Highly efficient and recyclable copper based ionic liquid catalysts for amide synthesis

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Supporting Information

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NMR investigation for [Bmim][OAc]-[Cu(OAc)₂] and its precursor compound

¹H NMR spectrum of [Bmim][OAc] (Fig. S1a) shows that all the protons (labeled a-g) associated with N-methyl imidazole ring, butyl and acetate groups are present except the (N)₂-C-H imidazole ring proton. This shows that (N)₂-C-H proton is in dynamic equilibrium between N-methyl imidazole ring and acetate anion. ¹³C NMR spectrum of [Bmim][OAc] (Fig. S1a) shows that all the carbons (labeled a-i) associated with N-methyl imidazole, butyl and acetate groups are present. ¹H-¹H correlation (COSY) spectrum (Fig. S1b) shows various H-H interactions present in the sample. ¹³C-¹H correlation spectrum (HETCOR) (Fig. S1b) further confirms the formation of [Bmim][OAc]. HETCOR spectrum confirms that no proton is correlated with (N)₂-C carbon present in the ¹³C spectrum of [Bmim][OAc], which clearly illustrates that (N)₂-C-H proton is in dynamic equilibrium between N-methyl imidazole ring and acetate anion. ¹H NMR spectrum of [Bmim][OAc]-[Cu(OAc)₂] (Fig. S2a) shows that protons (labeled a-h) associated with N-methyl imidazole ring and butyl groups are present but acetate protons are absent (Fig. S2). Due to the presence of paramagnetic Cu(II), ¹H spectrum of [Bmim][OAc]-[Cu(OAc)₂] is broad when compared with [Bmim][OAc]. ¹³C NMR spectrum of [Bmim][OAc] (Fig. S2a) confirms that all the carbons (labeled a-i) associated with N-methyl imidazole ring and butyl group are present but the acetate carbon does not exhibit any signal in ¹³C spectrum. ¹H-¹H and ¹³C-¹H correlation spectra (Fig. S2b) further confirm that acetate ions exhibit no signal in the NMR investigation. ¹H and ¹³C NMR investigations confirm that all the acetate ions present in the sample are in dynamic equilibrium with those complexed with paramagnetic Cu(II).
Table S1. Elemental analysis of supported catalysts investigated in this study.

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<tr>
<th>Sample</th>
<th>C (wt %)^a</th>
<th>N (wt %)^a</th>
<th>Cu (wt%)^b</th>
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<tr>
<td>Nano-S-1</td>
<td>0.24</td>
<td>0.04</td>
<td>None</td>
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<tr>
<td>Nano-S1-[Bmim][Cl]-[CuCl]</td>
<td>5.56</td>
<td>1.60</td>
<td>3.41</td>
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<tr>
<td>Nano-S1-[Bmim][Cl]-[CuCl₂]</td>
<td>5.64</td>
<td>1.63</td>
<td>3.50</td>
</tr>
<tr>
<td>Nano-S1-[Bmim][OAc]-[Cu(Oac)₂]</td>
<td>8.50</td>
<td>1.42</td>
<td>3.06</td>
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^aObtained from CHN elemental analyzer  
^bObtained from AAS analysis
Fig. S1 (Continued)
Fig. S1. (a) $^1$H and $^{13}$C, (b) COSY and HETCOR, NMR spectra of [Bmim][OAc].
Fig. S2 (Continued)
Fig. S2. (a) $^1$H and $^{13}$C (b) COSY and HETCOR, NMR spectra of [Bmim][OAc]-[Cu(OAc)$_2$].
Fig. S3: FT-IR spectra of Cu based ILs and functionalized ILs catalysts and their precursor compounds.
Fig. S4: Thermo gravimetric analysis of neat Cu based ILs and Nano-S-1 supported Cu based ILs and their precursor compounds.
Fig. S5: N$_2$-adsorption isotherm of Nano-S-1 (Inset shows pore size distribution).
Fig. S6: TEM images of Nano-S-1.
Fig. S7: UV-visible spectra of Cu based ILs and functionalized ILs catalysts and their precursor compounds.
Scheme S1: Changes in the color observed during the synthesis of ILs.