

Supporting Information (1) T. Sasaki, C. Zhong, M. Tada and Y Iwasawa.

**Synthesis of 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride (1):** The compound (**1**) was synthesized as follows. *N*-methylimidazole (56.7 g, 0.690 mol) and (3-chloropropyl)trimethoxysilane (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 five times repeatedly, and refluxed for 48 h. After cooling to room temperature, the resulting liquid was washed with dehydrated ethyl acetate five times and dried by evacuation at room temperature for 48 h. The finally obtained material was a liquid with a little yellow color and was stored at 253 K. Yield 70 %. Anal. Calcd. for  $C_{10}H_{21}N_2O_3SiCl$ : C, 42.77; H, 7.54; N, 9.98. Found: C, 40.53; H, 8.54; N, 10.13.

**Analysis:** NMR spectra were recorded using a Bruker DRX500 spectrometer at resonance frequencies of 500 MHz for  $^1H$  NMR, 125 MHz for  $^{13}C$  { $^1H$ } NMR and 99.36 MHz for  $^{29}Si$  { $^1H$ } NMR. HH-COSY, HMQC and HMBC measurements were performed for the assignments.  $CD_3CN$  was used as solvent and chemical shifts in ppm were described with respect to TMS below.

$^1H$  NMR: 9.81 (s, 1H, *NCHN*), 7.60 (d, 1H, *CHCHNCH\_2*), 7.58 (d, 1H, *MeNCHCH*), 4.23 (t, 2H, *NCH\_2*), 3.93 (s, 3H, *NCH\_3*), 3.51 (s, 9H, *O(CH\_3)\_3*), 1.91 (m, 2H, *CH\_2CH\_2Si*), 0.60 (t, 2H, *CH\_2Si*).

$^{13}C$  { $^1H$ } NMR: 138.3 (*NCHN*), 124.5 (*MeNCHCH*), 123.1 (*CHCHNCH\_2*), 52.3 (*NCH\_2*), 51.0 (*OCH\_3*), 36.7 (*NCH\_3*), 24.7 (*CH\_2CH\_2Si*), 6.3 (*CH\_2Si*).

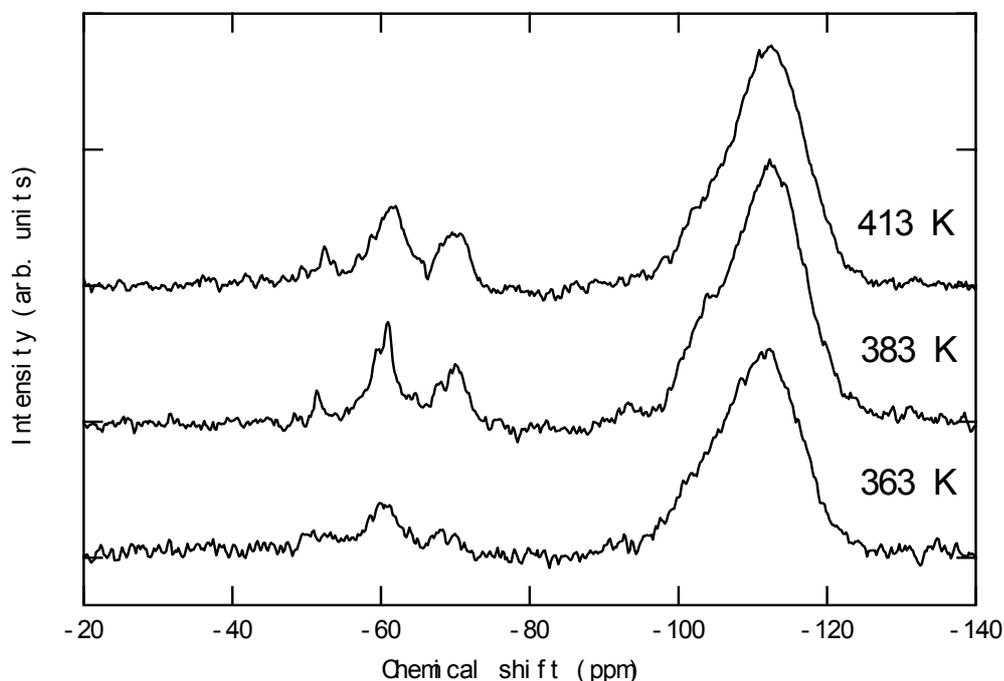
$^{29}Si$  { $^1H$ } NMR: -42.74 (*CH\_2Si(OMe)\_3*).

Supporting Information (2)

**Immobilization of the compound (1) on silica**

Preparation: Silica (Aerosil 300) was calcined at 573 K for 1.5 h in air and evacuated for 0.5 h, which was stored in dry nitrogen. In a glovebox pretreated silica and the compound (1) were weighted (weight ratio 1:1, *ca.* 6 ionic liquid molecules per nm<sup>2</sup>) and put into a Schlenk tube with toluene as a solvent. The mixture was refluxed for 48 h under nitrogen atmosphere. Toluene was removed under evacuation and the resulting material was transferred to a Soxhlet apparatus in nitrogen. The excess ionic liquid molecules were removed by Soxhlet extraction (48 h) with dichloromethane. Elemental analysis for the resulting solid (Imm-IL) was found to be C, 8.89; H, 1.90; N, 1.89.

The Imm-IL was characterized by Solid-state magic-angle-spinning (MAS) <sup>29</sup>Si NMR (59.67 MHz) using a Chemagnetics CMX-300 spectrometer using zirconia rotors of 5 mm diameter spinning at 4 kHz. Spectra were accumulated for 5000 scans with an interval of 30s. Three spectra were shown below with a specified bath temperature for reflux. A large peak around -110 ppm corresponds to silica support (Q4-Si and Q3-Si). In each spectrum three peaks appeared due to the immobilized silyl-functionalized imidazolium groups at -69 ppm (C-Si(OSi)<sub>3</sub>); -61 ppm (C-Si(OMe)(OSi)<sub>2</sub>), and -52 ppm (C-Si(OMe)<sub>2</sub>(OSi)). These spectra indicate that the bath temperature at 383 K is enough for the immobilization, which was adopted in experiments.



SS-MAS-<sup>29</sup>Si NMR spectra measured for the Imm-IL samples prepared at specified reflux bath temperatures for immobilization.

Supporting Information (3)

**Cu K edge EXAFS Fourier transforms and curve fittings for [Bmim]<sub>2</sub>CuCl<sub>4</sub> and Imm-Cu<sup>2+</sup>-IL**

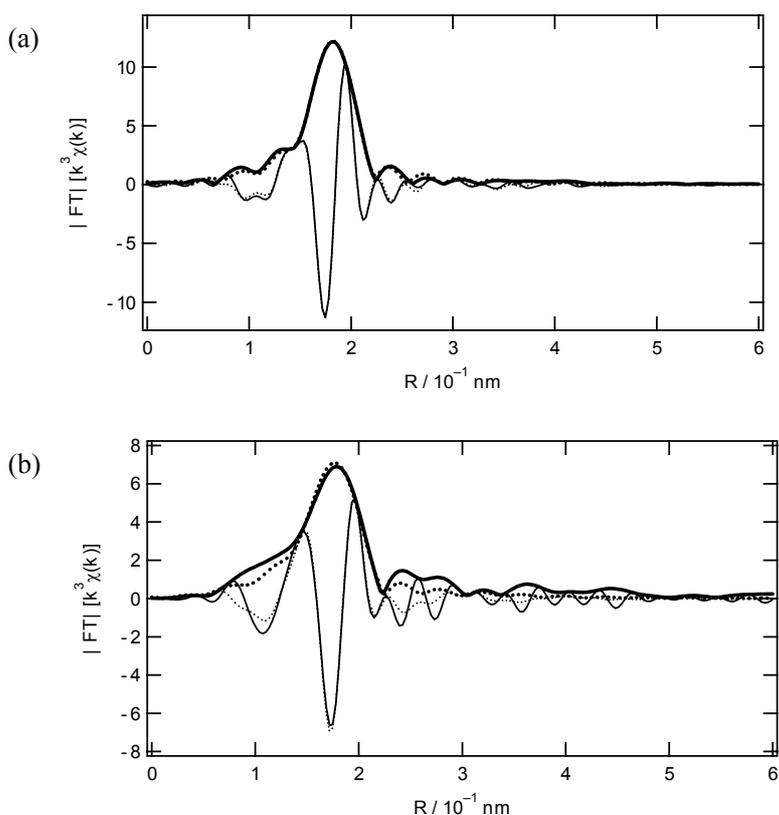
EXAFS spectra were measured at BL-12C station of KEK-IMSS-PF. The energy and current of electrons in the storage ring were 2.5 GeV and 250 - 400 mA, respectively. X-rays from the storage ring were monochromatized by Si(111) double crystals and were focused by Rh-coated bent cylindrical mirrors. Ionization chambers filled with pure N<sub>2</sub> and Ar/N<sub>2</sub> (50:50) mixed gas were used to monitor the incident and transmitted X-rays, respectively. The EXAFS spectra were analyzed with the UWXAFS package [ref 1]. The threshold energy E<sub>0</sub> was tentatively set at the inflection point of the absorption edge. The background was subtracted by the AUTOBK program. The k<sup>3</sup>-weighted EXAFS data were Fourier transformed into R-space. The curve-fitting analysis was carried out using the FEFFIT program in the R-space [ref 3]. The fitting parameters were coordination numbers (CN), interatomic distances ( R ), Debye-Waller factors ( σ ), amplitude factor ( S<sub>0</sub><sup>2</sup> ), and a correction-of-edge energy ( ΔE<sub>0</sub> ). The phase shifts and backscattering amplitudes were calculated by the FEFF8 code [ref 4].

[ref 1] E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, D. Haskel, *Physica B*, **208-209**, (1995) 117.

[ref 2] M. Newville, P. Livins, Y. Yacoby, E.A. Stern, J.J. Rehr, *Phys. Rev. B*, **47**, (1993) 14126.

[ref 3] M. Newville, B. Ravel, D. Haskel, J.J. Rehr, E.A. Stern, Y. Yacoby, *Physica B*, **208-209**, (1995) 154.

[ref 4] A.L. Ankudinov, B. Ravel, J. Rehr, S.D. Conradson, *Phys. Rev. B*, **58**, (1998) 7565.

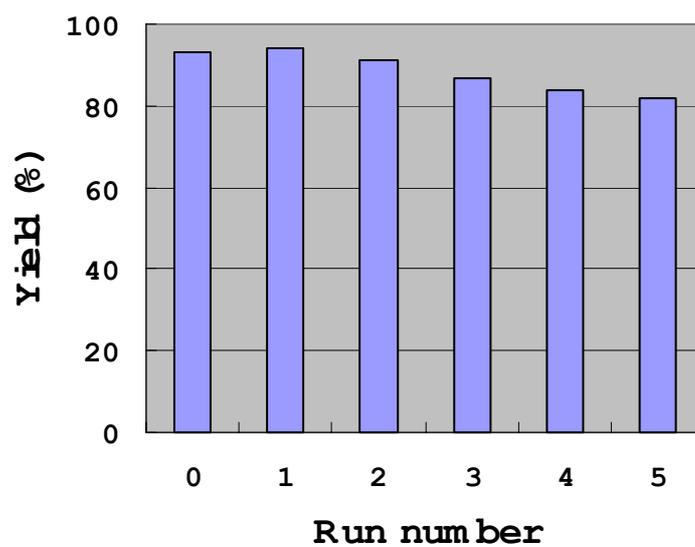


k<sup>3</sup>-weighted Cu K-edge EXAFS Fourier transforms and curve fitting results for [Bmim]<sub>2</sub>CuCl<sub>4</sub> (a) and Imm-Cu<sup>2+</sup>-IL (b). Two solid curves and dotted curves represent the absolute values (thick) and imaginary parts (thin) of the observed data (solid) and the fitted spectra (dotted), respectively.

Supporting Information (4)

### Reuse of Imm-Cu<sup>2+</sup>-IL

After 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. Catalytic performances upon repeated reuses are shown below.



Reusable performances of Imm-Cu<sup>2+</sup>-IL for Kharasch reaction between styrene and CCl<sub>4</sub>.