Chapter 3

Supported noble metal catalysts for hydrogenation of methyl levulinate
Several supported noble metal catalysts were screened for the hydrogenation of methyl levulinate (MeLA) to γ-valerolactone (GVL). Among these catalysts, 5% Ru/C showed the highest conversion of 95% of MeLA with 91% selectivity to GVL. A detailed characterization was carried out using TPR, XRD, XPS and BET techniques. XPS studies revealed that higher extent of Ru⁰ species in case of carbon supported Ru was responsible for its higher hydrogenation activity as compared to Ru on other supports. Effect of process parameters such as temperature, H₂ pressure, catalyst and substrate concentration and metal loading on MeLA conversion and selectivity to GVL also has been studied. 5% Ru/C catalyst was found to be stable up to five reuses.

<table>
<thead>
<tr>
<th>Lignocellulosic Biomass</th>
<th>Feedstock Carbohydrates</th>
<th>Platform Chemicals</th>
<th>Building Block</th>
<th>Applications</th>
</tr>
</thead>
</table>

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3.1. Introduction

As highlighted in chapter 1, cellulosic biomass constitutes a huge and renewable resource that can be converted into a wide variety chemical and fuel products [1-2]. In this context, \( \gamma \)-valerolactone (GVL) has drawn increasing attention because of its benign properties and versatility with which it can be converted to downstream applications for the next generation fuel and fuel additives [3-5]. Horvath et al. has already demonstrated that GVL after hydrogenation gives pentanoic acid that is a starting compound for several other fuel/fuel additives [6-9]. The low yields of levulinic acid due to polymeric humin formation during thermal decomposition of lignocellulosic biomass in aqueous acid medium alone can be significantly improved in presence of alcohols directly giving the corresponding levulinic esters [10-13]. The subsequent catalytic hydrogenation of levulinic esters to GVL (Scheme 3.1.) thus offers greater commercial potential due to (i) suppression of active metal leaching of hydrogenation catalyst caused by free carboxyl of levulinic acid and (ii) recyclability of alcohol formed during hydrogenation.

\[
\text{Scheme 3.1. Hydrogenation of methyl levulinate to GVL}
\]

The limited literature published so far, on conversion of LA esters or LA to GVL includes mainly the homogeneous catalyst systems having major drawbacks of catalyst separation and subsequent reuse, as well as poor selectivity to GVL. While in case of heterogeneous catalyst systems, leaching of active metal was observed with LA as a substrate [14-18].
Since in the literature Ru catalyst is reported for LA hydrogenation, we decided to carry out a systematic study on catalyst screening using other noble metals such as Pt and Pd and the results were compared with Ru catalyst. Our study also includes the influence of various supports such as carbon, silica and alumina on the activity for MeLA hydrogenation. Among several catalysts studied in this work, 5% Ru/C was found to be the best for selective catalytic hydrogenation of methyl levulinate giving 95% conversion and 91% selectivity to GVL. Further, the effect of various reaction parameters such as temperature, H₂ pressure, catalyst and substrate concentrations on methyl levulinate conversion and GVL selectivity was also studied over 5% Ru/C catalyst.

3.2. Experimental

Ru, Pd and Pt supported on C, SiO₂ and Al₂O₃ catalysts were prepared by wet impregnation method and the detailed experimental procedure of their preparation has been described in chapter 2 (section 2.2.1). The catalysts were characterized by various techniques according to the procedures described in section 2.4. Activity of the prepared catalysts was evaluated for the hydrogenation of levulinic acid to GVL and a typical experimental procedure is described in section 2.5.1.

3.3. Results and Discussion

Among the various catalysts screened (discussed in section 3.4.1), 5% Ru/C showed the highest activity and selectivity. Hence, detailed characterization of 5% Ru on various supports was carried out and the results are discussed below.

3.3.1. Catalyst Characterization

3.3.1.1. BET surface area

The specific BET surface areas of carbon, silica and alumina supported Ru catalysts are shown in Table 3.1. The highest surface area of 139 m²/g was observed for 5% Ru/C while several order of magnitude lower surface area namely, 64 and 1.7 m²/g were obtained for Ru on silica and alumina respectively. Least surface area for alumina supported catalyst is due to the higher extent of aggregation while, ruthenium encapsulation by silica is reported for Ru on silica [20].
Table 3.1. BET surface area for various supported Ru catalysts

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Catalysts</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5% Ru/C</td>
<td>139</td>
</tr>
<tr>
<td>2</td>
<td>5% Ru/SiO₂</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>5% Ru/Al₂O₃</td>
<td>1.7</td>
</tr>
</tbody>
</table>

3.3.1.2. X-ray diffraction

XRD patterns of the 5% Ru supported on carbon, silica and alumina are shown in Figure 3.1. For both Ru on carbon and silica samples, broad peaks were observed indicating highly amorphous nature of the material. In case of Ru/C catalyst, diffraction peak at $2\theta = 43.3^\circ$ was attributed to graphitic carbon phase (002) while the peak at $2\theta = 25.7^\circ$ for Ru/SiO₂ could be attributed to silica phase.

![Figure 3.1. XRD pattern for 5% Ru/C, 5% Ru/Al₂O₃ and 5%Ru/SiO₂](image-url)
While in case of alumina supported Ru catalyst, sharp diffraction peaks at $2\theta = 25.3^\circ$, $37.1^\circ$, $43.48^\circ$ and $57.21^\circ$ with higher intensities attributed to $\gamma$-alumina phases were observed due to highly crystalline nature of the sample. In all the samples no characteristic peaks of Ru were observed indicating either very high dispersion of Ru and/or Ru being diffused in the bulk matrix of the support [19].

3.3.1.3. $\text{H}_2$–TPR

Figure 3.2 shows temperature programmed reduction (TPR) profiles in the range of 50-250$^\circ\text{C}$ for Ru supported on C, $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$.

![Figure 3.2. $\text{H}_2$ TPR profiles for (a) 5% Ru/C (b) 5% Ru/Al$_2$O$_3$ (c) 5%Ru/SiO$_2$](image)

As shown in Figure 3.2, TPR profiles of Ru/C catalysts showed a major reduction peak extending from 200-220 $^\circ\text{C}$ which correspond to the reduction of Ru (III) to metallic Ru [21]. Silica supported Ru catalyst showed a peak at 107$^\circ\text{C}$ indicating only partial...
reduction of Ru (III) to Ru (II) while another small peak at 160-170°C could be due to second step reduction of Ru (II) to Ru (I) however, the possibility of Ru (II) to Ru⁰ cannot be ruled out. The lower temperature of reduction to Ru⁰ was due to the fact that ruthenium sites were encapsulated by silica, which partially dissolved during the ion-exchange under alkaline conditions and then precipitated on top of the exchanged surface during filtering/washing forming some other superficial ruthenium species [20-23]. 5% Ru/Al₂O₃ TPR profile showed a single peak at 90-100°C which corresponds to the reduction of metallic precursor or ruthenate (RuOH)₃ [24]. Among all these samples, only 5%Ru/C showed maximum reduction which was also in accordance with its high activity towards hydrogenation of methyl MeLA.

3.3.1.4. XPS

Figure 3.3 (A) presents the XPS of Ru 3d₅/₂-3d₃/₂ in Ru/C sample. After deconvolution, the most intense doublet at 279.9 and 283 eV (δ = 4.1 eV) was due to metallic Ru [22]. The second set of doublet at 284.3 and 286.9 eV (δ = 4.1 eV) could be assigned to Ru (VI) state as RuO₃. Figure 3.3 (B) shows XPS of O1s for Ru/C sample. After deconvolution an intense peak at 529.7 eV corresponds to (O²⁻) indicating formation RuO₃ [24-25]. The percentage of the Ru species calculated after deconvolution suggests that 40% of the Ru was present in the metallic state Ru⁰ while remaining 60% of Ru is present in the oxide form of ruthenium. It should be noted that the catalysts were prepared using sodium borohydride as a reducing agent having mole ratio of Ru:B is (5:1). XPS study revealed that no boron species was found hence possibility of Ru:B alloy formation was completely eliminated. Figure 3.4 (A) shows XPS of Ru 3d₅/₂-3d₃/₂ states in 5% Ru supported on mesoporous silica. A less intense doublet at 279.9 and 284 eV (δ = 4.1 eV) suggests Ru⁰ state. Another doublet at 283.3 and 287.4 eV (δ = 4.1 eV) suggests Ru (VI) state in accordance with O1s peak at 532.8eV as shown in Figure 3.4 (B)[20]. Figure 3.5 (A) shows XPS of Ru 3d₅/₂-3d₃/₂ for alumina supported ruthenium catalyst. An intense doublet at 280.3 and 285.4 eV (δ = 5.1 eV) corresponds to Ru (II) state in RuO₂. The second set of doublet at 283.3 and 287.4 eV (δ = 4.1 eV) could be assigned to the Ru (VI) state in RuO₃. Figure 3.5 (B) shows XPS of O1s of Ru on
alumina catalyst. Two intense peaks at 530.9 and 532.2 eV could be assigned to oxide and hydroxide (\(\text{OH}^-\)) species of Ru, respectively [25].

**Figure 3.3.** XPS spectra for carbon supported Ru catalysts. (A) Ru and carbon (B) O1s
Figure 3.4. XPS spectra for silica supported Ru catalysts. (A) Ru and silica (B) O1s
Figure 3.5. XPS spectra for alumina supported Ru catalysts. (A) Ru and alumina (B) O1s
3.3.2 Activity testing

3.3.2.1. Catalyst screening

Series of supported noble metal catalysts were screened for the hydrogenation of methyl levulinate and their activity results are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalysts</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5% Ru/C</td>
<td>95</td>
<td>91</td>
<td>09</td>
</tr>
<tr>
<td>2</td>
<td>5% Pt/C</td>
<td>18</td>
<td>47</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>5% Pd/C</td>
<td>14</td>
<td>65</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>5% Ru/SiO₂</td>
<td>15</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>5% Ru/Al₂O₃</td>
<td>7</td>
<td>47</td>
<td>28</td>
</tr>
</tbody>
</table>

**Table 3.2. Catalyst screening for methyl levulinate hydrogenation**

**Reaction conditions**: Methyl levulinate, 5% (w/w); Solvent, MeOH (95ml); H₂ pressure, 500 psi; temperature, 130 °C; reaction time, 2 h.

Although Pd and Pt showed some activity for hydrogenation of methyl levulinate, substantial amount of byproducts were also formed due to further hydrogenation of GVL. As ruthenium is known for hydrogenation of aliphatic carbonyl group, we evaluated ruthenium on various supports for the hydrogenation of methyl levulinate [23]. Among the three supports, carbon supported ruthenium catalyst showed the highest conversion of 95 % which was about 5–13 times higher than the ruthenium on silica and alumina, respectively. The activity of these catalysts was in the following order: Ru/C>Ru/SiO₂>Ru/Al₂O₃. Selectivity to GVL was also found to be highest (91 %) for 5 % Ru/C catalyst. Although the order of catalytic activity is same as the order of surface areas of these catalysts, the order of magnitude difference in activities cannot be explained only on the basis of surface area difference. For example, the difference of surface areas of 5 % Ru/C and 5 % Ru/SiO₂ was about two fold but the activity difference between these catalysts was about six folds. As seen from the TPR characterization, 5 % Ru/C showed the presence of Ru⁰ which is responsible for catalyzing the hydrogenation reaction. This
is also in accordance with XPS studies which revealed the presence of Ru\(^0\) species in 5 % Ru/C catalyst. On the contrary, 5 % Ru/SiO\(_2\) showed very less Ru\(^0\) species in both TPR and XPS analysis (Figures 3.2 c, 3.4). In case of 5 % Ru/SiO\(_2\), the major species present were Ru (IV) and Ru (VI). The incomplete reduction of 5 % Ru/SiO\(_2\) was due to the encapsulation of Ru by silica leading to its lower hydrogenation activity [20–23]. 5 % Ru/Al\(_2\)O\(_3\) catalyst did not show presence of any Ru\(^0\) species. This catalyst mainly contained ruthenium in the form of its oxide and hydroxide as revealed by its TPR and XPS characterizations (Figures 3.2 b, 3.5). Ruthenium hydroxide formation on alumina support could be due to Al–O–Al bridged species [20]. Since, we used NaBH\(_4\) reduction method, complete reduction of ruthenium precursors did not take place particularly, in case of silica and alumina supports where more stable other ruthenium species were formed [26].

Since, 5 % Ru/C showed the highest activity and selectivity, further studies on effect of reaction conditions on methyl levulinate hydrogenation was carried out using this catalyst and the results are discussed below.

### 3.3.3. Effect of parameters

#### 3.3.3.1. Effect of hydrogen pressure

Figure 3.6 shows the results of effect of hydrogen pressure on methyl levulinate hydrogenation at 130 °C. The conversion of methyl levulinate increased by a factor of two (45 to 95%) with increase in hydrogen pressure from 100 to 500 psi. the selectivity to GVL also increased from 78 to 91% with increase in hydrogen pressure. Increase in activity with increase in hydrogen pressure is obviously due to higher dissolved concentration of hydrogen according to Henry’s law [18].
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Figure 3.6. Effect of hydrogen pressure on hydrogenation of MeLA

**Reaction conditions:** Methyl levulinate, 5% (w/w); solvent, MeOH (95 ml); H₂-Pressure, 100-500 psi; temperature, 130 °C; catalyst, 0.5 g (5% Ru/C); reaction time, 2h.

3.3.3.2. Effect of reaction temperature

Figure 3.7 shows influence of reaction temperature on conversion and selectivity pattern in methyl levulinate hydrogenation over 5% Ru/C catalyst.

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Figure 3.7. Effect of temperature on hydrogenation of MeLA

**Reaction conditions:** Methyl levulinate, 5% (w/w); solvent, MeOH (95 ml); H₂ pressure, 500 psi; temperature, 110-130 °C; catalyst, 0.5 g (5% Ru/C); reaction time, 2 h.

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Methyl LA conversion increased from 88 to 98% with increase in temperature from 110 to 150 °C. GVL selectivity progressively increased from 79 to 83% with increase in temperature from 110-150 °C as the hydrogenation of the intermediate, 4-hydroxyl methyl levulinate also picked up with increase in temperature.

3.3.3.3. Effect of substrate concentration

The effect of methyl LA concentrations on hydrogenation reactions was studied in the range of 5-20 wt % methyl LA and the results are shown in Figure 3.8.

![Figure 3.8. Effect of substrate concentration on hydrogenation of MeLA](image)

**Reaction conditions:** Solvent, MeOH (74-95 ml); H₂ pressure, 500 psi; temperature, 130 °C; catalyst, 0.5 g (5% Ru/C); reaction time, 2 h.

The conversion of methyl LA decreased marginally from 95 to 81% as the concentration of methyl LA increased from 5-20 wt %. The decrease in methyl LA conversion was due to the limiting number of catalytic sites at high methyl LA concentration because the catalyst amount was constant. The decrease in conversion at higher concentration (20%) of methyl levulinate was also associated with increase in selectivity to 4-hydroxyl methyl pentanoate upto 19% at the cost of GVL selectivity.
3.3.3.4. Effect of catalyst concentration

Figure 3.9 shows the effect of catalyst concentration on the conversion of methyl levulinate and selectivity was also studied in the range of 0.250 to 0.750 g at 130 °C.

![Figure 3.9. Effect of catalyst concentration on hydrogenation of MeLA](image)

**Reaction conditions:** Methyl levulinate, 5% (w/w); solvent, MeOH (95 ml); H₂ pressure, 500 psi; temperature, 130 °C; catalyst, 0.25-0.75 g (5% Ru/C); reaction time, 2 h.

It was found that the conversion of methyl levulinate increased from 82 to 97% with increase in the catalyst concentration from 0.250 to 0.750 g. The increase in methyl LA conversion was mainly because of higher availability of active catalytic sites with increasing the catalyst concentration. There was no variation in selectivity with increase in catalyst concentration indicating neither further hydrogenation of GVL took place nor the possibility of any reversible reaction.

3.3.3.5. Effect of metal loading

Effect of active metal loading on carbon in range of 1-5% on conversion and selectivity of methyl LA hydrogenation is shown in Figure 3.10. The conversion of methyl LA
increased linearly by 5 times from 18 to 95% with increase in active metal loading from 1 to 5% on the carbon support.

**Figure 3.10.** Effect of metal loading on hydrogenation of MeLA

**Reaction conditions:** Methyl levulinate, 5% (w/w); solvent, MeOH (95 ml); metal loading, 1-5% Ru/C; H₂ pressure, 500 psi; temperature, 130 °C; catalyst, 0.5 g; reaction time, 2 h.

However, selectivity of GVL was slightly affected (87%) for the lowest metal loading of 1% due to the less availability of active component for the hydrogenation of carbonyl group of methyl LA.

### 3.3.3.6 Effect of substrate screening

In order to verify the versatility of 5% Ru/C catalyst few other derivatives of levulinic acid esters were also tested for hydrogenation and the results are shown in Figure 3.11. Although conversion remained the same, selectivity to the corresponding substituted
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GVL decreased from 91-60% with increase in chain length from methyl to butyl substituent as methyl is a better leaving group than butyl.

![Substrate screening for GVL synthesis](image)

**Figure 3.11.** Substrate screening for GVL synthesis

**Reaction conditions:** Substrate concentration 5% (w/w); solvent, (MeOH, EtOH, ButOH) (95 ml); H₂ pressure, 500 psi; temperature, 130 °C; catalyst (5% Ru/C), 0.5 g; reaction time, 2 h.

3.3.4 **Catalyst recyclability**

The catalyst reusability studies for 5% Ru/C catalyst was carried out as follows. After the first hydrogenation experiment, the reaction crude was allowed to settle down and the supernatant clear product mixture was separated out. To the catalyst left in the reactor, fresh charge was added and the subsequent hydrogenation was continued. This procedure was followed for four subsequent runs and the results are shown in Figure 3.12. Our 5% Ru/C catalyst showed almost the same activity as that of the fresh catalyst even after 4th
reuse. A slight decrease in conversion from 95 to 83% could be due physical losses during sampling of the reaction crude from time to time.

![Graph](image)

**Figure 3.12.** Catalyst recycle study for hydrogenation of methyl levulinate

**Reaction conditions:** Methyl levulinate, 5% (w/w); solvent, MeOH (95 ml); H$_2$ pressure, 500 psi; temperature, 403 K; catalyst, 0.5 g (5% Ru/C); reaction time, 2 h

### 3.3.4.1. Catalyst stability

In order to confirm the marginal drop in activity during catalyst recycle study was only due to the handling losses, a standard leaching test was also carried out [27, 28]. As can be seen from Figure 3.13, the hot reaction crude filtrate after the catalyst separation at partial levulinate conversion did not show any activity.
Figure 3.13 Catalyst stability study for hydrogenation of methyl levulinate

**Reaction conditions:** Methyl levulinate, 5% (w/w); solvent, MeOH (95 ml); H$_2$ pressure, 500 psi; temperature, 403K; catalyst, 0.5 g (5% Ru/C); reaction time, 2 h. L$_1$ - With catalyst under the reaction conditions same as above. L$_2$ - Without catalyst after ½ hr under reaction conditions same as above.
3.4. Conclusion

Among Pd, Pt and Ru supported catalysts, Ru/C catalyst showed the highest conversion and selectivity to GVL in methyl LA hydrogenation. As compared to C support, SiO₂ and Al₂O₃ supports showed several folds lower hydrogenation activity for Ru catalyst. TPR and XPS studies revealed that Ru⁰ species were in less concentration or absent in case of Ru/SiO₂ and Ru/Al₂O₃ catalyst, due to either encapsulation of Ru with silica or due to some other stable species such as Ru(OH)₃ formed on the surface.
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3.5. References


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