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Surface Species of Supported Ruthenium Catalysts in Selective Hydrogenation of Levulinic Esters for Bio-Refinery Application

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Abstract Several supported noble metal catalysts were screened for the hydrogenation of methyl levulinate to γ-valerolactone (GVL). Among these catalysts 5 % Ru/C showed the highest conversion of 95 % of methyl levulinate 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 Ru^0 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, H_2 pressure, catalyst and substrate concentration and metal loading on methyl LA conversion and selectivity to GVL also has been studied. 5 % Ru/C catalyst was found to be stable up to five reuses.

Keywords Biofeedstock · Methyl levulinate · Hydrogenation · γ-Valerolactone · 5 % Ru/C · XPS · H_2-TPR

Abbreviations

GVL	γ-Valerolactone
LA	Levulinate or levulinic acid
4-Hyd-pentanoate	4-Hydroxyl methyl pentanoate
MeOH	Methanol
EtOH	Ethanol
ButOH	Butanol

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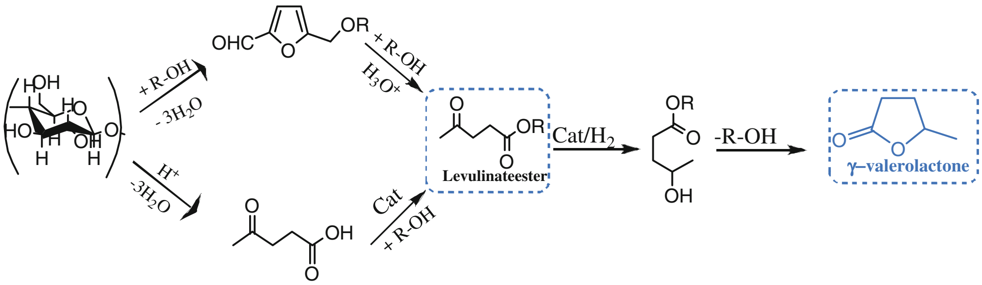
1 Introduction

Cellulosic biomass constitutes a huge and renewable resource that can be converted to chemical and fuel feedstocks [1, 2]. Hence, catalytic conversion of biomass derived compounds to variety of products will drastically shift the energy base of our world in the next decade from fossil to renewable feedstock. In this context, γ-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. [6–9] has already demonstrated that GVL after hydrogenation gives pentanoic acid that is a starting compound for several other fuel/fuel additives. 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 1) thus offers greater commercial potential due to (i) suppression of active metal leaching of hydrogenation catalyst caused by free carboxyl of levulinic acid [14], and (ii) recyclability of alcohol formed during hydrogenation.

Both homogeneous as well as heterogeneous catalyst systems have been reported for the hydrogenation of levulinic acid and its esters. Joo and Beck [15] reported the use of water soluble homogeneous ruthenium catalysts with sulfonated triphenylphosphine ligands (e.g. $HRuCl(Dpm)_3$, Dpm = diphenylphosphinobenzene-*m*-sulfonic acid) for the hydrogenation of LA as well as pseudo LA to give conversion of 99 % and GVL yield of 86 % in toluene. Horvath et al. [6] reported $[(h_6\text{-}C_6Me_6)Ru(bpy)(H_2O)][SO_4]$ catalyst in water for the transfer hydrogenation of LA, using



Scheme 1 Hydrogenation of bio-derived methyl levulinate to γ-valerolactone

formic acid as the hydrogen donor giving GVL and 1,4-pentanediol with 25 % yield. The hydrogenation of LA or ethyllevulinate to GVL using formic acid as the hydrogen donar over Ni, Pt and Re supported on silica has been reported with the highest GVL yield of 81 mol% using ethyllevulinate as substrate [16]. Schutte et al. [17] hydrogenated LA using a platinum oxide catalyst to give GVL with an yield of 87 %. Copper-chromite based catalysts were reported to give a complex mixture of GVL, 1,4-pentanediol, and methyltetrahydrofuran [17]. Yan et al. [18] hydrogenated levulinic acid to GVL over 5 % Ru/C catalyst in methanol as a solvent with a conversion of 92 %, and selectivity to γ-valerolactone achieved was 99 % however, the substantial decrease in both conversion (92–48 %) and selectivity (99–70) was observed in catalytic recycle studies, due to the active metal leaching. The limited literature published so far on conversion of LA esters or LA to GVL shows that the homogeneous catalyst systems have major drawbacks of catalyst separation and subsequent reuse, as well as poor selectivity to GVL. In case of heterogeneous catalyst systems, leaching of active metal was observed with LA as substrate [14].

We report here a stable 5 % Ru/C catalyst for selective catalytic hydrogenation of methyl levulinate with 95 % conversion and 91 % selectivity to GVL. For this purpose, a systematic study on catalyst screening using Pt, Pd, Ru on carbon, silica and alumina was carried out. Further, the effect of various reaction parameters such as temperature, H_2 pressure, catalyst and substrate concentrations on methyl levulinate conversion and GVL selectivity was also studied.

2 Experimental Section

2.1 Material

Methyl levulinate (99 %), $[(RuCl_3)\cdot 3H_2O]$ were purchased from Sigma-Aldrich, Bangalore, India while methanol was purchased from Rankem and, γ-Alumina, Fumed silica were purchased from Loba Chemie, Mumbai, India. Hydrogen of high purity (>99.99 %) was obtained from Inox-India.

2.2 Catalyst Preparation

Supported Ru, Pd, Pt catalysts were prepared by impregnation method. The synthesis was performed by suspending 2 g of activated carbon in aqueous medium using calculated amount of the respective metal precursors and then suspension was stirred for 1 h. It was then subsequently reduced using 5 mL of $NaBH_4$ (1 mol) as a reducing agent. The catalyst was filtered and dried at 110 °C for 12 h.

2.3 Catalyst Activity Tests

Methyl levulinate hydrogenation reactions were carried out in a 300 mL capacity autoclave (Parr Instruments Co., USA) at a stirring speed of 1000 rpm. The typical hydrogenation conditions were: temperature, 403 K; methyl levulinate concentration, 5 wt%; solvent 95 mL; catalyst loading, 0.5 g; and hydrogen pressure 3–4 MPa. Liquid samples were withdrawn periodically. Samples taken during the reaction were analyzed with a HP6890 series GC System (Hewlett Packard) coupled with FID detector and capillary column (HP-5 capillary column, 30 m length × 0.32 mm i.d.). The following temperature programme method was used for GC analysis: 60 °C (1 min)–10 °C/min–230 °C (5 min).

2.4 Catalyst Characterization

BET surface area of the Ru supported on carbon, SiO_2 and Al_2O_3 catalysts was measured by means of N_2 adsorption at 77 K preformed on Autoabsorb 3100 instrument. Temperature programmed reduction (TPR) experiment of prepared Ru supported catalysts were also performed on a Autochem (II) (2920 V 3.05).

In the TPR experiment, a U-tube (Quartz tube) was filled with solid catalyst. This sample holder was positioned in a furnace equipped with a temperature control. A thermocouple is placed in the solid for temperature measurement. Equal quantity of fresh vacuum dried catalyst was taken in the U-tube. Initially flow of inert gas (Nitrogen) was passed through U-tube to remove the air present in the lines, and then heated with a N_2 flow rate of

30 mL/min to 200 °C for 30 min, in order to remove the moisture and surface impurities present on the sample. The sample was then cooled to room temperature. Then nitrogen was replaced by mixture of 5 % H_2 in N_2 gas for the TPR experiment and the hydrogen uptake was measured by a thermal conductivity detector.

X-ray diffraction patterns were recorded on a PAnalytical PXRD Model X-Pert PRO-1712, using Ni filtered Cu Kα radiation ($\lambda = 0.154$ nm) as a source (current intensity, 30 mA; voltage, 40 kV) and X-celerator detector. The samples were scanned in the 2θ range of 20°–80°. The species present on the surface were identified by their characteristic 2θ values of the relevant crystalline phases. The software program X-Pert High Score Plus was employed to subtract contribution of copper Kα_2 line prior to data analysis. X-ray photoelectron spectra were recorded using an ESCA-3000 (VG Scientific Ltd. England) with a 9 channeltron CLAM4 analyzer under vacuum better than 1×10^{-8} Torr, using MgKα radiation (1253.6 eV) and a constant pass energy of 50 eV. The binding energy values were charge-corrected to the C1s signal (284.6 eV).

3 Results and Discussion

Among the various catalysts screened (discussed in Sect. 3.2), 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.

3.1 Catalyst Characterization

XRD patterns of the 5 % Ru supported on carbon, silica and alumina are shown in Fig. 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 $2\theta = 43.3°$ was attributed to graphitic carbon phase (002) while the peak at $2\theta = 25.7°$ for Ru/SiO_2 could be attributed to the silica phase. While in case of alumina supported Ru catalyst, sharp diffraction peaks with higher intensities 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].

The specific BET surface areas of carbon, silica and alumina supported Ru catalysts are shown in Table 1. The highest surface area of 139 m^2/g was observed for 5 % Ru/C while several order of magnitude lower surface area namely, 64 and 1.7 m^2/g were obtained for Ru on silica and alumina respectively. Least surface area for alumina supported catalyst is due to the higher extent of agglomeration while ruthenium encapsulation by silica is reported for Ru on silica [20].

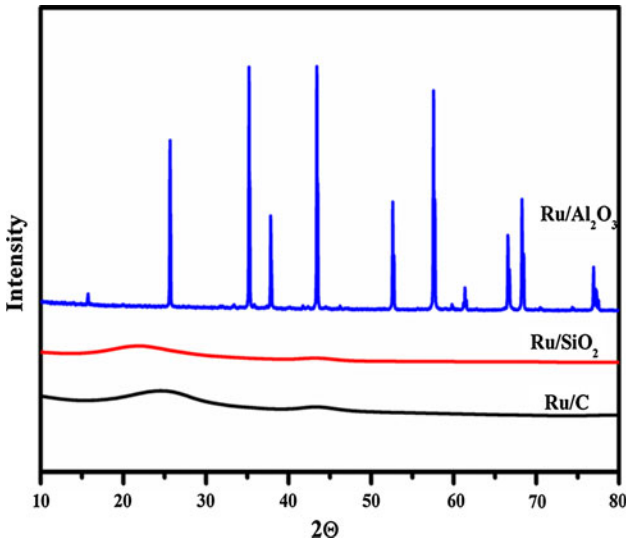


Fig. 1 XRD pattern for 5 % Ru/C, 5 % Ru/Al_2O_3 and 5 %Ru/SiO_2

Table 1 BET surface area for various supported Ru catalysts

S. No.	Catalysts	Surface area (m^2/g)
1	5 % Ru/C	139
2	5 % Ru/SiO_2	64
3	5 % Ru/Al_2O_3	1.7

Figure 2 shows TPR profiles in the range of 50–250 °C for Ru supported on C, SiO_2 and Al_2O_3. Moreover, the samples were exposed to air and they might suffer a surface oxidation. The TPR profiles of Ru/C catalysts showed a reduction peak extending from 200 to 220 °C which corresponds to the reduction of Ru (III) to metallic Ru [21]. Silica supported Ru catalyst showed a peak at 110 °C indicating only partial reduction Ru (III) to Ru (II) while another small peak at 160–170 °C could be due to second step Ru (II) to Ru (I) however, the possibility of Ru (II) to Ru^0 can not be ruled out. The lower temperature of reduction to Ru^0 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/Al_2O_3 TPR profile showed a single peak at 90–100 °C which corresponds to the reduction of metallic precursor or ruthanate $(RuOH)_3$ [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 levulinate.

Figure 3a presents the XPS of Ru $3d_{5/2}$–$3d_{3/2}$ in Ru/C sample. The most intense doublet at 279.9 and 284 eV

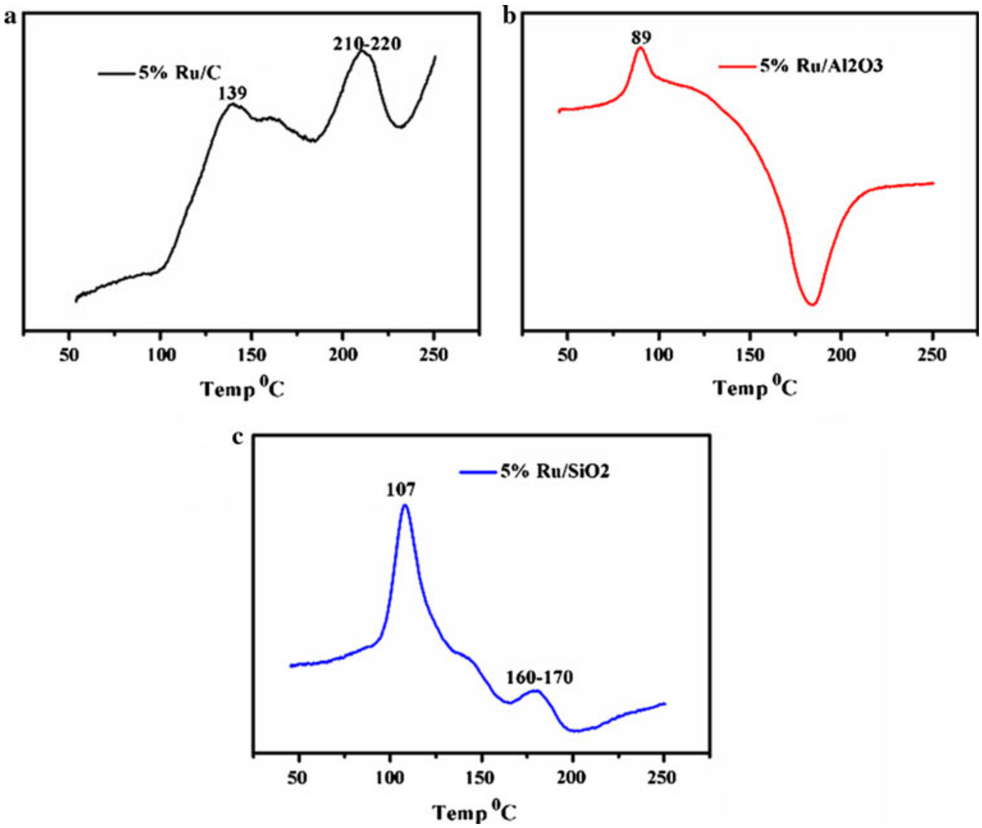


Fig. 2 H_2 TPR profiles for **a** 5 % Ru/C, **b** 5 % Ru/Al_2O_3, **c** 5 %Ru/SiO_2

($\delta = 4.1$ eV) is due to metallic Ru [22]. The second set of doublet at 283.3 and 286.9 eV ($\delta = 4.1$ eV) could be assigned to Ru (VI) state as RuO_3. Figure 3b shows XPS of O1s for Ru/C sample. An intense peak at 529.8 eV corresponds to (O^-) indicating formation RuO_3 [24, 25]. The percentage of the Ru species calculated after deconvulation suggests that 40 % of the Ru is present in the metallic state Ru^0 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 (5:1). XPS study revealed that no boron species was found hence possibility of Ru:B alloy formation was completely eliminated. Figure 4a shows XPS of Ru $3d_{5/2}$–$3d_{3/2}$ states in 5 % Ru supported on mesoporous silica. A less intense doublet at 279.9 and 284 eV ($\delta = 4.1$ eV) suggests Ru^0 state. Another doublet at 283.3 and 287.4 eV ($\delta = 4.1$ eV) suggests Ru (VI) state in accordance with O1s peak at 532.8 eV [20]. (Fig. 4b). Figure 5a shows XPS of Ru $3d_{5/2}$–$3d_{3/2}$ for alumina supported ruthenium catalyst. An intense doublet at 280.3 and 285.4 eV ($\delta = 5.1$ eV) corresponds to Ru (II) state in RuO_2. The second set of doublet at 283.3 and 287.4 eV ($\delta = 4.1$ eV) could be assigned to the Ru (VI) state in RuO_3. Figure 5b shows XPS of O1s of Ru on alumina catalyst. Two intense peaks at 530.9 and 532.2 eV could be assigned to oxide of ruthenium as well as hydroxide (OH^-) species of the catalyst [25].

3.2 Activity Testing

Series of supported noble metal catalysts were screened for the hydrogenation of methyl levulinate and their activity results are shown in Table 2. 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/SiO_2 > Ru/Al_2O_3. 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 surface areas of these catalysts, the order of magnitude difference in activities can not be explained only on the basis of surface area difference. For example, the difference of surface areas of 5 % Ru/C and 5 % Ru/SiO_2 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 Ru^0 which is responsible for catalyzing the hydrogenation reaction. This is also in accordance with XPS studies which revealed the presence

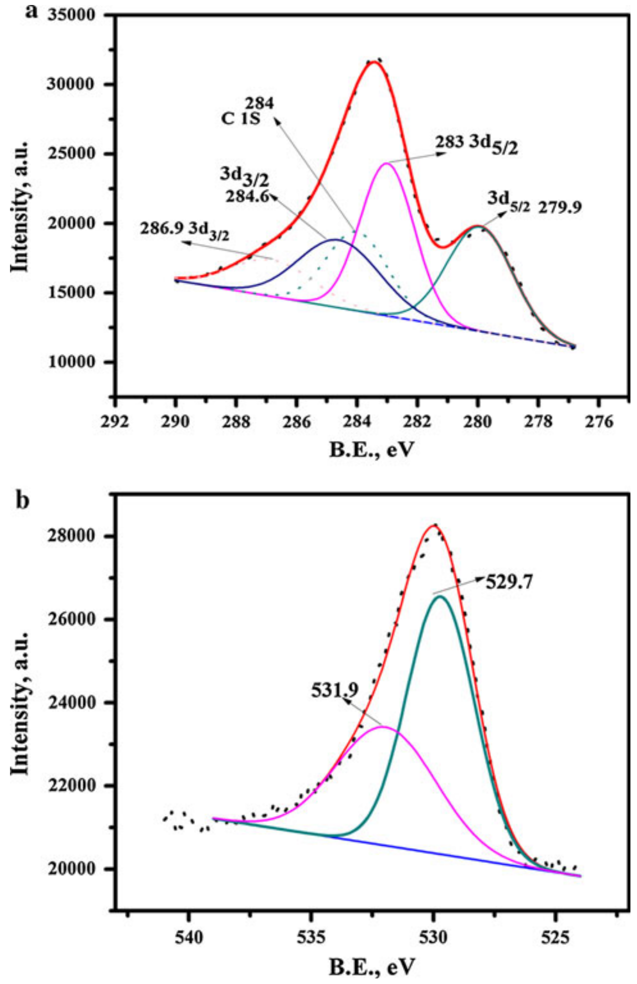


Fig. 3 XPS spectra for carbon supported Ru catalysts. **a** Ru and carbon, **b** O1s

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 (Figs. 3, 5). 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 lower hydrogenation activity [20–23]. 5 % Ru/Al_2O_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 (Figs. 4, 6). 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.

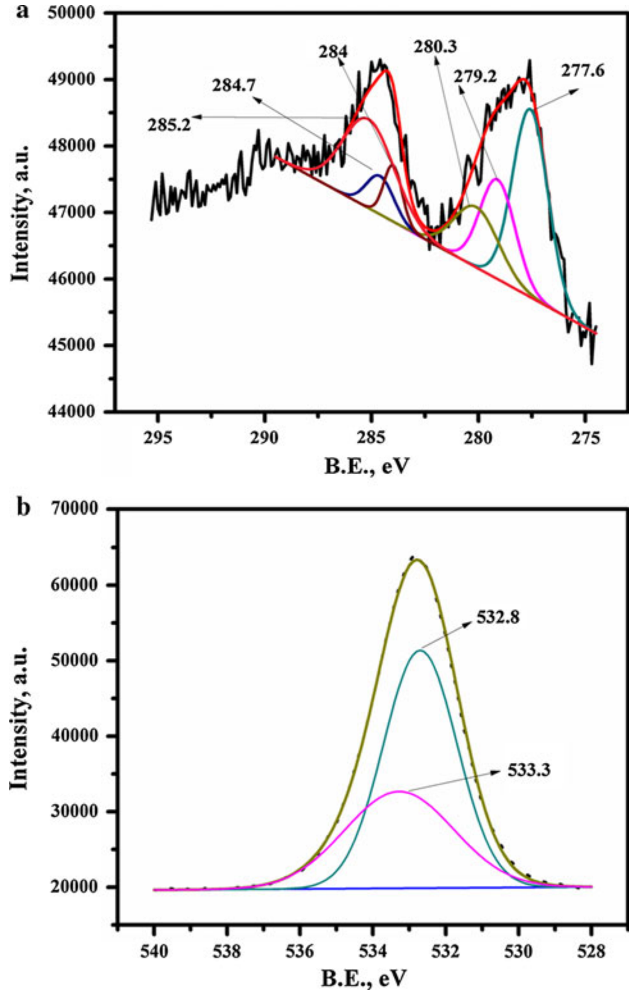


Fig. 4 XPS spectra for silica supported Ru catalysts. **a** Ru and silica, **b** O1s

3.3 Effect of Hydrogen Pressure

Figure 6 shows the results of effect of hydrogen pressure on methyl levulinate hydrogenation at 403 K. The conversion of methyl levulinate increased by a factor of two (45–95 %) 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 Henery’s law [18].

3.4 Effect of Temperature

Figure 7 shows influence of reaction temperature on conversion and selectivity pattern in methyl levulinate hydrogenation over 5 % Ru/C catalyst. Methyl LA conversion increased from 88 to 98 % with increase in temperature from 383 to 423 K. selectivity as low as 82 % was

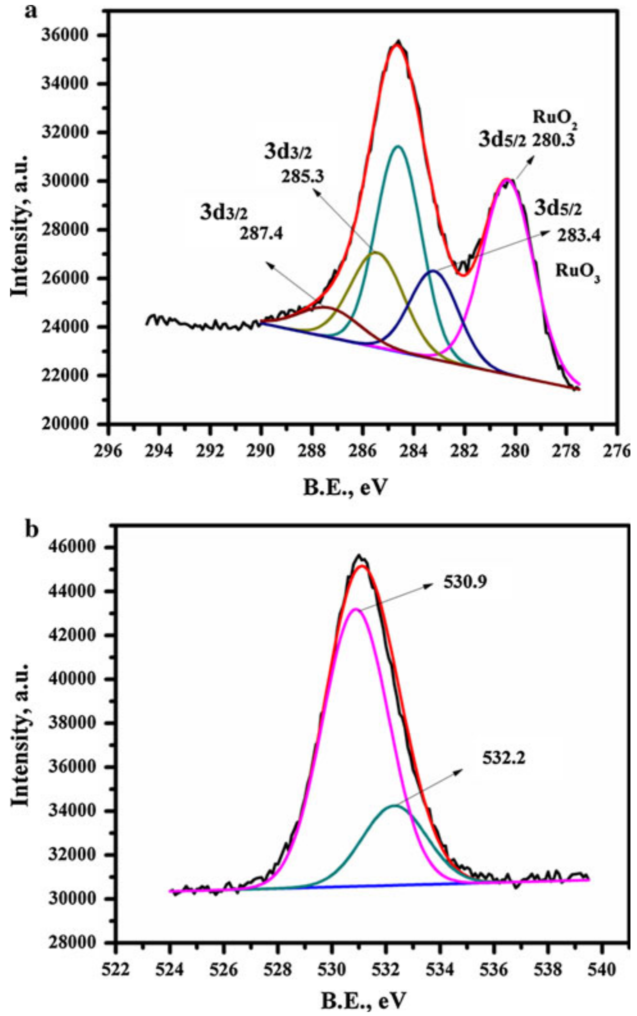


Fig. 5 XPS spectra for alumina supported Ru catalysts. **a** Ru and alumina, **b** O1s

observed due to slower rate of conversion of 4-hydroxyl methyl pentanoate to GVL.

3.5 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 Fig. 8. The conversion of

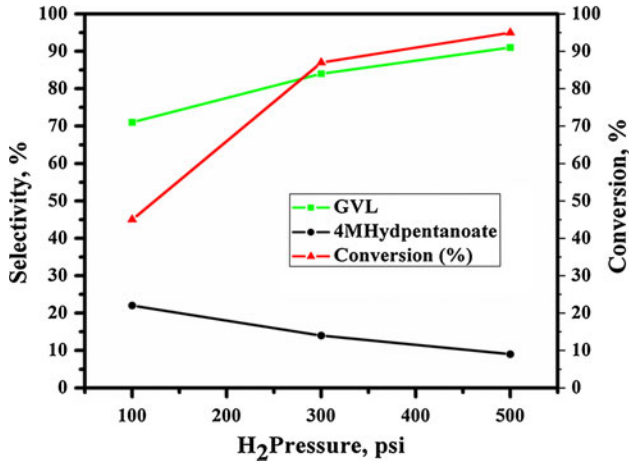


Fig. 6 Effect of hydrogen pressure. *Reaction conditions*: methyl levulinate, 5 % (w/w); solvent, MeOH (95 ml); temperature, 403 K; catalyst, 0.5 g (5 % Ru/C); reaction time, 2 h

methyl LA decreased marginally from 95 to 81 % as the concentration of methyl LA increased from 5 to 20 wt%. The decrease in methyl LA conversion is due the limiting number of catalytic sites at high methyl LA concentration because 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 up to 19 % at the cost of GVL selectivity.

3.6 Effect of Catalyst Concentration

Figure 9, shows the effect of catalyst concentration on the conversion of methyl levulinate and selectivity was also studied in the range of 0.250–0.750 g at 403 K. 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.

Table 2 Catalyst screening for methyl levulinate hydrogenation

Catalysts	Conversion (%)	Selectivity (%)		
		Gamma-valerolactone	Methyl 4-hydroxypentanoate	Others
5 % Ru/C	95	91	09	<0.01
5 % Pt/C	18	47	20	33
5 % Pd/C	14	65	15	20
5 % Ru/SiO_2	15	89	11	<0.01
5 % Ru/Al_2O_3	7	47	28	25

Reaction conditions: Methyl levulinate, 5 % (w/w); Solvent, MeOH (95 ml) H_2 pressure, 500 psi; temperature, 403 K; reaction time, 2 h

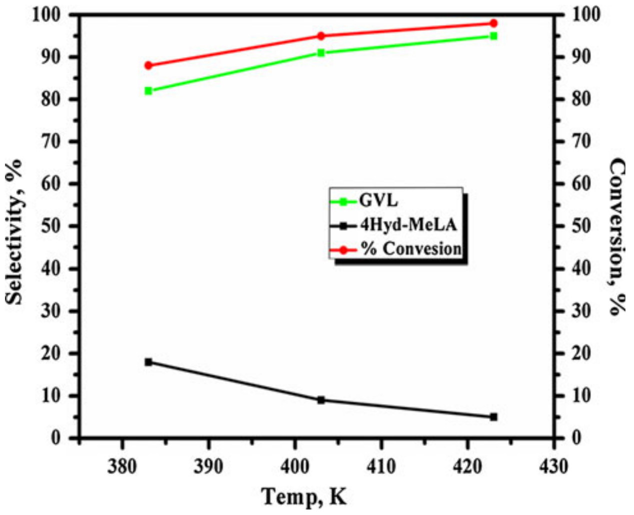


Fig. 7 Effect of temperature. *Reaction conditions*: methyl levulinate, 5 % (w/w); solvent, MeOH (95 ml); H_2 pressure, 500 psi; catalyst, 0.5 g (5 % Ru/C); reaction time, 2 h

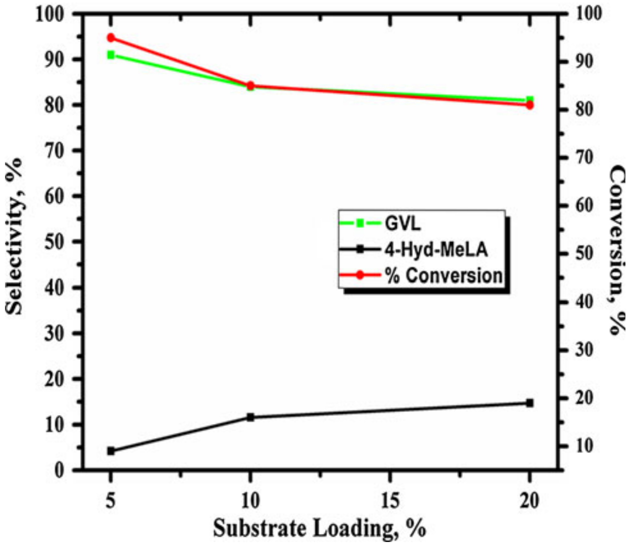


Fig. 8 Effect of substrate concentration. *Reaction conditions*: solvent, MeOH (74–95 ml); H_2 pressure, 500 psi; temperature, 403 K; catalyst, 0.5 g (5 % Ru/C); reaction time, 2 h

3.7 Effect of Metal Loading

Effect of active metal loading on carbon in the range of 1–5 % on conversion and selectivity of methyl LA hydrogenation is shown in Fig. 10. The conversion of methyl LA increased linearly by five times from 18 to 95 % with increase in active metal loading from 1 to 5 % on the carbon support. 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.

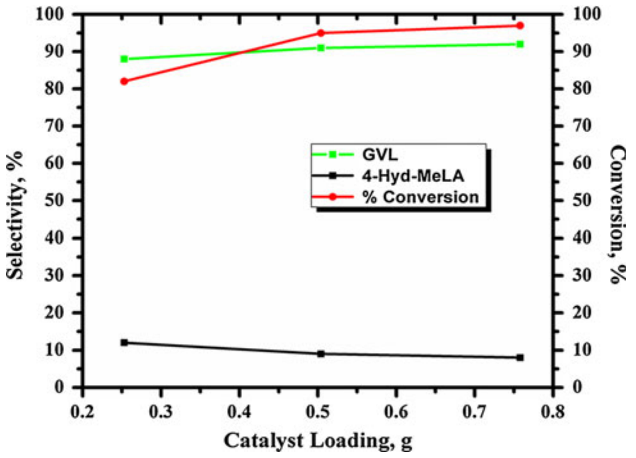


Fig. 9 Effect of catalyst concentration. *Reaction conditions*: methyl levulinate, 5 % (w/w); solvent, MeOH (95 ml); H_2 pressure, 500 psi; temperature, 403 K; catalyst, 0.25–0.75 g (5 % Ru/C);reaction time, 2 h

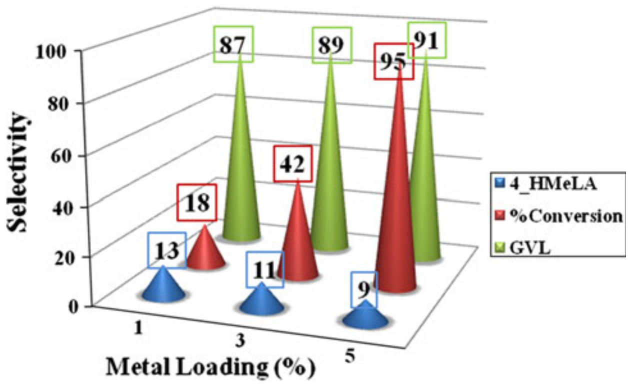


Fig. 10 Effect of metal loading. *Reaction conditions*: methyl levulinate, 5 % (w/w); Solvent, metal loading, 1–5 % Ru on carbon; MeOH (95 ml); H_2 pressure, 500 psi; temperature, 403 K; catalyst, 0.5 g; reaction time, 2 h

3.8 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 Fig. 11. Although the conversion remained same, the selectivity to the corresponding substituted GVL decreased from 91 to 60 % with increase in chain length from methyl to butyl substituent as methyl is a better leaving group than butyl.

3.9 Catalyst Recycle Study

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

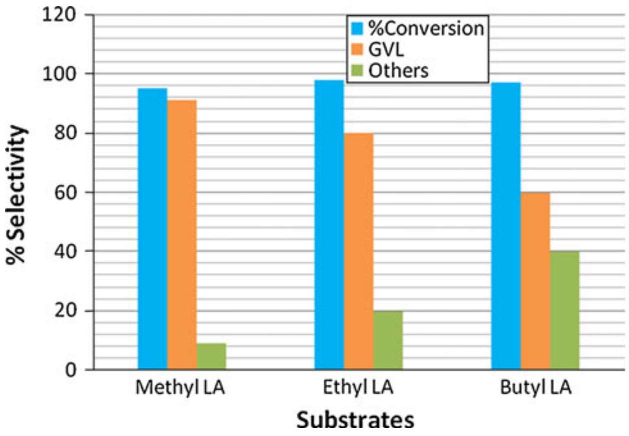


Fig. 11 Effect of substrate screening. *Reaction conditions*: Substrate concentration 5 % (w/w); solvent, (MeOH, EtOH, ButOH) (95 ml); H_2 pressure, 500 psi; temperature, 403 K; catalyst, 0.5 g (5 % Ru/C); reaction time, 2 h

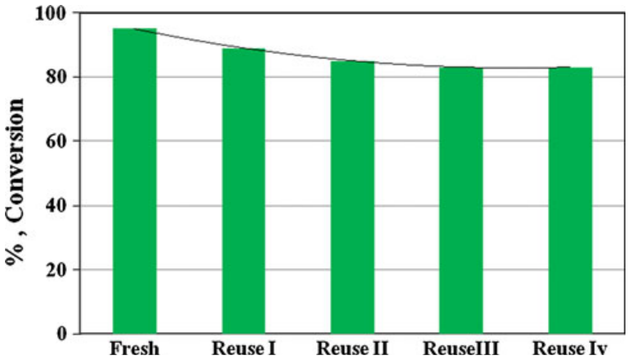


Fig. 12 Catalyst recycle study. *Reaction conditions*: methyl levulinate, 5 % (w/w); Solvent, MeOH (95 ml); H_2 pressure, 500 psi; temperature, 403 K; catalyst, 0.5 g (5 % Ru/C); reaction time, 2 h

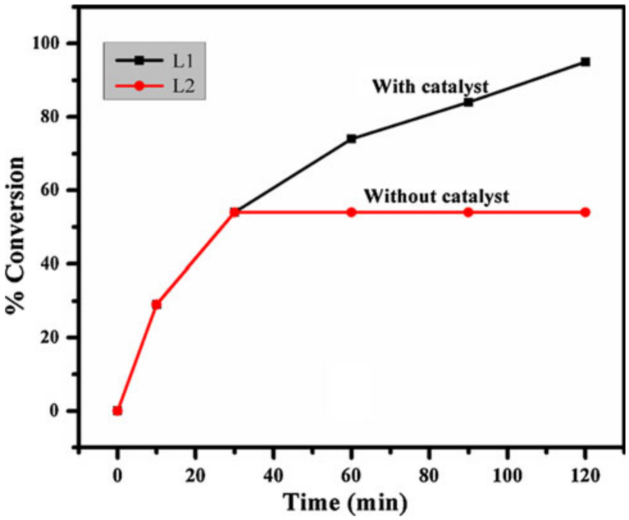


Fig. 13 Metal leaching experiment. *Reaction conditions*: methyl levulinate, 5 % (w/w); Solvent, MeOH (95 ml); H_2 pressure, 500 psi; temperature, 403 K; catalyst, 0.5 g (5 % Ru/C); reaction time, 2 h. L_1-With catalyst same above reaction conditions. L_2-Without catalyst after ½ hr same as above reaction conditions

out. To the catalyst, remaining in the reactor, fresh charge was added and the subsequent hydrogenation was continued. This procedure was followed for four subsequent runs and the result are shown in Fig. 12. Carbon supported ruthenium 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.

In order to confirm the marginal drop in activity during catalyst recycle study was only due to handling losses, a standard leaching test was also carried out [27, 28]. As can be seen from Fig. 13. The hot reaction crude filtrate after the catalyst separation at partial levulinate conversion did not show any activity.

4 Conclusion

Among Pd, Pt and Ru supported catalysts, Ru/C catalyst showed the highest conversion and selectivity to GVL in methyl LA hydrogenation. The comparison of various supports showed that SiO_2 and Al_2O_3 were responsible for decreasing the hydrogenation activity of Ru, by several folds. TPR and XPS studies revealed that Ru^0 species were in less concentration or absent in case of Ru/SiO_2 and Ru/Al_2O_3 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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References

1. Klass DL (1998) Fuels and chemicals. Academic Press, London
2. Grbz EI, Alonso DM, Bond JQ, Dumesic JA (2011) Chem Sus Chem 4:357
3. Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenschwander GG, Fitzpatrick SW, Bilski RJ, Jarnefeld JL (2000) Resour Conserv Recycl 28:227
4. Bourne RA, Stevens JG, Ke J, Poliakoff M (2007) Chem Commun 4632
5. Serrano-Ruiz JC, Wang D, Dumesic JA (2010) Green Chem 12:574
6. Horvath IT, Mehdi H, Fabos V, Boda L, Mika LT (2008) Green Chem 10:238
7. Mehdi H, Fabos V, Tuba R, Bodor A, Mika LT, Horvath IT (2008) Top Catal 48:49
8. Manzer E (2004) Appl Catal A 272:249
9. Lange JP, Vestering JZ, Haan RJ (2007) Chem Commun 3488
10. Windom BC, Lovestead TM, Mascal M, Nikitin EB, Bruno TJ (2011) Energy Fuels. doi:10.1021/ef200239x
11. Kim B, Jeong J, Shin S, Lee D, Kim S, Yoon H, Cho JK (2010) Chem Sus Chem 3:1273
12. Hu X, Zhu LC (2011) Green Chem. doi:10.1039/c1gc15272f

13. Lincai P, Lu L, Zhanga J, Jianbin S, Shijie L (2011) Appl Catal A 397:259
14. Lange JP, Price R, Ayoub PM, Louis J, Petrus L, Clarke L, Gosselink H (2010) Angew Chem Int Ed 49:1
15. Joo F, Beck MT (1975) React Kinet Catal Lett 2:257
16. Lange JP, Petrus L (2007) WO Patent 2007099111
17. Schutte HA, Thomas RW (1930) J Am Chem Soc 52:3010
18. Yan ZP, Lin L, Liu S (2009) Energy Fuels 23:3853
19. Zhao Y, Zhou J, Zhang J, Wang S (2009) Catal Lett 131:597
20. Bond GC, Rajaram R, Burch R (1986) Appl Catal A 27:379
21. Reinikainen M, Niemelä MK, Kakuta N, Suhonen S (1998) Appl Catal A 174:61
22. Guerrero-Ruiz A, Badenes P, RodrõÂguez-Ramos I (1998) Appl Catal A 173:313
23. Zou W, Gonzales RD (1992) J Catal 133:202
24. Lederhos RC, Pablo ACL, Fernando CP, Goli NSF (2006) Catal Lett 110:23
25. Foelske AZ, Barbieri O, Hahn M, Kötz R (2006) Electrochem Solid-State Lett 9:268
26. Pouilloux Y, Autin F, Guimon C, Barrault (1998) J Catal 176:215
27. Arends IWCE, Sheldon RA (2001) Appl Catal A 212:175
28. Sheldon RA, Wallau M, Arends IWCE, Schuchardt U (1998) Acc Chem Res 31:485