Organo-zincate molten salts as immobilising agents for organometallic catalysis

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The combination of 1-*n*-butyl-3-methylimidazolium chloride with $ZnCl_2$ affords ionic mixtures with different melting point temperatures depending on the zinc molar fraction. $RuCl_2(PPh_3)_3$ immobilised in the low melting mixture (60 °C) promotes the 1-hexene hydrogenation (turnover frequencies up to 44 min^{-1}) and the recovered solid catalyst phase can be reused several times.

KEY WORDS: molten salts; ionic liquids; ruthenium; hydrogenation

1. Introduction

Molten salts ("ionic liquids") are emerging as a new, simple and efficient class of immobilising agents for transition-metal catalyst precursors [1–3]. Among these melts, those that are liquid at room temperature, in particular 1,3-dialkylimidazolium cations associated with anions such as $AlCl_4^-$, BF_4^- and PF_6^-, have been successfully used as the "mobile phase" for the biphasic transition-metal-catalysed hydrogenations, hydroformylations, oligomerisations, telomerisations, oxidations, cross-couplings, etc. [1–3]. One of the greatest advantages of these immobilising agents is the ease of catalyst recycling and product isolation. Indeed, the products can be separated from the ionic catalyst solution by decantation, extraction with organic solvents or distillation. Transition-metal catalyst precursors can also be immobilised in molten salts with melting point temperatures just above room temperature. In these systems the products can be "poured off" from the solid catalyst medium at room temperature. Although these systems have great potential for technological applications, they have been investigated in few cases [4–7]. We wish to report here that the combination of 1-*n*-butyl-3-methylimidazolium chloride (BMI.Cl) with controlled amounts of zinc dichloride ($ZnCl_2$) affords ionic mixtures with different melting point temperatures depending upon the zinc molar fraction. The $RuCl_2(PPh_3)_3$ compound immobilised in these ionic mixtures promotes the hydrogenation of 1-hexene, typically via two-phase catalysis. Upon cooling the reaction mixture, the products can be separated from the ionic solid catalyst phase by simple filtration and the recovered catalyst ionic solution has been reused seven times.

2. Experimental

2.1. General

All manipulations were performed under dry, oxygen-free argon using standard Schlenk tube techniques. All solvents were dried over suitable desiccant agents and distilled under argon prior to use. Infrared (nujol mulls or KBr pellets) spectra were recorded in the 4000–400 cm^{-1} region using a Mattson 3020 FTIR spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.13 and 50.32 MHz, respectively, using a Varian VXR-200 instrument. Proton and carbon shifts (δ (ppm), J (Hz)) are positive downfield relative to external $SiMe_4$. Elemental analyses were carried out by the "Central Analítica IQ/UFRGS" (Porto Alegre, Brazil). The metal content in the organic phase was determined using a Perkin–Elmer 2380, HGA 400, atomic absorption spectrometer with graphite tube atomiser and auto sampler. Calorimetric experiments were carried out in a 1200 PL-DSC, under nitrogen, with the heating rate varying from 1 to 10 °C. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70 eV). The substrate conversions and product selectivities were analysed by gas chromatography on a Varian 3400 CX chromatograph equipped with an LM100 column ($20\,m \times 0.25\,mm \times 0.2\,\mu m$), equipped with a FID detector; N_2 was the carrier (1 ml/min); the temperature program was from 35 (5 min) to 200 °C (15 min) at a heating rate of 10 °C/min, using cyclohexane as internal standard. The organic compounds were characterised by CG-MS and by comparison of their CG retention times with those of authentic samples (Aldrich).

2.2. Materials

The $RuCl_2(PPh_3)_3$ was prepared according to a method described in the literature using reagents obtained from commercial sources [8]. 1-hexene was distilled under ar-

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gon and stored over molecular sieves (3 Å). The 1-butyl-3-methylimidazolium chloride was prepared according to literature procedures [9] and commercial zinc chloride was dried by benzene azeotropic distillation and stored under argon. All other chemical were obtained from commercial sources (Aldrich or Across) and used as received.

2.3. Preparation of the BMI.Cl/ZnCl$_2$ mixtures and catalyst immobilisation

Ionic organo-zincate mixtures were prepared by mixing appropriate amounts of solid BMI.Cl and ZnCl$_2$ over argon and then heated at 100 °C, under efficient stirring, until complete dissolution of the solid reagents. Alternatively, they could be obtained by adding acetone or acetonitrile to the solid reagents and then stirring the mixture for 1 h, followed by organic solvent distillation under vacuum. In both cases, pale-yellow viscous ionic liquids were formed that solidified on standing.

Catalyst ionic solutions were obtained by adding the powdered ruthenium complex to a molten organo-zincate mixture in a Schlenk tube under argon. The mixture was then left stirring, above the mixture melting point temperature, until complete dissolution of the ruthenium complex.

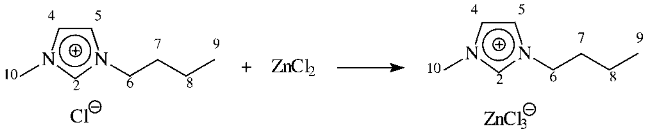
2.4. Typical procedure for the hydrogenation reaction

The catalyst ionic solution was transferred into the autoclave (130 ml internal volume, 4.6 cm of internal diameter and 8.0 cm of length) under argon. The substrate (10 ml, 80 mmol) was introduced and the reactor was pressurised with hydrogen at the desired temperature and stirring (300–350 rpm) was started. For the reaction, a well-stirred system is required, since the mass transfer between the phases is an important parameter in these systems (in the absence of stirring the consumption of hydrogen is completely stopped). The consumption of hydrogen was monitored by the drop of the reactor pressure. The reaction was stopped after complete hydrogen consumption. By cooling the reaction mixture, the ionic phase containing the ruthenium complex solidified and the organic phase, which contains the products, was separated by filtration and analysed by gas chromatography. In cases where the ionic phase was reused, this procedure was carried out under argon and the metal content in the organic phase checked by atomic absorption analysis.

3. Results and discussion

3.1. Preparation of ionic mixtures

The association of 1-butyl-3-methylimidazolium chloride and zinc chloride, as shown in scheme 1 for 50 mol% composition, yields a pale-yellow viscous liquid that solidifies on standing.



Scheme 1. Organo-zincate molten salt synthesis.

The physical–chemical properties of these ionic mixtures depend upon their composition, as can be seen in table 1. The different observed melting points can be attributed to the formation of different chlorozincate anions such as $ZnCl_3^-$, $ZnCl_4^{2-}$ and $Zn_2Cl_7^{3-}$ similar to the well-known chloroaluminate imidazolium molten salts [10]. It is also apparent that these anions interact through hydrogen bonds with the aromatic imidazolium hydrogens. In particular, the H2 undergoes an upfield shift (from 9.05 to 8.73 ppm) with the augmentation of the zinc chloride concentration. Moreover, hydrogen bond interactions are evident by the appearance of bands in the 3050–3150 cm^{-1} region in the IR spectra of these melts. Note that C–H stretching at 3063 cm^{-1}, due to the imidazolium hydrogen interaction with free chloride, only disappears when the molar ratio of imidazolium chloride/zinc dichloride is 1. This behaviour is similar to those observed with the analogous organo-aluminate imidazolium melts [11–13].

3.2. 1-hexene hydrogenation

The interaction of the complex $RuCl_2(PPh_3)_3$ (96 mg, 0.1 mmol) with 3 ml of the ionic mixture BMI.Cl/ZnCl$_2$ (0.33 ZnCl$_2$ molar fraction) produces a stable brown-red solution from which the transition metal complex is not removed by organic solvents.

The quantitative hydrogenation of 1-hexene (80 mmol) was observed after 18 min at 60 °C and 25 atm of hydrogen pressure, achieving a turnover frequency (TOF = mol of hexane/mol of Ru × min) of 44 min^{-1}. It is important to note that this activity is in the same magnitude of those obtained changing the organo-zincate melt by BMI.BF$_4$, using the same ruthenium complex and reaction conditions (TOF of 38 min^{-1}). The ionic catalytic solution solidifies upon cooling to room temperature and the product is separated by simple filtration. The recovered ionic solid was reused five times without showing any changes in its catalytic activity. Indeed, using the same amount of substrate, 100% conversion was achieved in all cases at comparable reaction times as can be seen in figure 1. The total amounts of 1-hexene

Table 1
Physical–chemical properties of imidazolium chloride/zinc dichloride ionic mixtures.

Composition (ZnCl$_2$ mol%)	Melting point temperature (°C)	H2 chemical shift (ppm relative to CD$_3$CN)	Wavenumber (cm^{-1}) relative aromatic C–H···X$^-$ stretching		
0.80	84	8.73	3149	3116	3097
0.75	105	8.74	3149	3116	
0.64	78	8.74	3148	3113	
0.50	96	8.82	3147	3110	
0.32	60	8.98	3140	3099	3061
0.26	64	8.99	3141	3100	3061
0.19	76	9.03	3140		3063
0.00	69	9.05			3063

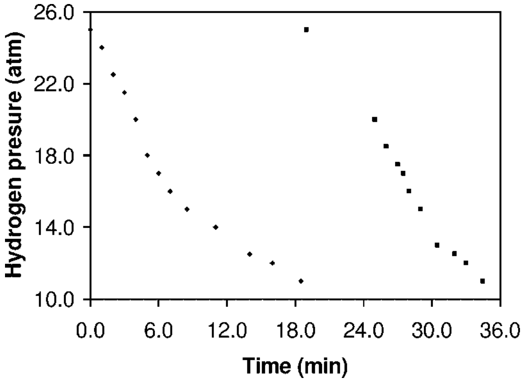


Figure 1. Hydrogen consumption in the first two recycling processes of the catalytic active ionic solution using 1-hexene as substrate.

hydrogenated represents an overall productivity of 350 g of hexane per gram of ruthenium. It is important to note that, since the ionic solution showed no apparent deactivation at the end of the 5th run, this is not the total productivity. The isolated yield in hexane was always greater than 91%. Note that the organic phase was not contaminated by metals (Ru and Zn) as checked by atomic absorption analysis. Moreover, no alkene isomerisation products have been detected even at low 1-hexene conversions (monitored by CG-MS). In these cases (low 1-hexene conversions, i.e., $<25\%$) also there was no observed catalyst deactivation or leaching.

4. Conclusions

In summary, we have shown that 1-butyl-3-methylimidazolium chloride and zinc dichloride form ionic mixtures with their physical–chemical properties depending upon the zinc composition. These ionic mixtures can be used as solvents for classical ruthenium complex catalysis, showing similar behaviour to the well-known 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. By cooling the two-phase system at the end of the reaction, the ionic solution solidifies, improving the separation of the organic product.

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