Conversion of Cellulose to Butyl Levulinate in Bio-Butanol Medium Catalyzed by Acidic Ionic Liquids

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The typical procedures for synthesis of SFILs: N-methylimidazole (8.21 g, 0.1 mol) and 1,4-butanesultone (13.64 g, 0.1 mol) were charged into a 50 mL round bottom flask and stirred at 50 °C for 20 h to get white zwitterionic-precursor 4-(3-methylimidazolium)butane sulfonate. After the precursor prepared was purified through washing with ether (3×20 mL), a stoichiometric amount of concentrated mineral acid (HCl, H₃PO₄ or H₂SO₄, 0.1 mol) was added dropwise. The mixture was reacting while stirred vigorously at 80 °C for 6 h. At last, the acidic ILs were obtained as colorless or yellowish viscous liquid after being washed with ether (3×20 mL) and then dried under vacuum at 80 °C for 24 h.

**Fig.S1** Catalysts used in this study

[C₄H₈SO₃Hmim]Cl: ¹H NMR (400 MHz, D₂O): δ=8.66 (s, 1H); 7.42 (s, 1H); 7.36 (s, 1H); 4.17 (t, J=8 Hz, 2H); 3.82 (s, 3H); 2.87 (t, J=8 Hz, 2H); 1.91-1.99 (m, 2H); 1.63-1.71 (m, 2H). ¹³C NMR (100 MHz, D₂O): δ=135.96; 123.64; 122.15; 50.03; 48.90; 35.64; 28.07; 20.90. ESI-MS: m/z (+): 219.1; m/z (−): 35.4. Onset decomposition temperature: 338.9 °C.

[C₄H₈SO₃Hmim]H₂PO₄: ¹H NMR (400 MHz, D₂O): δ=8.55 (s, 1H); 7.39 (s, 1H); 7.33 (s, 1H); 4.14 (t, J=8 Hz, 2H); 3.78 (s, 3H); 2.84 (t, J=8 Hz, 2H); 1.88-1.95 (m, 2H); 1.60-1.67 (m, 2H). ¹³C NMR (100 MHz, D₂O): δ=135.91; 123.61; 122.12; 50.01; 48.87; 35.61; 28.04; 20.87. ESI-MS: m/z (+): 219.3; m/z (−): 97.4. Onset decomposition temperature: 336.8 °C.

[C₄H₈SO₃Hmim]HSO₄: ¹H NMR (400 MHz, D₂O): δ=8.63 (s, 1H); 7.40 (s, 1H); 7.34 (s, 1H); 4.15 (t, J=8 Hz, 2H); 3.79 (s, 3H); 2.85 (t, J=8 Hz, 2H); 1.89-1.96 (m, 2H); 1.60-1.68 (m, 2H). ¹³C NMR (100 MHz, D₂O): δ=135.93; 123.63; 122.13; 50.02;
48.88; 35.62; 28.05; 20.88. ESI-MS: \(ml/z\) (+): 219.0; \(ml/z\) (−): 97.1. Onset decomposition temperature: 327.7 °C.

Table S1  Properties of the BuOH, BF, Dibutyl ether, and BL

<table>
<thead>
<tr>
<th>Sample</th>
<th>Boiling point (°C)</th>
<th>Solubility in water (w, %)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuOH</td>
<td>118</td>
<td>7.3 (25 °C)</td>
<td>1</td>
</tr>
<tr>
<td>BF</td>
<td>106</td>
<td>0.75 (27 °C)(^a)</td>
<td>2</td>
</tr>
<tr>
<td>Dibutyl ether</td>
<td>142</td>
<td>0.03 (25 °C)</td>
<td>1</td>
</tr>
<tr>
<td>BL</td>
<td>232</td>
<td>1.3 (25 °C)</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) calculated from the data (0.75 g/100 mL) given in Pubchem database

Distribution of catalysts in BuOH and H₂O

The distribution of acidic catalyst in BuOH/H₂O biphasic system was determined by comparing the weight of catalyst distributed in each phase after stirring at 25 °C.

Table S2  Distribution of catalysts in BuOH/H₂O

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Distribution(^a)/%</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BuOH</td>
<td>H₂O</td>
</tr>
<tr>
<td>[C₄H₈SO₃Hmim]Cl</td>
<td>4.8±0.13</td>
<td>95.2±0.13</td>
</tr>
<tr>
<td>[C₄H₈SO₃Hmim]H₂PO₄</td>
<td>4.5±0.11</td>
<td>95.5±0.11</td>
</tr>
<tr>
<td>[C₄H₈SO₃Hmim]HSO₄</td>
<td>3.9±0.15</td>
<td>96.1±0.15</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>47.1±0.46</td>
<td>52.9±0.46</td>
</tr>
</tbody>
</table>

\(^a\) 0.5 mmol catalyst, 10 mL H₂O and 10 mL BuOH at 25 °C

Table S3  BuOH soluble chemicals determined by GC-MS (Table 1, entry 4)

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Compound(^a)</th>
<th>Percentage (%(^b))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>Structure</td>
</tr>
</tbody>
</table>
3.07 butyl formate  \[
\text{\begin{center}
\begin{tikzpicture}
\draw (-0.5,0) -- (0.5,0);
\draw (0,-0.5) -- (0,0.5);
\end{tikzpicture}
\end{center}}\]
11.45

5.51 dibutyl ether  \[
\text{\begin{center}
\begin{tikzpicture}
\draw (-0.5,0) -- (0.5,0);
\draw (0,-0.5) -- (0,0.5);
\end{tikzpicture}
\end{center}}\]
48.94

8.82 butyl levulinate  \[
\text{\begin{center}
\begin{tikzpicture}
\draw (-0.5,0) -- (0.5,0);
\draw (0,-0.5) -- (0,0.5);
\end{tikzpicture}
\end{center}}\]
39.61

*a* identified according to the NIST MS library; *b* measured using peak area normalization method

**Fig.S2**  TG curves of fresh IL and spent IL after 6 runs

Oven temperature: 50 to 550 °C at a rate of 10 °C·min⁻¹

**References**

