Chapter 6

Dehydration/hydrogenation of furfuryl alcohol to GVL via LA esters
Functionalized ionic liquids with various acidic anions were designed as novel heterogeneous solid acid catalysts for alcoholsysis of furfuryl alcohol (FAL) in presence of methanol, ethanol, n-butanol and isopropyl alcohol (IPA) to the corresponding levulinic acid esters under mild temperature (90–130 °C) conditions. The extended alkyl chain length of 1-methyl imidazole [MIm] using 1,4-butane sultone enhanced the Brønsted acidity of [BMIm-SH][HSO₄] catalyst resulting into the highest selectivity of >95% to Me-LA with >99% conversion of FAL. Using a combination of ionic liquid, [BMIm-SH][HSO₄] and 5% Ru/C catalyst, single-pot transformation of FAL to γ-valerolactone (GVL) is shown successfully for the first time with complete FAL conversion the selectivity as high as 68% to GVL. Our catalyst system could be efficiently recycled five times retaining the original activity and selectivity levels.
6.1. Introduction
The exploitation of bio-based fuels and fuel additives is imperative due to its role in effective remediation of greenhouse gas levels in the atmosphere and to mitigate the economic consequences of the depleting fossil resources [1, 2]. First-generation biofuels (i.e. ethanol and biodiesel) are presently produced from sugars, starch and vegetable oils creating important compatibility and energy density issues. One promising alternative to overcome these limitations of oxygenated fuels is to use more abundant, cheaper and potentially more sustainable non-edible lignocellulosic biomass [3, 4]. We report here the most promising route to achieve this transformation by developing the selective and versatile catalyst system involving acid and metal functions together for alcoholysis and hydrogenation reactions respectively, in a single step. These two are the primary unit processes for conversion of the monomeric carbohydrate building blocks, i.e., mainly C₅ sugars, such as xylose and arabinose, and C₆ sugars in the form of glucose and their respective secondary products, furfural and levulinic acid into the potential fuel additives [5,6]. Furfural produced by the hydrolysis and dehydration of xylan contained in lignocellulose can be easily hydrogenated to furfuryl alcohol. Hence, direct conversion of furfuryl alcohol to levulinic esters followed by its in-situ hydrogenation to γ-valerolactone (GVL) becomes a new alternative route for the production of biofuels [7]. Levulinic esters (LA) are mainly obtained by a series of reactions involving first, acid catalyzed esterification of levulinic acid produced from hexose sugars. LA is then hydrogenated to give 4-hydroxy LA followed by its ring cyclization to GVL [8-10]. GVL along with levulinic esters which can be also used as diesel additives, form sustainable liquid transportation fuels replacing ethanol in a gasoline ethanol blend [11, 12]. In addition, another product of single step catalytic hydrogenation of levulinic acid is methyl tetrahydrofuran (MTHF) which has been also approved by US-DOE as a component of P-Series type fuel [13,14]. The formation of levulinic acid and its esters from cellulose and hemicelluloses is possible by two different routes i) hexose triple dehydration to 5-hydroxymethylfurfural (5-HMF) and its rehydration with two water molecules to produce levulinic and formic acids, and ii) hydrolysis of pentose sugars to produce a mixture of C₅ monomers, mainly furfural which is then reduced to furfuryl alcohol followed by its rehydration to produce levulinic acid/ester [15-18].
A commercial Biofine process for the production of levulinic acid requires 3.5 tons of 3.5 wt% sulfuric acid, thus creating a serious environmental pollution and involving tedious work up for the recovery of pure LA [19, 20]. Attempts are being made to overcome such drawbacks by developing heterogeneous catalysts. Several catalytic systems were reported for production of esters of levulinic acid and GVL from biomass and its derivative 5-HMF and FAL [21-26].

In the present chapter, we report a single pot catalytic conversion of furfuryl alcohol to levulinic acid ester and GVL via alcoholysis/hydrogenation sequence using sulfonic acid-functionalized ionic liquids (SO$_3$H-ILs) and carbon supported Ru, Re, Ir and Ag catalysts. Our novel approach of direct conversion of furfuryl alcohol to GVL has several advantages: (i) yield of methyl levulinate is higher than that for hydrolysis of C$_6$ sugars due to humin elimination in alcohol medium, (ii) no separation step required for downstream conversion of levulinic acid/esters (iii) complete atom efficiency in the conversion of FAL to GVL (iv) elimination of metal leaching and deactivation of catalysts used for LA hydrogenation to GVL. To the best of our knowledge, this approach of direct conversion of C$_5$ furfuryl alcohol to C$_5$ GVL has not been reported so far. We found that 5%Ru/C + [BMIm-SH][HSO$_4$] showed complete alcoholysis of furfuryl alcohol with 95% selectivity to methyl levulinate followed by its hydrogenation with the highest selectivity of 94% to GVL in a batch reactor.

### 6.2. Experimental

All acid functionalized ILs were prepared by using a ion exchange method while, supported Ru, Pd, Re, Pd and Ag catalysts were prepared by the impregnation method and the detailed experimental procedures of their preparation have been described in chapter 2, section 2.2.4. The catalysts were characterized by various techniques according to the procedure described in section 2.4. The activity of the prepared catalysts was evaluated for the hydrogenation of levulinic acid to $\gamma$-valerolactone and a typical experimental procedure is described in section 2.5.1. The quantitative analysis of liquid samples was carried out by gas chromatography method using FID detector, HP-5 capillary column and helium as a carrier gas. Other details of temperature programming method (60-190 °C) etc. are described in chapter II, section 2.6.
6.3. Results and discussion

6.3.1. Alcoholysis of furfuryl alcohol to esters of levulinic acid

6.3.1.1. Activity testing

Two major objectives of the present work were (i) to design a novel, environmentally benign acid catalyst for efficient alcoholysis of furfuryl alcohol to levulinic esters and (ii) to develop a tandem approach to synthesize GVL directly from furfuryl alcohol. For the first stage of this work, we prepared several acid functionalized ILs and their performance evaluation results are shown in Table 6.1.

Table 6.1. Catalyst screening for alcoholysis of furfuryl alcohol to methyl levulinate

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion %</th>
<th>% Selectivity Methyl LA</th>
<th>Methoxy FAL</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No Catalyst</td>
<td>2</td>
<td>&lt;0.01</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>[H₂SO₄]</td>
<td>68</td>
<td>74</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Amberlyst-15</td>
<td>99</td>
<td>40</td>
<td>51</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>SO₄-ZrO₂</td>
<td>99</td>
<td>74</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>20% DTP-SiO₂</td>
<td>69</td>
<td>25</td>
<td>61</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>20% DTP-MMT</td>
<td>73</td>
<td>24</td>
<td>63</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>[MIm][HSO₄]</td>
<td>96</td>
<td>65</td>
<td>21</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>[MIm][TFA]</td>
<td>10</td>
<td>1</td>
<td>95</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>[NMP][HSO₄]</td>
<td>99</td>
<td>98</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>[NMP][TFA]</td>
<td>11</td>
<td>2</td>
<td>94</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>[BMIm-SH][ClSO₃H]</td>
<td>98</td>
<td>90</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>12</td>
<td>[BMIm-SH][PTSA]</td>
<td>95</td>
<td>76</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>13</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>95</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Reaction conditions: Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N₂ atm; catalyst, 0.3 g; reaction time, 2 h.

The initial control experiment without any catalyst (entry 1, Table 6.1) showed that furfuryl alcohol conversion was <2% confirming that the alcoholysis of furfuryl alcohol was a catalytic reaction. Among the various solid acid catalysts, almost complete conversion was obtained with Amberlyst-15 and SO₄-ZrO₂ but the selectivity to MeLA was only 40 and 74%, respectively, with the remaining FAL ethers (entries 3, 4 Table 6.1). With other two solid acid catalysts, conversion achieved was less than 75% with a very poor selectivity of 25% to Me-LA. Thus, the simultaneous high activity and
selectivity for furfuryl alcoholysis to Me-LA was not possible using any of the solid acid catalysts screened in this work (entries 5, 6, Table 6.1). This fact is also evident from the reported literature [10, 22, 26]. Therefore, we explored the use of ILs having Brønsted acidity which was systematically varied with anions such as ClSO₃H, SO₃H, PTSA and TFA with the same cation MIm. It was observed that furfuryl alcohol conversion of >95% was achieved with cations such as HSO₄ and Cl-SO₃H (entries 7, 11 Table 6.1) and 10% conversion was obtained with TFA anion (entry 8, Table 6.1). However, with only HSO₄ anion, the selectivity to methyl levulinate was the highest, 98% (entry 9, Table 6.1). As can be seen from Table 6.1, the choice of anion was critical, because with TFA both the cations MIm and NMP exhibited very poor activities in terms of furfuryl alcohol conversion in the range of only 10-11 %. HSO₄ with both the cations, MIm and NMP showed very high conversion (>95%) while the selectivity to methyl levulinate was only 65% in case of [MIm][HSO₄]. Hence this catalyst was further modified by extending its alkyl chain length with 1, 4-butane sultone so that the resulting IL (BMIm-SH) would be more stable and also acquires the enhanced Brønsted acidity. To our expectation, this was actually observed as the [BMIm-SH][HSO₄] catalyst gave dramatic increase in selectivity of methyl levulinate up to 95% [entry 13, Table 6.1]. The appropriate combination of anion and the cation is emphasized by the fact that incomplete alcoholysis gave appreciable formation of intermediate FAL ethers (Scheme 6.1) in case of [MIm][HSO₄] and [BMIm-SH][PTSA] catalysts (entries 7,12 Table 6.1).

**Scheme 6.1.** Alcoholysis of furfuryl alcohol to methyl-levulinate

A typical gas-chromatogram of the reaction mixture is shown in Figure 6.1 while, the intermediate, methoxy FAL and the final product methyl levulinate formed in this
alcoholysis reaction were identified by GC-MS as shown in Figures 6.2 and 6.3. Using HSO$_4$ as the anion, NMP showed almost complete conversion of furfuryl alcohol and selectivity to methyl levulinate [entry 9, Table 6.1].

Figure 6.1. GC spectra of furfuryl alcohol alcoholysis
However, this catalyst when recovered and was attempted to recycle, its activity dropped down by 50% as shown in Figure 6.4 as against the successful complete recyclability of [BMIm-SH] [HSO₄] catalyst for several times (discussed later). Hence, further study on effect of parameters was carried out using [BMIm-SH] [HSO₄] catalyst.

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**Figure 6.2.** Mass spectra of methoxy FAL

**Figure 6.3.** Mass spectra of methyl levulinate
Recycle study of NMP[HSO₄] catalyst for FAL to methyl levulinate

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 ºC; N₂ atm, catalyst, 0.3 g; reaction time, 2 h.

Along with the catalyst, equally important was choice of the reaction medium as the selectivity to levulinic acid dropped down to 31% in an aqueous medium over the same active catalyst [BMIm-SH][HSO₄], obviously due to the humin formation [27]. The humin formation also makes separation of catalyst and product very much tedious. Hence, direct alcoholysis of furfuryl alcohol in presence of methanol without formation of levulinic acid is the most advantageous strategy from process point of view [8, 28].

### 6.3.2. Reaction parameters study for FAL alcoholysis

#### 6.3.2.1. Solvent Screening

The efficiency of our [BMIm-SH] [HSO₄] catalyst was further established for the synthesis of a variety of alkyl levulinates, by carrying out the alcoholysis of furfuryl alcohol in presence of different alcohols. Figure 6.5 shows that a consistent activity (99% conversion) was achieved for all the alcohols studied in this work. However, alkyl levulinate selectivity was found to decrease from 99 to 85% with increase in alcohol
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chain length from ethanol to n-butanol. The decrease in Me-LA selectivity was associated with the formation of respective ethers of FAL depending on the alcohols used (shown as blue and green bars in Figure 6.5). In case of a branched alcohol like isopropanol, corresponding ester (IPA-LA) selectivity decreased to the extent of 68%. This indicates that the steric factor played an important role in the alcoholsysis of furfuryl alcohol.

![Figure 6.5. Screening of solvent for alcoholsysis of furfuryl alcohol](image)

**Figure 6.5.** Screening of solvent for alcoholsysis of furfuryl alcohol

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH, EtOH, n-PrOH, n-BuOH and IsoPrOH (95 mL); temperature, 130 °C; N₂ atm, catalyst (Acidic IL), 0.3 g; reaction time, 2 h

### 6.3.2.2. Effect of temperature

The influence of temperature on the alcoholsysis of furfuryl alcohol was studied in a range from 100 to 150 °C keeping other parameters constant and the results are shown in Figure 6.6. Almost complete conversion could be achieved as the temperature increased from 100 to 130 °C, and remained constant beyond 130 °C up to 150 °C. Similarly, the selectivity to Me-LA also increased linearly from 65 to 95% with increase in temperature from 100 to 130 °C.
Figure 6.6. Effect of temperature on alcoholysis of furfuryl alcohol

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH, (95 mL); temperature, 90-130°C; N₂ atm, catalyst, 0.3 g (Acidic IL); reaction time, 2 h.

At higher temperature, the conversion of ethers of FA L to Me-LA was facilitated, proving the reaction pathway given in Scheme 6.1 which involves first, the etherification of FAL followed by rehydration of the intermediate ethers to methyl levulinate.

### 6.3.2.3. Effect of catalyst concentration

The study on effect of catalyst loading on the alcoholysis of furfuryl alcohol showed that the conversion of furfuryl alcohol increased from 84 to 99% with increase in catalyst loading from 0.1 to 0.3 g as shown in Figure 6.7. Moreover, the selectivity to methyl levulinate increased by 1.5 times (>80%) due to increased rehydration of the intermediate, FAL ethers. The higher catalyst concentration resulted into the higher availability of Brønsted acid sites, facilitating faster consumption of furfuryl alcohol and rehydration of the intermediates to methyl levulinate.
Figure 6.7. Effect of catalyst loading on alcoholysis of furfuryl alcohol

Reaction conditions: Furfuryl alcohol, 5% (w/w); solvent, MeOH, (95 mL); temperature, 130 °C; N₂ atm; reaction time, 2 h.

6.3.2.4. Effect of substrate concentration

One of the important process parameters was substrate concentration, the effect of which on conversion and selectivity pattern was studied by systematically varying the furfuryl alcohol concentration from 5 to 15% and the results are shown in Figure 6.8. With increase in substrate concentration from 5 to 15%, both the conversion of furfuryl alcohol and the Me-LA selectivity decreased significantly. At higher substrate concentration, the accumulation of higher concentration of the first step alcoholysis products viz. FAL ethers, on the active sites retarded further rehydration to Me-LA. The substrate concentration of 5% was the optimum to obtain complete conversion and suppression of methoxy FAL intermediates. This minimum substrate concentration can be compensated for higher productivity as our catalyst system was found to show more than three reuses as discussed later.
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Figure 6.8. Effect of substrate loading on alcoholysis of furfuryl alcohol

**Reaction conditions:** Furfuryl alcohol, 5-15% (w/w); solvent, MeOH, (95 mL); temperature, 130 °C; N₂ atm, catalyst, 0.3 g (Acidic IL); reaction time, 2 h.

6.3.3. Alcoholysis followed by hydrogenation of furfuryl alcohol to GVL via LA esters

6.3.3.1. Batch Activity

Encouraged by the results on modified ILs for efficient alcoholysis of furfuryl alcohol to Me-levulinate, we thought it most desirable to obtain GVL directly from furfuryl alcohol in a single pot synthesis.
Table 6.2. Screening of catalysts for alcoholysis/hydrogenation of furfuryl alcohol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>MeLA</th>
<th>GVL</th>
<th>HMeL A</th>
<th>FAL</th>
<th>Ethers</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5% Ru/C</td>
<td>H₂SO₄</td>
<td>99</td>
<td>47</td>
<td>31</td>
<td>9</td>
<td>13</td>
<td>13</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2</td>
<td>5% Ru/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>24</td>
<td>68</td>
<td>8</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>3</td>
<td>5% Ru/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>12</td>
<td>58</td>
<td>1</td>
<td>3</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5% Rh/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>92</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>5</td>
<td>5% Re/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>85</td>
<td>9</td>
<td>2</td>
<td>4</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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</tr>
<tr>
<td>6</td>
<td>5% Pd/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>94</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>6</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>7</td>
<td>5% Ir/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>65</td>
<td>6</td>
<td>26</td>
<td>3</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>8</td>
<td>10% Ag/C</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>84</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>9</td>
<td>10% Ag/ZrO₂</td>
<td>[BMIm-SH][HSO₄]</td>
<td>99</td>
<td>81</td>
<td>9</td>
<td>3</td>
<td>7</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>10</td>
<td>5% Ru/C</td>
<td>Amberlyst-15</td>
<td>99</td>
<td>76</td>
<td>14</td>
<td>6</td>
<td>14</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>11</td>
<td>5% Ru/C</td>
<td>SO₄-ZrO₂</td>
<td>99</td>
<td>79</td>
<td>18</td>
<td>1</td>
<td>2</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N₂ atm. + H₂ pressure*, 500 psi; catalyst, 0.3+0.5 g; reaction time, 2h+3h.

For this purpose, a combination of acidic ILs and metal catalyst was used in a tandem synthesis of GVL. We therefore screened several combinations of various supported noble metals and the ILs selected from Table 6.1. All the combinations studied in this work were indeed very successful showing an excellent activity in terms of furfuryl alcohol conversion >99% Table 6.2. The selectivity to GVL varied depending on the noble metal used for the hydrogenation of the intermediate Me-LA. It is very interesting to note that under hydrogenation conditions, selectivity to GVL was only 58% and to the...
intermediate ester was also only 12% while almost all the remaining (26%) byproduct was (entry 3, Table 6.2) tetrahydrofurfuryl alcohol (THFAL). THFAL was formed due to the ring hydrogenation of furfuryl alcohol and it was found to be a very stable product as observed from the conversion/selectivity vs. time profile shown in Figure 6.9.

![Figure 6.9](image)

**Figure 6.9.** CT profile for direct hydrogenation of furfuryl alcohol

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 403 K; H₂ pressure, 500 psi; catalyst, 0.3 (acidic IL) + 0.75 g (5% metal catalyst); reaction time, 5 h.

A novel strategy adopted by us involved conducting the initial alcoholysis reaction under an N₂ atmosphere for 2 h after which N₂ was replaced by H₂. This time period of changeover was arrived at from the optimum time of alcoholysis as studied previously (Table 6.1). This approach worked very well to completely suppress the ring hydrogenation product, THFAL (entry 2, Table 6.2), enhancing the selectivities to the desired products such as MeLA and GVL. Hence, further studies were carried out initially under N₂ and then replacing it by H₂. Under these conditions, among several
noble metal catalysts, 5% Ru/C in combination with IL [BMIm-SH][HSO₄] showed the highest selectivity to GVL (68%). For the same IL, other metals gave GVL selectivity in the range of 2–9%, which was in accordance with our earlier results [28]. The GVL selectivity is important not only from the process point of view but also it is necessary to dissolve the unwanted humin associated with cellulose hydrolysis [29]. The best performance of our Ru/C + [BMIm-SH][HSO₄] catalyst system for the direct conversion of FAL to GVL could be distinctly visible when compared with the performance of Ru/C in combination with the best solid acids chosen from Table 6.1 (entries 10 and 11, Table 6.2). Ru/C with both amberlyst and SO₄-ZrO₂ gave <20% selectivity to GVL, as the major product was Me-LA. Our catalyst showed ten times higher activity (TOF, 160 h⁻¹) than the reported catalysts such as Ru/C + H₂SO₄ for the synthesis of GVL shown in Table 6.3.

**Table 6.3.** Comparison study of our Ru/C with other reported catalysts systems for synthesis of GVL

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity (GVL) (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10%Ru/C+ [BMIm-SH][HSO₄]</td>
<td>Furfuryl alcohol</td>
<td>5</td>
<td>99</td>
<td>&gt;95</td>
<td>53ᵃ (160)ᵇ</td>
</tr>
<tr>
<td>2</td>
<td>5%Ru/C</td>
<td>Levulinic acid</td>
<td>24</td>
<td>90</td>
<td>&gt;99</td>
<td>15ᵃ</td>
</tr>
<tr>
<td>3</td>
<td>10% Ru/C + TFA</td>
<td>Fructose</td>
<td>8</td>
<td>99</td>
<td>62</td>
<td>7ᵃ</td>
</tr>
</tbody>
</table>

[a] The total turnover frequency is calculated on the basis of moles of Ru on support [b]. Numbers in parenthesis refer to the TON estimated on the basis of dispersion of Ru atoms.

This was because of deactivation of Ru catalyst due to sulfur leaching from H₂SO₄, which was evidenced by an intense peak at 169.3 eV of S 2p as seen from Figure 6.10 [30, 31].
6.3.4. Reaction parameters study for tandem reaction

6.3.4.1. Effect of Ru/IL ratio

Since both acid as well as metal sites are important for the direct conversion of FAL to GVL, the effect of compositions of 5% Ru/C + ILs was also studied. For this purpose, loading of 5% Ru/C was varied from 0.25 g to 0.75 g at a constant loading IL of 0.3 g. Figure 6.11 shows that for all the loadings of Ru, the conversion of FAL remained constant at >99% while the product selectivity was significantly affected. With an increase in 5% Ru/C catalyst loading from 0.25 to 0.75 g, the selectivity to hydrogenation product GVL gradually increased from 35 to 83% at the cost of Me-LA indicating that an optimum Ru catalyst loading was necessary to achieve the highest selectivity to GVL. In another control experiment, IL loading was decreased to 0.15 g which resulted in significant lowering of the furfuryl alcohol conversion to 80%. More importantly, Me-LA selectivity was also minimum (10%) which in turn adversely affected the selectivity to GVL.
Figure 6.11. Effect of catalyst ratio on hydrogenation of furfuryl alcohol to GVL

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; H₂ pressure, 500 psi; catalyst, 0.15-0.3g (acidic IL) +0.25-0.75g (5% metal catalyst); reaction time, 5 h.

This study suggests that the direct conversion of furfuryl alcohol to GVL involves acid catalyzed first step alcoholysis of furfuryl alcohol to Me-LA followed by its metal catalyzed hydrogenation to 4- hydroxy methyl levulinate and subsequent cyclization to GVL (Scheme 6.2). During the cyclization, R–O is released as the corresponding alcohol, methanol in this case.

Scheme 6.2. Direct conversion of furfuryl alcohol to GVL
6.3.4.2. Effect of hydrogen pressure

In order to maximize the selectivity to GVL, hydrogen pressure was varied from 250 to 750 psi and the results are shown in Figure 6.12.

Figure 6.12. Effect of hydrogen pressure on hydrogenation of furfuryl alcohol to GVL

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; H₂ pressure, 250-750 psi; catalyst, 0.3g (acidic IL) +0.5g (5% metal catalyst); reaction time, 5 h.

A complete conversion of furfuryl alcohol was achieved over the entire range of H₂ pressures studied in this work. The H₂ pressure effect was very positive to enhance the selectivity to GVL from 35 to 85% with complete disappearance of FAL ethers. However, even at the highest H₂ pressure of 750 psi, marginal Me-LA and 4-MeLA remained unreacted indicating that rather than higher H₂ concentration, a higher extent of metal sites would be necessary for complete hydrogenation of the intermediates to GVL.
6.3.4.3. Effect of metal loading

The effect of active metal (Ru) loading on carbon was varied in the range of 5–10% with a constant amount of IL. As can be seen from Figure 6.13, conversion of the intermediate methyl LA increased from 76 to 95% with an increase in selectivity to GVL up to 94% for the active metal (Ru) loading of 10% on the carbon support. Thus, the availability of active metal content plays an important role in hydrogenation of methyl levulinate to GVL.

**Figure 6.13.** Effect of metal loading on hydrogenation of furfuryl alcohol to GVL

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; H₂ pressure, 500 psi; catalyst, 0.3g (acidic IL) +0.5g (5-10% metal catalyst); reaction time, 5h.

6.3.4.4. Concentration Vs time study

The role of acidic and metal sites could be further understood for the direct single pot conversion of furfuryl alcohol to GVL under nitrogen and hydrogen atmosphere. Figure 6.14 shows the conversion and selectivity vs. time pattern for a single pot conversion of
furfuryl alcohol to GVL over acidic as well as metal sites. Initially, under an N₂ atmosphere, Brønsted acid sites of IL gave complete formation of methyl levulinate within the first 2 h of the reaction with complete conversion of furfuryl alcohol while changeover from N₂ to H₂ facilitated the hydrogenation of MeLA to 4-hydroxy MeLA followed by its cyclization to GVL. However, under only hydrogenation conditions, the ring hydrogenation product THF alcohol was obtained to the extent of 25–31% which remained stable, affecting the selectivity to GVL (entry 3, Table 6.2).

![CT profile for furfuryl alcohol alcoholysis and hydrogenation](image)

**Figure 6.14.** CT profile for furfuryl alcohol alcoholysis and hydrogenation

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N₂ atm. + H₂ pressure, 500 psi; catalyst, 0.3 (acidic IL) +0.75 g (5%metal catalyst); reaction time, 2h+3h.

The mechanistic pathway for alcoholysis of furfuryl alcohol to methyl levulinate catalyzed by IL in alcoholic medium involves first the formation of methoxy FAL followed by ring hydration in the form of 1,4- addition to form the intermediate A formed by subsequent deprotonation and the evolution of alkyl alcohol gave rise to the 1,3- diene B as shown in Scheme 6.3. Protonation of this diene yielded the cyclic oxonium compound, C. By electron-pair transfer, the cyclic oxonium compound was converted...
into exocyclic oxonium D, which was attacked by water to form compound E, which then isomerized to form levulinate as the final product. In a single pot tandem approach we could achieve GVL synthesis from FAL.

Scheme 6.3. Plausible mechanistic pathway for MeLA formation

6.3.5. Catalyst recycle study

The recycle experiments for [BMIm-SH][HSO4] catalyst for alcoholysis were also carried out at 130 °C. After completion of the reaction, methanol was evaporated using a rotavapour. To this concentrated solution, 80 mL of ethyl acetate was added and the IL was extracted with three portions 40 mL each of distilled water, in a separating funnel.
After evaporation of the aqueous layer, IL catalyst was recovered for its reuse in the subsequent alcoholysis experiment. This procedure was repeated up to the third recycle of the catalyst which showed the consistent activity as shown in Figure 6.15. A decrease in selectivity to methyl levulinate from 99 to 83% associated with the corresponding increase in intermediate selectivity was observed due to handling loss from time to time extraction. This was confirmed by adding a makeup amount (~20%) of the catalyst after the third recycle due to which the original selectivity to methyl levulinate was regained in the fourth recycle.

**Figure 6.15.** Catalyst recycle study for alcoholysis of furfuryl alcohol to methyl levulinate (B) direct hydrogenation of FAL to GVL

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N₂ atm, catalyst, 0.3 g [BMIm-SH][HSO₄]; reaction time, 2 h; catalyst,
Figure 6.16. Catalyst recycle study for direct hydrogenation of FAL to GVL.

**Reaction conditions:** Furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N₂ atm, catalyst, 0.3 g + 0.5 g [BMIm-SH][HSO₄] + Ru/C; reaction time, 2 h; H₂ pressure, 500 psi; catalyst, 0.75 g;

The results of a catalyst recycle study for a single pot conversion of furfuryl alcohol to GVL are also shown in Figure 6.16. Both the activity and selectivity were consistent for 5% Ru/C in combination with [BMIm-SH][HSO₄] up to three recycles, confirming the stability of our catalyst system under reaction conditions. GC analysis of the organic layer showed GVL with 100% purity while the aqueous layer did not show any GVL. Figures 6.17 and 6.18. This confirms the easy protocol of solvent extraction for the recovery of pure product (GVL).
Figure 6.17. GC spectra of extracted GVL
Figure 6.18. GC spectra of aqueous layer for GVL
6.4. Conclusion

A novel tandem approach for direct conversion of furfuryl alcohol to GVL via the alcoholysis/hydrogenation sequence was demonstrated by designing sulfonic acid-functionalized ionic liquids (SO3H-ILs) and 5% Ru/C catalyst system. Furfuryl alcohol conversion as high as 99% could be achieved with ILs modified with HSO4 and Cl-HSO3 anions in the alcoholysis reaction. The catalyst could be further tuned by increasing the alkyl chain of IL 1-methyl imidazole with 1,4-sultone to give an enhanced selectivity of 95% to methyl levulinate. Combining furfural alcoholysis with a subsequent hydrogenation of Me-LA in a single pot synthesis using our catalyst system comprising [BMIm-SH][HSO4] + 5% Ru/C successfully resulted in the formation of GVL with 68% selectivity and complete conversion of furfuryl alcohol. Under the hydrogenation conditions, the ring hydrogenation to THFAL is a competing reaction adversely affecting the GVL selectivity; hence, the first stage alcoholysis can be carried out under N2 and then changeover to H2 eliminates the THFAL formation. Among the various parameters studied in this work, an increase in Ru loading from 5 to 10% dramatically enhanced the GVL selectivity from 68 to 94%, indicating that the availability of active metal sites is more significant in the tandem reactions of alcoholysis and hydrogenation of methyl levulinate. 5% Ru/C in combination with IL could be satisfactorily recycled three times with consistent performance, confirming its stability under reaction conditions.
6.5. References