{Inconel}$ supported [Rh(nbd)Cl]$_2$ catalyst, PPh$_3$ as ligand and an acid (H$_3$PO$_4$ or HBF$_4$) in ionic liquids ([bmim][BF$_4$] and [bmim][PF$_6$]) , found that with [bmim][BF$_4$]:HBF$_4$ of 0.5 and PPh$_3$:Rh of 8, the reaction was fast *i.e.* 285 h^{-1}. Further investigation showed that addition of excess acid favoured the formation of a cationic dihydride species (Figure 3).
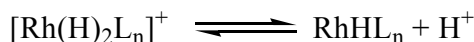
$$[Rh(H)_2L_n]^+ \; \rightleftharpoons \; RhHL_n + H^+$$

Fig. 3. Acid equilibrium for cationic dihydride species

Excellent work was carried out by Kernchen *et al.*[24] in which the hydrogenation of 1,4-cyclooctadiene was performed using a [bmim][n-C$_8$H$_{17}$OSO$_3$] coated Ni catalyst in *n*-dodecane. This IL/ *n*-dodecane biphasic system allows effective partitioning of the intermediate (in this case cyclooctene) into the hydrocarbon layer, preventing over-reduction to cyclooctane. Table 3 depicts the values of partition coefficients of COD, COE and COA.

T in °C	K_N in (kg i/kg IL)/(kg i/kg *n*-dodecane) With i = COD, COE or COA		
	COD	COE	COA
20	0.30	0.25	0.20
50	0.37	0.31	0.25

Table 3. Nernst participation coefficients K_N for COD, COE and COA in biphasic system *n*-dodecane and ionic liquid [bmim][n-C$_8$H$_{17}$OSO$_3$]

For the hydrogenation of COD with uncoated Ni catalyst at 50 °C Kernchen obtained 40 % yield for COE (c.f. IL coated catalyst under the same conditions, 70 % yield). The K_N values from Table 3 offer a reasonable explanation for the results obtained. The low solubility of COE in the ionic liquid facilitates transfer to the n-dodecane layer and hence over-reduction is avoided. Further studies showed that the reaction follows first order kinetics with respect to COD and is zero order with respect to H$_2$ gas. An example of arene reductions by Rh

nanoparticles supported on an ionic liquid-like co-polymer was reported by *Zhao et al.*[31] In this case most of the intermediate dienes were found to be soluble in [bmim][BF$_4$] which was used as a solvent, hence hydrogenation did not stop at the diene and further hydrogenated products predominate. *Dyson et al.*[32] have also performed reductions of benzene, exploiting solubility differences using K$_2$PtCl$_4$/[*N*-octyl-3-picolinium][AlCl$_4$]. The group also put forward a mechanism to account for the superior activity of K$_2$PtCl$_4$ (99 % yield of cyclohexane, at 100 °C, 50 bar H$_2$ in 240 mins) over other catalysts screened (Figure 4) in which a trimetal face is coordinated by the aromatic π-system of benzene.
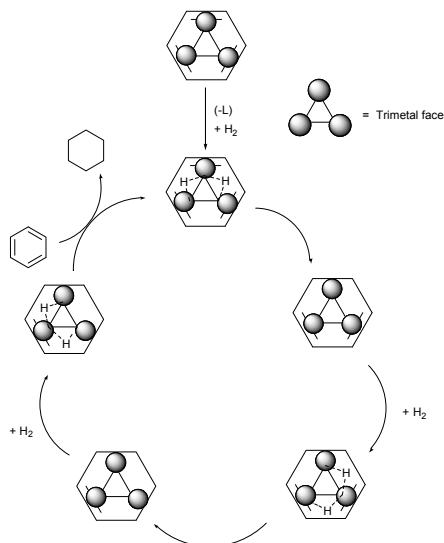

Fig. 4. The arene-exchange mechanism that could operate at a metal face

Interestingly when   *Silveira et al.*[33] studied the partial hydrogenation of benzene to cyclohexene using Ru(0) nanoparticles, under solvent-free conditions and in ionic liquids ([bmim][PF$_6$] and [bmim][BF$_4$]) at 75 °C and 4 atm H$_2$, it was found that in the absence of a solvent, the reactions were faster (Table 4). Similar results were observed for the reduction of cyclohexanone using Ir(0) nanoparticles[34] and for other arenes using Ir(0) and Rh(0) nanoparticles.[35] The authors indicate that the reactions in ionic liquids may have been slowed by mass transfer effects. Correspondingly, when the reduction of 1,3-butadiene was attempted using Pd(0) particles at 40 °C and 4 atm H$_2$[25] under solvent-free conditions, 1,3-butadiene was consumed in under 2 h, compared to 6 h when [bmim][BF$_4$] was used as the solvent.

Mass transfer limitations have been a major challenge in many ionic liquid-based hydrogenations. For example, even in the biphasic reduction of caffeate in [bmim][PF$_6$] and tetradecane although the initial reaction rate was high (880 mmol kg^{-1} h^{-1}), after 1 hour this decreased to 12.4 mmol kg^{-1} h^{-1}[36]. *Wolfson et al.*[37] have overcome this problem by addition of water in their biphasic asymmetric hydrogenation reactions which were carried out with 2-acetamidoacrylate using Rh-EtDuPHOS as a catalyst in [bmim][PF$_6$]. When the reaction was performed with the ionic liquid in isolation, no conversion was observed. However, when water was included as a cosolvent, the product was isolated in 68 % yield with 96 % ee, with a 50 % v/v ratio of ionic liquid to water giving optimal reaction rates (TOF ≈ 1000 h^{-1} at 20 °C and 5 bar H$_2$).

Entry	Medium	Substrate	t [h]	Conv. [%]	TON[a]	TOF [h-1][b]
1	-	1-hexene	0.7	> 99	500	714
2	[bmim][BF$_4$]	1-hexene	0.6	> 99	500	833
3	[bmim][PF$_6$]	1-hexene	0.5	> 99	500	1000
4	-	cyclohexene	0.5	> 99	500	1000
5	[bmim][BF$_4$]	cyclohexene	5.0	> 99	500	100
6	[bmim][PF$_6$]	cyclohexene	8.0	> 99	500	62
7	-	2,3-dimethyl-2-butene	1.2	76	380	316
8	-	benzene	5.5	90	450	82
9	[bmim][BF$_4$]	benzene	17.3	30	150	9
10	[bmim][PF$_6$]	benzene	18.5	73	365	20
11	[bmim][CF$_3$SO$_3$]	benzene	17.5	50	240	14
12	-	benzene[c]	2.0	> 99	250	125
13	-	toluene[c]	5.6	> 99	250	45
14	-	isopropylbenzene[c]	6.4	> 99	250	39
15	-	tert-butylbenzene[c]	14.1	> 99	250	18
16	-	anisole	18	< 1	-	-

[a] Turnover number TON = mol of hydrogenated product/mol of Ru.
[b] Turnover frequency TOF = TON/h. [c] Arene/Ru = 250.

Table 4. Hydrogenation of alkenes and arenes by Ru^0 nanoparticles under multiphase and solventless conditions (75 °C and 4 atm, constant pressure, substrate/Ru = 500)

While studying the asymmetric hydrogenation of acetophenone Fow et al.[38] investigated supported Ru and Rh-based catalysts containing either BINAP or chiraphos ligands immobilised in phosphonium ionic liquids, with the bases, K$_2$CO$_3$ and K$_3$PO$_4$ as additives. Fow proposed a kinetic model to rationalise the results of these experiments (Figure 5). For full details for catalysts structure and preparation see Fow et al.[38]
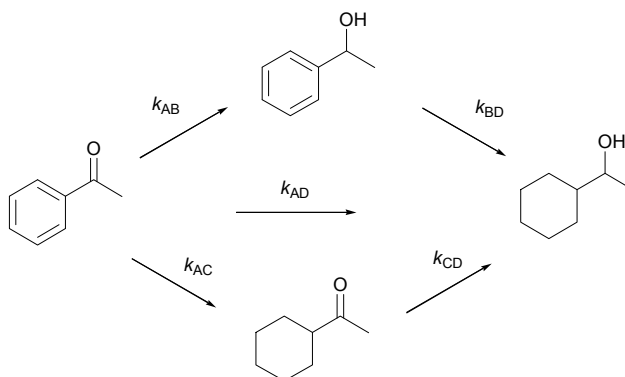

Fig. 5. Kinetic model for the reduction of acetophenone with supported catalysts.

Using a series of supported Ru and Rh catalysts immobilised in ionic liquids, reductions were carried out at between 30 and 80 °C (results Table 5) and rate constants were calculated (Table 6).

Catalyst	Temp. (°C)	Time (h)	Conv. (%)	Selectivity[a] (%)	ee[b] (%)	Configuration[b]
Ru/dec/PO$_4$	50	15	22	35	49	S
Ru/tos/CO$_3$	50	17	36	19	55	S
Rh/dec/PO$_4$	30	30	95	41	13	R
Rh/dec/PO$_4$	50	15	90	70	30[c]	R
Rh/dec/PO$_4$	80	4	100	45	5	R
Rh/dbp/PO$_4$	30	29	20	58	19	R
Rh/tos/CO$_3$	50	22	100	6	74	S
Rh(chi)/tos/CO$_3$	50	24	63	38	2	S

[a] Chemoselectivity to 1-phenylethanol, [b] Enantiomeric excess (ee) and configuration of 1-phenylethanol were determined by gas chromatography, [c] 49 % ee at 10 % conversion

Table 5. Conversion and selectivity in the hydrogenation of acetophenone

Catalyst	Temp (°C)	k_{AB} (h^{-1})	k_{AC} (h^{-1})	k_{BD} (h^{-1})	k_{CD} (h^{-1})	k_{AD} (h^{-1})	Ratio (k_{AB}/k_{AC})	Ratio ($k_{AB} + k_{CD})/(k_{AC} + k_{BD}$)
Rh/dec/PO$_4$	30	0.064	0.038	0.018	0.043	0.006	1.7	1.9
Rh/dec/PO$_4$	50	0.169	0.046	0.008	0.065	0.005	3.7	4.3
Rh/dec/PO$_4$	80	0.678	0.177	0.062	0.038	0.299	3.8	3.0
Rh/dbp/PO$_4$	30	0.185	0.099	0	0.391	0.036	1.9	5.8
Rh/tos/CO$_3$	50	0.136	0.117	0.137	0.017	0	1.2	0.6
Ru/dec/PO$_4$[a]	50	0.108	0.109	0.100	0.012	0.045	1.0	0.6
Ru/tos/CO$_3$[a]	50	0.044	0.145	0	0.356	0.036	0.3	2.8

[a] Catalyst deactivation was taken into account.

Table 6. Rate constants for the hydrogenation of acetophenone with supported catalysts

As expected the reaction rates are temperature dependent. A higher ratio for k_{AB}/k_{AC} supports the obtained selectivities of 2-phenylethanol. It was found that Rh/dec/PO$_4$ proved a more effective catalyst for the reduction at 50 °C in terms of reaction rate, conversion and selectivity. The activation energies calculated for reaction AB (42 kJmol^{-1}) were measured higher than reactions AC and BD (28 and 24 kJmol^{-1} respectively) which again supports the higher selectivities at high temperatures.
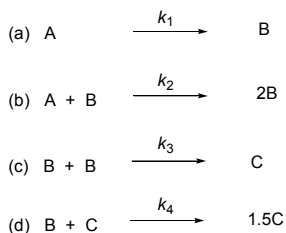
When chemoselective hydrogenation of cinnamaldehyde was carried out by Kume et al.[39] using Pd nanoparticles at 80 °C and 5 MPa of H$_2$, they found that the reaction which uses Pd nanoparticles immobilized on ionic liquid modified silica gel in m-xylene has high reaction rates than that of reactions with Pd(OAc)$_2$ immobilized in ionic liquids in terms of TOFs (Table 7). In case of Pd/SiO$_2$-IL (PF$_6$) the reaction took only 20 minutes for completion with TOF > 47,000 h^{-1} whereas the analogous reaction in [bmim][PF$_6$] using Pd(OAc)$_2$ as catalyst took 6 h to complete with TOF 18 h^{-1}. The increase in reaction rates are proposed to be due to the high surface area of the silica gel which promotes adsorption of substrate and H$_2$ on to the Pd nanoparticles. The low yields in cases when ionic liquids were used as the solvent were ascribed to low solubility of H$_2$ in the medium.

Run	Catalyst	Time	Yield (%)	TOF (h⁻¹)
1[b]	Pd/[bmim][Cl]	6 h	56.2	18
2[b]	Pd/[bmim][PF$_6$]	6 h	100	33
3[b]	Pd/[bmim][BF$_4$]	6 h	75.3	23
4[b]	Pd/[bmim][NO$_3$]	6 h	90.1	29
5[c]	Pd/SiO$_2$-IL[Cl]	20 min	20.7	270
6[d]	Pd/SiO$_2$-IL[PF$_6$]	20 min	100	> 47,000
7[e]	Pd/SiO$_2$-IL[BF$_4$]	20 min	70.8	24,260
8[e]	Pd/SiO$_2$-IL[NO$_3$]	20 min	100	> 33,000
9[e]	Pd/SiO$_2$	20 min	64.8	22,200

[a] Temperature 80 °C; H$_2$ 5 MPa; cinnamaldehyde 2.7 mmol; *m*-xylene 2 g, [b] Pd(OAc)$_2$ 0.0134 mmol; ionic liquid 5 mmol., [c] Pd 0.108 mg, [d] Pd 0.016 mg, [e] Pd 0.022 mg.

Table 7. Hydrogenation of cinnamaldehyde catalyzed by Pd catalyst

While discussing reaction rates, one has to consider the rates of formation of metal nanoparticles as well. When Scheeren *et al.*[40] studied the hydrogenation of cyclohexene by catalyst precursor PtO$_2$ dispersed in [bmim][PF$_6$] at 75 °C, they proposed a mechanism of formation of Pt(0) nanoparticles and calculated the rate of their formation. This mechanism suggests nanoparticles are formed in four stages, nucleation, autocatalytic surface growth, agglomeration and autocatalytic agglomeration to form large agglomerates (Figure 6).

$$(a) \quad A \xrightarrow{k_1} B$$

$$(b) \quad A + B \xrightarrow{k_2} 2B$$

$$(c) \quad B + B \xrightarrow{k_3} C$$

$$(d) \quad B + C \xrightarrow{k_4} 1.5C$$

* The four equations correspond to: (a) slow nucleation of catalyst precursor A to a nanocluster B, (b) autocatalytic surface growth, (c) agglomeration step leading to the formation of bulk metal C, and (d) autocatalytic agglomeration of smaller nanoparticles with larger bulk metal particles.

Fig. 6. Four-step mechanism for transition-metal nanocluster nucleation, growth and agglomeration

Rate constants were calculated for the four step formation of nanoparticles. The kinetic data was found to be consistent with formation of large agglomerates of bulk metal catalyst (Table 8) and shows that the autocatalytic surface growth is faster than other steps.

Floris *et al.*[41] have discussed the effect of ion pairs of the catalyst and ionic liquid in the asymmetric hydrogenation of methyl acetoacetate at 60 °C and a hydrogen pressure of 50 bars. The [PF$_6^-$] based ionic liquids showed around 50 % lower activity in terms of TOF than [NTf$_2^-$] salts. (Table 9)

PtO$_2$/ C$_6$H$_{12}$ (molar ratio)	Equations in kinetic model[a]	k_1 (h^{-1})[b]	k_2 (M^{-1}h^{-1})[b]	k_3 (M^{-1}h^{-1})[b]	k_4 (M^{-1}h^{-1})[b]
1/4000	a, b	0.143	204.00	-	-
1/4000	a, b, c	0.184	329.88	15.96	-
1/1000	a, b	0.094	58.10	-	-
1/1000	a, b, c	0.086	78.72	7.26	-
1/1000	a, b, c, d	0.677	904.39	9.40	146.17

[a] From Figure 6. [b] Rate constants corrected for reaction stoichiometry

Table 8. Kinetic constants for hydrogenation of cyclohexene by PtO$_2$ in [bmim][PF$_6$][a]

IL	TOF$_{90}$ (h^{-1})	ee$_{90}$ (%)	S$_{90}$ (%)	ee^{re-use} (%)
MeOH	1100	98	79	-
[N$_{6222}$][NTf$_2$]	390	93	87	54
[bmim][NTf$_2$]	340	97	91	54
[N$_{6222}$][PF$_6$]	210	55	86	-
[bmim][PF$_6$]	160	78	88	32

Reaction conditions: 2 g MAA, 17 mL IL-MeOH 1/1 wt., S/C = 1580, 333 K, 50 bar H$_2$.

Table 9. The ion pair effect

There are two rate limiting factors which can be considered. First is the hydrogen gas solubility, and second is the structural modification of active catalytic centre by anion pairing. Figure 7 depicts plausible catalyst-IL interactions in the case of the [NTf$_2^-$] based IL.
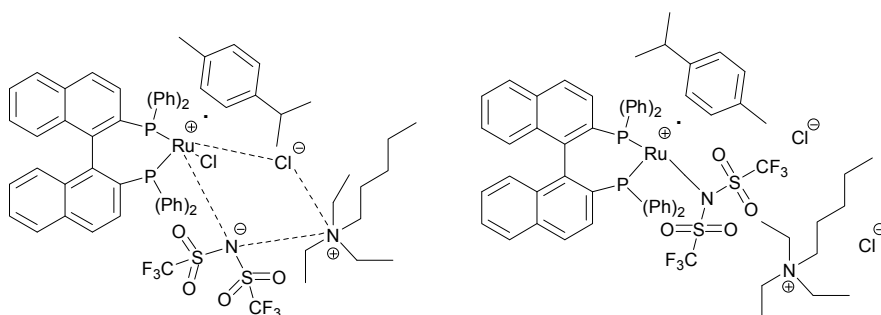
Fig. 7. Plausible catalyst-IL interactions in an [NTf$_2^-$] IL

3. Transition metal catalysis in ILs

Commonly used heterogeneous catalysts such as palladium or platinum on solid supports are among the catalysts employed for the hydrogenation of substrates in ILs. Although increased temperature and pressure may be a requirement when using the IL, classic palladium, platinum and ruthenium catalysts have been shown to give superior results when used in an IL compared with a common organic solvent.

Xu *et al.*[42] used a range of imidazolium ILs containing $[BF_4]$ and $[PF_6]$ anions for the catalytic heterogeneous hydrogenation of halonitrobenzenes to the corresponding haloanilines (Figure 8).
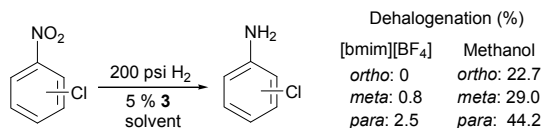

	Dehalogenation (%)	
	$[bmim][BF_4]$	Methanol
	ortho: 0	*ortho*: 22.7
	meta: 0.8	*meta*: 29.0
	para: 2.5	*para*: 44.2

Fig. 8. Hydrogenation of halonitrobenzenes to haloanilines

Raney nickel (**1**), platinum on carbon (**2**) and palladium on carbon (**3**) were employed as metal catalysts, and methanol was used as a reference organic solvent due to its wide application in heterogeneous catalytic hydrogenations. Although increased temperatures and pressures were required for the IL systems (100 °C, 31.0 bar (**1**), 13.8 bar (**2** and **3**)) in comparison with the methanol systems, i.e. 80 °C, 13.8 bar for (**1**) and 30 °C, 2.8 bar for (**2**) and (**3**), the ILs performed better as solvents for these reactions, with the undesirable dehalogenation being greatest for all substrates tested in methanol rather than the ILs (Figure 8). Taking for example *ortho*-, *meta*- and *para*-chloronitrobenzene, and 5 % (**3**), for which the greatest differences in results between IL and organic solvent were evident, in $[bmim][BF_4]$ dehalogenation ranged from as little as 0 % with *o*-chloronitrobenzene to 0.8 % with the *meta* derivative and at most 2.5 % with the *para* substituted derivative. However, when methanol was used as the solvent, dehalogenation ranged from 22.7 % for *ortho* to 44.2 % for the *para*-chloro isomer (Figure 8). The same trend was evident using 5 % (**2**) and (**1**) as catalyst, albeit to a lesser extent. The reaction rates were found to be lower in $[bmim][BF_4]$ than in methanol, which was attributed to mass transfer processes.

Anderson *et al.*[43] selected the α,β-unsaturated aldehydes, citral and cinnamaldehyde (Figure 9 and Figure 10), to demonstrate the superior selectivity obtained using pyridinium, imidazolium and ammonium ILs over common organic solvents in hydrogenation reactions. A palladium on carbon catalyst (**3**) was used for the reactions.

In the case of cinnamaldehyde, although the temperature was increased for the reaction carried out in the IL (60 °C), superior selectivity towards hydrocinnamaldehyde was obtained (78-100 %) compared with several conventional organic solvents (78-89 %). Worth noting for these hydrogenations is the variation of selectivities across a series of [bmim] ILs. $[Bmim][PF_6]$ showed a selectivity of 100 %, $[bmim][OTf]$ 91 %, and $[bmim][OAc]$ 78 % for formation of hydrocinnamaldehyde. Recycling of the $[bmim][BF_4]$ system showed catalyst activity to decrease by 50 % upon the first recycle but remained constant thereafter for five successive reactions. The selectivity however remained almost constant for all recycles carried out. The authors note that if the IL system without a substrate is treated with hydrogen gas for one hour prior to the reaction, the recycling ability of the system can be improved. In the case of citral hydrogenation, similar trends were observed. The selectivity towards citronellal obtained using ILs ($[bmim][PF_6]$, $[bmim][BF_4]$, $[C_8Py][BF_4]$, $[C_6mim][NTf_2]$, and $[emim][NTf_2]$) ranged from 81-100 %, with the organic solvents giving only 62-77 % selectivity (cyclohexane: 62 %, toluene: 77 %, and dioxane: 77 %). The authors concluded that due to the high viscosity of the ILs the rate of diffusion of aldehyde was reduced compared with conventional solvents and reactions rates were correspondingly lower. Using the dicyanamide IL $[bmim][N(CN)_2]$ Arras *et al.*[44] also achieved the selective
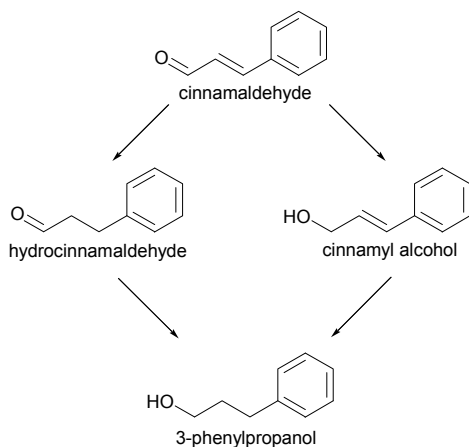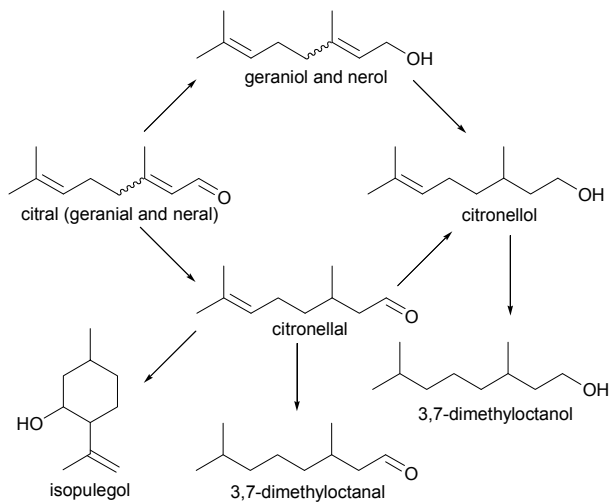
Fig. 9. Reaction pathway of cinnamaldehyde hydrogenation

Fig. 10. Reaction pathway of citral hydrogenation

hydrogenation of citral to citronellal using 10 % (**3**) at 50 °C and 1.0 MPa H_2. In the IL-free system 100 % conversion and 41 % selectivity towards the desired product was obtained. They found that with the IL as bulk solvent, 100 % conversion was obtained with 97 % selectivity. However, using the catalyst coated with IL the selectivity increased to > 99 % with 100 % conversion. When the IL was only present as an additive a reduction in the conversion (42 %) was observed while the selectivity remained high (> 99 %).

The same group continued this work by investigating the use of ILs as additives and coatings on palladium supported catalysts for the hydrogenation of citral.[45] They compared the results obtained by using ILs containing perfluorinated anions ([bmim][NTf$_2$], [bmim][PF$_6$] and [BMPL][NTf$_2$]) and the dicyanamide anion ([bmim][N(CN)$_2$], [BMPL][N(CN)$_2$] and [B3MPYR][N(CN)$_2$]). The performance of the dicyanamide ILs as either additives or coatings improved in comparison the ditriflimide or hexafluorophosphate ILs regardless of the heterocyclic cation. Using Pd/SiO$_2$ (**4**) as catalyst, at 50 °C and 2.0 MPa H_2, the highest conversions and selectivities towards citronellal were achieved using the dicyanamide ILs. Conversions ranging from 63 – 75 % and selectivities from 59 – 62 % were obtained using the ditriflimide or hexafluorophosphate ILs as a catalyst coating. The results for conversion obtained with [bmim][NTf$_2$] and [BMPL][NTf$_2$] were comparable with those obtained in the absence of an IL under the same reaction conditions, although the selectivity obtained was higher (79 % conversion, 45 % selectivity). Using [bmim][N(CN)$_2$], [BMPL][N(CN)$_2$] and [B3MPYR][N(CN)$_2$] conversion was > 99 % and selectivity ranged from 81 – 99 %. Almost quantitative yield of citronellal was obtained using [BMPL][N(CN)$_2$] (conversion = 100 %, selectivity = 99 %). The authors attribute the improved results of the hydrogenation using dicyanamide ILs to the sensitivity of the hydrogenation reaction to halide impurities from the fluorinated anions and also an electronic interaction between the dicyanamide anion and the palladium catalyst. Curiously the low hydrogen solubility in ILs did not affect the conversion, indicating no mass transport limitations. When the research was extended to Ru/Al$_2$O$_3$ catalyzed hydrogenation of citral in ditriflimide ILs[46], it was determined that addition of the ionic liquid reduces the initial TOF of the catalyst. For [bmim][NTf$_2$] the initial TOF decreased from 14.0 x 10^{-2} s^{-1} (initial TOF for reaction without IL) to 7.2 x 10^{-2} s^{-1}.

Geldbach *et al.*[32] investigated the generation of catalysts from metal chlorides in the Lewis acidic IL, [*N*-octyl-3-picolinium]AlCl$_4$ (Figure 11), by dissolving a series of metal chlorides in the IL and adding benzene as the substrate. The hydrogenation of benzene to cyclohexane is an important petrochemical process and research in this area is in continuous evolution.[47,48,49]
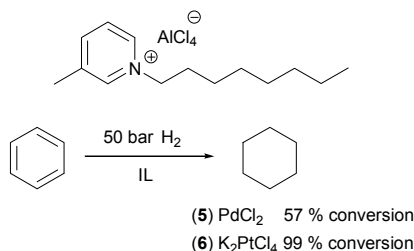

(**5**) PdCl$_2$ 57 % conversion
(**6**) K$_2$PtCl$_4$ 99 % conversion

Fig. 11. [*N*-octyl-3-picolinium]AlCl$_4$ in the hydrogenation of benzene

Hydrogen was added to the biphasic mixture and the conversions to cyclohexane recorded. Of all the metal chlorides used, only the palladium catalyst, PdCl$_2$, (**5**) and platinum catalyst, K$_2$PtCl$_4$, (**6**) showed any significant activity, with 57 and 99 % conversion respectively. K$_2$PtCl$_4$ was investigated further in relation to catalyst concentration and temperature due to the impressive result. Generally, higher K$_2$PtCl$_4$ catalyst loadings gave increased conversion, and raising the temperature also led to an increase in conversion (e.g. 0.0071 mol% (**6**): 18 % conversion at 20 °C and 80 % conversion at 75 °C; and 0.14 mol% (**6**): 67 % conversion at 20 °C and > 99 % conversion at 75 °C). This groups research also extends to the examination of a ruthenium cluster catalyst in [bmim][BF$_4$] for the same hydrogenation reactions however no activity was observed using the IL.[23] The importance of the IL-promoted reduction can be appreciated when one considers that much higher temperatures have been recommended to achieve conversion of benzene to cyclohexane under conventional conditions. Jasik *et al.*[47] using a temperature of 175 °C to achieve complete hydrogenation and Bakar *et al.*[48] recommended 200 °C for maximum conversion.

Deshmukh *et al.*[50] also used a Lewis acidic IL ([bmim][AlCl$_4$]) for the hydrogenation of a selection of arenes, in the presence of a Pd/C catalyst. Although the hydrogenation of benzene can require harsh conditions, this group combined the concept of the activation of aromatics by Lewis acids (using the IL) and the activation of molecular hydrogen by Pd/C to achieve > 99 % conversion of benzene to cyclohexane under ambient conditions (1 bar H$_2$, RT). Under the same conditions they were able to achieve > 99 % conversion of biphenyl, naphthalene and napthacene and 97 % conversion of anthracene. Deshmukh[50] also tackled the problem of the hydrogenation of fullerene with their novel system. Harsh conditions are usually necessary for hydrogenation of this substrate (120 bar H$_2$, 400 °C),[51] however hydrogenation was achieved with only 5 bar H$_2$ at RT using this system.

Although ILs has many 'green' attributes, in hydrogenation reactions there are some cases, in which conventional organic solvents are preferred. Using the bimetallic catalyst system, Ag-In/SiO$_2$ (**7**) for the hydrogenation of citral to selectively form the acyclic/allylic terpene alcohols, geraniol and nerol, Steffan *et al.*[52] showed the non-polar solvent hexane to be superior to [bmim][NTf$_2$]. The chemoselective hydrogenation of citral to geraniol and nerol was lower in the IL compared to the organic solvent. Steffan explained the lower conversion of citral in ILs compared with hexane by suggesting that the lower solubility of hydrogen in the IL (0.77 x 10^{-3} molL^{-1} at 298 K and 0.1 MPa of H$_2$, estimated from the H$_2$ solubility at 10.1 MPa assuming a linear relationship with partial pressure)[10] was the limiting factor. Information pertaining to hydrogen solubility in ILs can be found in recent sources.[53,54,55]

While investigating mass transfer effects in the hydrogenation of phenylacetylene to styrene and ethyl benzene (Figure 12) using a rotating disc reactor, Hardacre *et al.*[56] found [bmim][NTf$_2$] to give lower reaction rates than a non-polar hydrocarbon solvent.
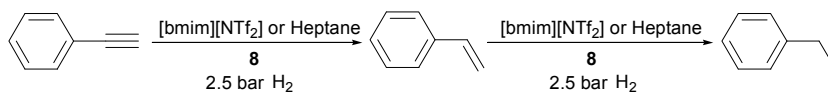
Reaction rate: reduced in [bmim][NTf$_2$] compared to heptane

Fig. 12. Hydrogenation of phenylacetylene

Using palladium on calcium carbonate (**8**) as a catalyst, they investigated several parameters in [bmim][NTf$_2$] and heptane, including the effect of phenyl acetylene concentration in the

solvent and the rotation speed. The rate of reaction was reduced in the IL (0.942 mmol min^{-1} at 6.0 bar) compared with the organic solvent (12.976 mmol min^{-1} at 5.5 bar), postulated to be due to the varying rate of diffusion of gaseous hydrogen through the liquid medium to the catalyst surface. The liquid to solid mass transfer coefficient ($k_{LS}a$) was calculated to vary from 0.144 to 0.150 s^{-1}, over a range of phenylacetylene concentrations and hydrogen pressures. These values indicate that the reaction is limited by liquid to solid mass transfer process, in particular the transport of dissolved hydrogen. This fact was supported by the calculated activation energies for conversion of phenylacetylene to ethyl benzene in heptane and [bmim][NTf$_2$] obtained between 9 and 33 kJ mol^{-1}.

Recently Khodadadi-Moghaddam *et al.*[28] investigated the kinetic parameters of the hydrogenation of cyclohexene, in mixtures of 2-hydroxyethylammonium formate and various alcohols (methanol, ethanol and IPA). Using a Pt-Al$_2$O$_3$ (**9**) catalyst, the rate constant for the reaction carried out in the IL/IPA mixture was twenty eight times higher than when IPA was used as the reaction medium. From studying solvent effects on the reaction the authors explain the discrepancy in rate to be due to the varying polarities of solvent and substrate – specifically that because of the polarity of the IL, the non-polar cyclohexene is more abundant on the catalyst surface, promoting the reaction. Furthermore, Khodadadi-Moghaddam and co-workers state that low gas solubility in many ILs is compensated by fast gas diffusion in reactions involving hydrogen gas.[57] This group extended their work to investigate this effect using acetone as the hydrogenation reaction substrate.[58] They postulate that the presence of the polar carbonyl group in acetone lowers the extent of adsorption on the catalyst surface compared with cyclohexene. The first-order rate constant of the hydrogenation reaction of cyclohexene to cyclohexane was found to be 8.7 times higher using the IL as solvent than compared to IPA. The rate constant of the hydrogenation reaction of acetone to propan-2-ol was also higher in the IL than IPA, albeit only 3.3 times.

Biphasic reaction conditions are one important method for hydrogenations using homogeneous catalysts when efficient recycling of catalyst is of importance. Hydrogenation reactions have been carried out using rhodium and ruthenium catalysts in biphasic systems using imidazolium based ILs ([bmim], [hmim] and [omim] [BF$_4$]). With the use of a rhodium catalyst ([Rh(η^4-C$_7$H$_8$)(PPh$_3$)$_2$][BF$_4$]) (**10**), Dyson *et al.*[59] demonstrated a biphasic hydrogenation of an alkyne using [omim][BF$_4$] containing the catalyst and an aqueous phase containing the substrate, 2-butyne-1,4-diol (Figure 13).
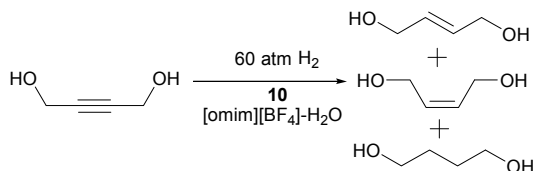

Fig. 13. Hydrogenation of butyne-1,4-diol

At room temperature, the phases were immiscible; however at the reaction temperature of 80 °C homogeneity was attained. Hydrogenation reactions were carried out under 60 atm H$_2$ with facile separation of the reduced products from the catalyst/IL phase being achieved simply by cooling the reaction. The products dissolved in the aqueous layer were isolated and reuse of the IL/catalyst system demonstrated. The limitations of this system were shown with maleic acid, when the reduced product, succinic acid, was found to be soluble

in both the IL and aqueous phase. This type of cationic rhodium catalyst has been also used by Esteruelas *et al.*[60] employing an organic solvent to selectively hydrogenate phenylacetylene to styrene ([Rh(2,5-norbornadiene)(PPh$_3$)$_2$] (**11**) in DCM at 25 °C and 1 atm. H$_2$ pressure). At 50 °C and 39.48 atm. H$_2$ with scCO$_2$ as reaction solvent (157.91 atm. CO$_2$) Zhao *et al.*[61] selectively hydrogenated the same substrate as Dyson *et al.*,[59] 2-butyne-1,4-diol, to butane-1,4-diol (84 % at 100 % conversion) using a stainless steel reactor wall (SUS 316) to promote the reaction with no catalyst.

Wolfson *et al.*[37] used [bmim][PF$_6$] as reaction medium in the hydrogenation of 2-cyclohexen-1-one with Rh(PPh$_3$)$_3$Cl (**12**) (Wilkinson's catalyst) (Figure 14) and methyl 2-acetamidoacrylate with Rh-EtDuPHOS (**13**).
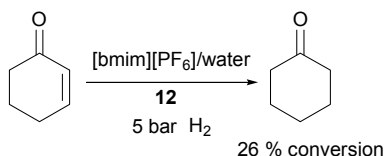

Fig. 14. Hydrogenation of 2-cyclohexen-1-one

As water was shown by this group to enhance the activity of Wilkinson's catalyst (**12**), they studied this parameter in the biphasic hydrogenation of 2-cyclohexen-1-one. Diethyl ether and hexane were screened but demonstrated low hydrogenation activity. The conversion to cyclohexanone increased from 4 % (100 % selective) in diethyl ether and 7 % (100 % selective) in hexane as co-solvent to 26 % in water (90 % selective). In the analogous homogeneous reaction with Wilkinson's catalyst (**12**) and only ethanol as solvent, 100 % conversion was achieved, albeit with low selectivity (27 %). Increased selectivity was achieved using DCM as solvent (100 %), although a compromise in conversion was observed (17 %).

Water was also used as solvent in conjunction with the [bmim][PF$_6$] for the biphasic hydrogenation of methyl 2-acetamidoacrylate at 5 bar H$_2$ and 20 °C. 68 % conversion was obtained (66 % upon re-use) with 96 % ee (97 % upon re-use). The group proposes that the use of water as the second solvent in biphasic IL reactions has a beneficial effect on activities due to the creation of a well mixed 'emulsion-like' system. Using methanol as the sole phase in a homogeneous reaction, 54 % conversion with 97 % selectivity was obtained. However, using the IL as sole reaction phase, no reaction was observed.

Scurto *et al.*[62] used biphasic hydrogenation conditions with scCO$_2$ and a rhodium catalyst (**14**) for the hydrogenation of 2-vinyl-naphthalene (Figure 15).
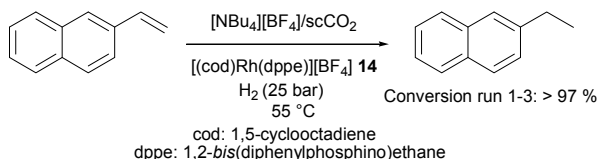

Fig. 15. Hydrogenation of 2-vinyl-naphthalene

[TBA][BF$_4$] was pressurised with CO$_2$ to give a high melting point depression of the salt for subsequent use as a reaction solvent in the liquid phase. Conversions for the first three runs

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