Immobilized metal ion-containing ionic liquids: preparation, structure and catalytic performance in Kharasch addition reaction†

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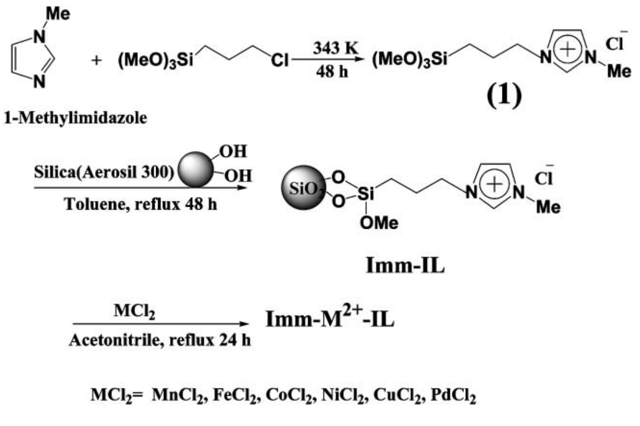
Immobilized metal ion-containing ionic liquid catalysts were prepared by the reaction between silyl-functionalized imidazolium ionic molecules and surface silanol groups of silica, followed by addition of $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, or $PdCl_2$; only the immobilized copper catalyst, which has a sandwiched $CuCl_4^{2-}$ moiety, was very active for the Kharasch reaction between styrene and CCl_4.

Design and preparation of a new class of immobilized single-reaction-site catalysts derived from structurally well-defined metal ion-containing ionic liquids, may provide an opportunity to exploit new catalytic materials with good performance from fundamental interests as well as the practical aspects of an environmentally-friendly system.[1,2] Ionic liquids, or molten salts, composed entirely of ions, have received much attention as they are versatile functionalities[3–5] and can be regarded as new key precursor materials for catalysts. Imidazolium ions commonly used as the cationic moiety are 1-ethyl-3-methylimidazolium (Emim) and 1-butyl-3-methylimidazolium (Bmim). In ionic liquids, common counter anions to date are BF_4^-, PF_6^-, halogen anions and haloaluminates (*e.g.*, $AlCl_4^-$). Ionic liquids are utilized as electrolytes in electrochemistry, green solvents for organic syntheses and immobilizing phases for biphasic catalysis. $AlCl_4^-$-containing ionic liquids were applied to catalytic reactions.[4,5] The crystal structures of Emim- and Bmim-salts with transition metal chloride anions such as $CoCl_4^{2-}$, $NiCl_4^{2-}$ and $PdCl_4^{2-}$ were also reported,[6,7] and the $PdCl_4^{2-}$-containing Bmim-ionic liquid was active in the hydrodimerization of butadiene.[7] Ionic liquids are regarded as catalytic precursors and they can be immobilized on inorganic oxide surfaces like SiO_2, which minimizes the consumption of ionic liquids in catalytic reactions, facilitates the reuse of catalysts, and finds a promising use in gas-phase catalytic reactions, with easier operation and higher performance. There are some reports of immobilization of ionic liquids involving $FeCl_3$, $SnCl_2$, and $AlCl_3$, but there is still the need to develop well-characterized immobilized ionic liquids with good catalytic performances.[2,8–11]

Recently, we have synthesized a series of metal ion-containing Bmim salts ([Bmim]MCl_x), and performed X-ray crystal structure analysis, TGA, and ionic conductivity measurements, which showed that the synthesized metal ion-containing imidazolium salts were unambiguously of ionic liquid character.[12] The aim of the present study is to find a metal ion-containing immobilized ionic liquid catalyst having a good catalytic property and to characterize it by physical methods.

Immobilized metal ion-containing ionic liquid catalysts were prepared as shown in Scheme 1. 1-Methyl-3-(trimethoxysilylpropyl)imidazolium chloride (**1**) was synthesized by refluxing 1-methylimidazole with (3-chloropropyl)trimethoxysilane [See ESI (1)†]. Silica (Aerosil® 300, surface area 300 $m^2\ g^{-1}$, Japan Aerosil Co.) was added to a toluene solution of **1** and refluxed for 48 h. Then toluene was removed and the functionalized silica was washed with boiling dichloromethane using a Soxhlet apparatus under a nitrogen atmosphere for 48 h, followed by drying under vacuum to remove dichloromethane. The silica thus treated is denoted as Imm-IL hereafter. The amount of immobilized **1** was determined to be 1.6 molecules per nm^2 by the elemental analysis of nitrogen. Solid state ^{29}Si-NMR revealed that immobilized Si atoms exhibited chemical shifts corresponding to the formation of one or two Si–O bonds with the silica surface [See ESI (2)†].

The complexation of $CuCl_2$ with the Imm-IL was achieved by refluxing the Imm-IL and $CuCl_2$ in acetonitrile for 24 h, subsequently washing with acetone in a Soxhlet apparatus for 48 h and drying by evacuation, resulting in Imm-Cu^{2+}-IL. The loading of Cu was determined to be 3.3 wt% by X-ray fluorescence analysis. The ratio of Cu atoms to immobilized imidazolium groups is close to 1:2. In order to evidence the local structure around the Cu ion, EXAFS spectra were measured at the BL-12C station of the Photon Factory in the Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The k^3-weighted Cu K-edge



Scheme 1

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† Electronic supplementary information (ESI) available: synthesis, elemental analysis, and NMR assignments of **1**. Solid state ^{29}Si NMR spectra for Imm-IL, Cu-K edge EXAFS Fourier transforms and curve fittings for $[Bmim]_2CuCl_4$ and Imm-Cu^{2+}-IL. Results for reuse of the Imm-Cu^{2+}-IL. See http://www.rsc.org/suppdata/cc/b5/b500349k/

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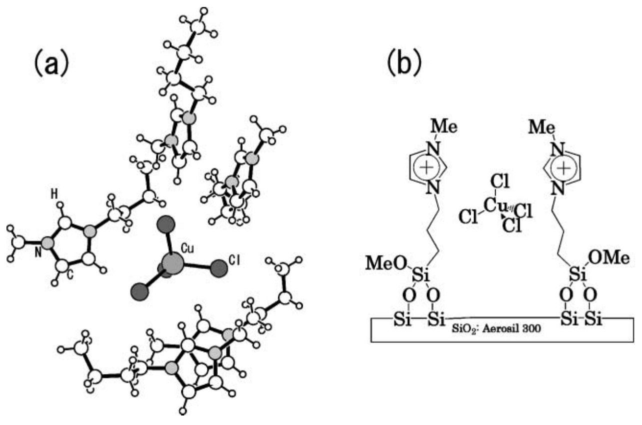


Fig. 1 Structure determined by X-ray crystal structure analysis for $[Bmim]_2CuCl_4$ (a),[12] and schematic illustration of Imm-Cu^{2+}-IL (b).

EXAFS Fourier transforms for $[Bmim]_2CuCl_4$ and Imm-Cu^{2+}-IL [See ESI (3)†] were almost the same as each other. We have succeeded in determining the single crystal X-ray structure of $[Bmim]_2CuCl_4$, which reveals that a tetrahedral $CuCl_4$ with a flattened distortion is surrounded by Bmim cations as shown in Fig. 1(a).[12] Table 1 summarizes the results of the EXAFS analysis. The EXAFS analysis for $[Bmim]_2CuCl_4$ was performed by fixing the coordination number (CN) as 4.0, while for the EXAFS analysis for the Imm-Cu^{2+}-IL the amplitude factor (S_0^2) was fixed to be 0.83. It was found that a Cu atom in the Imm-Cu^{2+}-IL is coordinated by 4 Cl atoms at the Cu–Cl distance of 0.225 nm. These results lead to a schematic view for Imm-Cu^{2+}-IL shown in Fig. 1(b). In the same way, various metal ion-containing immobilized catalysts (Imm-M^{2+}-IL) (M: Mn, Fe, Co, Ni, and Pd) were also prepared and characterized by XAFS, DR-UV/Vis, and XRF.

Immobilized ionic liquid catalysts were used for the Kharasch reaction between styrene and CCl_4 in the absence of solvent. Kharasch *et al.* reported the addition of carbon tetrachloride and chloroform to the C=C double bond of alkenes in the presence of peroxide.[13] The Kharasch reaction has been studied in homogeneous systems using iron and copper chlorides,[14–17] ruthenium complexes,[18–21] a palladium complex,[22] a nickel pincer complex,[23,24] a rhodium–ruthenium bimetallic complex,[25] and $Eu(OTf)_3$.[26] To our knowledge the only preceding example of a heterogeneous metal complex catalyst active in the reaction is an immobilized ruthenium complex.[27]

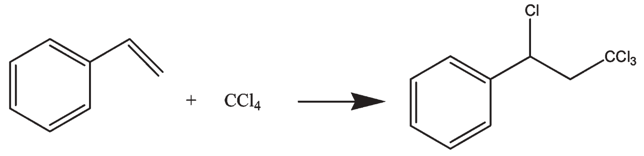
The reactions using the Imm-M^{2+}-IL catalysts were monitored by FID-GC and GC-MS. In a separate experiment the product, $PhCHClCHCCl_3$, was synthesized and used for the GC calibration. Serious by-products of the reaction are oligomers of styrene. Table 2 compares the performances of different Imm-M^{2+}-IL catalysts. Only Imm-Fe^{2+}-IL and Imm-Cu^{2+}-IL were active for the Kharasch reaction, and the product yield using Imm-Cu^{2+}-IL was three times better than that using Imm-Fe^{2+}-IL. Thus we have optimized the catalytic performance of Imm-Cu^{2+}-IL as shown in Table 3. By changing the amount of catalyst, the CCl_4:styrene ratio and the reaction temperature, the best performance (entry 6) showed 98% conversion, 95% selectivity, and 93% yield. When acetonitrile was added as a solvent (entry 7), the conversion, selectivity, and yield were reduced. A silica-supported $CuCl_2$ catalyst with the same Cu loading (entry 8) was also examined to find the effect of immobilized imidazolium groups. The silica-supported Cu catalyst produced a negligible amount of the product, with 0.3% yield, and styrene oligomerization mainly occurred, indicating that the catalytic activity is not the result of free Cu ions and that the existence of the immobilized imidazolium groups is essentially important for the reaction. Unsupported ionic liquid catalyst $[Bmim]_2CuCl_4$ was also compared after performance optimization (entry 9). The conversion (98%) was the same, irrespective of the three times larger Cu quantity, and the selectivity and yield were 69% and 68% respectively, which were much worse than those for the Imm-Cu^{2+}-IL. The yield of 68% is

Table 1 Curve-fitting results of the Fourier-transformed EXAFS data for $[Bmim]_2CuCl_4$ and Imm-Cu^{2+}-IL, measured at room temperature

Sample	Shell	CN	Distance (10^{-1} nm)	Debye–Waller factor (10^{-5} nm^2)	R_f (%)
$[Bmim]_2CuCl_4$[a]	Cu–Cl	4.0 (fix)	2.256 ± 0.002	5.56 ± 0.3	0.25
Imm-Cu^{2+}-IL[b]	Cu–Cl	3.9 ± 0.6	2.25 ± 0.01	10.4 ± 2	3.36

[a] $k = 3.0$–12.0, $R = 1.0$–3.0, $\Delta E_0 = -0.1 \pm 0.4$ eV. S_0^2 was fitted to be 0.83 ± 0.03. [b] $k = 3.0$–11.0, $R = 1.0$–3.0, $\Delta E_0 = -3 \pm 2$ eV. S_0^2 was fixed at 0.83.

Table 2 Kharasch reaction catalyzed by Imm-M^{2+}-IL[a]



Entry	Imm-M^{2+}-IL	M loading (wt%)	Conversion (%)	Selectivity (%)	Yield (%)
1	Mn	3.2	14	0	0
2	Fe	3.1	43	28	12
3	Co	2.9	28	0	0
4	Ni	3.3	31	0	0
5	Pd	3.4	60	0	0
6	Cu	3.3	65	55	36

[a] Reaction conditions: M: 0.1 mol%, styrene: 15 mmol, CCl_4: 30 mmol, 383 K, 20 h. The M mol% was defined with respect to styrene.

Table 3 Kharasch reaction performances of the ImmCu^{2+}-IL catalyst, CuCl$_2$–SiO$_2$, and [Bmim] $_2$CuCl$_4$[a]

Entry[b]	Cu (mol%)[c]	Ratio of CCl$_4$:styrene	*T* (K)	Conversion (%)	Selectivity (%)	Yield (%)
1	0.1	2:1	333	4	0	0
2	0.1	2:1	353	51	68	35
3	0.1	2:1	383	65	55	36
4	0.1	4:1	383	67	70	47
5	0.1	6:1	383	46	82	38
6	1.0	4:1	383	98	95	93
7[d]	1.0	4:1	383	37	76	28
8[e]	0.1	4:1	383	67	0.4	0.3
9[f]	3.0	2:1	383	98	69	68

[a] Reaction conditions: styrene 15 mmol, 20 h. [b] Entries 1–7: Cu loading was 3.3 wt%. [c] The Cu mol% was defined with respect to styrene. [d] 2 ml of CH$_3$CN was used. [e] CuCl$_2$–SiO$_2$ (3.3 wt%) was used as catalyst. [f] Performances of [Bmim]$_2$CuCl$_4$ after condition optimization.

similar to the reported value (78%) for the homogeneous catalysis of CuCl$_2$.[14] The immobilization on SiO$_2$ surfaces seems to restrict the conformation of reactants and favor the formation of the PhCHClCHCCl$_3$ product rather than the oligomerization of styrene. It is noted that the Imm-Cu^{2+}-IL catalyst is reusable. After the 5th reuse the yield was maintained above 80% [ESI (4)†]. DR UV-VIS measurements revealed that a fresh catalyst, a post-reaction catalyst and a reused catalyst exhibited almost the same features, indicating that the Imm-Cu^{2+}-IL is a durable catalyst.

In summary, immobilized metal ion-containing ionic liquid catalysts were prepared by the reaction between silyl-functionalized imidazolium ionic molecules (**1**) and silanol groups of silica surfaces, followed by addition of metal chloride (MnCl$_2$, FeCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and PdCl$_2$). Only the immobilized copper catalyst (Imm-Cu^{2+}-IL) among the obtained immobilized metal ion-containing ionic liquid catalysts was very active for the Kharasch reaction between styrene and CCl$_4$; 98% conversion, 95% selectivity, and 93% yield. The Imm-Cu^{2+}-IL catalyst was analyzed by EXAFS and the sandwiched CuCl$_4^{2-}$ moiety was confirmed by the comparison with that for single crystal [Bmim]$_2$CuCl$_4$. The Imm-Cu^{2+}-IL catalyst was also reusable. The present method provides an active single-site heterogeneous catalyst prepared by two simple steps.

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