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Synthesis of multicarboxylic acid appended imidazolium ionic liquids and their application in palladium-catalyzed selective oxidation of styrene†

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A series of multicarboxylic acid appended imidazolium ionic liquids (McaILs) with chloride $[Cl]^-$ or bromide $[Br]^-$ as anions have been synthesized and characterized. Deprotonation of these ionic acids gives the corresponding zwitterions. Re-protonation of the zwitterions with strong Brønsted acids gives a series of new ionic acid-adducts, many of which remained as room-temperature ionic liquids. A new catalytic system, McaIL/$PdCl_2$ for the selective catalytic oxidation of styrene to acetophenone with hydrogen peroxide as an oxidant has been attempted. In the presence of McaILs, it is found that the quantity of palladium chloride $PdCl_2$ used can be greatly reduced while the activity (TOF) and selectivity towards acetophenone are enhanced sharply. It is also shown that the catalytic properties of this system could be finely tuned through the molecular design of the McaILs. The best TOF value obtained so far is 146 h^{-1} with 100% conversion of styrene at 93% selectivity to acetophenone. In addition, the catalytic activity has been maintained for at least ten catalytic cycles.

Introduction

Ionic liquids (ILs) incorporating functional groups on their cations and/or anions as new solvent media have started to receive considerable attention, particularly in the areas of homogeneous and heterogeneous catalysis.[1] Functional moieties attached in the cations or anions often show a significant influence on certain processes, so that much effort has been devoted to the design of the functionalized ILs in order to control processes where the IL is involved as solvent or catalyst.[2] It is without doubt that the imidazolium based ILs are the focus of most investigations, due, in part, to the flexibility of varying the nature of the groups attached to the N-atoms, as well as on the ring carbons, in order to modify the physical and chemical properties of the designed ILs. Pyridinium,[3] and ammonium based ILs have also been functionalized,[4] but to a much lesser extent. Upon incorporating a functional group into an ionic liquid structure specific properties are imparted to the liquid. For example, ILs with groups containing lone pairs of electrons such as imidazole,[5] pyridine,[6] pyrazole[7] or even weaker nitrile groups[8] can coordinate effectively to transition metals. They often show an extraordinary stabilizing effect for zero-valent transition metals such as Pd(0) and Pt(0), and thus can increase their catalytic activities (formation of smaller metal nanoparticles of high surface area through the stabilization effect) and reduce the extent of metal leaching into solution.[9] Strong sulfonic acid ILs are typical examples of functionalized ILs that can be used as solvents and catalysts for etherification reactions.[10] Imidazole[11] and imidazolium salts[12] with carboxylic groups have known for many years, many of them being valuable starting materials for organic synthesis. Zwitterionic imidazolium salts with carboxylic group attached in the 2-position,[13] giving weaker acidic properties are also well studied.[14] Most recently, a series of Brønsted acidic ionic liquids with one or two carboxylic acid groups attached to the imidazolium backbone have been reported.[15] These ILs show stronger acidic properties compared to the corresponding non-ionic carboxylic acids, and can dissolve many group II metal carbonates and readily react with many transition metals such as elemental zinc and cobalt, forming coordination polymers with interesting topologies.[16] However, the potential applications of these acids ILs in organic processes have been seldom explored. By varying the cations and anions, many of these ionic carboxylic acids can be obtained as room-temperature ionic liquids, and it would be interesting to investigate their potential application as catalysts or co-catalysts.

The Wacker oxidation reaction was chosen because it is an important process widely used in industry[17] and is also a classical reaction for many catalytic studies.[18] The traditional process for Wacker reaction involves the use of organic solvent and excess of H_2O_2.[19] Recently, a technique for the use of a much more convenient oxygen source, such as air and

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molecular oxygen was adopted.[17b] HCl is often used in the system in order to re-oxidize the zero-valent palladium to Pd(II). Since olefins are usually poorly soluble in water, expensive phase-transfer agent has to be used. Oxidation reactions of styrene with H_2O_2 or O_2 using an ionic liquid or mixture of ionic liquid and water as solvents have previously been reported, but problems related to the solubility and the recycling of the catalyst ($PdCl_2$) apparently remained.[20] The low selectivity of this system often leads to the formation of a mixture including acetophenone, benzaldehyde, benzoic acid and other products which require further separation. Another major drawback is that the ionic liquids and catalyst ($PdCl_2$) can be hardly reused due to the contamination of the side-products that are formed during the oxidation process. Moreover, the variety of products in the oxidation of styrene with H_2O_2 could be oriented through careful design of the catalyst system,[21] which has a wider significance both in theoretical design of catalyst and industrial production process.

In this paper we describe the synthesis, characterization and the reactivity of a novel series of imidazolium ionic liquids incorporating multicarboxylic acid functionalities. In addition, a new catalyst system, McaILs/$PdCl_2$ employing these McaILs and $PdCl_2$ for selective oxidation of styrene was investigated. The presence of the carboxylic groups not only renders the catalysts to display higher conversion and selectivity towards desirable products but also significantly reduces the need for a high level of Pd content.

Results and discussion

Synthesis of multicarboxylic acid imidazolium halide precursors

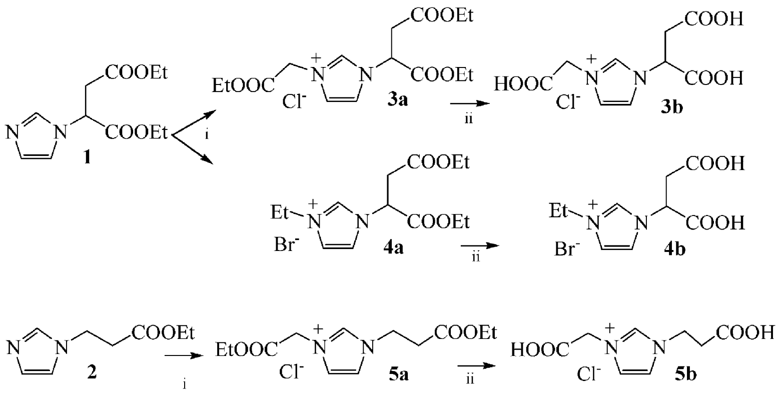
The synthetic route for novel multicarboxylic acid imidazolium halide precursors (McaILs) is illustrated in Scheme 1. The precursors **1** and **2** were synthesized following a literature method by Michael addition of acrylate to imidazole.[11] Quaternization of **1** and **2** with chloroacetic acid ethyl ester or ethyl bromide gave the corresponding imidazolium salts **3a**, **4a** and **5a**, respectively, with the carboxylic acid ester groups being attached. The ester compounds were all very hygroscopic. They were found to be soluble in common polar solvents such as acetonitrile, acetone, dichloromethane and chloroform, but insoluble in diethyl ether or hexane. Heating **3a** under reflux in an aqueous solution of hydrochloric acid (37% w/w) gave ionic acid **3b** in quantitative yield. A slight excess of HCl was essential in order to give full conversion of the esters to the acids. After the reaction was complete, the side product and the solvent were easily removed by heating the reaction mixture under mild vacuum.

Similarly, **4b** and **5b** were obtained in high yield by reacting **4a** and **5a** with aqueous HBr or HCl. Unlike the ester precursors, compounds **3b**, **4b** and **5b** were found to be well soluble in water, slightly soluble in DMSO and totally insoluble in other solvents such as dichloromethane and chloroform. The insolubility of these acids may be due to the formation of extended polymeric networks in the solid state arising from hydrogen bonds (for example through COO–H···F, COO–H···O). Compared to the 1,3-dialkylimidazolium based ILs, there is increased tendency of formation of hydrogen bonding in carboxylic acid ILs.[15,16]

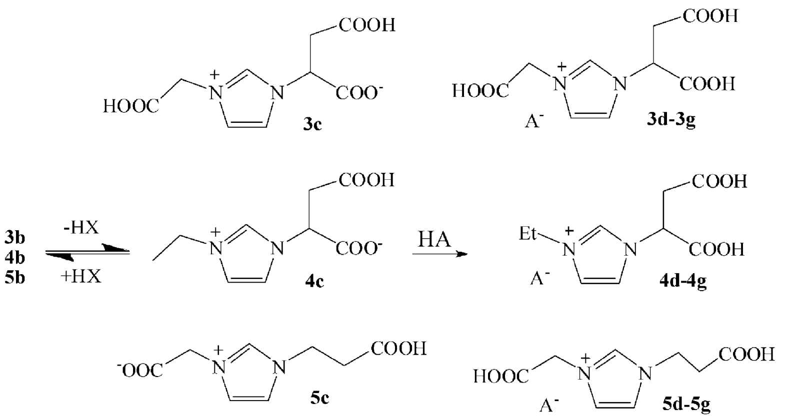
In the IR spectrum (data available in ESI†), **3b**, **4b** and **5b** displayed strong absorptions at 3350–3500 cm^{-1}, representing the O–H···O/O–H···Cl(Br) hydrogen bonds. In addition, strong–medium absorptions in the region 2500–2800 cm^{-1} were also observed, representing the C–H···Cl or C–H···Cl interactions, typical of imidazolium halides.[22] The ^{13}C NMR spectrum of **3b** in D_2O exhibited three sharp signals at 169, 170 and 171 ppm, indicative of the presence of three different carboxylic groups. Similar results were also obtained from **4b** and **5b**.

Synthesis of multicarboxylic acid imidazolium zwitterions and McaILs

Reaction of the ionic acids **3b**, **4b** and **5b** with the organic base triethylamine in 1 : 1 molar ratio gave corresponding zwitterions **3c**, **4c** and **5c** (Scheme 2). Similar to the ionic acids **3b**, **4b** and **5b**, these zwitterions were found to be very soluble in water, but only slightly soluble in DMSO and totally insoluble in other common organic solvents. This enabled the facile separation of the zwitterions from the



Scheme 1 Synthetic route of acidic imidazolium salts **3a**/**3b**–**5a**/**5b**: *Reagents and conditions*: (i) $ClCH_2COOEt$ (for **3a** and **5a**), BrEt (for **4a**), 60 °C, 24 h; (ii) 37% HCl (**3b** and **5b**) or 48% HBr (for **4b**) aqueous solution, 100 °C, 2 h.



Scheme 2 Synthetic route to acidic imidazolium salts **3c–5c** and **3d–3g**, **4d–4g** and **5d–5g**: **d**, A = BF_4, **e**: A = PF_6, **f**: A = CF_3CO_2, **g**: A = CF_3SO_3.

reaction mixture, since the zwitterions were insoluble in this solvent whereas the formed ammonium salts were well solubilised. Formation of zwitterions using other bases such as tributylamine or pyridine was also studied. **3c**, **4c** and **5c** were characterized using standard spectroscopic methods. In D_2O solution, the protons of the carboxylic groups can not be observed, and even the 2-H of the imidazolium ring undergoes rapid H–D exchange. It is interesting to note that for all the zwitterions **3c**, **4c** and **5c**, use of excess base did not lead to further deprotonation of the other carboxylic protons. Synthetic route to acidic imidazolium salts **3c–5c** and **3d–3g**, **4d–4g** and **5d–5g**: **d**, A = BF_4, **e**: A = PF_6, **f**: A = CF_3CO_2, **g**: A = CF_3SO_3.

The carboxylic group COO^- can act as a proton acceptor, and thus may be protonated using stronger acids. This differs significantly from other zwitterions, for example $-SO_3^-$ groups, which can not be easily protonated. Imidazolium based zwitterions with SO_3^- attached to the side-chain react with aqueous HCl gave a mixture of the zwitterion and HCl. Upon washing the obtained mixture with cold acetone the HCl can be removed, giving the zwitterion back. Reaction of the zwitterions **3c**, **4c** and **5c** with strong Brønsted acids HBF_4, HPF_6, CF_3COOH and CF_3SO_3H gave a series of new ionic acids **3d–3g**, **4d–4g** and **5d–5g**. Since all the precursors were acids, the products **3d–3g**, **4d–4g** and **5d–5g** can be considered as acid–acid adducts. All these new acids were viscous liquids at room temperature and become waxes on cooling at a temperature of −20 °C; only glass transitions were observed and no obvious melting point was detected (data available in ESI†). These acids were found to be stable and showed no decomposition even up to 250 °C with decomposition only at a temperature above 280 °C (data available in ESI†).

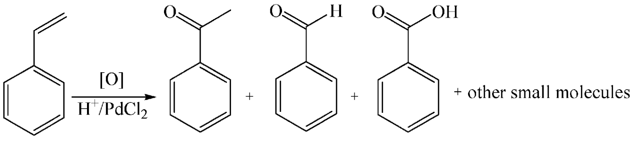
The IR and NMR spectroscopic data of the acid–acid adducts **3d–3g**, **4d–4g** and **5d–5g** showed a close similarity to the acids **3b**, **4b** and **5b**, and the anions had little effect on the chemical shifts in the ^1H and ^{13}C NMR spectra. In the ESI-MS spectra, all the ILs showed strong absorptions of the cation, anions and their aggregates (*e.g.* $[(Cation)_3(Anion)_2]^+$, $[(Cation)_4(Anion)_3]^+$ in the positive mode). Similar results have been observed in other ionic compounds.[23]

Application of McaILs in Wacker oxidation process

The ionic and acidic nature of **3b**, **3d–3g**, **4b**, **4d–4g** and **5b**, **5d–5g** made these compounds interesting candidates as catalysts. The oxidation process of styrene is always complicated and often leads to the formation of mixtures including acetophenone, benzaldehyde, benzoic acid and other products (Scheme 3).

The initial screening of the ionic carboxylic acids, **3b**, **4b** and **5b** and **3d–3g**/**4d–4g**/**5d–5g** in the absence of palladium chloride suggested that all these McaILs show little catalytic activities on their own: oxidation of styrene took place slowly (entry 1, Table 1) and the selectivity of acetophenone was very poor with the main product being benzaldehyde. Without the presence of the McaILs, styrene could be catalytically oxidized to acetophenone by palladium chloride with relatively higher selectivity although such oxidation took place very slowly with a TOF value of only 21 h^{-1} after 8 h reaction time. (entry 2, Table 1).

When a combination of McaILs and palladium chloride was used, all the McaIL/$PdCl_2$ systems showed better catalytic properties with the yield and selectivity improved significantly. After investigating all the possible combinations we found that the reaction temperature was the most important factor for the rate of the oxidation, independent of the nature of the cation and anions. Another important factor was the particular structure of the McaIL used. In general, the ILs with Cl^- or Br^- as anions, namely the ILs **3b**, **4b** and **5b** gave the highest conversions of the styrene and highest selectivities towards acetophenone. This is probably due to the favorable interactions of $PdCl_2$ with ILs **3b**, **4b** and **5b**. Addition of $PdCl_2$ to the acidic ILs **3b** gave immediately an orange solution. Apparently, the $PdCl_2$ reacted with the coordinating anion Cl^- or Br^- to form $PdCl_4^{2-}$/$PdCl_2Br_2^{2-}$ anions, as evidenced by the presence of a peak at 124 from the negative mode



Scheme 3 Oxidation of styrene.

Table 1 Selective oxidation of styrene catalyzed by McaILs/$PdCl_2$ [a]

Entry	IL	IL/Pd (mol/mol)	TOF[d]/h^{-1}	*C* (%)	*S* (%)
1	**3b**[b]	—	—	8	7
2	—[c]	0	21	25	86
3	**3b**	1.1	146	100	93
4	**3d**	2.0	125	100	91
5	**4b**	1.4	116	84	92
6	**5b**	2.3	92	80	92

[a] *Reaction conditions*: reaction was carried out in a 250 mL round-bottomed flask fitted with a condenser; styrene (250 mmol, 26.03 g), 30% H_2O_2 (287.5 mmol, 32.59 g), $PdCl_2$ (0.25 mmol, 0.0446 g), temperature = 55 °C. [b] Without $PdCl_2$, 8 h. [c] Without McaIL, 8 h. [d] TOF: turnover frequency: number of moles of styrene converted per mole of palladium catalyst per hour. *C* (%): conversion of styrene; *S* (%): selectivity of acetophenone.

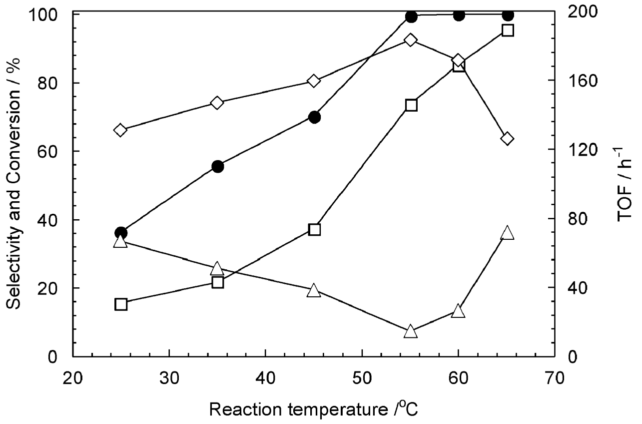


Fig. 1 Effect of temperature on the oxidation of styrene with H_2O_2 in the presence of **3b**/$PdCl_2$: selectivity of acetophenone (◇), selectivity of benzaldehyde (△), conversion (●) and TOF value (□). *Reaction conditions*: reactions were carried out in a 250 mL round-bottomed flask fitted with a condenser until the conversion of styrene maintained invarient; styrene (250 mmol, 26.03 g), 30% H_2O_2 (287.5 mmol, 32.59 g), $PdCl_2$ (0.25 mmol, 0.0446 g), **3b** : $PdCl_2$ = 1.1 : 1.0; TOF: turnover frequency, number of moles of styrene converted per mole of palladium catalyst per hour; *C* (%): conversion of styrene; *S* (%): selectivity of acetophenone.

ESI-MS (for **3b** and **5b**) and 168 (for **4b**) representing the presence of $[PdCl_4]^{2-}$, $[PdCl_2Br_2]^{2-}$ ($\frac{1}{2}$ m/z due to the -2 charge).

Using the ionic acid **3b** and $PdCl_2$, the optimal temperature was found at 55 °C (Fig. 1), under which conditions the conversion of styrene was virtually 100% within 7 h of reaction time and the measured TOF value (146 h^{-1}) was six times higher than that of $PdCl_2$ catalyst. Furthermore, the selectivity of acetophenone was as high as 93%. For all McaIL/$PdCl_2$ catalyst systems, with the increase of molar ratio of McaIL to $PdCl_2$, the selectivity of acetophenone increased, however, it was found that the conversions of styrene and the TOF values peaked at a certain molar ratio, which was different in different McaIL systems. For example, using the same cation the optimized molar ratio for **3b** to $PdCl_2$ was 1.1 (entry 3), 2.0 for **3d** (entry 4) while the optimized molar ratio for **3b**, **5b** with Cl^- anion and **4b** with Br^- to $PdCl_2$ was 1.1 (entry 3), 2.3 (entry 6) and 1.4 (entry 5), respectively.

Other acids with BF_4^-, PF_6^-, CF_3COO^- and $CF_3SO_3^-$ anions gave slightly lower conversions than **3b**/$PdCl_2$, **4b**/$PdCl_2$ and **5b**/$PdCl_2$. In most cases, the conversion can reach as high as 90%, but the selectivity to the side-product benzaldehyde was significantly increased (2–23%) at the expense of acetophenone. Anion effects have been observed in other catalytic systems where the anions of the ionic liquids played a major role in the catalytic performance.[24] As in this case, the reduced activity of **3d–3g**, **4d–4g** and **5d–5g**/$PdCl_2$ systems could be attributed to the interaction(s) between palladium chloride and the McaILs. In contrast to the ILs **3b**, **4b** and **5b**, ILs **3d–3g**, **4d–4g** and **5d–5g** did not form a homogeneous solution upon addition of $PdCl_2$. The suspensions obtained instead can be partially dissolved upon heating the mixture to 55 °C. The solids, isolated from the suspension through centrifugation, all showed an absorption at 1650 cm^{-1} in the IR spectra, a remarkable shift compared to the absorption value of the corresponding free acid (1720 cm^{-1}), which strongly indicates a coordination of Pd ion with carboxylic groups as (COO–Pd).[25] Though the coordination mode the carboxylic groups to the palladium could be complicated, we believe, due to the presence of the multi-carboxylic groups, formation of polymeric structures is possible. Phenylformic acid, which is always the by-production of the selective oxidation of styrene, cannot be detected upon any McaIL/$PdCl_2$ samples, implying that McaILs/$PdCl_2$ could inhibit the generation of deep oxidation products of styrene. This could be rationalised in that the deep oxidation products are suppressed as the transition process of the intermediate transient state is prevented to form carboxylic groups by these carboxyl groups present in the McaIL/$PdCl_2$ systems. Further study on the detailed catalytic mechanism of McaILs/$PdCl_2$ is ongoing in our laboratory and the results will be communicated elsewhere.

To illustrate the advantage of the McaIL/$PdCl_2$ catalytic systems we compared our McaILs/$PdCl_2$ with C_4mimBF_4/$PdCl_2$, C_4mimPF_6/$PdCl_2$, oxalic acid/$PdCl_2$, succinic acid/$PdCl_2$ and acetic acid/$PdCl_2$ systems. For the C_4mimBF_4/$PdCl_2$ and C_4mimPF_6/$PdCl_2$ systems we achieved similar results as those reported in the literature with the selectivity of acetophenone being slightly lower.[26] In the presence of palladium chloride, these neutral carboxylic acid–$PdCl_2$ systems could catalyze the oxidation of styrene but they all gave consistently lower conversions (28–46%) with lower selectivity towards acetophenone (73–84%).

A further major advantage of using McaILs was reflected in their facile separation and recycling with the palladium catalyst. After distillation of the reaction mixture,[27] the impurities formed during the oxidation process can all be removed by washing the McaIL–palladium containing mixture with cold acetone. Due to the low solubility of the McaILs, most of the McaILs/Pd can be recovered. In our previous paper, the susceptibility of dialkylimidazolium ionic liquids to oxidative degradation under oxidizing conditions was reported,[28] but it should be mentioned here that the oxidation of McaILs could not be observed in the present work. Thus, the obtained McaIL/$PdCl_2$ mixtures can be

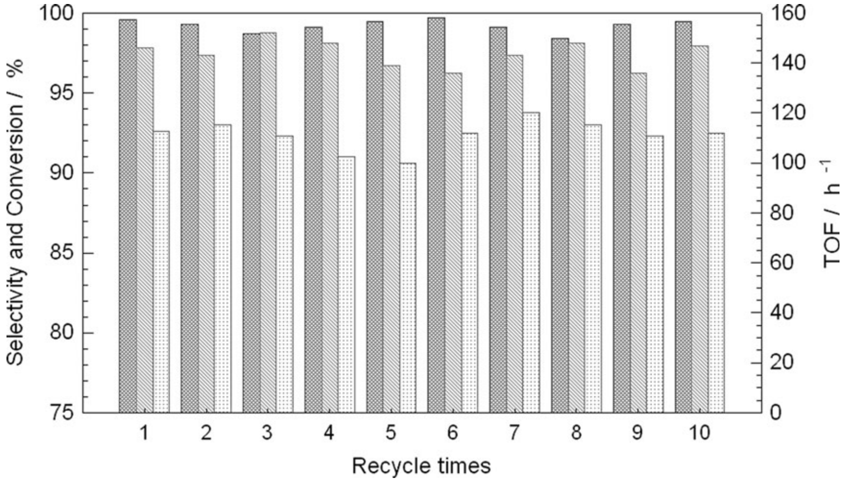


Fig. 2 Repeated testing of **3b**/$PdCl_2$ for the oxidation of styrene with H_2O_2: conversion (left), TOF (middle) and selectivity (right).

reused without a significant loss of catalytic activity (see Fig. 2). Though a very slight trace of Pd could be detected by ICP elemental analysis, this does not indicate a significant leakage of Pd, since the activity of **3b**/$PdCl_2$, conversion of styrene, and the selectivity towards acetophenone were all maintained after ten repeated cycles. In contrast, when $C_4mimBF_4/PdCl_2$ was used, the impurities remained in the residue after distillation, and were hardly removed due to the solubility of the C_4mimBF_4 in most common solvents. The activity decreased after three runs and the selectivity was lowered to less than 20%. For the $C_4mimPF_6/PdCl_2$ system although the impurities were partly removed after distillation followed by washing the residue with water, a significant amount of benzaldehyde and formic acid were always present in the remaining ionic liquids systems as indicated by ^1H NMR spectroscopy. As a result, the selectivity was remarkably reduced even after the second run.

Conclusions

We have synthesized a series of multicarboxylic acid appended imidazolium ionic liquids (McaILs). Novel McaIL/$PdCl_2$ systems have been investigated for the selective oxidation of styrene to acetophenone in the presence of hydrogen peroxide with excellent catalytic performances. Compared to non-functionalized ILs, these McaILs show a much higher selectivity at a relatively lower level of $PdCl_2$ content. The exceptionally low solubility of the acidic ILs has enabled a facile separation of the reaction products from catalyst without a significant loss of catalytic activity.

Experimental

General

Bromoethane, ethyl chloroacetate and styrene were purchased from Aldrich and used without further purification. Solvents used in this study were purchased from Guangzhou Jinhuada Chemical Reagent Co., Ltd. 1-Butyl-3-methylimidazolium tetrafluoroborate, $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$, were prepared according to the literature.[29] All NMR spectra were measured using a Bruker AVANCE Digital 400 spectrometer in D_2O or DMSO-d_6 at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded by a ThermoFinnigan LCQ Deca XP Plus ion trap mass spectrometer.[30] FT-IR spectra were recorded with a Bruker EQUINOX55 infrared spectrometer. Elemental analysis data were recorded on an Elementar Vario EL CHNS Elemental Analyzer. Water contents were determined by Karl Fischer volumetry using a Metrohm 758 KFD Titrino. TGA–DSC measurements were carried out on a STA 449C (Netzsch) apparatus at a scanning rate of 10 °C min^{-1}.

Wacker oxidation

The reaction was carried out in a 250 mL round-bottomed flask equipped with a condenser and a thermometer. In a typical experiment, styrene (26.03 g, 250 mmol), H_2O_2 (30% w/w) (32.59 g, 287.5 mmol) and $PdCl_2$ (0.0446 g, 0.25 mmol) were loaded into the reactor, the usage of McaILs was varied according to the designed molar ratio of McaIL to $PdCl_2$ in the range of 0.5 to 3.0 with fixed $PdCl_2$ molar value. The reaction mixture was heated to 55 °C under vigorous stirring. The reaction was monitored by a Shimadzu GCMS-QP2010 equipped with a DB-5MS capillary column (30 m × 0.25 mm × 25 μm) under a temperature programmed heating from 50 to 200 °C at 10 °C min^{-1}. The reaction was terminated as soon as no further conversion of styrene was observed.

Synthesis of 3a

Ethyl chloroacetate (8.09 g, 66 mmol) was added dropwise to a stirred solution of **1** (14.41 g, 60 mmol) at 75 °C under an argon atmosphere. The reaction mixture was stirred vigorously at 75 °C for 24 h. The residue was washed with diethyl ether (3 × 20 ml) and then residual solvent removed in vacuum. The product was dried in high vacuum to give **3a** as a viscous liquid (20.24 g, 93%).

Synthesis of 4a

Bromoethane (7.19 g, 66 mmol) was added dropwise to a stirred solution of **1** (14.41 g, 60 mmol) at 50 °C under an argon atmosphere. The reaction mixture was stirred vigorously at 50 °C for 24 h. The residue was washed with diethyl ether (3 × 20 ml), then residual solvent removed in vacuum. The product was dried in high vacuum to give **4a** as a viscous liquid (17.60 g, 84%).

Synthesis of 5a

Ethyl chloroacetate (8.09 g, 66 mmol) was added dropwise to a stirred solution of **2** (10.09 g, 60 mmol) at 70 °C under a argon atmosphere. The reaction mixture was stirred vigorously at 70 °C for 24 h. The residue was washed with diethyl ether (3 × 20 ml), then residual solvent removed in vacuum. The product was dried in high vacuum to give **5a** as a viscous liquid (16.57 g, 95%).

Synthesis of 3b

A mixture of **3** (21.77 g, 60 mmol) and HCl (37% aqueous solution, 19.51 g, 198 mmol) was refluxed for 1 h. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (3 × 20 ml) and then residual solvent removed in vacuum. The product was dried in high vacuum to give **3b** as a viscous liquid (15.88 g, 95%).

Synthesis of 4b

A mixture of **2** (20.95 g, 60 mmol) and HBr (48% aqueous solution, 13.00 g, 132 mmol) was refluxed for 1 h. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (3 × 20 ml) and then residual solvent removed in vacuum. The product was dried in high vacuum to give **4b** as a viscous liquid (17.06 g, 97%).

Synthesis of 5b

This compound was prepared using the same procedure as described for **3b**.

Synthesis of 3c, 4c and 5c

Synthesis of **3c** as a typical procedure, compounds **4c** and **5c** are prepared similarly.

A mixture of IL **3b** (16.72 g, 60 mmol) and triethylamine (6.68 g, 66 mmol) in dichloromethane (100 mL) was stirred at 25 °C for 36 h under a dry argon atmosphere. The white solid product was filtered off and washed with dichloromethane (3 × 30 mL) and dried in high vacuum to give the zwitterion.

Synthesis of 3d–3g, 4d–4g and 5d–5g

During the addition of Brønsted acids to zwitterions **3c**, **4c** and **5c**, exactly 1 : 1 molar ratio of zwitterion and the Brønsted acids was combined. The preparation of **3d** is described as a typical procedure, other compounds **3e–3g**, **4d–4g** and **5d–5g** were prepared using the same method.

Zwitterion **3c** (14.48 g, 60 mmol) was dissolved in 10 mL deionized water, then each acid was added to the aqueous solution. The mixture was stirred at 25 °C for 24 h under a dry argon atmosphere. The aqueous solvent was removed under reduced pressure. The residue was washed with diethyl ether (3 × 20 ml) and then residual solvent removed in vacuum. The product was dried in high vacuum to give **3d** as a viscous liquid (59 mmol, 98%). Similarly synthesized **3e–3g**, **4d–4g** and **5d–5g** were all viscous liquids obtained in yields >98%.

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References

1 (*a*) S. Doherty, P. Goodrich, C. Hardacre, H. Luo, D. W. Rooney, K. R. Seddon and P. Styring, *Green Chem.*, 2004, **6**, 63; (*b*) A. R. Katritzky, H. Yang, D. Zhang, K. Kirichenko, M. Smiglak, J. D. Holbrey, W. M. Reichert and R. D. Rogers, *New J. Chem.*, 2006, **30**, 349; (*c*) J. Dupont, R. Souza and P. A. Suarez, *Chem. Rev.*, 2002, **102**, 3667; (*d*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*e*) Z. Fei, T. J. Geldbach, D. Zhao and P. J. Dyson, *Chem.–Eur. J.*, 2006, **12**, 2122; (*f*) J. H. Davis, Jr, *Chem. Lett.*, 2004, **33**, 1072; (*g*) W. Dobbs, L. Douce, L. Allouche, A. Louati, F. Malbosc and R. Welter, *New J. Chem.*, 2006, **30**, 528.

2 (*a*) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr and R. D. Rogers, *Chem. Commun.*, 2001, 135; (*b*) E. Amigues, C. Hardacre, G. Keane, M. Migaud and M. O'Neill, *Chem. Commun.*, 2006, 72.

3 (*a*) R. P. Singh and J. M. Shreeve, *Chem. Commun.*, 2003, 1366; (*b*) D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *J. Am. Chem. Soc.*, 2004, **126**, 15876.

4 (*a*) C. Wang, L. Guo, H. Li, Y. Wang, J. Weng, L. Wu and Lianhai, *Green Chem.*, 2006, **8**, 603; (*b*) Z. B. Zhou, H. Matsumoto and K. Tatsumi, *Chem.–Eur. J.*, 2006, **12**, 2196; (*c*) Z. B. Zhou, H. Matsumoto and K. Tatsumi, *Chem. Lett.*, 2004, **33**, 886; (*d*) D. R. MacFarlane, S. A. Forsyth, J. Golding and R. B. Deacon, *Green Chem.*, 2002, **4**, 444.

5 J. C. Xiao, B. Twamley and J. M. Shreeve, *Org. Lett.*, 2004, **6**, 3845.

6 J. C. Xiao, C. Ye and J. M. Shreeve, *Org. Lett.*, 2005, **7**, 1963.

7 (*a*) R. Wang, M. M. Piekarski and J. M. Shreeve, *Org. Biomol. Chem.*, 2006, **4**, 1878; (*b*) R. Wang, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2006, **71**, 426.

8 K. Sasaki, S. Matsumura, K. Toshima and Kazunobu, *Tetrahedron Lett.*, 2004, **45**, 7043.

9 (*a*) D. Zhao, Z. Fei, W. H. Ang and P. J. Dyson, *Small*, 2006, **2**, 879; (*b*) S. R. Dubbaka, D. Zhao, Z. Fei, C. M. Rao Volla, P. J. Dyson and P. Vogel, *Synlett*, 2006, 5388.

10 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, Jr, *J. Am. Chem. Soc.*, 2002, **124**, 5962.

11 (*a*) M. S. Gil, F. Cruz, S. Cerdán and P. Ballesteros, *Bioorg. Med. Chem. Lett.*, 1992, **2**, 1717; (*b*) S. Gil, P. Zaderenko, F. Cruz, S. Cerdán and P. Ballesteros, *Bioorg. Med. Chem. Lett.*, 1994, **2**, 305; (*c*) P. Zaderenko, M. S. Gil, P. López, P. Ballesteros, I. Fonseca and A. Albert, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1997, **53**, 961; (*d*) N. E. Leadbeater and H. M. Torenius, *J. Org. Chem.*, 2002, **67**, 3145; (*e*) Y. Cai, S.-P. Yao, Q. Wu and X.-F. Lin, *Biotechnol. Lett.*, 2004, **26**, 525.

12 (*a*) N. Gathergood and P. J. Scammells, *Aust. J. Chem.*, 2002, **55**, 557; (*b*) D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 741; (*c*) W. A. Herrmann, L. J. Goossen and M. Spiegler, *J. Organomet. Chem.*, 1997, **547**, 357.

13 D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi and R. D. Rogers, *Chem. Commun.*, 2003, 28.

14 M. Aresta, I. Tkatchenko and I. Tommasi, *Ionic Liquids as Green Solvents: Progress and Prospects*, ACS Symposium Series, Washington, DC, 2003, vol. 856, p. 93.

15 (*a*) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Chem.–Eur. J.*, 2004, **10**, 4886; (*b*) P. Wasserscheid, B. Drießen-Hölscher, R. Hal, H. C. Steffens and J. Zimmermann, *Chem. Commun.*, 2003, **1**, 2038; (*c*) Z. Fei, W. H. Ang, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Chem.–Eur. J.*, 2006, **12**, 4014.

16 (*a*) Z. Fei, T. J. Geldbach, D. Zhao, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2005, **44**, 5200; (*b*) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti, P. J. Dyson, S. Antonijevic and G. Bodenhausen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5720; (*c*) Z. Fei, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 6331.

17 (*a*) M. Roussel and H. Mimoun, *J. Org. Chem.*, 1980, **45**, 5387; (*b*) T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329; (*c*) H. Jiang, L. Jia and J. Li, *Green Chem.*, 2000, **2**, 161.

18 J. M. Takacs and X. T. Jiang, *Curr. Org. Chem.*, 2003, **7**, 369.

19 N. Alandis, I. Rico-lattes and A. Lattes, *New J. Chem.*, 1994, **18**, 1147.

20 V. V. Namboodiri, R. S. Varma, E. Sahle-Demessie and U. R. Pillai, *Green Chem.*, 2002, **4**, 170.

21 M. Johansson, A. A. Lindén and J.-E. Baäckvall, *J. Organomet. Chem.*, 2005, **690**, 3614.

22 (*a*) A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, 1994, 3405; (*b*) A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton and J. A. Zora, *J. Chem. Soc., Dalton Trans.*, 1995, 3467.

23 Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Eur. J. Inorg. Chem.*, 2005, 860.

24 C. Chiappe, D. Pieraccini, D. Zhao, Z. Fei and P. J. Dyson, *Adv. Synth. Catal.*, 2006, **348**, 68.

25 See, for example: T. R. Jack and J. Powell, *Can. J. Chem.*, 1975, **53**, 2558.

26 We repeated carefully in our lab the experiments reported in ref. 20 (*Green Chem.*, 2002, **4**, 170); the conversion and selectivity were achieved were all slightly lower (3–5%) than reported.

27 The main product can be extracted using diethyl ether as described in ref. 20, however, side-products can not be fully removed. After extraction, some side-products can be partially, but not fully, removed through distillation under vacuum (0.1 mmHg) even at elevated temperature.

28 X. Li, J. Zhao, Q. Li, L. Wang and S. C. Tsang, *Dalton Trans.*, 2007, 1875.

29 (*a*) P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168; (*b*) J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133; (*c*) C. M. Gordon, J. D Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 1998, 2627.

30 P. J. Dyson, J. S. McIndoe and D. Zhao, *Chem. Commun.*, 2003, 508.