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Greener, Recyclable and Reusable $RuCl_3$/PEG-400/H_2O System for the Selective Hydrogenation of Biomass Derived Levulinic acid to γ-valerolactone

Nilesh M. Patil[a] and Bhalchandra M. Bhanage*[a]

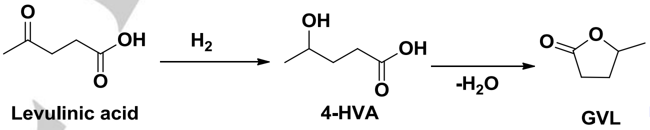
Abstract: This work reports a versatile and an efficient catalyst for the hydrogenation of biomass derived levulinic acid to γ-valerolactone (GVL) using $RuCl_3$/PEG-400/H_2O catalyst system. The developed catalytic system is also found to be active for levulinate ester hydrogenation. The present protocol furnished 99% conversion with 99% selectivity towards γ-valerolactone (GVL) without formation any side products. Remarkably, reaction does not require sensitive phosphine ligands, base and additives or co-catalyst to promote the reaction. This methodology uses environmentally benign poly-(ethylene glycol) (PEG-400) and water as a solvent which is nontoxic, inexpensive, commercially available, nonflammable and easy to handle. $RuCl_3$/PEG-400/H_2O catalyst system could be easily recycle and reused six times with high activity and selectivity.

Introduction

Due to the increasing demand of energy and environmental problem the utilization of biomass into value added chemical or fuel has gained considerable attention.[1-2] Acid hydrolysis of an inexpensive and abundantly available biomass can be converted into carbohydrate such as glucose, fructose, and sucrose. Furthermore acidic dehydration of these carbohydrates gives 5-hydroxymethylfurfural (HMF) and it further converted Levulinic acid (LA) via hydrolysis.[3-4] LA is an important class of compound having a ketone carbonyl group and an acidic carboxyl group and is wildly used for production of fuel additives and also used for synthesis of polymer, resin, organic chemical, flavor substances with numerous applications in many industries. [5]

γ-valerolactone (GVL) is an essential renewable compound as it is useful for the synthesis of various range of biofuels and wide range of fine chemical compounds.[6-7] Since, GVL is highly water soluble, its biodegradation and bioremediation can be easily achieved. GVL is a key intermediate for synthesis of MeTHF, 1,4-pentanediols, alkyl-4-alkoxyvalerates, mixtures of alkanes, butenes, adipic acid 4-hydroxypentane amides via pentenoic acids.[8-12] GVL is not only applicable for chemical industries but also used in petroleum industries. Non toxic GVL has unique physical and chemical properties and also have been found to be present in fruits, thereby making it useful in food industries and pharmacy industries. Nowadays, GVL is extensively used as a fuels additive derived from petroleum industries in comparison with ethanol. Recently, Horvath et al. studied comparison of GVL and ethanol, and results reveals that mixture of 90 vol% gasoline with 10 vol% ethanol or 10 vol% GVL has similar octane number and also observed that the mixture with GVL better the combustion because of its lower vapor pressure. Even though GVL has not been used as a clean fuel, still GVL and ethanol have similar combustion energy (35 MJ L^{-1}) and a higher energy density. Hence, in future GVL can be use as an alternative liquid fuel. [13]

Catalytic hydrogenation of levulinic acid (LA) to form 4-hydroxyvaleric acid (4-HVA) then followed by dehydration of 4-HVA produces γ-valerolactone (GVL) as shown in Scheme 1. To date, numerous heterogeneous and homogenous metal catalytic systems have been developed for hydrogenation of LA to GVL using molecular hydrogen.[14] Among these catalysts, ruthenium catalysts are found to be the best catalyst providing excellent conversion and selectivity towards the GVL.[15] Yan *et al*. studied 5% of Ru/C catalyzed hydrogenation of LA to GVL and this system show that excellent conversion (92%) and selectivity (99%) towards GVL at 130 °C and 1.16 MPa hydrogen pressures.[16] Of note, highly active 1 wt% Ru/TiO_2 catalyst was studied for reduction of LA at 200 °C and 40 bar under neat reaction conditions for 4h.[17] Further, hydrogenation of LA has also been carried out in presence of bimetallic catalysts such as Ru–Sn and Ru–Re/C at high temperatures.[18]



Scheme 1. Hydrogenation of LA into GVL.

In the last decades, homogenous recyclable or biphasic catalytic systems have been of paramount interest to researchers for LA hydrogenation.[19] In this regard, several homogenous methods such as $RuCl_3$ or $Ru(acac)_3$ with phosphine or sulfonated phosphine ligands have been demonstrated for GVL synthesis in excellent yields.[20] The aqueous biphasic Ru/TPPTS system for conversion of LA to GVL has also been explored with 95% yields.[21] Heeres *et al*. showed Ru with modified TPPTS catalyst in CH_2Cl_2/H_2O biphasic system for the hydrogenation of LA.[22] The selective synthesis of GVL, 1,4-pentanol, and 2-methyl-tetrahydrofuran (2-MTHF) have been achieved by hydrogenation of LA using Ru/1,1,1-tris-(diphenylphoshinomethyl)ethane (Ru/TriPhos) as a catalyst as well. [23] The homogeneous system of iridium pincer complex provides good yield of GVL by reduction of LA at 100 °C and 10 MPa of hydrogen pressure in ethanol solvent in presence of base.[24] Recently, Beller and coworkers have shown $RuCl_2(p\text{-cymene})]_2$ with various mono and bidentate-diNHC ligands in dioxane solution for the reduction of LA.[25] Although these catalytic systems provide high yield of GVL, the use of phosphine or nitrogen containing ligands, flammable organic solvents, non-recyclable catalytic system and harsh reaction conditions limits its applicability. Therefore, the exploration of greener and recyclable catalytic system for reduction of LA is highly desirable.

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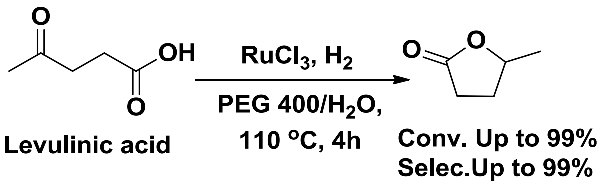
Nowadays, the use of poly(ethylene glycols) (PEGs), as a solvent has captured considerable attention due to its non toxicity, negligible vapor pressure, commercially available, inexpensive, recoverable and thermally stable. Recently, eco-friendly PEGs have been used in many organic transformations.[26] In continuation of our ongoing research toward the development of environmentally benign, greener, recyclable catalyzed hydrogenation, [27] herein, we showed $RuCl_3$/PEG-400/H_2O as a versatile catalytic system for hydrogenation of LA to GVL using molecular hydrogen without using any additives (Scheme 2).



Scheme 2. $RuCl_3$/PEG-400/H_2O catalyzed hydrogenation of LA into GVL.

Experimental Section

Materials

Levulinic acid (LA, 98%) and ethyl levulinate (EL, 98%) were purchased from Alfa Aesar. Ruthenium chloride and methyl levulinate (EL, 98%) were obtained from Aldrich. PEG 400 was procured from Spectrochem (India). All the chemicals and solvents were purchased from reputed firm and used without further purification. The products are well-known in the literature and were confirmed by GCMS (Shimadzu GC-MS QP 2010).

Results and Discussion

Optimization study for selective hydrogenation of LA to GVL.

The reaction conditions (i.e. solvent, pressure, temperature and time) were optimized and for which preliminary studies were conducted using levulinic acid (5 mmol), solvent (10 ml) and $RuCl_3$ as a catalyst without using any additives, base and ligand (Table 1). At first, we employed non polar solvents such as toluene and dioxane and both solvents gave low conversion of LA (Table 1, entries 1,2). In polar solvent like ethanol, conversion (96%) was good but it gave poor selectivity (42%) due to the formation of ethyl levulinate (Table 1, entry 3). The transesterification of LA acid with ethanol forms ethyl levulinate as a by-product. Generally, water favors the LA hydrogenation, hence, we employed water as a solvent and it was noticed that water furnished highest conversion (99%) with 99% selectivity towards desired product (Table 1, entry 4). When only PEG-400 was employed as a solvent 69% conversion was obtained. (Table 1, entry 5). The use of PEG-400 and water mixture in the ratio of 7:3 was found to be very effective for LA hydrogenation as this system gave 99% conversion and excellent selectivity of 99% for GVL. No formation any side products were noted (Table 1, entry 6). The use of PEG 400/H_2O solvent system makes this protocol greener, recyclable and reused of precious metal. Hence, this PEG 400/H_2O solvent system was chosen for further investigations. Low conversion of LA was noted when the reaction was carried out under neat condition (Table 1, entry 7). Increasing the temperature up to 130 °C led to the full conversion of LA within 1 h (Table 1, entry 8). There was no formation of any side product when reaction was performed at high pressure (up to 40 bar) at 130 °C for 12 h (Table 1, entry 9). At room temperature, conversion was also very low (Table 1, entry 10).

Table 1. Hydrogenation of LA to GVL in different solvents at different tempe and pressures.[a]

Entry	Solvent	H_2 (bar)	Temp (°C)	Time (h)	Conv./ (%
1	Toluene	20	110	4	52/
2	Dioxane	20	110	4	10/
3	Ethanol	20	110	4	99/
4	Water	20	110	4	99/
5	PEG 400	20	110	4	64/
6	PEG 400/H_2O (7:3)	20	110	4	99/
7	Neat	20	110	4	51/
8	PEG 400/H_2O (7:3)	20	130	1	99/
9	PEG 400/H_2O (7:3)	40	130	12	99/
10	PEG 400/H_2O (7:3)	20	RT	12	15/

[a] Reaction conditions: LA (5 mmol), $RuCl_3$ (2.5 mol%), solvent (10 mL), mo hydrogen, temperature and time.

[b] Conversion and selectivity based on GC-MS analysis.

In the beginning, the reaction was carried out in the absence of transition metal catalyst, but the reaction did not proceed which indicated the necessity of catalyst (Table 2, entry 1). The activity of $RuCl_3$ catalysed hydrogenation of LA in PEG400/H_2O was compared with other transition metal catalysts such as $PdCl_2$, $CoCl_2$•$6H_2O$ and $NiCl_2$•6H2O (Table 2, entries 2-4). Among them $RuCl_3$ catalyst was found to be the best catalyst

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furnishing highest 99% conversion and excellent selectivity toward the desired product (Table 2, entry 5).

Table 2. Hydrogenation of LA to GVL with different catalyst.[a]

Entry	Catalyst	Catalyst loading (mol %)	Conversion (%)[b]	Selectivity (%)[b]
1	No catalyst	-	00	00
2	$PdCl_2$	2.5	00	00
3	$CoCl_2{\cdot}6H_2O$	2.5	00	00
4	$NiCl_2{\cdot}6H_2O$	2.5	00	00
5	$RuCl_3$	2.5	99	99

[a] Reaction conditions: LA (5 mmol), 10 mL of $PEG400/H_2O$ (v/v=7/3) (10 mL), H_2 (20 bar), temperature (110 °C) and time (4h).

[b] Conversion and selectivity based on GC-MS analysis.

Effect of temperature and hydrogen pressure on LA hydrogenation.

To investigate the effects of the reaction temperature and hydrogen pressure a series of hydrogenation experiments were conducted over $RuCl_3$ as the catalyst in $PEG400/H_2O$ system and the results are shown in Figure 1. The increase in temperature from 50 to 110 °C led to the significant increase in the conversion along with maximum 99% selectivity for this reaction (Figure 1a). A rapid decrease in the conversion of LA was found when pressure decrease from 20 to 5 bar. No effect on selectivity was noted when hydrogen pressure was decreased (Figure 1b). These results clearly indicate that the hydrogenation reaction is very sensitive to the temperature and pressure.

Effect of time and catalyst loading on LA hydrogenation

Next, the effect of reaction duration on conversion was explored and it was found that the conversion of LA increases during the course of reaction from 1 to 4h. Thus, minimum 4h duration is needed to complete the conversion (Figure 2a.) In transition metal-catalyzed LA hydrogenation reactions, the use of minimum amount of expensive and precious transition metal catalyst is an important aspect. Considering this aspect in mind, we determined the optimum concentration of the catalyst by varying the catalyst loading ranging from 1 to 2.5 mol%. It was observed that 2.5 mol% catalysts required to complete conversion of LA to GVL (Figure 2b).

Hydrogenation of biomass derived levulinate ester to GVL.

Encouraged by these results, the reduction of Levulinate Ester into GVL was investigated under the same optimized reaction conditions. At first, we check our present catalyst system for

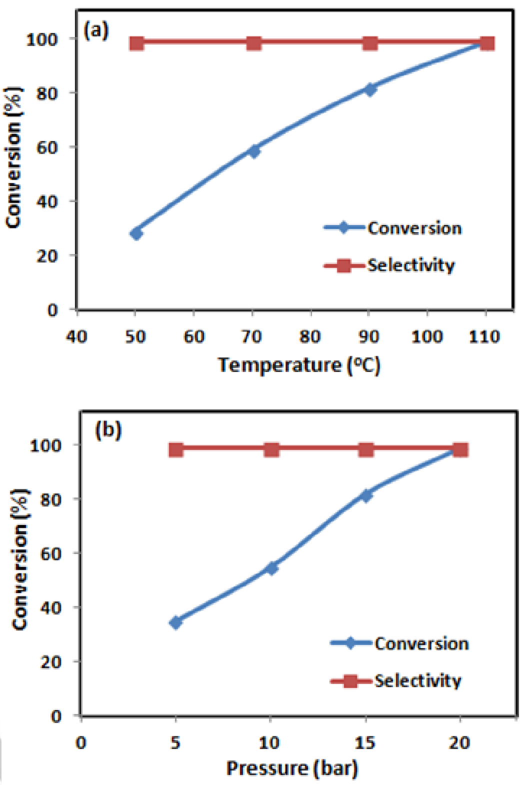

Figure 1. a) effect of temperature b) effect of pressure

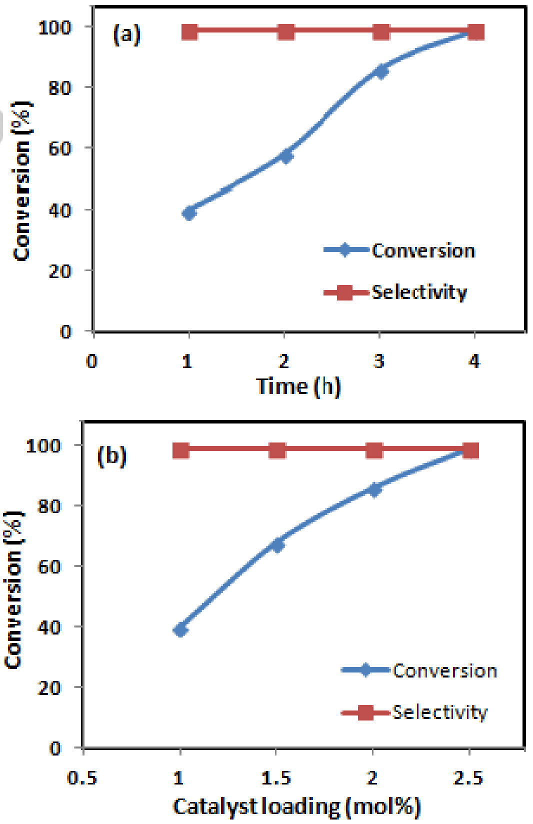

Figure 2. a) effect of time b) effect of catalyst loading.

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hydrogenation of methyl levulinate (ML) and 99% conversion of ML was observed with excellent 99 % selectivity of GVL (Table 3, entry 1).Next, we employed EL hydrogenation under optimized condition but only 48% conversion was obtained (Table 3, entry 2). In both the cases, no formation of any side products was observed during the course of reaction.

Firstly, Fu and co-workers used homogenous iron complex with phosphine ligands for ethyl levulinate hydrogenation.[28] Thereafter, various groups attempted for the reduction of ethyl levulinate (EL) to GVL. Rinaldi and co-workers studied Raney nickel catalyst for reduction of alkyl levulinates using 2-propanol as hydrogen source.[29] Nadgeri *et al*. reported liquid-phase hydrogenation of methyl levulinate [ML] using ruthenium support on graphite- and zeolite in water.[30] Guan and co-workers reported ethyl levulinate hydrogenation using Pd–AC doped with Nb_2O_5 as a catalyst.[31] Although, these reports are highly efficient but there was a need to develop a simple environment friendly protocol for the reduction of levulinate esters to GVL under mild reaction conditions.

Table 3. Hydrogenation of biomass derived levulinate ester to GVL.[a]

Entry	Substrate	Catalyst loading (mol %)	Conversion (%)^b	Selectivity (%)^b
1	Methyl levulinate	2.5	99	99
2	Ethyl levulinate	2.5	48	99

[a] Reaction conditions: levulinate ester (3 mmol), $RuCl_3$ (2.5 mol%), 10 mL of PEG400/H_2O (v/v=7/3), H_2 (20 bar) temperature (110 °C) and time (4h).

[b] Conversion and selectivity based on GC-MS analysis.

Recycle study

In an effort to make the present catalytic system more economically and ecofriendly, the recycling of precious metal is definitely important tasks in the catalytic reactions. Hence, we tested the recyclability and the stability of $RuCl_3$/PEG-400/H_2O for LA hydrogenation under identical conditions as shown in figure 3. After the completion of reaction, GVL was extracted using diethyl ether from $RuCl_3$/PEG-400/H_2O system before it was subjected to the next run. The current catalytic system could be reused effectively for six successive recycles without loss in its activity and selectively (Figure 4).

In situ nano particles formations

Literature study reveals that several methods have been explored for the synthesis of metal nanoparticles from the corresponding metal salts in polyethylene glycol.[32] Recently, Tay *et al*. report reduction of LA to GVL in presence of Ru-NPs which is *in situ* generated from homogenous Ru-NHC complexes.

We observed that in situ formation of ruthenium nanoparticles (Ru-NPs) during the reaction. The nanoparticles were isolated by centrifugation at 8000 rpm for 20 min from the reaction mixture. The collected Ru-NPs were confirmed using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. The TEM image shows the generation of spherical Ru-NPs having size range 100 nm to 200 nm (Figure 5). The XPS spectrum (Figure 6) of Ru-NPs showed the peaks at 284.84 eV correspond to Ru $3d_{3/2}$ and 280.34 eV correspond to Ru $3d_{5/2}$ respectively which similar to the literature.[33] The XPS spectrum confirms that the Ru is in zero state.

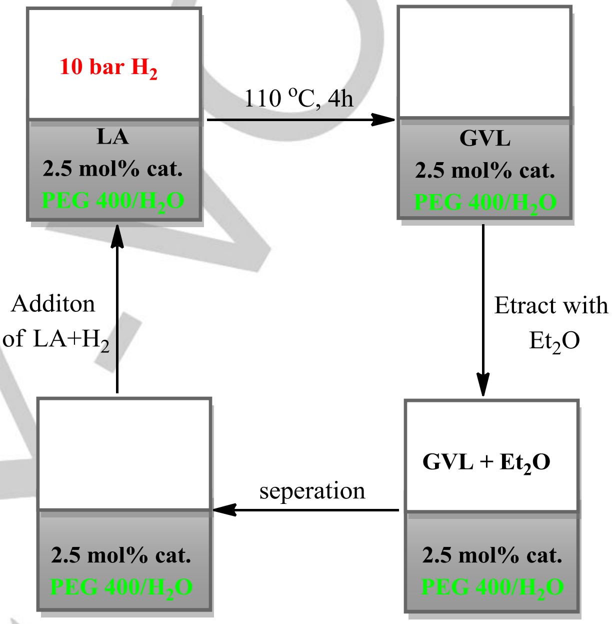

Figure 3. Diagrammatic representation for catalyst and product separation and recycle study.

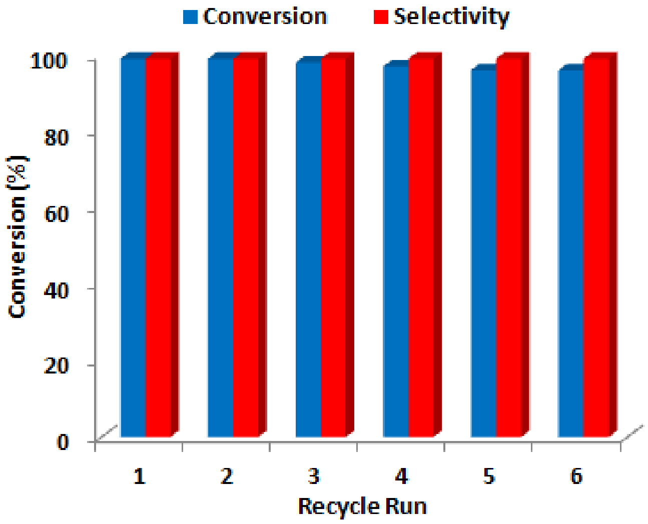

Figure 4. Recycle study.

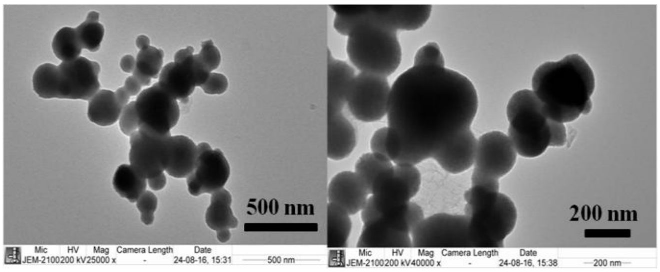

Figure 5. TEM images of Ru-NPs.

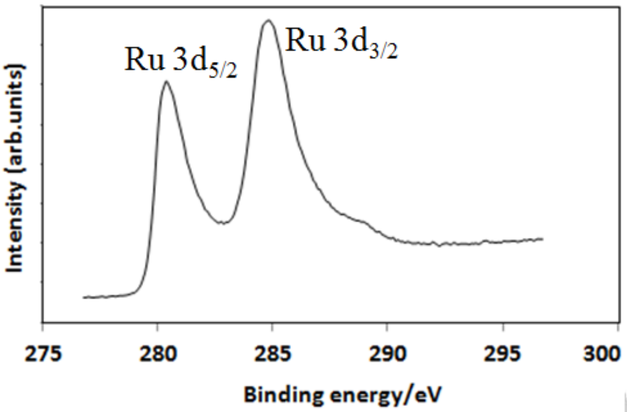

Figure 6. XPS specra of Ru-NPs.

Typical procedure for LA hydrogenation

To a 100 mL stainless steel high pressure reactor (autoclave), levulinic acid (5 mmol) and 10 mL of PEG400/H_2O (v/v=7/3) were added with $RuCl_3$ (2.5 mol%).The reaction mixture was then pressurized to 20 bar of hydrogen pressure at room temperature. Then the reactor was heated to 110 ^oC and stirred for 4 h. After completion of reaction, the reactor (autoclave) was cooled to room temperature and the remaining hydrogen gas was carefully vented and then the reactor was opened. The product (GVL) was extracted in diethylether and then reaction mixture was analyzed by GCMS (Shimadzu GC-MS QP 2010).

Experimental procedure for recycling of the $RuCl_3$/PEG-400/H_2O for LA hydrogenation.

For recycle study, the reaction was carried out as mentioned above in a typical experimental procedure. After completion of reaction, the reactor (autoclave) was cooled to room temperature and the remaining hydrogen gas was carefully vented and then the reactor was opened. The product (GVL) was extracted in diethylether, and the $RuCl_3$/PEG-400/H_2O system was then subjected to a next run with the same substrates (LA) without addition of $RuCl_3$.

Conclusions

In summary, a highly efficient and reusable $RuCl_3$/PEG-400/H_2O catalyst system for selective hydrogenation of biomass derived levulinic acid and levulinate ester has been demonstrated. Notably, the reaction works smoothly under base free, ligand free and additives free conditions in 99% conversion with excellent 99% selectivity towards γ-valerolactone (GVL) without formation of any side products. The present protocol uses a stable homogenous recyclable catalyst, easily available molecular hydrogen and eco-friendly PEG 400/water as a solvent, thus contribute towards development of greener methodologies in hydrogenation reaction.

Acknowledgements

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Keywords: biomass • levulinic acid • hydrogenation • greener • reusable.

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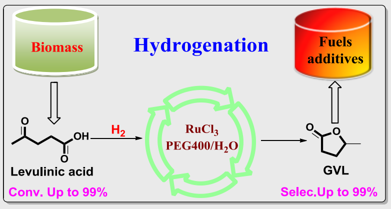
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Highly efficient and reusable $RuCl_3$/PEG-400/H_2O catalyst system for selective hydrogenation of biomass derived levulinic acid and levulinate ester has been developed. The reaction works smoothly under base free, ligand free and additives free conditions in 99% conversion with excellent 99% selectivity towards γ-valerolactone (GVL) without formation of any side products. The present protocol reused the catalyst as well as solvent system.



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Greener, Recyclable and Reusabl RuCl3/PEG-400/H2O System for th Selective Hydrogenation of Biomas Derived Levulinic acid to γ-valerolactone