Chapter 4

Copper catalyzed hydrogenation of levulinic acid and its methyl ester
For developing non-noble metal catalyst systems for LA hydrogenation, several copper-based catalysts were prepared, characterized and evaluated for their activity. Among these, nanocomposites of Cu-ZrO$_2$ and Cu-Al$_2$O$_3$ quantitatively catalyzed the hydrogenation of levulinic acid and its methyl ester to give 90-100% selectivity to γ-valerolactone in methanol and water respectively. Both Cu-ZrO$_2$ and Cu-Al$_2$O$_3$ nanocomposites were prepared by co-precipitation method using mixed precursors under controlled conditions. XRD results showed that the main active phase of the reduced Cu-ZrO$_2$ catalyst was metallic copper and particle size was found to be of 10-14 nm by HRTEM. The active metal leaching was maximum for Cu-Al$_2$O$_3$ catalyst in water medium due to formation of a blue color copper-carboxylate complex. Surprisingly, copper leaching was completely suppressed in case Cu-ZrO$_2$ catalyst in methanol in spite of the substrate loading was increased from 5 to 20% w/w. The excellent recyclability of Cu-ZrO$_2$ catalyst with complete LA conversion and >90% GVL selectivity makes it a sustainable process having a commercial potential.
4.1. Introduction

A tremendous impetus worldwide has been laid on ‘Biorefinery’ concept with the aim for developing new catalytic routes for the conversion of several biobased platform molecules into fuels and multiple commodity products [1, 2]. The major challenge in this endeavor is the selective hydro-deoxygenation with minimum number of processing steps by designing appropriate catalyst systems and at the same time would require less number of processing steps as compared to as compared to the fossil derived hydrocarbons [3, 4]. As mentioned previously (chapters 1 and 3), downstream processing of LA gives several useful molecules and one of these is γ-valerolactone (GVL) obtained by the catalytic hydrogenation of LA. GVL is a sustainable commodity chemical having great commercial importance due to its applications as a solvent in lacquers, as a food additive and can be converted to a variety of monomers. It is also considered as a potential fuel additive for replacing ethanol in gasoline-ethanol blends [3-5].

As shown in Scheme 4.1, GVL synthesis from LA involves the first step of hydrogenation to give an intermediate, 4-hydroxy levulinic acid followed by its subsequent cyclization either by homogeneous or heterogeneous catalysts. Recently, a process for GVL from LA with high yield was reported using noble metal homogeneous catalysts systems [6, 7]. Homogeneous catalyst systems obviously have serious drawbacks of catalyst recovery and its recycle in addition to multistep synthesis of ligands, thus far from the commercial application. Heterogeneous catalyst systems, reported for the hydrogenation of LA include supported Ru, Pt, Pd and Re as well as chromium containing copper catalysts [8-16]. Similar studies were carried out using homogeneous as well as heterogeneous Ru based catalysts however, substantial leaching of the precious noble metals was observed [17].
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Scheme 4.1. Reaction pathway for hydrogenation of levulinic acid

The potential commercial application of LA hydrogenation to GVL process can thus be possible by developing a two way strategy viz. (i) a route which eliminates/minimizes the active metal leaching; and (ii) developing a non noble metal catalyst for an improved process economics. In the present chapter we demonstrate for the first time, the efficiency of a non noble Cu-ZrO$_2$ and Cu-Al catalysts for the hydrogenation of LA to GVL. Between the two catalysts, metal leaching was also drastically reduced for Cu-ZrO$_2$ catalyst (34 ppm) as compared to Cu-Al$_2$O$_3$ (174 ppm) in water medium due to stable tetragonal phase formation of ZrO$_2$ which strongly binds to the active Cu. The extent of metal leaching was further reduced to almost nil (2 ppm) with in situ formation of methyl levulinate in methanol solvent, followed by its subsequent hydrogenation to GVL. Hence, the catalyst reusability was also possible for three times unlike Ru based catalysts [11]. Our copper based catalyst will thus have a significant potential of commercial development since the lignocellulose decomposition is increasingly carried out in presence of alcohol to enhance overall yield of LA ester as compared to LA, due to substantial reduction in humin formation [18].
4.2. Experimental

All copper catalysts tested in this work (Cu–ZrO$_2$, Cu–Al$_2$O$_3$, Cu–BaO, Cu–Cr$_2$O$_3$, Cu–Cr$_2$O$_3$–Al$_2$O$_3$, Cu–BaO–Al$_2$O$_3$) were prepared by using a co-precipitation method and the detailed experimental procedure of their preparation has been described in chapter 2 (section 2.2.2). The catalysts were characterized by various techniques according to the procedure described in section 2.4. 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 2.5.

4.3. Results and discussion

4.3.1. Catalyst characterization

As Cu-ZrO$_2$ catalyst showed the highest performance and stability for the hydrogenation of LA and its methyl ester, a detailed characterization of Cu-ZrO$_2$ was carried out and the results were also compared with those of other Cu based catalysts studied in this work.

4.3.1.1. BET surface area and isotherms

BET surface area of Cu-ZrO$_2$ was found to be 22.1 m$^2$/g with pore volume of 0.06 cc/g and pore size of 2.7 nm (Table 4.1). The microporous nature of the material was confirmed by type I adsorption isotherm as shown in Figure 4.1. The characteristic feature of a Type I isotherm is a long horizontal plateau, which extends up to relatively high $P/P_0$. Such sorption isotherms can be described by the Langmuir equation which was developed on the assumption that adsorption, was limited to at the most one monolayer. Any factor that can limit the quantity adsorbed to a few monolayer which is relevant to a type I isotherm prevailing for micropores, where the small pore width prevents multilayer adsorption and limits the amount adsorbed as shown in Figure 4.1.
Table 4.1. Textural properties of Cu-ZrO\textsubscript{2} catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area m\textsuperscript{2}/g</th>
<th>Pore Volume cc/g</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zr (1:1)</td>
<td>22.1</td>
<td>0.061</td>
<td>2.7</td>
</tr>
</tbody>
</table>

4.3.1.2. X-ray diffraction

XRD patterns of activated and used Cu-ZrO\textsubscript{2} catalyst samples are shown in Figure 4.2. The appearance of indexed diffraction lines at \(2\theta = 43.5^\circ\) (111), 50.6\(^\circ\) (200), 60.2\(^\circ\) (202) and 74.3\(^\circ\) (220) indicate the presence of the crystalline phases of metallic Cu in all the samples [19]. The particle size evaluated from Scherrer equation using the peak at \(2\theta = 43.5^\circ\) having maximum intensity was found to be 13.5 nm, that matched very well with the HRTEM results (discussed later). XRD results showed that the main active phase of the reduced Cu-ZrO\textsubscript{2} catalyst was metallic copper and a peak at \(2\theta = 30.5^\circ\) (particle size = 8 nm) indicated the tetragonal phase of zirconia [19-20]. While, the sample recovered...
after the reaction carried out in water, showed that metallic copper phase remained intact as evidenced by a peak at $2\theta = 43.5^\circ$, however appearance of a new peak at $2\theta = 36.5^\circ$ indicated the formation of Cu$_2$O as shown in Figure 4.2 (c). The increased sharpness of the peak at $2\theta = 30.5^\circ$ in the used sample, could be due to the increase in crystallite size (from 8 to 11 nm) of ZrO$_2$. In contrast to this, XRD of Cu-ZrO$_2$ recovered from the methanol medium (Figure 4.3) showed the presence of metallic copper phase without any characteristic peak of Cu$_2$O.

![XRD patterns for nano Cu-ZrO$_2$ catalyst](image)

**Figure 4.2.** XRD patterns for nano Cu-ZrO$_2$ catalyst (a) calcined Cu-ZrO$_2$ (b) activated Cu-ZrO$_2$ (c) used Cu-ZrO$_2$ in water.
Figure 4.3. XRD patterns for nano Cu-ZrO₂ catalyst (a) calcined Cu-ZrO₂ (b) activated Cu-ZrO₂ (c) used Cu-ZrO₂ in methanol.

Figure 4.4. XRD patterns for nano Cu-Al₂O₃ catalyst (a) Activated Cu-Al₂O₃ (b) Used Cu-Al₂O₃ in water.

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Although XRD pattern of activated Cu-Al₂O₃ catalyst in Figure 4.4 showed metallic copper and Cu₂O phases at $\theta = 43.5^\circ$ (111) and $\theta = 36.5^\circ$ respectively, in contrast to Cu-ZrO₂ both these phases disappeared and appearance of peaks at $\theta = 38.1^\circ$, 44.7°, 48.72° and 71.9° and another peak at $\theta = 27.8^\circ$ indicate the presence of CuO and alumina phases, respectively.

### 4.3.1.3. XPS

In order to evaluate the extent of various copper species formed, XPS of Cu-ZrO₂ was also studied and XPS spectrum is shown in Figure 4.5. The Cu 2p XPS of the activated Cu-ZrO₂ catalyst sample showed a broad peak in the range of 932–935 eV, which was ascribed to the presence of various Cu species. The wide Cu 2p₃/₂ signals showed the presence of two peaks of different binding energies namely, 932.4 eV and 933.08 eV corresponding to metallic Cu and Cu⁺ in Cu₂O, respectively. The extent of Cu metal and Cu⁺ was evaluated as 67 % and 33%, respectively.

![Figure 4.5. XPS of used Cu-ZrO₂ catalyst](image-url)
4.3.1.4. Raman study

In Raman spectra of freshly activated (Figure 4.6, a) and recovered (Figure 4.6, b) Cu-ZrO$_2$ catalyst samples, weak and strong bands at 144, 436 and 627 cm$^{-1}$ could be assigned to tetragonal ZrO$_2$, which was in accordance with the XRD results. In addition, the bands at 248 and 308 cm$^{-1}$ were of surface CuO due to the exposure of the sample to air. Although these bands in the recovered sample shifted to new values nevertheless, these are characteristics of tetragonal ZrO$_2$ phase which is in good agreement with the XRD results. Also, the absence of sharp bands in the spectra after the reaction indicates the semi crystalline nature due to exposure under reaction conditions [20].

![Raman spectra of nano Cu-ZrO$_2$ catalyst](image)

**Figure 4.6.** Raman study of nano Cu-ZrO$_2$ catalyst (a) activated Cu-ZrO$_2$ (b) used Cu-ZrO$_2$ in water.

4.3.1.5. NH$_3$-Temperature programmed desorption

Figures 4.7 (A) and (B) show NH$_3$-TPD profiles and Py-IR respectively, for various copper catalysts. Among these catalysts, Cu-Al$_2$O$_3$ and Cu-ZrO$_2$ showed broad peaks of NH$_3$ desorption in a high temperature region of 500-700 °C, indicating the presence of...
strong acid sites, while other two catalysts (Cu-Cr2O3 and Cu-BaO) did not show any 
NH3 desorption peaks indicating the absence of detectable acid sites.

![Figure 4.7. NH3 TPD and Py-IR profiles of copper based catalysts (A) NH3 TPD profiles of copper catalysts (B) Pyridine IR of copper with Al and Zr catalysts.](image)

*Figure 4.7. NH3 TPD and Py-IR profiles of copper based catalysts (A) NH3 TPD profiles of copper catalysts (B) Pyridine IR of copper with Al and Zr catalysts.*
In order to distinguish between the acid sites, Py-IR of both Cu-ZrO$_2$ and Cu-Al$_2$O$_3$ samples were also studied which showed distinct peaks at 1539 and 1558 cm$^{-1}$ due to mixed Lewis-Brønsted and only Brønsted acid sites respectively. The strong acidity of Cu-ZrO$_2$ evidenced by NH$_3$ TPD and Py-IR, resulted into its higher activity for acid catalyzed esterification of LA in methanol as discussed later [19-21].

4.3.1.6. TG-DTA

Catalyst stability was studied by TG-DTA and the results are shown in Figures 4.8 (A) and (B). TG profiles of Cu-Cr$_2$O$_3$ and Cu-BaO showed the decomposition of these catalysts after 400 ºC and 600 ºC, respectively. On the other hand, both Cu-ZrO$_2$ and Cu-Al$_2$O$_3$ showed excellent stability upto 700 ºC. DTA of TG profiles of all the samples in Figure 4.8, (B) showed 8-9% weight loss around 100-120 ºC, due to the loss of water molecules.
The broad exothermic peaks for Cu-Cr$_2$O$_3$ and Cu-BaO catalysts could be due to the loss of Cu in the form of CuO, to the extent of 30% which was much higher than that observed for Cu-ZrO$_2$ and Cu-Al$_2$O$_3$ (8-9%) catalysts [22-23]. This confirms the higher stability of Cu-ZrO$_2$ catalyst as well as retention of active Cu for higher hydrogenation activity than that of other Cu catalysts.

4.3.1.7. H$_2$-TPR

Figure 4.9 shows the H$_2$ TPR of all the copper catalysts studied in this work. All the samples exhibited a broad band of H$_2$ consumption in the range of 180–356 °C. The shape of the H$_2$ consumption peak was asymmetric with a shoulder or a tail, as a result of a complex overlapping of several elemental reduction processes such as sequential reduction of CuO to Cu via Cu$_2$O [24-25]. The highest reduction temperature (359 °C) of Cu.
Cu-ZrO₂ sample confirms the strong interaction of Cu and ZrO₂, contributing to its greater stability under reaction conditions.

![Graphs showing H₂ TPR profiles of copper based catalysts.](image)

**Figure 4.9.** H₂ TPR profiles of copper based catalysts.

### 4.3.1.8. HRTEM

Figure 4.10 (A) and (B) shows HRTEM images of Cu–ZrO₂ before and after reaction in the water medium respectively. The TEM image (Figure 4.10, A) shows the well dispersed nature of the Cu nanoparticles on the zirconia surface with particle sizes in the range of 10–14 nm which is close to the particle size estimated from XRD (13–14 nm) [26]. HRTEM of the used Cu–ZrO₂ sample (Figure 4.10, B) showed minor agglomeration of Cu particles giving the particle size of 13–15 nm.
The ‘d’ spacing of the used catalyst determined from the pattern of fringes (inset right bottom, Figure 4.10, B) was found to be 3.2 Å which was also close to that obtained by XRD (2.9 Å) for $2\theta = 43.5^\circ$ (111) plane of metallic copper. On the contrary, fresh Cu–Al$_2$O$_3$ (Figure 4.10, C) showed agglomeration of the particles and did not allow to specify the fringes pattern. In case of recovered Cu–Al$_2$O$_3$ (Fig. 4.10, D) the particles got oriented into a distinct rod like structure without any fringes. This could be due to substantial leaching of Cu, as discussed in detail later (Table 4.3).
4.3.2. Catalyst activity measurement

4.3.2.1. Catalyst screening

The preliminary results on hydrogenation of LA to GVL using various copper catalysts in both water and methanol solvents are presented in Table 4.2. The desired product GVL was identified by $^1$H-NMR, $^{13}$C-NMR, DEPT and the respective spectra are given in Figures 4.11-4.13.

Table 4.2. Catalyst screening for hydrogenation of LA in water and methanol

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalysts</th>
<th>Water</th>
<th>Methanol</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conversion, %</td>
<td>Selectivity, %</td>
<td>Conversion, %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GVL</td>
<td>MeLA</td>
<td>GVL</td>
</tr>
<tr>
<td>1</td>
<td>Cu-ZrO$_2$ (1:1)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Cu-Al$_2$O$_3$ (1:1)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Cu-Cr$_2$O$_3$ (1:1)</td>
<td>9</td>
<td>100</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>Cu-BaO (1:1)</td>
<td>12</td>
<td>100</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>Cu-Cr$_2$O$_3$-Al$_2$O$_3$ (4:4:2)</td>
<td>40</td>
<td>100</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>Cu-BaO-Al$_2$O$_3$ (4:4:2)</td>
<td>45</td>
<td>100</td>
<td>92</td>
</tr>
</tbody>
</table>

**Reaction conditions:** Levulinic acid, 5% (w/w); solvent, water and MeOH (95 ml); temp, 200 °C; H$_2$ pressure, 500 psi; catalyst, 0.5 g; reaction time, 5h.

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Figure 4.11. NMR spectra of γ-valerolactone

$^1$H-NMR (CDCl$_3$, 200MHz) : $\delta$ 1.39-1.43 (d, 3H), 1.73-1.93 (m, 1H), 2.28-2.43 (m, 1H), 2.51-2.59 (m, 2H), 4.56-4.73 (m, 1H).

Figure 4.12. C$^{13}$NMR spectra of γ-valerolactone

$^{13}$C NMR (CDCl$_3$, 50MHz) : $\delta$ 20.86, 28.93, 29.50, 77.18, 177.26.
It is interesting to note that copper in combination with Zr and Al showed complete LA conversion in water while, copper with other metals showed very poor LA conversion in the range of 4–45%, although complete GVL selectivity was obtained in all the cases. On the other hand, in methanol solvent, a maximum GVL selectivity of up to 90% was achieved only in the case of Cu–ZrO₂ and Cu–Al₂O₃ catalysts. Copper, in combination with other metals, gave LA conversion of <90% with GVL selectivity ranging from 45–86%. The lowering of the GVL selectivity was due to unconverted 4-HMeLA and MeLA (Scheme 4.1). The poor surface acidity of the Cu catalysts with metals other than Zr and Al, as evidenced by NH₃-TPD, was responsible for the slower rate of esterification Figure 4.7. This also affected the further steps of Cu catalyzed hydrogenation and acid catalyzed cyclization to GVL leading to accumulation of 4-HMeLA and MeLA. The marginal lower selectivity to GVL in methanol over Cu–ZrO₂ catalyst was due to less facile cyclization of 4-hydroxyl methyl levulinate having a bulkier methyl group as compared to that of 4-hydroxyl levulinic acid. The excellent catalytic performance of our copper–zirconia catalyst could be due to (i) its strong surface acidity that catalyzes cyclization of
the intermediate hydroxyl levulinic acid–ester due to the protonation of hydroxyl group, [27] (ii) the microporous nature of Cu–ZrO₂ as evidenced by the type I isotherm (Figure 4.1, Table 4.1), [28] (iii) ZrO₂ also plays a role in the first step of hydrogenation in which hydrogen adsorbs dissociatively on ZrO₂, [29] (iv) among the dopent oxides of other metals such as barium, chromium and aluminium, ZrO₂ is the most stable to “decoking” conditions during repeated catalyst regeneration cycles, and (v) ZrO₂ shows much higher stability against its leaching in aqueous LA solution in high temperature reaction conditions, as proven by the catalyst recycles studies described later [12, 13].

4.3.2.2. Stability of the catalyst

As stability is critical for the efficient use of any catalyst, Cu metal leaching was studied for the Cu–ZrO₂ and Cu–Al₂O₃ catalysts since almost complete conversion of LA with similar selectivities to GVL were obtained for both catalysts. The extent of Cu metal leaching was dramatically affected by change in the reaction medium. As can be seen from Table 4.3, the active metal leaching was maximum (174 ppm) for the Cu–Al₂O₃ catalyst while, it was only 34 ppm in case of the Cu–ZrO₂ catalyst in the water medium. Even in methanol solvent, metal leaching up to 31 ppm was observed for Cu–Al₂O₃ while, it was almost completely suppressed in the case of the Cu–ZrO₂ catalyst. However for the Cu–ZrO₂ catalyst, no metal leaching was observed when methyl levulinate was used as a substrate in spite of the substrate loading being increased from 5 to 20% w/w. Copper metal leaching was evident visibly by observing the blue colour of the crude reaction in the case of the Cu–Al₂O₃ catalyzed reaction, as shown in Figure 4.14. The blue colour of the solution was due to the formation of a soluble metal carboxylate complex with levulinic acid [30].
Table 4.3. Catalytic activity and stability for synthesis of GVL

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
<th>Metal Leaching (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GVL Me-LA 4-hydroxy Me-LA</td>
<td></td>
</tr>
<tr>
<td>Cu-ZrO₂</td>
<td>Levulinic Acid</td>
<td>Water</td>
<td>100</td>
<td>&gt;99.9 0.01 0.01</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Levulinic acid</td>
<td>Methanol</td>
<td>100</td>
<td>90 2 8</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Methyl levulinate</td>
<td>Methanol</td>
<td>95</td>
<td>92 SM 8</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>*Methyl levulinate</td>
<td>Methanol</td>
<td>81</td>
<td>79 SM 21</td>
<td>ND</td>
</tr>
<tr>
<td>Cu-Al₂O₃</td>
<td>Levulinic acid</td>
<td>Methanol</td>
<td>100</td>
<td>&gt;99.9 0.01 0.01</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>Methyl levulinate</td>
<td>Methanol</td>
<td>93</td>
<td>88 SM 12</td>
<td>ND</td>
</tr>
</tbody>
</table>

Reaction conditions: LA, *MeLA, (5%, 20% w/w); temp, 200 °C; H₂ pressure, 500 psi; catalyst, 0.5 g; reaction time, 5 h.
Figure 4.14. Final reaction sample of LA hydrogenation in water and methanol (A) final reaction sample of LA in water with Cu-Al$_2$O$_3$ catalyst (B) final reaction sample of MeLA in methanol with Cu-ZrO$_2$ catalyst.

**Reaction Conditions**: Levulinic acid, 5% (w/w); solvent, water, methanol (95 mL); temp, 200 °C; catalyst, 0.5 g; (Cu–Al$_2$O$_3$, Cu–ZrO$_2$) reaction time, 5 h.

This was also confirmed by FT-IR (Figures 4.15 A and B) in which the frequency of the carbonyl group of levulinic acid shifted from 1702 cm$^{-1}$ to 1565 cm$^{-1}$, while no change was observed for methyl levulinate as a substrate [30]. Thus metal leaching could be avoided at least in the case of Cu–ZrO$_2$ in the presence of methanol, where the carboxyl group undergoes trans-esterification thus rendering the free carboxylic group unavailable, so cannot form a soluble copper complex [30].
Figure 4.15. FTIR study LA hydrogenation (A) LA hydrogenation in water (B) Methyl LA hydrogenation in methanol

Reaction Conditions: Levulinic acid, Methyl Levulinate 5% (w/w); solvent, water, methanol (95 ml); Temp, 200 °C; catalyst, 0.5 g; (Cu-Al, Cu-Zr) reaction time, 5h.
The proposed reaction mechanism as shown in Scheme 4.1, is believed to proceed differently in methanol than in water. In presence of methanol, the first step of esterification of the carboxyl group forms methyl levulinate and its subsequent hydrogenation to GVL involves the elimination of methanol, which can be recycled. On the other hand, in water the first step is the direct hydrogenation of the keto group to give 4-hydroxy levulinic acid followed by its dehydration to give cyclic GVL.

4.3.2.3. Concentration Vs time activity

The role of acidity of Cu–ZrO$_2$ and Cu–Al$_2$O$_3$ catalyst was further studied by the kinetics of the first step esterification reaction. Figure 4.16 shows selectivity vs. time pattern for conversion of LA to methyl levulinate over various copper based catalysts in methanol. Copper with Zr and Al gave complete formation of methyl levulinate within first 30 min of the reaction while, other metals like Ba and Cr showed lower activity for the esterification step.

![Selectivity profile for methyl levulinate formation](image)

**Figure 4.16.** Selectivity profile for methyl levulinate formation

**Reaction Conditions:** Levulinic acid, 5% (w/w); solvent, water, methanol (95 mL); temp, 200 °C; catalyst, 0.5 g; reaction time, 5 h.
It is also interesting to note that the hydrogenation of methyl levulinate begins only after the complete formation of methyl levulinate, indicating the competitive adsorption of LA and methyl levulinate (Figures 4.17, A and B).

**Figure 4.17.** Conversion selectivity pattern of LA Hydrogenation in (A) water (B) methanol
**Reaction Conditions:** Levulinic acid, 5% (w/w); solvent, water, methanol (95 mL);
temp, 200 °C; catalyst, 0.5 g; reaction time, 5 h.

4.3.3. Catalyst recycle study

The catalyst reuse studies for Cu–ZrO$_2$ catalyst were carried out as follows. After the first hydrogenation was complete, the reaction crude was allowed to settle down and supernatant clear product mixture was removed from the reactor. A fresh charge of reactants was added to the catalyst residue retained in the reactor and the subsequent run was continued. This procedure was followed for three subsequent runs and the results are shown in Figure 4.18 and Figure 4.19. Our copper zirconia catalyst showed almost the same activity with slight decrease in selectivity for LA hydrogenation in methanol even after the third recycle. A marginal decrease in selectivity from 90 to 80% could be due to sintering of the active sites of metal particles. Figure 4.19 (b) shows reuse of copper zirconia catalyst with a lower catalyst loading of 0.15 g which gave consistent activity as indicated by complete conversion after the third recycle. The catalyst activity dropped down to 70% in an aqueous medium due to copper leaching in the reaction crude (Table 4.3).

![Figure 4.18. Recycle study of LA hydrogenation in water](image-url)
Figure 4.19. Recycle study of LA hydrogenation in methanol (a) 0.500 mg catalyst loading (b) 0.150 mg catalyst loading

4.3.4. Continuous hydrogenation of levulinic acid and its methyl ester to GVL

Since Cu on zirconia was established as the best non noble metal catalyst in batch reactor studies for LA hydrogenation to GVL, its time on stream activity was also studied. For this purpose, continuous hydrogenation of methyl levulinate and levulinic acid was studied over a fixed bed of catalyst (4 g) packed in a single tube reactor. Figure 4.20 shows a consistent conversion of 80 to 85% was obtained for both the substrates, methyl LA and levulinic acid over a total period of 100 h. the selectivity to GVL achieved was >90%. This time on stream study confirms the suitability of the catalyst and process from scale up point of view.
Figure 4.20. TOS of Cu-ZrO\textsubscript{2} catalyst for the hydrogenation of MeLA and LA

**Reaction Conditions:** Catalyst, 4 gm palletized (Cu: Zr); LA & MeLA Concentration, 5\% (w/ w); Solvent, Methanol; Reaction Temperature, 200 °C; Feed Flow Rate, 0.5 ml/min; Hydrogen pressure, 500 psi; Reaction time, 100 h.
4.4. Conclusion

Non-noble metal nanocomposite catalysts were developed for the first time by incorporating Zr and Al with copper, for selective hydrogenation of levulinic acid and its methyl ester to GVL. HRTEM revealed the particle size of copper in a range of 10–14 nm. Both XRD and Raman spectroscopy confirmed the formation of the Cu–ZrO$_2$ nanocomposite and also the presence of mixed oxide phases along with Cu$^0$. Both the catalysts showed complete conversion of LA and its ester with $>90\%$ selectivity to GVL. Interestingly, for LA hydrogenation in methanol only Cu–ZrO$_2$ could be recycled efficiently four times, with almost no leaching of the active metal. In methanol, the hydrogenation was found to proceed via the first step of the trans-esterification to the corresponding ester followed by its in situ hydrogenation to GVL.
4.5. References


