Electronic Supplementary Information

Ionic Liquids as Recycling Solvents for The Synthesis of Magnetic Nanoparticles

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1. Experimental details

Synthesis of ionic liquids

The synthesis of BMI.NTf₂ and BMI.PF₆ were done by modification of the process developed by Cassol et al.( C. C. Cassol, G. Ebeling, B. Ferrera, J. Dupont, Adv. Synth. Catal. 348 (2006) 243) and involves the following steps:

**Synthesis of Butyl Methanesulfonate**: Methanesulfonyl chloride (1.60 mol) was added under vigorous stirring to a solution of n-butanol (1.60 mol) and triethylamine (1.60 mol) in dichloromethane. The reaction temperature was kept between 10-20 °C. Then, the organic layer was washed with water. The combined organic extracts were dried over MgSO₄ and the solvent was removed under reduced pressure to give a colorless liquid.

**Synthesis of 1-Butyl-3-methylimidazolium Methanesulfonate**: equimolar amounts of butyl methanesulfonate and 1-methylimidazole (1.59 mol) were mixed and the reaction mixture was kept at room temperature. One crystal of 1-butyl-3-methylimidazolium methanesulfonate was added and the resulting crystalline reaction mass was kept at room temperature for 24 h. Recrystallization was performed using acetone as solvent.

**Synthesis of 1-n-butyl-3-methylimidazolium trifluoromethanesulfonimide (BMI.NTf₂)**: A mixture of 1-butyl-3-methylimidazolium methanesulfonate (165 mmol), LiNTf₂ (174 mmol) and distilled water (65 mL) were vigorously stirred for 30 min and dichloromethane (200 mL) was added. The organic phase was separated, washed with water and dried with MgSO₄ and filtered through a basic alumina column. Solvent evaporation system was used to dichloromethane evaporation. The final product was a viscous and colorless liquid, the BMI.Tf₂N ionic liquid. The purity (> 97%) of the ionic liquid was determined by ¹H NMR using the intensity of the ¹³C satellites of the imidazolium N-methyl group as internal standard. The ¹H NMR spectrum was recorded on a Varian Mercury Plus spectrometer (300 MHz) at room temperature.

**Synthesis of 1-n-butyl-3-methylimidazolium hexafluorophosphate (BMI.PF₆)**: A mixture of 1-butyl-3-methylimidazolium methanesulfonate (470 mmol), KPF₆ (493 mmol) and distilled water (250 mL) were vigorously stirred for 30 min. The upper aqueous phase was separated and discarded. Then KPF₆ (23 mmol) and distilled water (40 mL) were added to the remaining layer. The mixture was stirred for 15 min followed by the addition of 200 mL of dichloromethane. The organic phase was separated, dried with MgSO₄ and filtered through a basic alumina column. Solvent evaporation system was used to dichloromethane evaporation. The purity (> 94%) of the product was verified as described above for the BMI.NTf₂.
2. Characterization techniques

*NIR spectra of Fe₃O₄ NPs obtained at 150 °C (a) and 250 °C (b)*

Figure S-1. NIR spectra of Fe₃O₄ NPs obtained at 150 °C (a) and 250 °C (b). The spectra were recorded from a thin film of the sample dispersed in hexane in a NaCl window.

*FTIR spectra of Fe₃O₄ NPs obtained at 250 °C*

Figure S-2. Infrared spectra of: (a) BMI.NTf₂ ionic liquid before the reaction; (b) a thin film of the magnetite NPs covered by oleylamine as obtained in the synthesis; (c) BMI.NTf₂ ionic liquid after the 20th reaction is completed at 250 °C in 1.5 h of reaction.

Figure S-3. Photographs of a magnetic fluid (Fe₃O₄ NPs dispersed in cyclohexane) exposed to a permanent magnet (Nd): far from the sample (a), closer (b) and touching the glass wall (c).
**CHN Analysis**

Table S-1. Results of CHN analysis for samples prepared at 150 °C

<table>
<thead>
<tr>
<th>IL</th>
<th>%C (m/m)</th>
<th>%H (m/m)</th>
<th>%N (m/m)</th>
<th>%oleylamine (m/m)</th>
<th>%oleylamine (m/m) calc.¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI.NTf₂</td>
<td>11.42</td>
<td>2.17</td>
<td>0.62</td>
<td>14.13</td>
<td>12.7</td>
</tr>
</tbody>
</table>

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm².

**TGA results**

![TGA curves](image)

**Figure S-4.** TGA curves for the indicated samples (magnetite/OA obtained at 150 °C in BMI.NTf₂). Note the weight loss of 13.5% begins near 250 °C and ends near 400 °C (red curve). This is due to the release of OA from the magnetite surface. This weight % corresponds to nearly one monolayer of OA.

**¹H-NMR analysis**

![¹H-NMR spectra](image)

**Figure S-5.** ¹H-NMR spectra of pure cyclohexene (upper curve) and of the cyclohexene solution containing Pd(OAc)₂ as catalyst after ten minutes of purging with the gas liberated in the synthesis of Fe₃O₄ nanoparticles (lower curve). The Pd(OAc)₂ catalyst promotes the hydrogenation of cyclohexene leading to the formation of cyclohexane.
Results for the BMI.PF₆

Figure S-6. FTIR spectra of (a) BMI.PF₆ and (b) Fe₃O₄ NPs obtained in BMI.PF₆ at 250 °C after 1.5 h of reaction.

TEM and HRTEM (BMI.PF₆)

Figure S-7 (left) TEM image and histogram (inset, mean diameter 6.2 ±0.9 nm) of Fe₃O₄ NPs obtained in BMI.PF₆ at 150 °C and 1.5 h of reaction in the presence of OA. (right) a HRTEM image of a Fe₃O₄ nanocrystal.

Table S-2 CHN Analysis for the Fe₃O₄ obtained in BMI.PF₆ at 150 °C in 1.5 h of reaction

<table>
<thead>
<tr>
<th>IL</th>
<th>%C (m/m)</th>
<th>%H (m/m)</th>
<th>%N (m/m)</th>
<th>%oleylamine (m/m)</th>
<th>%oleylamine (m/m) calc.¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI.PF₆</td>
<td>12.28</td>
<td>2.29</td>
<td>0.55</td>
<td>15.12</td>
<td>16.7</td>
</tr>
</tbody>
</table>

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm²
Magnetization measurements

![Hysteresis loop at 300 K for the Fe₃O₄ NPs obtained at 150 °C in BMI.PF₆.](image)

**Figure S-8.** Hysteresis loop at 300 K for the Fe₃O₄ NPs obtained at 150 °C in BMI.PF₆.

TEM Results for NiFe₂O₄ and MnFe₂O₄ obtained in BMI.NTf₂

![TEM micrographs and histograms of NiFe₂O₄ (e,f) and MnFe₂O₄ (g,h) NPs. (e,g) were obtained after 1.5 h and (f,h) after 3.0 h of reaction at 200 °C.](image)

**Figure S-9.** TEM micrographs and histograms of NiFe₂O₄ (e,f) and MnFe₂O₄ (g,h) NPs. (e,g) were obtained after 1.5 h and (f,h) after 3.0 h of reaction at 200 °C.

![HRTEM images of Fe₃O₄ NPs obtained after 1.5 h (a) and 3.0 h of reaction at 200 °C.](image)

**Figure S-10.** HRTEM images of Fe₃O₄ NPs obtained after 1.5 h (a) and 3.0 h of reaction at 200 °C.
Magnetic measurements

Figure S-11. Hysteresis loops at 300 K for (c) Fe$_3$O$_4$ and (d) MnFe$_2$O$_4$ obtained at 200 °C for (○) 1.5 h and (●) 3 h reaction times. The insets show the hysteresis loops at lower magnetic fields.

FTNIR and FTIR spectra

Figure S-12. NIR spectra of Fe$_3$O$_4$ (a) and CoFe$_2$O$_4$ (b) NPs obtained at 200 °C in 1.5 h reaction. The spectra were recorded from a thin film of the sample dispersed in hexane in a NaCl window. The NIR spectrum of CoFe$_2$O$_4$ NPs shows two main absorptions near 1640 and 1350 nm, as observed before for CoFe$_2$O$_4$ NPs obtained by the co-precipitation method.

Figure S-13. FTIR spectra of Fe$_3$O$_4$ (a), CoFe$_2$O$_4$ (b), NiFe$_2$O$_4$ (c), and MnFe$_2$O$_4$ (d) NPs obtained in BMI.NTf$_2$ after 1.5 h of reaction at 200 °C.
Table S-3 CHN Analysis for the ferrite NPs obtained in BMI.NTf₂ at 150 °C after 1.5 h of reaction

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C (m/m)</th>
<th>%H (m/m)</th>
<th>%N (m/m)</th>
<th>%oleylamine (m/m) exp.</th>
<th>%oleylamine (m/m) calc.</th>
<th>Weightloss%²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄</td>
<td>14.13</td>
<td>2.71</td>
<td>0.77</td>
<td>13.30</td>
<td>14.6</td>
<td>12.3</td>
</tr>
<tr>
<td>CoFe₂O₄</td>
<td>13.53</td>
<td>2.25</td>
<td>0.30</td>
<td>16.08</td>
<td>19.7</td>
<td>13.8</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>11.83</td>
<td>1.98</td>
<td>0.72</td>
<td>14.51</td>
<td>14.6</td>
<td>12.2</td>
</tr>
<tr>
<td>MnFe₂O₄</td>
<td>11.77</td>
<td>1.53</td>
<td>0.42</td>
<td>13.72</td>
<td>13.8</td>
<td>12.8</td>
</tr>
</tbody>
</table>

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm²
² Mass percent of OA as obtained by TGA (see Fig.S-14)

TGA results

Figure S-14. TGA measurements for Fe₃O₄ (a), CoFe₂O₄ (b), NiFe₂O₄ (c), and MnFe₂O₄ (d) samples obtained after 1.5 h of reaction in BMI.NTf₂ at 200 °C. (See Table S-3 for the weightlosses corresponding to the OA decomposition).
Results for the synthesis in DPE

TEM Results for $\text{Fe}_3\text{O}_4$ obtained in DPE and OA

![TEM micrograph and size distribution histogram](image)

**Figure S-15.** TEM micrograph and size distribution histogram (lognormal function) of $\text{Fe}_3\text{O}_4$ NPs prepared by decomposition of $\text{Fe}($Acac)$_3$ in DFE and oleylamine.

**CHN Analysis**

**Table S-4.** Results of CHN analysis for samples prepared in DPE

<table>
<thead>
<tr>
<th>%C (m/m)</th>
<th>%H (m/m)</th>
<th>%N (m/m)</th>
<th>% oleylamine (m/m)</th>
<th>% oleylamine (m/m) calc.(^1)</th>
<th>Wheightloss%(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.07</td>
<td>1.60</td>
<td>0.68</td>
<td>19.9</td>
<td>18.5</td>
<td>9.1</td>
</tr>
</tbody>
</table>

\(^1\) Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm\(^2\)

\(^2\) Mass percent of OA as obtained by TGA (see Fig.S-16)

TGA results

![TGA measurement](image)

**Figure S-16.** TGA measurements for $\text{Fe}_3\text{O}_4$ obtained in DPE. (See Table S-4 for the weightloss corresponding to the OA decomposition).