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Selective hydrogenation of levulinic acid to γ-valerolactone over a Ru/Mg–LaO catalyst†

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Ruthenium supported on magnesium–lanthanum mixed oxide (Ru/Mg–LaO) obtained from Mg–La hydrotalcite (a base support) catalyzes the hydrogenation of biomass derived levulinic acid (LA) to γ-valerolactone (GVL). The conversion of LA to GVL in toluene was found to be 92% with the selectivity >99% at 80 °C and 0.5 MPa hydrogen pressure in 4 h. It is the first example on the basic support under mild reaction conditions. The Ru nanoparticles on the Mg–LaO support exhibited excellent GVL yields for 5 cycles, making it a sustainable process.

Fossil fuel is a main source for the production of energy and carbon based chemical products. A rapid depletion of fossil fuel resources has driven researchers to develop sustainable alternatives to renewable resources.[1,2] Of the many, natural resources for energy production, biomass is the only renewable resource which could produce carbon based intermediates or building blocks of valuable chemicals and synthetic fuels.[3] Levulinic acid (LA) a keto-carboxylic acid, is one of the biomass-derived platform chemical that is obtained by acid hydrolysis of carbohydrates. The active functional groups of LA (keto and carboxylic acid) help in producing several derivatives which can be used in the synthesis of materials that are bio-degradable with good strength, and can be solvents and fuel additives.[4] Some of the important chemicals such as lactones can be synthesized by hydrogenation of LA. GVL is a water soluble, saturated lactone which is used as food and fuel additives,[5] as a solvent,[6] plastics[7] and fine chemicals.[8] Therefore, synthesis of GVL has received more attention in recent times. Several homogeneous systems such as complexes of $RuCl_3$ or $Ru(acac)_3$ with BINAP, PPh_3, sulfonated phosphine ligands or combination of PPh_3 and TPPTs were explored in the synthesis of GVL in excellent yields (>99%).[9] The homogeneous iridium pincer complex afforded high yields of GVL by hydrogenation of LA at 100 °C and 10 MPa of hydrogen pressure in ethanol, but external bases were used.[10]

However, it should be noted that the use of heterogeneous catalysts is much more desirable than those of using complexes under homogeneous conditions; they offer easy separation and multiple reaction cycles without significant drop in both yield and catalytic activity of the reaction. Many heterogeneous catalysts were applied for this hydrogenation reaction in batch reactor, vapor phase and in supercritical conditions. Christian *et al.* reported 94% of GVL from LA at 220 °C and 4.82 MPa H_2 using RANEY®Ni as catalyst. They also examined the copper–chromium oxide as a catalyst and obtained 11% of GVL at 245 °C and 20 MPa.[11] Fu and co-workers used RANEY®Ni in the catalytic transfer hydrogenation of ethyl levulinate to yield 99% GVL, where isopropanol is used as hydrogen source at room temperature in Ar atmosphere for 9 h.[12] Broadbent *et al.* showed 71% of GVL yield on rhenium heptoxide at 100 °C and 15 MPa pressure.[13] Cao and his group developed gold supported on zirconia catalyst for the hydrogenation of LA using formic acid as the hydrogen source and achieved 99% of GVL at 150 °C in nitrogen atmosphere.[14] Z.-P. Yan *et al.* evaluated 5% of Ru/C catalyst that gave 99% selectivity for GVL with 92% conversion of LA at 130 °C and 1.16 MPa hydrogen pressure.[15] It is noteworthy to report 1 wt% Ru/TiO_2 as highly active catalyst for hydrogenation of LA under neat reaction conditions at 40 bar (4 MPa) hydrogen pressure and 200 °C in 4 h.[16] Many Ru based catalysts were reported in the presence of water soluble phosphine ligands,[17] co-catalysts[18] and ionic liquid.[19] Using Pd nanoparticles on γ-Al_2O_3, Yan and his group reported 63% conversion of LA with 96% selectivity towards GVL in water at 160 °C, 4.5 MPa hydrogen pressure in 6 h.[20] Recently, Rode and Hengne reported Cu/ZrO_2 for the conversion of LA to GVL in methanol at 200 °C and 3.4 MPa of hydrogen pressure with 90% GVL selectivity.[21] Bimetallic catalysts such as Ru–Re/C, Ru–Sn, Cu–Cr were tested for the hydrogenation of LA at high temperatures. However, development of catalyst system

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which is lucrative under mild conditions is still a challenge as most of these reports adopted severe and harsh experimental conditions in order to obtain higher GVL yields. In recent years, Mg–La mixed oxide derived from hydrotalcite has received much attention as support and base catalyst in many organic transformations.[22,23]

In the present study, we report an efficient Ru(0) nanoparticles supported on Mg–LaO mixed oxide as a recyclable heterogeneous catalyst for the hydrogenation of LA under mild experimental conditions (80 °C and 0.5 MPa H_2) with consistent activity and selectivity towards the desired product. In addition, the method is base, additive or phosphine free.

The powder XRD patterns of Mg–La catalysts were depicted in Fig. 1. As prepared (oven dried) Mg–La-HT (Fig. 1a) shows well resolved XRD reflections due to lanthanum carbonate hydroxide hydrate (JCPDS-46-0368, $2\theta = 30.19$, 24.18, 20.65, 38.30, 16.02, 33.82) and magnesium hydroxide (JCPDS-75-0447) phases, indicating a biphasic system as reported in the literature.[22] Upon calcination at 650 °C, the HT is transformed to form mixed oxides along with lanthanum hydroxide is presented in Fig. 1b, and the reflections are related to lanthanum oxide (JCPDS-74-1144, hexagonal symmetry),[24] lanthanum hydroxide (JCPDS-36-1481, hexagonal)[24] and magnesium oxide (JCPDS-75-0447, cubic with face-centered)[25] phases. Fig. 1c depicts the XRD pattern of the reduced Ru/Mg–LaO sample. The pattern shows the presence of Ru(0) in two phases, the peaks that are indexed as (101), (100) and (102) planes (marked red) corresponds to hexagonal (JCPDS-06-0663)[26] and the diffraction lines that are indexed as (111) and (200) to face centered cubic (FCC) phase (JCPDS-88-2333).[26] The other peaks represent the metal phases as in Fig. 1b and lanthanum oxide carbonate. The TEM image of reduced Ru/Mg–LaO (Fig. 2a and b) displays the Ru nanoparticles an average size of <10 nm is dispersed on the support. The SEM-EDX studies of reduced (Ru/Mg–LaO) catalyst revealed the presence of Ru, Mg, La, Cl and O and are found to be 23.53% atomic oxygen, 4.92% atomic ruthenium, 12.82% atomic magnesium, 57.45% of atomic lanthanum and 1.27% atomic chlorine.

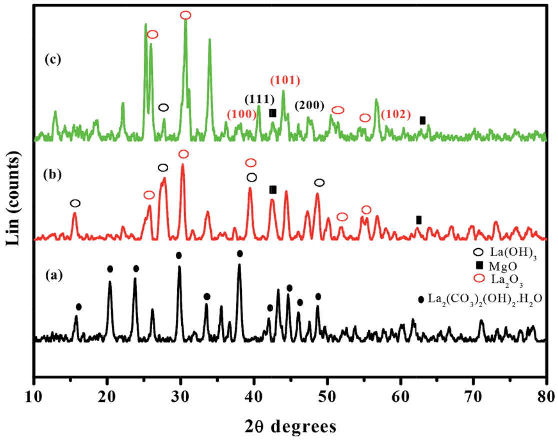


Fig. 1 XRD pattern of (a) Mg–La-HT, (b) Mg–LaO (calcined at 650 °C) and (c) Ru/Mg–LaO (reduced at 450 °C).

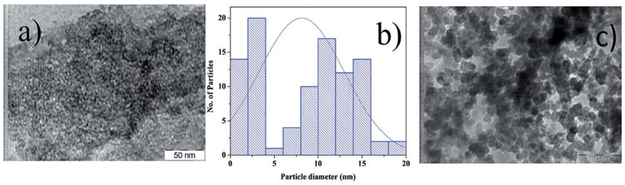


Fig. 2 TEM images of (a) reduced Ru/Mg–LaO (50 nm), (b) particle size analysis and (c) used Ru/Mg–LaO (200 nm).

The TPR profile of the calcined Ru impregnated Mg–LaO catalyst (Fig. 3) shows two reduction peaks at about 224 °C and 376 °C. The low temperature peak is related to Ru cations that are well dispersed on the surface; the peak at about 376 °C is assigned to the reduction of RuO_2 and Ru-oxychloride.[27] The XPS analysis of reduced catalyst shows (Fig. 4a) the characteristic binding energy (BE) for Ru $3d_{5/2}$ at 280.2 eV, which is in the overlapped portion with the C 1s (carbon) 285 eV. The Ru $3p_{3/2}$ signal at 464.15 eV and Ru $3p_{1/2}$ signal at 485.61 eV clearly indicate the presence of surface Ru(0) phase (Fig. 4b).[28–30]

The Ru/MgLaO allowed the hydrogenation of LA in a batch reactor (Scheme 1), the hydrogen pressure was maintained manually. The samples were collected periodically and analysed by GC and the product components were identified by GC-MS-QP-5050 (M/s. Shimadzu Instruments, Japan).

From the activity data (Table 1) it is understood that support seems to play an important role in the hydrogenation of LA to GVL. All the catalysts were prepared by a similar procedure as is adopted for Ru/Mg–LaO. The catalysts Ru/MgO and Ru/Mg–AlO (Table 1, entries 3 & 4) show low LA conversions than Ru/Mg–LaO although with similar ruthenium content, metal dispersion, metal surface area (obtained from CO chemisorption) and particle size (see ESI†) is being used. Interestingly, when Mg–LaO (Table 1, entry 2) support alone was used, about 4% LA conversion with 99% selectivity for GVL is obtained. In controlled experiment (Table 1, entry 1) the conversion was found to be 3% in 16 h but the selectivity for GVL remained >99%.

In order to optimize the reaction conditions (*i.e.* solvent, pressure, temperature and weight of the catalyst), a series of experiments were carried out using levulinic acid (2.0 g, 17.24 mmol), solvent (18.0 ml) and Ru/Mg–LaO catalyst. Initially, catalytic runs were conducted at 130 °C and 1.2 MPa of

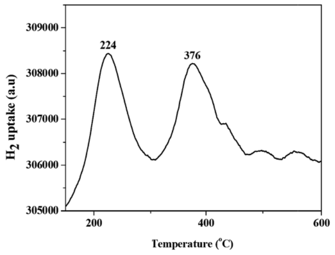


Fig. 3 TPR profile of Ru(II)/Mg–LaO calcined.

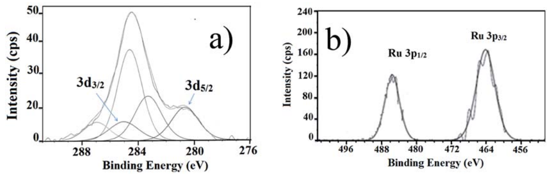
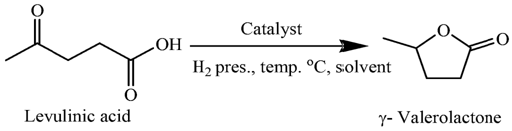


Fig. 4 XPS spectra of Ru/Mg–LaO (a) Ru 5d and (b) Ru 3p.



Scheme 1 Hydrogenation of levulinic acid.

hydrogen pressure in different solvents (Table 2). Using polar solvents such as methanol and ethanol, good conversions were obtained but the selectivity towards the GVL is decreased due to the formation of LA-esters (Table 2, entries 1, 5 & 6). The formation of levulinate esters by transesterification as byproducts ruled out reforming of ethanol. In case of water (Table 2, entry 2) the conversion (99%) and selectivity (>99%) towards desired product was excellent but the catalyst could not be recovered due to lower pH. When dioxane (a polar aprotic solvent) was used, the reaction was very sluggish; with 50% conversion and 45% GVL selectivity even after prolonged reaction times (overnight) (Table 2, entry 3). Interestingly, toluene (a non-polar aromatic solvent) was proved to be the most promising one that displayed excellent selectivity for GVL (>99%) (Table 2, entry 4). However at this temperature catalyst recovery became difficult due to formation of insoluble organic matter called humins on the surface of the catalyst. In order to prevent formation of humins Dumesic *et al.*[31] used biphasic system with GVL as one of the solvent. In our case for the complete recovery of the catalyst and for the prevention of formation of humins, we have tried to decrease the reaction temperature, pressures and by neutralization of the reaction medium with bases such as KOH and NEt_3.

On the contrary at 80 °C good conversion with excellent selectivity was obtained in different solvents (Table 2, entries 6–10). The reaction in water (Table 2, entry 7) gave good results hence; we tried to neutralize the water medium using bases, in order to recover the catalyst. When NEt_3 (2 mmol) (Table 2, entry 9) was used as base, the LA conversion was found to be moderate (68%) but the selectivity for GVL was 99%, and with KOH (2 mmol) (Table 2, entry 8) the conversion was 93% and GVL selectivity was 99%. But the solid catalyst could not be recovered quantitatively (20 mg). For the complete recovery of the catalyst, stoichiometric amount of KOH was used it shows a decrease in selectivity towards GVL, indicating that formed product is reacting with KOH.[5,32]

The results on solvent screening have shown toluene to be the best solvent, this could be due to its non-polar nature, it will be unable to solvate the reaction intermediates, rather the intermediates are stabilized by the surface of the catalyst and enables them to come in close proximity to each other and facilitates reaction of the unsolvated species.[33] Further screening at different temperatures, pressures and catalyst weight were performed in toluene solvent. It seems temperature has sturdy affect on the reaction, by reducing the temperature from 80 to 50 °C, there is a decrease in the conversion of LA from 92 to 48% (Table 2, entries 10–13). Similarly, when the reaction was conducted at different pressures *i.e.* 0.5, 0.3 and 0.1 MPa at 80 °C, the conversion of LA is lowered from 92, 65 to 21% respectively (Table 2, entries 10, 14 and 15). Upon decreasing the catalyst loading from 5 to 3.65 wt%, the conversion of LA is dramatically fallen to 35% (Table 2, entry 10e) which is in consistent with literature.[15] From the above results, the derived optimum parameters for 5% Ru/Mg–LaO are 80 °C, 0.5 MPa of H_2 pressure, 5 wt% of 5 wt% Ru/Mg–LaO catalyst (with respect to LA) in toluene. At these conditions the maximum normalized reaction rate achieved for the Ru/MgLaO was 13.345 mol h^{-1} $(mol_{Ru})^{-1}$ (see ESI†).

The recyclability results on Ru/Mg–LaO are reported in Fig. 5. For the reusability studies, after completion of reaction the mixture was centrifuged, the solid was washed with ethyl acetate to remove organic substances from the surface, later oven dried. To this recovered catalyst, fresh aliquots of reactants were added and reused for 4 cycles with consistent activity and selectivity. A small decrease in activity was observed in 5th cycle. The TEM image (Fig. 2c) of used catalyst shows some carbon deposition. The XPS of the used catalyst shows two broad peaks at 465.23 eV and 485.64 eV, which are characteristic of Ru 3p (Fig. 6).[28–30] The CHNS elemental analysis of used catalyst shows the presence of 1.15% carbon on the catalyst and it could be one of the reasons for lower activity.

Table 1 Hydrogenation of levulinic acid catalyzed by different catalysts[a]

Entry	Catalyst	Temp. (°C)	Time (h)	Conv.[b] (%)	Selec.[b] (%)	Rate[c] mol h^{-1} $(mol_{Ru})^{-1}$
1	—	80	16	3	>99	—
2	MgLaO	80	4	4	>99	—
3	Ru(0)/MgO	80	4	62	>99	9.00
4	Ru(0)/MgAlO	80	4	68	>99	9.86
5	Ru(0)/MgLaO	80	4	92	>99	13.345

[a] Reaction conditions: levulinic acid 2.0 g (17.24 mmol), 5% of 5 wt% catalyst (0.100 g), toluene + levulinic acid (20.0 ml), hydrogen pressure 0.5 MPa H_2. [b] The conversion and selectivity were determined by GC. [c] Rate is calculated as per normalized rate equation (see ESI section).

Table 2 Hydrogenation of levulinic acid catalyzed by Ru/Mg–LaO in different solvents at different temperatures and pressures[a]

					Selec.[b] (%)		
Entry	Solvent	Temp. (°C)	Pres. (MPa)	Conv.[b] (%)	GVL	LA ester	Others AL
1	Methanol	130	1.2	92	72	28	
2	H_2O	130	1.2	99	>99		
3	Dioxane[c]	130	1.2	50	45		55
4	Toluene	130	1.2	98	>99		
5	EtOH	130	0.5	84	76	24	
6	EtOH + H_2O (1 : 1)	80	0.5	92	86	14	
7	H_2O	80	0.5	92	>99		
8	KOH + water	80	0.5	93	98		
9	Et_3N + water	80	0.5	68	99		
10	Toluene	80	0.5	92, 90[d], 35[e]	>99, 98, >99		
11	Toluene	70	0.5	90	99		
12	Toluene	60	0.5	81	99		
13	Toluene	50	0.5	48	99		
14	Toluene	80	0.3	65	>99		
15	Toluene	80	0.1	21	>99		

[a] Reaction conditions: levulinic acid 2.0 g (17.24 mmol), 5% of 5 wt% Ru/Mg–LaO (0.100 g), solvent + levulinic acid 20.0 ml, time 4 h. [b] The conversion and selectivity were determined by GC. [c] Overnight (16 h). [d] 5th cycle. [e] 3.65% of catalyst.

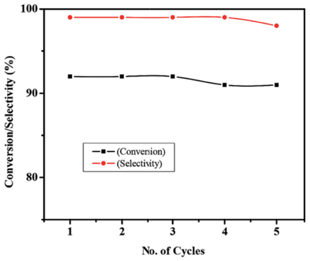


Fig. 5 Recyclability studies on Ru/Mg–LaO for hydrogenation of LA at 80 °C, 0.5 MPa H_2 pressure.

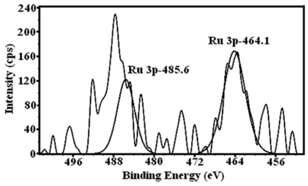


Fig. 6 XPS spectra of Ru $3p_{3/2}$ of used Ru/Mg–LaO.

Experimental section

Materials & methods

Levulinic acid (LA, 98%), γ-valerolactone (GVL, 98%), ruthenium trichloride anhydride were purchased from Aldrich. Lanthanum nitrate hexahydrate, aluminum nitrate nonahydrate, magnesium nitrate hexahydrate, sodium hydroxide, sodium carbonate, magnesium oxide and solvents were purchased from SD Fine chemicals Ltd., India. All of them were used without any further purification. The powder X-ray powder diffraction data were collected on a Siemens/(D5000) diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) with a scan speed of $2\theta = 0.045/0.5$ s in the range of 2–80°. TEM was performed on a TECNAI 12 FEI TEM instrument. The samples were suspended in ethanol, treated with ultrasound, and was applied to a carbon carrier foil (LaB_6, KO-AP3, $D = 50$ μm, single tilt holder). XPS measurements were conducted with Kratos XPS Axis 165 spectrometer, equipped with a hemispherical energy analyzer. The non-monochromatized Mg Kα X-ray source ($h\nu = 1253.6$ eV) was operated at 5 kV and 15 mA, with pass energy of 80 eV and a step of 0.1 eV. The samples were degassed for several hours in the XPS chamber to minimize air contamination to sample surface. In order to overcome the charging problem, charge neutralizer of 2 eV was applied and the binding energy of C 1s core level (BE = 284.6 eV) of adventitious hydrocarbon is taken as standard. The TPR profile was recorded on Micromeritics (Auto Chem 2910) using 0.05 g of catalyst sample. In a typical method the catalyst was loaded in an isothermal zone of a quartz reactor (i.d = 6 mm, length = 300 mm) heated by an electric furnace at a rate of 10 °C min^{-1} to 573 °C min^{-1} in flowing helium gas at a rate of 30 ml min^{-1}, which facilitates desorption of the physically adsorbed water. After degassing, the sample was cooled to room temperature and the helium gas was switched to 36 ml min^{-1} reducing gas of 5% H_2 in argon and the temperature was increased to 725 °C at a ramping rate of 10 °C min^{-1}. Hydrogen consumption is measured by analyzing effluent gas by means of thermal conductivity detector. The consumption of hydrogen was calibrated measuring the TPR of Ag_2O (20 mg), with the same protocol. GC analysis was done by GC-2010, gas chromatograph Shimadzu, with ZB5 capillary column, internal diameter 0.53 mm, film thickness 1.50 μm, length 30 m, initial temperature 80 °C (hold 10 min), ramp 7 °C min^{-1} – 279 °C (hold 7 min), injection temperature 250 °C and detector temperature 280 °C (FID). CO chemisorption measurements were carried out on AutoChem 2910 (Micromeritics, USA) instrument. Prior to adsorption measurements, *ca.* 100 mg of the sample was reduced in a flow of hydrogen (50 ml min^{-1}) at 250 °C for 3 h and flushed out subsequently in a pure helium gas flow for an hour at 250 °C. The sample was subsequently cooled to ambient temperature in the same He stream. CO uptake was determined by injecting pulses of 9.96% CO balanced helium from a calibrated on-line sampling valve into the helium stream passing over the reduced samples at 250 °C. Ruthenium surface area, percentage dispersion and Ru average particle size were calculated assuming the stoichiometric factor (CO/Ru) as 1. Adsorption was deemed to be complete after three successive runs showed similar peak areas.

Catalyst preparation

The magnesium–lanthanum mixed oxide was prepared by the co-precipitation method as described in the earlier literature.[22,23] The calcined sample of Mg–La-HT (Mg–LaO mixed oxide) (1.9 g) was stirred with $RuCl_3$ (0.205 g, 9.9 mmol) in 75 ml of freshly prepared deionized water at RT for 24 h under nitrogen atmosphere. The catalyst was filtered, washed with deionized water, acetone and dried overnight at 110 °C in an oven. The catalyst was reduced by loading in an isothermal zone of the reactor and was degassed at a ramping rate of 10 °C min^{-1} to 300 °C in nitrogen flow of 30 ml min^{-1}, which facilitates desorption of physically adsorbed water. After degassing, the sample was cooled to room temperature and the nitrogen gas was replaced by 5% H_2/Ar at a flow rate of 30 ml min^{-1} and the temperature is increased to 800 °C with a ramping rate of 10 °C min^{-1} (Ru/Mg–LaO). The SEM EDX analysis of Ru was found to be 4.92%. For comparison, Mg–AlO catalyst supported Ru was prepared by co-precipitation and followed by impregnation. The Ru/MgO catalyst was synthesized by impregnation method.

Hydrogenation of LA

Hydrogenation of levulinic acid was carried out in a 100 ml mechanically stirred Parr autoclave equipped with a PID controller 4848. In a typical experiment about 2.0 g (17.3 mmol) of LA and 18.0 g of solvent were added to 0.10 g of 5 wt% Ru/Mg–LaO and stirred at 1000 rpm by applying 80 °C and 0.5 MPa H_2 pressure. The products were periodically analyzed during the course of the reaction by using gas chromatography (GC) equipped with ZB5 capillary column and flame ionization detector (FID) and GC-MS.

Conclusions

In conclusion, Ru-heterogenized on Mg–LaO, a hydrotalcite derivative has been synthesized, characterized by an array of sophisticated analytical techniques. The catalytic activity has been tested for the hydrogenation of LA to GVL. It is demonstrated that Ru/Mg–LaO performs efficiently as a recyclable heterogeneous catalyst in toluene under mild reaction conditions. The key findings are that it does not require any external bases, ligands, additives or co-catalyst to promote the reaction. Further studies on the reaction mechanism are ongoing.

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