

# Immobilized metal ion-containing ionic liquids: Preparation, structure and catalytic performances in Kharasch addition reaction and Suzuki cross-coupling reactions

Takehiko Sasaki<sup>a,\*</sup>, Mizuki Tada<sup>b</sup>, Chongmin Zhong<sup>b</sup>, Takao Kume<sup>b</sup>, Yasuhiro Iwasawa<sup>b</sup>

<sup>a</sup> Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

<sup>b</sup> Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Available online 17 June 2007

## Abstract

A series of immobilized metal ion-containing ionic liquids on silica surfaces (ImmM\_IL) were prepared and characterized by EXAFS, UV–vis, TGA, and elemental analysis. The prepared ImmCu<sup>2+</sup>\_IL was found to be more active than unsupported [Bmim]<sub>2</sub>CuCl<sub>4</sub> ionic liquid and reusable for Kharasch addition reaction between CCl<sub>4</sub> and styrene. The prepared ImmPd<sup>2+</sup>\_IL was active and reusable for Suzuki cross-coupling between phenylboronic acid and arylhalide. Throughout this study the present catalyst preparation method was confirmed to give efficient and reusable catalysts.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Immobilization; Reusability; EXAFS; Kharasch addition reaction; Suzuki cross-coupling reaction

## 1. Introduction

Recently ionic liquids have received much attention as immobilizing phases in biphasic catalytic reactions [1–3]. The charged nature of ionic liquids makes them ideal immobilizing phases for ionic complex catalysts in biphasic reactions with organic substrates. However, the biphasic reaction systems require a large amount of ionic liquids, which is undesirable from economic and environmental points of view. On the other hand, the danger of catalyst leaching and the difficulties of extracting products from ionic liquids when polar products are produced [4] are still big challenges to overcome. The immobilization of ionic liquids on solid supports can solve these problems and satisfy the requirements from chemical industry of the ease of separation and recovery of catalyst from reaction mixture and the possibility to use a fixed bed reactor [5]. By transferring the catalytic property of a homogeneous catalyst to a heterogeneous catalyst, the immobilization can combine the advantages of homogeneous ionic liquids with those of heterogeneous catalysts. An approach to immobilize ionic liquids is to impregnate

solid supports with pre-formed ionic liquids [5–12], in which no covalent bonds are formed between inorganic anions and the support material except the case of strong Lewis acid anions and there is the danger of leaching. Another method is to immobilize ionic liquids on solid supports by covalent bonding between silyl groups on the ionic liquid cations and silanol groups on support surfaces [4,11,13]. To date, hydroformylation reactions [5,11], Friedel–Crafts acylation and alkylation [6–8,13], hydrogenation [9,12], nucleophilic substitution reactions [4], and catalytic hydrodechlorination of CCl<sub>4</sub> [10] have been investigated using immobilized ionic liquids as catalysts

Recently, we have synthesized a series of metal ion-containing Bmim based ionic liquids [14]. Their crystal structures and physical properties were characterized by X-ray crystal structure analysis, melting point, TGA and ionic conductivity. We also reported that a chlorine ion containing ionic liquid was covalently immobilized on a SiO<sub>2</sub> surface by reacting the silyl groups with silanol groups on the surface and that the functionalized silica was reacted with metal chloride salts to form immobilized metal ion-containing ionic liquids [15]. The catalytic property of a Cu<sup>2+</sup>-containing immobilized ionic liquid was explored for the Kharasch addition reaction between styrene and CCl<sub>4</sub> [15]. Moreover, the catalytic property of a Ni<sup>2+</sup>-containing immobilized ionic liquid was found to be active

\* Corresponding author. Fax: +81 4 7136 3910.  
E-mail address: [takehiko@k.u-tokyo.ac.jp](mailto:takehiko@k.u-tokyo.ac.jp) (T. Sasaki).

for Suzuki cross-coupling reaction between chloroarenes and arylboronic acids [16].

In the present study the structures of these new materials were characterized by EXAFS and diffuse reflectance UV–vis spectroscopy, and the thermal stability was evaluated by TGA. The catalytic property of a  $\text{Cu}^{2+}$ -containing immobilized ionic liquid was explored for the Kharasch addition reaction between styrene and  $\text{CCl}_4$ . Catalytic activity of a  $\text{Pd}^{2+}$ -containing immobilized ionic liquid was also examined for the Suzuki cross-coupling reaction between phenylboronic acid and arylhalide. Pd-catalyzed Suzuki cross-coupling reactions in ionic liquid media have been reported for bromoarene in a homogeneous system [17] and for iodoarenes immobilized on a resin [18].

## 2. Experimental

### 2.1. Material

*N*-Methylimidazole (99+%) and 3-trimethoxysilylpropyl chloride (97+%) were purchased from Aldrich. Anhydrous  $\text{MnCl}_2$  (99+%) was obtained from Aldrich. Anhydrous  $\text{CoCl}_2$  (97.0%),  $\text{ZnCl}_2$  (99.9%),  $\text{NiCl}_2$  (99.9%),  $\text{PtCl}_2$  (98.0%),  $\text{FeCl}_2$  (98%),  $\text{PdCl}_2$  (99.0%), and  $\text{CuCl}_2$  (99.99%) were purchased from WAKO. Anhydrous redistilled 1-methylimidazole (99+%) was purchased from Aldrich. All the dehydrated solvents were obtained from WAKO. Aerosil 300 ( $300 \text{ m}^2/\text{g}$ ) was obtained from Japan Aerosil Co. and calcined at 573 K for 1.5 h in air and 30 min in vacuum before use as support.

### 2.2. Synthesis of 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride

This compound was synthesized according to step 1 in Scheme 1. *N*-methylimidazole (55.0 ml, 56.7 g, 0.690 mol) and 3-trimethoxysilylpropyl chloride (126.9 ml, 137.17 g, 0.690 mol) were mixed in a dry 300 ml flask under nitrogen flow. The system was evacuated and refilled with nitrogen, and this procedure was repeated five times, and refluxed for 48 h. After cooling to room temperature, the resultant liquid was washed with dehydrated ethyl acetate five times and dried at room temperature under reduced pressure for 48 h. The finally obtained material was a liquid and stored at 253 K under dry nitrogen.

### 2.3. Preparation of immobilized metal ion-containing ionic liquids (ImmM\_IL)

The preparation process is shown in Scheme 1 for ImmM\_IL ( $M = \text{Ni}, \text{Cu}, \text{Co}, \text{Fe}, \text{Mn}, \text{Zn}, \text{Pt}, \text{and Pd}$ ). In a glovebox, the pretreated Aerosil 300 and 1-methyl-3-(3-trimethoxysilylpropyl)imidazole chloride (weight ratio 1:1) were dispersed in dehydrated toluene in a Schlenk tube and the mixture was refluxed for 48 h under nitrogen. The toluene solvent was removed at a reduced pressure and the resulting material was transferred to a Soxhlet tube in nitrogen. The excess ionic liquid was removed by Soxhlet extraction with dichloromethane. The resulting solid is

denoted as Imm\_IL. Anal. Found: C, 7.36; H, 1.92; N, 1.54. The number of ionic liquids on the  $\text{SiO}_2$  surface was estimated to be ca  $1.2 \text{ nm}^{-2}$  by the nitrogen content in the material. The number of silanol groups on the surface of Aerosil 300 is ca.  $4 \text{ nm}^{-2}$  before pretreatment. The pretreatment reduced the number of silanol groups to  $2\text{--}3 \text{ nm}^{-2}$  and the number of ionic liquids that can be immobilized is  $1.3\text{--}2 \text{ nm}^{-2}$ . If there are 2.4 hydroxyl groups per  $\text{nm}^2$  for the pretreated silica and one ionic liquid consumes two hydroxyl groups, almost all of the surface hydroxyl groups were used in the immobilization process. The Imm\_IL was characterized by MAS-SS- $^{29}\text{Si}$  NMR (59.67 MHz):  $\delta$   $-69$  ( $\text{C-Si}(\text{OSi})_3$ );  $-61$  ( $\text{C-Si}(\text{OMe})(\text{OSi})_2$ );  $-52$  ( $\text{C-Si}(\text{OMe})_2(\text{OSi})$ ).

In the next step, Imm\_IL was added to an acetonitrile solution of metal chloride in a 50 ml Schlenk tube and refluxed for 24 h. Acetonitrile was removed at a reduced pressure and excess of metal chloride was removed by Soxhlet extraction with acetone for 48 h. The prepared immobilized ionic liquids are denoted as ImmM\_IL, where M represents the associated metal ions. The metal loadings were determined by XRF to be 3.3 wt% for ImmNi\_IL, ImmCu\_IL and ImmZn\_IL, 3.4 wt% for ImmPt\_IL and ImmPd\_IL, 3.2 wt% for ImmMn\_IL, 3.1 wt% for ImmFe\_IL, and 2.9 wt% for ImmCo\_IL.

### 2.4. UV–vis spectra measurement

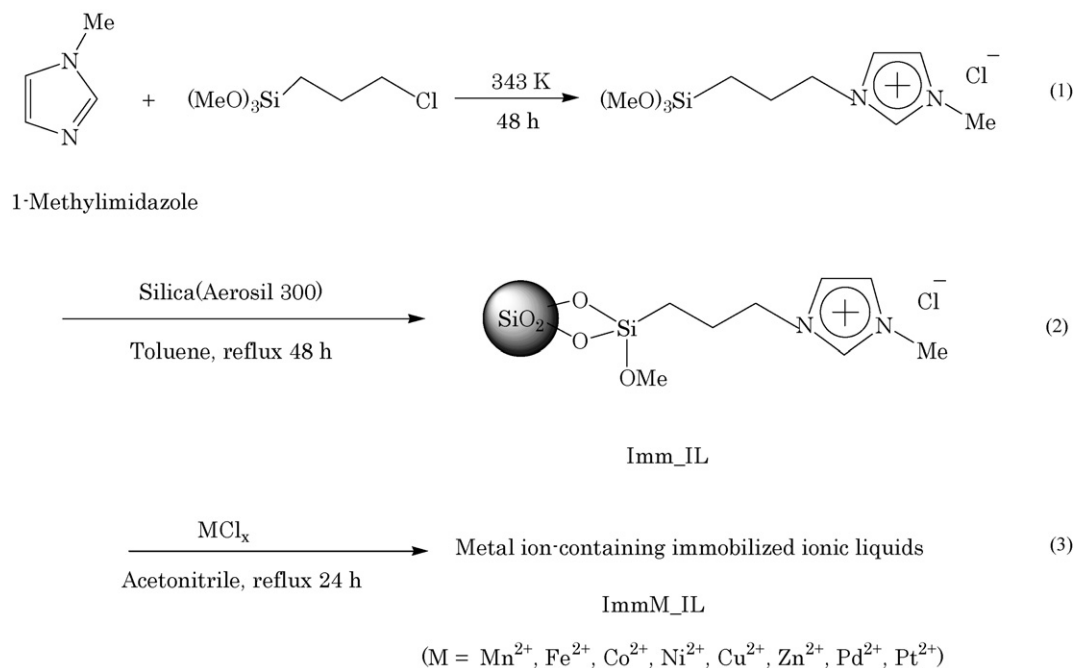
Diffuse reflectance UV–vis spectra were measured on a Jasco V-550 spectrophotometer equipped with a diffuse reflectance integrating sphere (ILV-471). The spectra were measured in reflectance mode and converted with the Kubelka-Munk function  $f(R_d)$ . The spectra were obtained by plotting  $\log f(R_d)$  versus wavelength (nm), which can be used to compare with spectra measured in a transmission method. The samples were handled under dry nitrogen atmosphere.

### 2.5. X-ray fluorescence measurement (XRF)

XRF was measured on a SEA-2010 spectrometer (Seiko Electronic Industrial Co.). Physical mixtures of metal chloride salts and support Aerosil 300 with various ratios were used to make calibration lines to estimate the metal loadings in the immobilized ionic liquids.

### 2.6. EXAFS measurement

Measurements of extended X-ray absorption fine structure (EXAFS) were carried out at the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The measurements were made in a transmission mode. Spectra were measured at BL-7C for  $[\text{Bmim}]_2[\text{NiCl}_4]$  and ImmNi\_IL, at BL-9A for  $[\text{Bmim}]_2[\text{CoCl}_4]$ , at BL-9C for  $[\text{Bmim}]_2[\text{MnCl}_4]$ , ImmMn\_IL, ImmCo\_IL and ImmFe\_IL, at BL-12C for  $[\text{Bmim}]_2[\text{FeCl}_4]$ , at BL-10B for  $[\text{Bmim}]_2[\text{MCl}_4]$  ( $M = \text{Cu}, \text{Pt}, \text{Zn}, \text{Pd}$ ) and ImmPd\_IL. The electron storage ring was operated at 2.5 GeV and 300–400 mA at BL-7C, 9A, 9C and 12C stations, and 3.0 GeV and 400 mA at BL-10B. Synchrotron radiation from



Scheme 1. Preparation of metal ion-containing immobilized ionic liquids.

the storage ring was monochromatized by a Si(3 1 1) channel cut crystal at BL-10B, and Si(1 1 1) at BL-7C, 9A, 9C and 12C. Ionization chambers, which were used as detectors for incident X-ray ( $I_0$ ) and transmitted X-ray ( $I$ ), were filled with 1 to 1 volume ratio of Ar/N<sub>2</sub> mixture gas and Ar gas, respectively. The angles of the monochromators were calibrated with metal foils of the same element as that in the samples. The samples were handled in dry nitrogen. The EXAFS raw data were analyzed with UWXAFS analysis package [19], including background subtraction program AUTOBK [20], curve fitting program FEFFIT, [21]. The amplitude reducing factor,  $S_0^2$  was found from a reference compound with known structure and applied to unknown samples.

### 2.7. Catalytic reaction: Kharasch addition reaction

Carbon tetrachloride (99.8%), styrene (99.0%), pentane (98%) and dehydrated acetonitrile were purchased from Wako and used as received. The addition products were analyzed by FID-GC, GC-MS and <sup>1</sup>H NMR. The copper loading of ImmCu<sup>2+</sup>\_IL was determined to be 3.3 wt% by XRF.

#### 2.7.1. General procedure for Kharasch addition reaction

ImmCu<sup>2+</sup>\_IL (290 mg, 0.15 mmol) was weighted in air and put into 50 ml Schlenk tube. Styrene (15 mmol, 1.73 ml) and CCl<sub>4</sub> (60 mmol, 5.8 ml) were added. The mixture was degassed three times and then refluxed in an oil bath at 383 K with stirring under nitrogen atmosphere. After the reaction, the solution was filtrated and the catalyst was washed with pentane five times. The catalyst was dried under vacuum at room temperature for 1 h and used in the next reaction.

### 2.8. Catalytic reaction: Suzuki cross-coupling reaction

ImmPd<sup>2+</sup>\_IL (0.03 mmol) was weighted in air and put into 50 ml Schlenk tube, to which phenylboronic acid (2.75 mmol), arylhalide (2.5 mmol), base (5.3 mmol) and 8 ml of solvent were added. The mixture was degassed three times and then refluxed in an oil bath at 383 K for 24 h with stirring under nitrogen atmosphere. The products were analyzed by FID-GC and GC-MS. After reaction, the solution was filtrated and the catalyst was washed with the solvent five times. The catalyst was dried under vacuum at room temperature for 1 h and used in the next reaction.

## 3. Results and discussion

### 3.1. EXAFS

The prepared ImmM\_ILs were characterized by K-edge EXAFS for M = Ni<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Pd<sup>2+</sup>, and L<sub>3</sub>-edge EXAFS for M = Pt<sup>2+</sup>. In order to determine the coordination number (CN) of the metal ions in these immobilized ionic liquids, parameters  $S_0^2$  were determined using reference compounds with known structures. The structures of corresponding ionic liquids [Bmim]<sub>2</sub>[MCl<sub>4</sub>] (M = Ni, Cu, Fe, Mn, Zn, Co, Pt, and Pd) have already been characterized by single crystal X-ray structure analysis, and the CNs of the metal ions in these compounds were determined to be 4 [14,15]. These ionic liquids were used as reference compounds and the EXAFS of them were also measured. The value of parameter  $S_0^2$  for a given metal element in an ImmM\_IL was determined by fitting the experimental EXAFS functions of its reference compounds with EXAFS equation, in which parameter CN was fixed at 4. The reference compounds for ImmMn<sup>2+</sup>\_IL, ImmFe<sup>2+</sup>\_IL, ImmCo<sup>2+</sup>\_IL, ImmNi<sup>2+</sup>\_IL, ImmCu<sup>2+</sup>\_IL, ImmZn<sup>2+</sup>\_IL, ImmPd<sup>2+</sup>\_IL, ImmPt<sup>2+</sup>\_IL were

Table 1

Summary of the EXAFS fitting results for [Bmim]<sub>2</sub>[MCl<sub>4</sub>] and ImmM\_IL (M = Ni<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, and Pd<sup>2+</sup>)

	Shell	CN	$R (\times 10^{-1} \text{ nm})$	$DW (\times 10^{-5} \text{ nm}^2)$	$\Delta k (\times 10 \text{ nm}^{-1})$	$\Delta r (\times 10^{-1} \text{ nm})$	$S_0^2$	$\Delta E_0 (\text{eV})$	$R_f (\%)$
[Bmim] <sub>2</sub> [PdCl <sub>4</sub> ]	Pd–Cl	4.0	2.31 ± 0.002	2.0 ± 0.3	3.0–12.5	1.1–3.0	0.89 ± 0.04	6.5 ± 0.6	0.42
ImmPd <sup>2+</sup> _IL	Pd–Cl	4.3 ± 0.3	2.31 ± 0.004	2.7 ± 0.4	3.0–14.0	1.0–2.9	0.89	7.2 ± 0.9	1.45
[Bmim] <sub>2</sub> [CuCl <sub>4</sub> ]	Cu–Cl	4.0	2.26 ± 0.002	5.6 ± 0.4	3.0–12.0	1.0–3.0	0.83 ± 0.03	−0.1 ± 0.4	0.25
ImmCu <sup>2+</sup> _IL	Cu–Cl	3.9 ± 0.6	2.25 ± 0.01	10 ± 2	3.0–11.0	1.0–3.0	0.83	−3.0 ± 2.0	3.36
[Bmim] <sub>2</sub> [NiCl <sub>4</sub> ]	Ni–Cl	4.0	2.27 ± 0.003	4.6 ± 0.3	3.0–13.0	1.0–3.0	0.83 ± 0.04	1.6 ± 0.6	0.53
ImmNi <sup>2+</sup> _IL	Ni–Cl	3.6 ± 0.2	2.27 ± 0.003	6.1 ± 0.4	3.0–13.0	1.0–3.0	0.83	2.1 ± 0.6	0.65
[Bmim] <sub>2</sub> [MnCl <sub>4</sub> ]	Mn–Cl	4.0	2.38 ± 0.005	3.9 ± 0.7	3.0–11.5	1.2–2.5	0.73 ± 0.06	3.0 ± 1.0	0.73
ImmMn <sup>2+</sup> _IL	Mn–Cl	3.8 ± 0.4	2.36 ± 0.008	7 ± 1	3.0–10.0	1.2–3.0	0.73	0.3 ± 1.2	0.77
[Bmim] <sub>2</sub> [ZnCl <sub>4</sub> ]	Zn–Cl	4.0	2.28 ± 0.004	5.7 ± 0.5	3.0–13.0	1.0–3.0	0.97 ± 0.6	5.8 ± 0.7	0.99
ImmZn <sup>2+</sup> _IL	Zn–Cl	3.6 ± 0.2	2.28 ± 0.004	6.1 ± 0.5	3.0–13.0	1.0–3.0	0.97	5.5 ± 0.7	1.03
[Bmim] <sub>2</sub> [CoCl <sub>4</sub> ]	Co–Cl	4.0	2.27 ± 0.005	3.1 ± 0.7	3.0–12.0	1.0–2.5	0.73 ± 0.08	3.3 ± 1.4	1.8
ImmCo <sup>2+</sup> _IL	Co–Cl	3.7 ± 0.3	2.28 ± 0.006	4.7 ± 0.9	3.0–10.0	1.5–3.0	0.73	4.0 ± 1.0	0.47

[Bmim]<sub>2</sub>[MnCl<sub>4</sub>], [Bmim]<sub>2</sub>[FeCl<sub>4</sub>], [Bmim]<sub>2</sub>[CoCl<sub>4</sub>], [Bmim]<sub>2</sub>[NiCl<sub>4</sub>], [Bmim]<sub>2</sub>[CuCl<sub>4</sub>], [Bmim]<sub>2</sub>[ZnCl<sub>4</sub>], [Bmim]<sub>2</sub>[PdCl<sub>4</sub>], and [Bmim]<sub>2</sub>[PtCl<sub>4</sub>], respectively. Then the  $S_0^2$  values obtained from the reference compounds were used to determine the CNs of metals in immobilized ionic liquids. The fitting parameters for the reference compounds [Bmim]<sub>2</sub>[MCl<sub>4</sub>] and the immobilized ionic liquids ImmM\_IL (M = Ni<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, and Pd<sup>2+</sup>) are summarized in Table 1. The EXAFS raw data for [Bmim]<sub>2</sub>[CuCl<sub>4</sub>] and ImmCu<sup>2+</sup>\_IL, which were applied to Kharasch addition reaction, are shown in Fig. 1(a) and (b),

respectively; and the EXAFS raw data for [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] and ImmPd<sup>2+</sup>\_IL, which were used as catalysts for Suzuki cross-coupling reaction, are shown in Fig. 2(a) and (b), respectively. The ionic liquids and immobilized ionic liquids of the same metal showed similar EXAFS oscillations. The  $k^3$ -weighted Fourier transforms of the EXAFS data for ImmM\_IL (M = Pd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, and Co<sup>2+</sup>) are shown in Fig. 3(a–f), respectively.

The EXAFS results of ImmM\_IL were similar to those for the corresponding [Bmim]-metal ion-containing ionic liquids with four CN of M–Cl bonds. Within the fitting uncertainties, the average distances of M–Cl in these ImmM\_ILs were the same

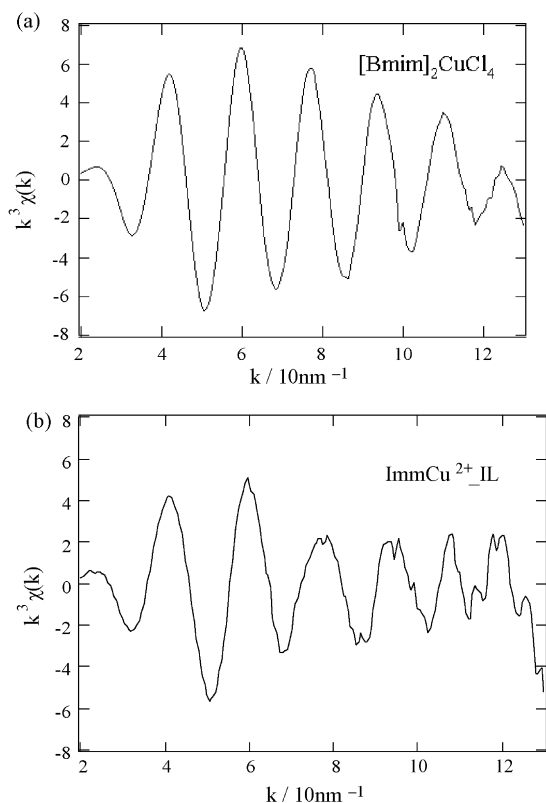


Fig. 1. EXAFS data for [Bmim]<sub>2</sub>[CuCl<sub>4</sub>] (a) and ImmCu<sup>2+</sup>\_IL (3.3 wt% Cu) (b).

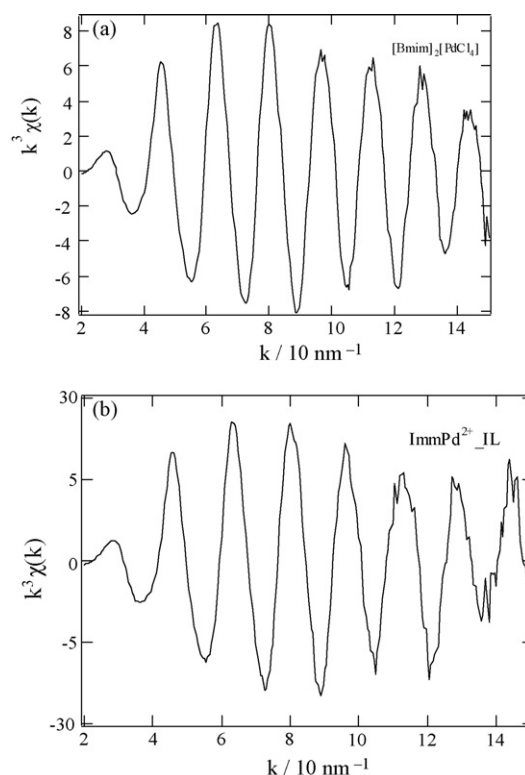


Fig. 2. EXAFS data for [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] (a) and ImmPd<sup>2+</sup>\_IL (3.4 wt% Pd) (b).

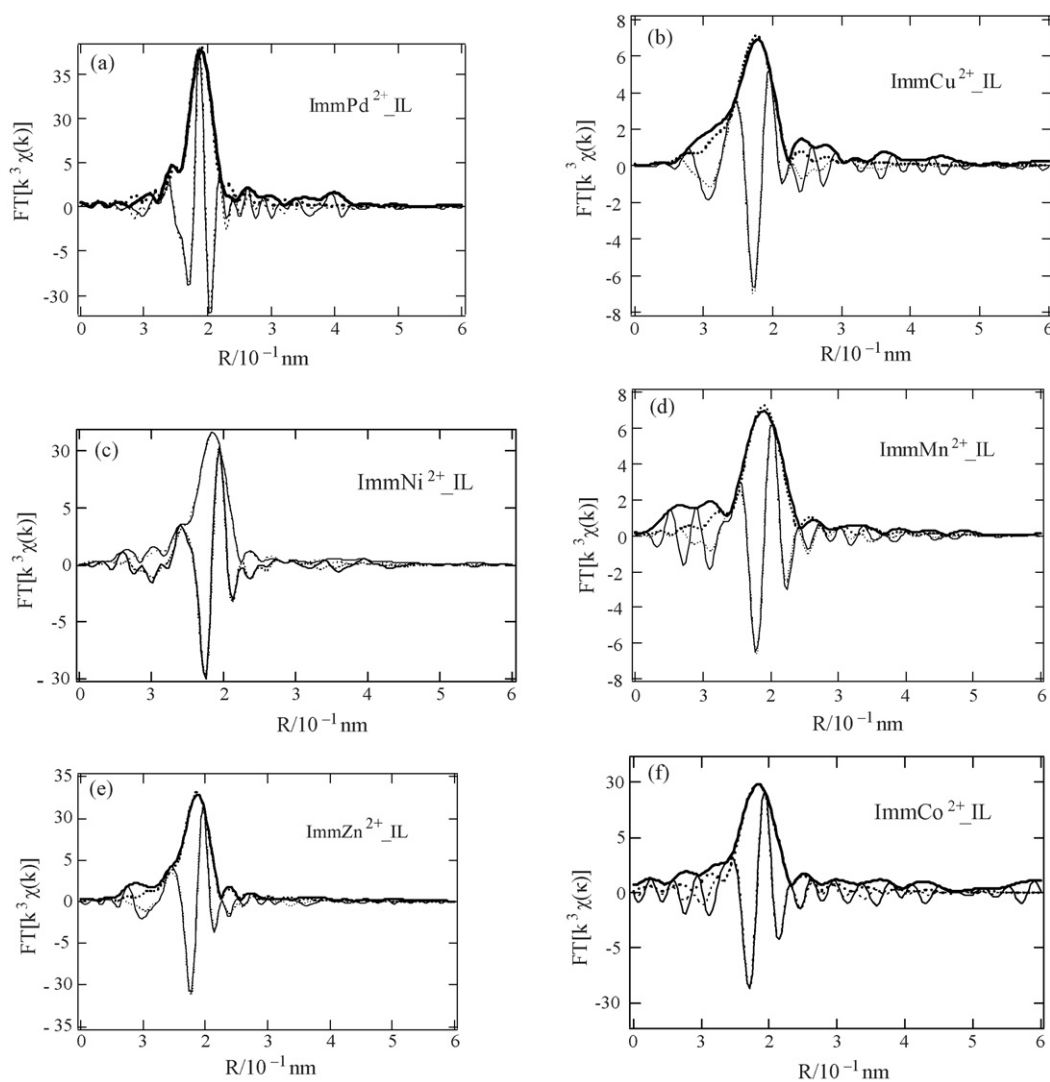


Fig. 3.  $k^3$ -Weighted Fourier transform (amplitude (thick curve) and imaginary part (thin curve)) of K-edge EXAFS for ImmM\_IL ( $M = \text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$ ). Observed data: solid lines; fitting data: dotted lines.

as those of the corresponding ionic liquids of the same metal (e.g. ImmCu<sup>2+</sup>\_IL has the same average bond distance of Cu–Cl as [Bmim]<sub>2</sub>[CuCl<sub>4</sub>], etc.). In all of the ImmM\_ILs, no metal–metal bond was observed. These results led to a schematic view of ImmM\_IL ( $M = \text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Co}^{2+}$ ) shown in Fig. 4, where the metal ions are held between two imidazolium ions. As to ImmFe<sup>2+</sup>\_IL and ImmPt<sup>2+</sup>\_IL almost similar results were obtained, where a remaining acetonitrile affected the EXAFS oscillation.

TGA curves of ImmM\_IL ( $M = \text{Cl}^-$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pt}^{2+}$ , and  $\text{Pd}^{2+}$ ) were measured (not shown) and it was found that ImmM\_ILs were stable up to 500 K, above which a decomposition process of immobilized groups started.

### 3.2. Kharasch addition reaction

Immobilized ionic liquids ImmM\_IL ( $M = \text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Mn}^{2+}$ ) were subjected to the Kharasch addi-

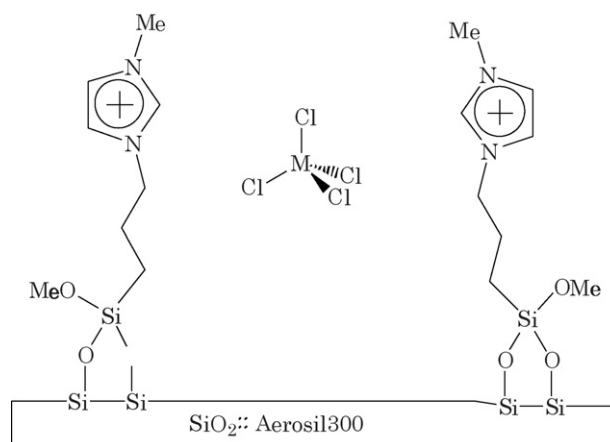
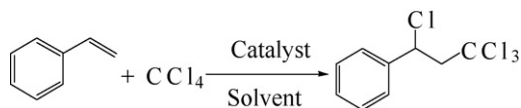
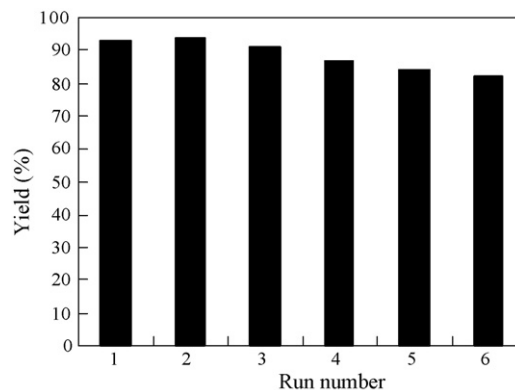


Fig. 4. A schematic view of ImmM\_IL ( $M = \text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$ ).

Scheme 2. Kharasch addition reaction between styrene and  $\text{CCl}_4$ .

tion reaction between styrene and  $\text{CCl}_4$  (Scheme 2) in the absence of additional solvent. Kharasch et al. reported the addition of carbon tetrachloride or chloroform to C=C double bond of alkenes in the presence of peroxide [22]. The Kharasch reactions have been studied in homogeneous systems by using iron and copper chlorides [23–26], ruthenium complexes [27–30], palladium complex [31], nickel pincer complex [32,33], rhodium–ruthenium bimetallic complex [34], and  $\text{Eu}(\text{OTf})_3$  [35].

The reactions on the ImmM\_IL catalysts were monitored by FID-GC and GC-MS. In a separate experiment the product  $\text{PhCHClCH}_2\text{CCl}_3$  was synthesized and used for the calibration of GC. Serious by-products of the reaction are oligomers of styrene. Table 2 compares the performances of different ImmM\_IL catalysts (entries 1–6). Only  $\text{ImmFe}^{2+}$ \_IL and  $\text{ImmCu}^{2+}$ \_IL were active for the Kharasch addition reaction, and the yield of product on  $\text{ImmCu}^{2+}$ \_IL was three times larger than that on  $\text{ImmFe}^{2+}$ \_IL. Thus the catalytic performances of  $\text{ImmCu}^{2+}$ \_IL were optimized as shown in Table 2 (entries 7–12). By changing the amount of catalysts, the molar ratio of  $\text{CCl}_4$ /styrene and the reaction temperature, the best performance (entry 12) showed 98% conversion, 95% selectivity, and 93% yield. When acetonitrile was added as a solvent (entry 13), the conversion, selectivity, and yield were reduced. A silica-supported  $\text{CuCl}_2$  catalyst with the same Cu loading (entry 14) was also applied to the Kharasch addition reaction under the identical conditions. The silica-supported Cu catalyst produced a negligible amount of the product with 0.3% yield, where the main products are

Fig. 5. Reuse of  $\text{ImmCu}^{2+}$ \_IL catalyst in Kharasch addition reaction.

oligomers of styrene. The result of unsupported ionic liquid  $[\text{Bmim}]_2[\text{CuCl}_4]$  was also listed after the performance optimization (entry 15). The conversion (98%) was similar irrespective of three times larger Cu quantity, and the selectivity and yield were 69% and 68%, respectively, which were much worse than those of the  $\text{ImmCu}^{2+}$ \_IL. It is well known that the mechanism of the Kharasch addition reaction catalyzed by transition metals involves a radical process [36] and the main reaction intermediate is a radical containing the metal center. It is reasonable to think that the mobility of the metal center, and thus that of the radical formed during the reaction, will be limited to a smaller range in the immobilized ionic liquid, compared to unsupported ionic liquid. The low mobility of radicals might be unfavorable to the formation of oligomers and be responsible for the higher selectivity of  $\text{ImmCu}^{2+}$ \_IL than that of  $[\text{Bmim}]_2[\text{CuCl}_4]$ . It is to be noted that the  $\text{ImmCu}^{2+}$ \_IL catalyst is reusable (Fig. 5). After the 5th reuse the yield was maintained above 80%. DR UV–vis measurements (Fig. 6) revealed that a fresh catalyst, a post-reaction catalyst and a reused catalyst exhibited almost

Table 2  
Performances of the ImmM\_IL catalyst in Kharasch addition reaction

Entry	M	M mol%	Ratio of $\text{CCl}_4$ /styrene	T (K)	Conversion (%)	Selectivity (%)	Yield (%)
1	$\text{Mn}^{2+}$	0.1	2	383	14	0	0
2	$\text{Fe}^{2+}$	0.1	2	383	43	28	12
3	$\text{Co}^{2+}$	0.1	2	383	28	0	0
4	$\text{Ni}^{2+}$	0.1	2	383	31	0	0
5	$\text{Pd}^{2+}$	0.1	2	383	60	0	0
6	$\text{Cu}^{2+}$	0.1	2	383	65	55	36
7	$\text{Cu}^{2+}$	0.1	2	333	4	0	0
8	$\text{Cu}^{2+}$	0.1	2	353	51	68	35
9	$\text{Cu}^{2+}$	0.1	2	383	65	55	36
10	$\text{Cu}^{2+}$	0.1	4	383	67	70	47
11	$\text{Cu}^{2+}$	0.1	6	383	46	82	38
12	$\text{Cu}^{2+}$	1.0	4	383	98	95	93
13 <sup>a</sup>	$\text{Cu}^{2+}$	1.0	4	383	37	76	28
14 <sup>b</sup>	$\text{Cu}^{2+}$	0.1	4	383	67	0.4	0.3
15 <sup>c</sup>	$\text{Cu}^{2+}$	3.0	2	383	98	69	68

For comparison, the results of  $\text{CuCl}_2/\text{SiO}_2$ , and  $[\text{Bmim}]_2[\text{CuCl}_4]$  were also shown here. Reaction conditions: styrene 15 mmol, 20 h. The M mol% was defined with respect to styrene.

<sup>a</sup> Two milliliters of  $\text{CH}_3\text{CN}$  was used.

<sup>b</sup>  $\text{CuCl}_2/\text{SiO}_2$  (3.3 wt%) was used as catalyst.

<sup>c</sup> Performances of  $[\text{Bmim}]_2[\text{CuCl}_4]$  after condition optimization.

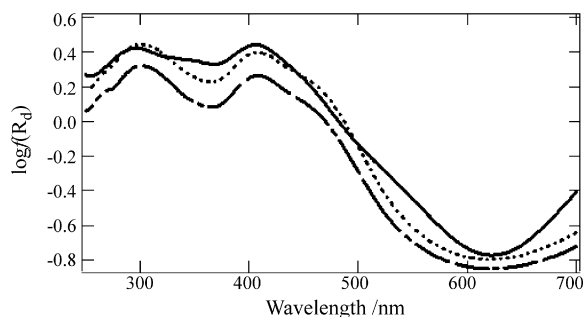


Fig. 6. DR UV-vis spectra of as-prepared ImmCu<sup>2+</sup>\_IL (solid curve), after reaction (dash-dot curve), and after 5th reuse (dotted curve).

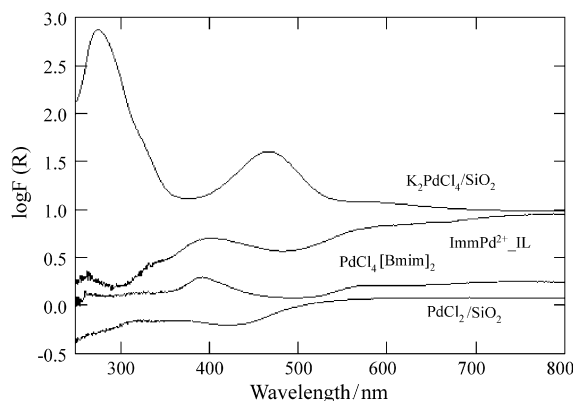
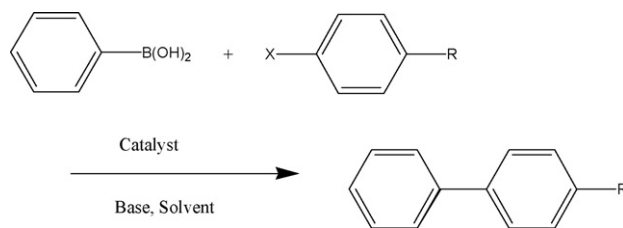


Fig. 7. Diffusion reflectance UV-vis spectra for K<sub>2</sub>PdCl<sub>4</sub>/SiO<sub>2</sub>, ImmPd<sup>2+</sup>\_IL, [Bmim]<sub>2</sub>PdCl<sub>4</sub>, and PdCl<sub>2</sub>/SiO<sub>2</sub>.

the same feature, indicating that ImmCu<sup>2+</sup>\_IL was a durable catalyst.

### 3.3. Suzuki cross-coupling reactions by ImmPd<sup>2+</sup>\_IL

Next, ImmPd<sup>2+</sup>\_IL were examined as a catalyst for Suzuki cross-coupling reaction. [Bmim]<sub>2</sub>[PdCl<sub>4</sub>], whose synthesis and structure was already reported by Dullius et al. [37], was also examined as a reference catalyst. The PdCl<sub>4</sub> unit exhibits the square planar structure. As mentioned above, the EXAFS analysis showed that the Pd–Cl bond distance is the same for ImmPd<sup>2+</sup>\_IL and [Bmim]<sub>2</sub>[PdCl<sub>4</sub>]. Fig. 7 shows the DR UV-vis spectra for silica supported K<sub>2</sub>PdCl<sub>4</sub>, ImmPd<sup>2+</sup>\_IL,



Scheme 3. Suzuki cross-coupling reaction between phenylboronic acid and *p*-substituted halobenzene in the presence of base and solvent.

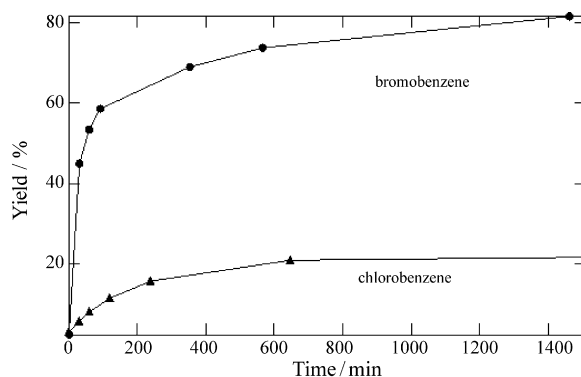


Fig. 8. Yield vs. reaction time for bromobenzene and chlorobenzene adopted as arylhalide, respectively, catalyzed by ImmPd<sup>2+</sup>\_IL corresponding to Table 4 entries 1 and 2 with K<sub>2</sub>CO<sub>3</sub> as base.

[Bmim]<sub>2</sub>[PdCl<sub>4</sub>] and silica supported PdCl<sub>2</sub>. ImmPd<sup>2+</sup>\_IL and [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] exhibit almost the same feature, while K<sub>2</sub>PdCl<sub>4</sub>/SiO<sub>2</sub> and PdCl<sub>2</sub>/SiO<sub>2</sub> show different peak positions, indicating that ImmPd<sup>2+</sup>\_IL and [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] have the similar coordination environment around the PdCl<sub>4</sub> unit.

Suzuki cross-coupling reaction [38] is a facile C–C bond forming catalytic reaction between phenylboronic acid and arylhalide in the presence of base, as indicated in Scheme 3, where Pd is the most commonly used element. Fig. 8 represents the yield of biphenyl catalyzed by ImmPd<sup>2+</sup>\_IL in *m*-xylene at 383 K as a function of time for bromobenzene and chlorobenzene as reactants. Obviously bromobenzene exhibits a higher activity than chlorobenzene, that is in agreement with a general trend. Table 3 summarizes the results for ImmPd<sup>2+</sup>\_IL with various substituted arylhalides using K<sub>2</sub>CO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub> as base. For *p*-substituted bromobenzene cross-coupling product and

Table 3  
Yields for Suzuki cross-coupling reactions catalyzed by ImmPd<sup>2+</sup>\_IL in the presence of either K<sub>2</sub>CO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub> as solid base

Entry	X	R	K <sub>2</sub> CO <sub>3</sub> yield (%) (homo coupling (%))	K <sub>3</sub> PO <sub>4</sub> yield (%) (homo coupling (%))
1	Br	H	89.1	94.3
2	Cl	H	21.7	26.1
3	I	H	80.8	88.5
4	Br	Me	79.5 (7.3)	81.1 (5.0)
5	Br	OMe	74.2 (4.5)	76.1 (4.4)
6	Br	NO <sub>2</sub>	93.2 (4.0)	61.1 (1.5)
7	Br	CF <sub>3</sub>	94.3	
8	Br	H	55.3 in dioxane	
9	Br	H	77.4 1 ml water	

Reaction conditions—catalyst: 0.03 mmol; arylhalide: 2.5 mmol; phenylboronic acid: 2.75 mmol; 383 K, *m*-xylene 8 ml, 24 h. Yield was calculated with respect to arylhalide.

Table 4

Yields for Suzuki cross-coupling reactions catalyzed by [Bmim]<sub>2</sub> PdCl<sub>4</sub> in the presence of either K<sub>2</sub>CO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub> as solid base

Entry		X	R	K <sub>2</sub> CO <sub>3</sub> yield (%) (homo coupling (%))	K <sub>3</sub> PO <sub>4</sub> yield (%) (homo coupling (%))
1		Br	H	99.9	89.5
2		Cl	H	21.0	14.0
3		I	H	62.3	88.3
4		Br	Me	66.0 (12.8)	58.6 (14.9)
5		Br	OMe	73.2 (11.6)	
6		Br	NO <sub>2</sub>	96.1 (3.9)	
7		Br	CF <sub>3</sub>	100.0	
8	Reuse 2nd	Br	H	74.1	
9	Reuse 3rd	Br	H	28.9	
10	In DMF	Br	H	94.6	
11	Carbene complex	Br	H	86.1	
12	Silica supported	Br	H	90.8	
13	1 ml water	Br	H	83.2	

Reaction conditions—catalyst: 0.03 mmol; arylhalide: 2.5 mmol; phenylboronic acid: 2.75 mmol; 383 K, *m*-xylene 8 ml, 24 h. Yield was calculated with respect to arylhalide.

homo-coupling product can be discriminated and each yield was specified. Bromobenzene with an electron-withdrawing group such as -NO<sub>2</sub> and -CF<sub>3</sub> exhibited a high yield [38]. The choice of solvent is important for the activity. When the solvent was changed from *m*-xylene to dioxane (entry 8), which is commonly used for Suzuki reaction, the yield fell by a factor of 35%. The addition of water (entry 9) also deteriorated the activity. The solid base K<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> are two good bases among various bases, as mentioned later. Table 4 shows the results for [Bmim]<sub>2</sub>[PdCl<sub>4</sub>], where a similar trend with a little better activity were obtained as compared with ImmPd<sup>2+</sup>·IL (Table 3). Entries 8 and 9 show that the activity is rapidly lost upon the reuse of [Bmim]<sub>2</sub>[PdCl<sub>4</sub>]. Pd carbene complex prepared from Pd(OAc)<sub>2</sub> and two equivalents of BmimCl [39] was also used to catalyze Suzuki cross-coupling reaction (entry 11) and exhibited the yield of 86.1%. [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] supported on SiO<sub>2</sub> (Aerosil 300) were also reactive (entry 12). The addition of water (entry 13) decreased the activity.

Table 5 compares various Pd catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and bromobenzene. Commercially available Pd/C(10%) (Wako Co.) has low activity (entry 1, 23.9% yield). Pd halides (entries 6, 7, 8), silica supported PdCl<sub>2</sub> (entry 3) gave yields lying around 60–80%. Pd acetate (entry 2) was as active as ImmPd<sup>2+</sup>·IL (entry 4) and

Table 5

Suzuki cross-coupling reactions catalyzed by various catalysts

Entry	Catalyst	X	R	Yield (%)
1	Pd/C(10%)	Br	H	23.9
2	Pd(OAc) <sub>2</sub>	Br	H	86.0
3	PdCl <sub>2</sub> /SiO <sub>2</sub>	Br	H	81.5
4	ImmPd <sup>2+</sup> ·IL	Br	H	89.1
5	[Bmim] <sub>2</sub> PdCl <sub>4</sub>	Br	H	99.9
6	PdBr <sub>2</sub>	Br	H	68.3
7	PdI <sub>2</sub>	Br	H	77.0
8	K <sub>2</sub> PdCl <sub>4</sub>	Br	H	65.2

Reaction conditions—catalyst: 0.03 mmol; arylhalide: 2.5 mmol; phenylboronic acid: 2.75 mmol; 383 K, *m*-xylene 8 ml, 24 h. Yield was calculated with respect to arylhalide.

[Bmim]<sub>2</sub>[PdCl<sub>4</sub>] was the most active catalyst (99.9% yield, entry 5).

Selection of base is an important factor for the reactivity. Table 6 summarizes the use of various base for ImmPd<sup>2+</sup>·IL. K<sub>3</sub>PO<sub>4</sub> (entry 2) and K<sub>2</sub>CO<sub>3</sub> (entry 1) are the best and the second best solid base, respectively. It is interesting to note that this order is inverse for [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] as shown in Table 4. The activity decreased when other base was adopted (entries 3–6). PdCl<sub>2</sub>/MgO (entry 7) was examined to check whether MgO support acts as a base, resulting in a very low activity.

In the yield change as a function of time (Fig. 8) a plateau appeared after 200 min. In order to check whether this means the lost of the activity or the consumption of reactants, the addition of reactants after the plateau was performed for both ImmPd<sup>2+</sup>·IL and [Bmim]<sub>2</sub>[PdCl<sub>4</sub>], as shown in Fig. 9. The immediate rise of the yield was found for both cases, indicating that the activity of catalysts are kept. Table 7 summarizes the initial rates for the Suzuki cross-coupling reactions catalyzed by ImmPd<sup>2+</sup>·IL and [Bmim]<sub>2</sub>[PdCl<sub>4</sub>]. Both catalysts exhibit almost the same trend in the initial rates. Substituted bromobenzene exhibited the larger initial rates.

Reusability of the immobilized catalyst was examined as shown in Fig. 10. The activity was kept after the third reuse, while the activity of [Bmim]<sub>2</sub>[PdCl<sub>4</sub>] was reduced at the sec-

Table 6

Comparison of various bases in the yields of the Suzuki cross-coupling reactions catalyzed by ImmPd<sup>2+</sup>·IL

Entry	Base	X	R	Yield (%)
1	K <sub>2</sub> CO <sub>3</sub>	Br	H	89.1
2	K <sub>3</sub> PO <sub>4</sub>	Br	H	94.3
3	KF	Br	H	60.6
4	NaHCO <sub>3</sub>	Br	H	6.3
5	NEt <sub>3</sub>	Br	H	3.2
6	Ba(OH) <sub>2</sub>	Br	H	12.8
7	PdCl <sub>2</sub> /MgO	Br	H	3.8

Reaction conditions—catalyst: 0.03 mmol; arylhalide: 2.5 mmol; phenylboronic acid: 2.75 mmol; 383 K, *m*-xylene 8 ml, 24 h. Yield was calculated with respect to arylhalide.



Table 7

Initial rates for the Suzuki cross-coupling reactions catalyzed by ImmPd<sup>2+</sup>\_IL and [Bmim]<sub>2</sub>PdCl<sub>4</sub>

Entry	X	R	ImmPd <sup>2+</sup> _IL ( $\times 10^{-5}$ mol/min)	[Bmim] <sub>2</sub> PdCl <sub>4</sub> ( $\times 10^{-5}$ mol/min)
1	Br	H	7.93	10.25
2	Cl	H	0.73	0.83
3	I	H	2.71	4.30
4	Br	Me	20.81	16.39
5	Br	OMe	21.02	32.09
6	Br	NO <sub>2</sub>	13.72	11.61
7	Br	CF <sub>3</sub>	29.32	19.20

Reaction conditions—catalyst: 0.03 mmol; arylhalide: 2.5 mmol; phenylboronic acid: 2.75 mmol; 383 K, *m*-xylene 8 ml, 24 h. Yield was calculated with respect to arylhalide.

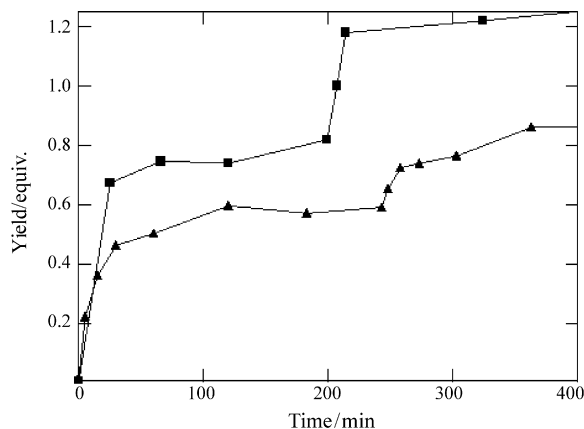


Fig. 9. Yield change as a function of time for the Suzuki cross-coupling reactions catalyzed by ImmPd<sup>2+</sup>\_IL (square symbols) and [Bmim]<sub>2</sub>PdCl<sub>4</sub> (triangular symbols). The same amount of reactants were added at 200 min for the former case and at 250 min for the latter case.

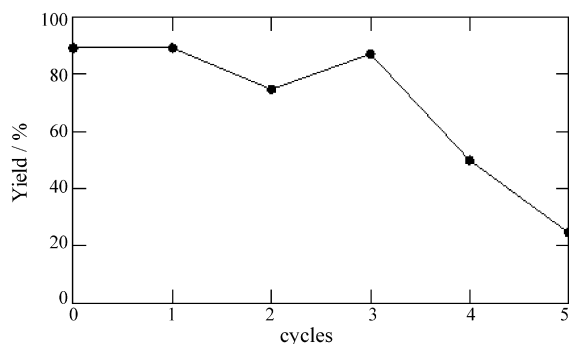


Fig. 10. Yield as a function of reused cycles for the Suzuki cross-coupling reaction catalyzed by ImmPd<sup>2+</sup>\_IL.

ond reuse as shown in Table 4. In this way, we could prepare the immobilized Pd catalyst active and reusable for the Suzuki cross-coupling reaction according to the immobilization of ionic liquid molecules. The present results for the Pd catalyst is in contrast to our recent results for a Ni catalyst active for Suzuki cross-coupling reaction with chloroarene where activation procedure and phosphine were necessary [16].

#### 4. Conclusions

- (1) A series of immobilized metal ion-containing ionic liquids on silica surfaces (ImmM\_IL) were prepared and

characterized by EXAFS, UV-vis, TGA, and elemental analysis.

- (2) The coordination environment around the metal ions were the same as the corresponding [Bmim]<sub>2</sub>MCl<sub>4</sub>.
- (3) The prepared ImmCu<sup>2+</sup>\_IL was found to be an active and reusable catalyst for Kharasch addition reaction between CCl<sub>4</sub> and styrene, where no other solvent is necessary. The performance of the ImmCu<sup>2+</sup>\_IL was better than that of unsupported [Bmim]<sub>2</sub>CuCl<sub>4</sub>.
- (4) The prepared ImmPd<sup>2+</sup>\_IL catalyst was much more active than a commercial Pd/C catalyst but a little more than [Bmim]<sub>2</sub>PdCl<sub>4</sub> for Suzuki cross-coupling between phenylboronic acid and arylhalide in *m*-xylene.
- (5) The selection of solid base was important for the Suzuki cross-coupling reaction and K<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> gave good yields.
- (6) Throughout this study the present catalyst preparation method provides efficient and reusable catalysts.

#### Acknowledgements

This work was supported by the 21st Century COE Program of MEXT, Japan. T.S. was supported by a Grand-in-Aid for Scientific Research (19550008) from the Japan Society for the Promotion of Science (JSPS). The XAFS measurements were performed at KEK-IMSS-PF with the approval of the Photon Factory Advisory Committee (projects 2004G081 and 2007G151).

#### References

- [1] T. Welton, Chem. Rev. 99 (1999) 2071.
- [2] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
- [3] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.
- [4] D.W. Kim, D.Y. Chi, Angew. Chem. Int. Ed. 43 (2004) 483.
- [5] A. Riisager, P. Wasserscheid, R. van Hal, R. Fehrmann, J. Catal. 219 (2003) 452.
- [6] C. deCastro, E. Sauvage, M.H. Valkenberg, W.F. Holderich, J. Catal. 196 (2000) 86.
- [7] M.H. Valkenberg, C. deCastro, W.F. Holderich, Appl. Catal. A: Gen. 215 (2001) 185.
- [8] M.H. Valkenberg, C. deCastro, W.F. Holderich, Top. Catal. 14 (2001) 139.
- [9] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, Chem. Commun. (2002) 3010.
- [10] X. Wu, Y.A. Letuchy, D.P. Eyman, J. Catal. 161 (1996) 164.
- [11] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afework, J. Am. Chem. Soc. 124 (2002) 12932.
- [12] R.T. Carlin, J. Fuller, Chem. Commun. (1997) 1345.

- [13] M.H. Valkenberg, C. deCastro, W.F. Holderich, *Green Chem.* 4 (2002) 88.
- [14] C. Zhong, T. Sasaki, A. Jimbo-Kobayashi, E. Fujiwara, A. Kobayashi, M. Tada, Y. Iwasawa, in preparation.
- [15] T. Sasaki, C. Zhong, M. Tada, Y. Iwasawa, *Chem. Commun.* (2005) 2506.
- [16] C. Zhong, T. Sasaki, M. Tada, Y. Iwasawa, *J. Catal.* 242 (2006) 357.
- [17] C.J. Mathews, P.J. Smith, T. Welton, *Chem. Commun.* (2000) 1249.
- [18] J.D. Revell, A. Ganesan, *Org. Lett.* 4 (2002) 3071.
- [19] E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, D. Haskel, *Physica B* 208–209 (1995) 117.
- [20] M. Newville, P. Livins, Y. Yacoby, E.A. Stern, J.J. Rehr, *Phys. Rev. B* 47 (1995) 14126.
- [21] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, *Phys. Rev. B* 58 (1998) 7565.
- [22] M.S. Kharasch, E.V. Jensen, W.H. Urry, *Science* 102 (1945) 128.
- [23] M. Asscher, D. Vofsi, *J. Chem. Soc.* (1963) 1887.
- [24] S. Murai, S. Tsutsumi, *J. Org. Chem.* 31 (1966) 3000.
- [25] D.J. Burton, K.J. Kehoe, *J. Org. Chem.* 35 (1970) 1339.
- [26] D.J. Burton, K.J. Kehoe, *J. Org. Chem.* 36 (1971) 2596.
- [27] O. Tutusaus, S. Delfosse, A. Demonceau, A.F. Noels, C. Vinas, F. Teixidor, *Tetrahedron Lett.* 44 (2003) 8421.
- [28] F. Simal, L. Wlodarczak, A. Demonceau, A.F. Noels, *Eur. J. Org. Chem.* (2001) 2689.
- [29] O. Tutusaus, C. Vinas, R. Nunez, F. Teixidor, A. Demonceau, S. Delfosse, A.F. Noels, I. Mata, E. Molins, *J. Am. Chem. Soc.* 125 (2003) 11830.
- [30] B. De Clercq, F. Verpoort, *J. Organomet. Chem.* 672 (2003) 11.
- [31] D. Motoda, H. Kinoshita, H. Shinokubo, K. Oshima, *Adv. Synth. Catal.* 344 (2002) 261.
- [32] L.A. Van de Kuil, D.M. Grove, R.A. Gossage, J.W. Zwikker, L.W. Jennekens, W. Drenth, G. Van Koten, *Organometallics* 16 (1997) 4985.
- [33] R.A. Gossage, L.A. Van de Kuil, G. Van Koten, *Acc. Chem. Res.* 31 (1998) 423.
- [34] L. Quebatte, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* 43 (2004) 1520.
- [35] E.J. Enholm, A. Bhardawaj, *Tetrahedron Lett.* 44 (2003) 3763.
- [36] F. Minisci, *Acc. Chem. Res.* 8 (1975) 165.
- [37] J.E.L. Dullius, P.A.Z. Suarez, S. Einloft, R.F. de Souza, J. Dupont, *Organometallics* 17 (1998) 815.
- [38] N. Miyaura, A. Suzuki, *Chem. Rev.* 95 (1995) 2457.
- [39] L.J. Xu, W.P. Chen, J.L. Xiao, *Organometallics* 19 (2000) 1123.