

Supporting information

for

Influence of Support for Ru and Water Role on Product Selectivity in the Vapor-Phase Hydrogenation of Levulinic Acid to γ -Valerolactone: Investigation by Probe-Adsorbed Fourier Transform Infrared Spectroscopy

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2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. Sigma-Aldrich A. R. grade (99.9%) chemicals such as $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ were used. Additional chemicals, purchased from Sigma-Aldrich, that were used as received were as follows: Activated Carbon (BET-surface area (S_{BET}) = $344.2 \text{ m}^2 \text{ g}^{-1}$), levulinic acid (LA; 98%), γ -valerolactone (GVL; 99%), α -angelica lactone (AL; 98%), acetone, methanol (>99%), formic acid (98%), anisole (99.7%) and pyridine (99.8%) were used as received. The $\gamma\text{-Al}_2\text{O}_3$ (Harshaw Al-3945; S_{BET} = $209.7 \text{ m}^2 \text{ g}^{-1}$), MgO (Sud. Chemie. Pvt. Ltd.; S_{BET} = $87.9 \text{ m}^2 \text{ g}^{-1}$) obtained were used as supports. A double distilled H_2O was used for the preparation of catalysts and also for the dilution of substrates.

2.2. Catalyst Preparation. The Ru supported on carbon, Al_2O_3 and MgO catalysts are prepared by incipient wetness impregnation method. In a typical procedure, the impregnation of support with the aqueous salt containing corresponding metal precursor $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (required for 2wt% of Ru) mixed with desired amounts of supports under a constant stirring at $100 \text{ }^\circ\text{C}$ until the excess water evaporated. The obtained powder samples were dried at $120 \text{ }^\circ\text{C}$ for overnight followed by calcination in static air; both Ru/MgO and Ru/ Al_2O_3 catalysts and Ru/C is annealed in flowing N_2 atmosphere at $450 \text{ }^\circ\text{C}$ for 4 h. The metal contents in the catalysts are denoted by their weight percentages.

2.3. Catalyst Characterization

2.3.1 Powder X-ray Diffraction (XRD). The powder XRD patterns of the catalysts are recorded with Bruker D4 Endeavor wide angle X-ray diffractometer (M/s. Bruker Corporation, Germany) using Ni filtered Cu $K\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) with a scan rate of 5° min^{-1} in the 2θ range of $10\text{-}90^\circ$ at 40 kV and 20 mA. The XRD phases present in the catalysts are identified with the help of powder diffraction file from the international centre for diffraction data (PDF-ICDD).

2.3.2 Physisorption Measurements. The N₂ physisorption experiments are carried for all the catalysts to determine the surface area of all the catalysts were recorded using N₂ adsorption at -196 °C, in Micromeritic ASAP 2010 surface area analyzer. The samples were degassed at 250 °C for 12 h in N₂ flow prior to the physisorption experiment. Specific surface areas (m² g⁻¹) were calculated applying BET (Brunnauer-Emmett-Teller) method.

2.3.3 CO-Pulse Chemisorption. The CO-pulse chemisorption experiments are carried out using a pulse titration procedure at 40 °C on an AUTOSORB-iQ automated gas sorption analyzer (M/s. Quantachrome Instruments, USA). Prior to the experiment, the catalyst was reduced at 450 °C for 2 h followed by flushing the catalyst for 1 h in helium flow. The CO pulses of 0.5 mL each is then injected on to the sample until its saturation point. The CO uptake is monitored using GC equipped with a thermal conductivity detector and Carboxen-1000 column. The active dispersion, metal surface area and metal particle sizes are calculated using standard equation presented below:

$$\text{Dispersion (\%)} = \frac{\text{CO uptake } \left(\frac{\mu\text{mol}}{\text{g}_{\text{cat}}}\right)}{\text{Total metal } \left(\frac{\mu\text{mol}}{\text{g}_{\text{cat}}}\right)} \times 100$$

Metal area = Metalcross sectional area × No. of metal atoms on surface

$$\text{Particle size (nm)} = \frac{6000}{\text{Total metal } \left(\frac{\text{m}^2}{\text{g}_{\text{cat}}}\right) \times \rho \left(\frac{\text{g}}{\text{cc}}\right)}; \rho: \text{metal density}$$

2.3.4 Pyridine and Water Adsorbed DRIFT Spectroscopy. FT-IR (Carry-660; Agilent technologies) connected with MCT detector is used to investigate the nature and strength of surface acid-base sites by using different probes such as pyridine/water adsorption in a DRIFT (Harrick) cell. After probe adsorption, the DRIFT spectra were collected in the range of 1000-2000 cm⁻¹ with 4 cm⁻¹ resolution and 64 no. of scans. All the experiments are performed in situ using a purpose-made IR cell connected to a conventional vacuum-

adsorption apparatus. Prior to analysis, samples were degassed in N₂ at 300 °C for 1 h and subsequently reduced the samples in 4.97% H₂ balanced Ar at 450 °C 30 min⁻¹ followed by cooling down to desired temperature for probe adsorption; 150 °C for pyridine and 125 °C for water is maintained. Then the samples were exposed to subsequent doses of probe molecule and the spectrum was recorded. The DRIFT spectrum collected after probe adsorption is subtracted with that of untreated sample spectrum to obtain the vibrational bands only due to interaction of probe with surface active sites followed by the quantification of the obtained spectra with Kubelka-Munk (K-M) function.

2.3.5 H₂-Temperature Programmed Reduction (TPR). The H₂-TPR analysis was carried out in a quartz micro-reactor interfaced to a GC (6820 A, Agilent technologies) equipped with a TCD unit. The catalyst was loaded in an isothermal zone of reactor and then degassed the sample at 300 °C in He flow to remove the physisorbed water. The furnace is cooled to room temperature after degassing at 300 °C and the He gas is switched to reducing gas (4.97% H₂ in Ar) with a flow rate of 30 mL min⁻¹ and the temperature was increased to 800 °C at a ramping rate of 5 °C min⁻¹. Hydrogen consumption was measured by analyzing the effluent gas using a calibration curve of Ag₂O TPR under identical conditions.

2.3.6 X-ray Photo Electron Spectroscopy (XPS). XPS analysis of the catalysts was performed on Thermo K α X-ray photoelectron spectrometer using monochromated Al K α X-ray ($E_{\text{photon}} = 1486.7$ eV) radiation as the excitation source at room temperature. The samples were maintained in a strict vacuum typically in the order of less than 10⁻⁸ Pa. Background subtraction was processed by Shirley method and the spectrum fitting (for each peak) was done with a linearly combined Gaussian functions using Avantage-XPS software.

2.3.7 Temperature Programmed Desorption (TPD) of NH₃. The acid site distribution of the catalysts were recorded in a gas flowing system equipped with quadrupole mass analyzer by temperature programmed desorption (TPD) of NH₃. In a typical method, about 0.2 g of

the sample was reduced at 450 °C for 1 h in 4.97% H₂/Ar (v/v) at a flow rate of 30 mL min⁻¹. After reductive pre-treatment, the sample was cooled to 100 °C and saturated with NH₃ pulses and subsequently flushed in helium flow at 100 °C for 1 h to remove the physisorbed ammonia. The desorption of NH₃ was then carried out by heating the sample up to 700 °C at a ramping rate of 10 °C min⁻¹. The total amount of desorbed NH₃ was calculated based on (m/z) 15 for NH₃.

2.3.8 CHNS and AAS Analyses. The coke contents of the fresh and used samples were measured using a VARIO EL, CHNS analyzer instrument in order to confirm the potential coking after time stream study. The elemental analysis of the fresh and used samples was carried out by atomic absorption spectroscopy (AAS) PerkinElmer, Analyst-300 after digestion of samples in aqua regia and required dilution thereof.

2.4. Catalytic Activity Measurements. Vapour phase conversion of levulinic acid (LA) is carried out in a fixed bed quartz reactor (i.d. = 12 mm, length = 420 mm) in down flow mode. Prior to the reaction, the catalyst sample (~0.1 to 0.2 g -18/+25 BSS sieved particles) were reduced in situ at 450 °C for 4 h in 4.97% H₂ (balance Ar) at a flow rate of 30 mL min⁻¹. After reduction, the catalyst zone was brought to the desired reaction temperature and the aqueous LA (10wt.%) was fed (2-10 mL h⁻¹) with a syringe operated using a HPLC pump along with 20 cc min⁻¹H₂ flow. The gas flow rates were monitored using mass flow controllers (Alicat Scientific) to regulate the flow. The product mixture was collected in an ice cold trap for each 1 h. The collected product mixture was then subjected to sufficient dilution with an organic solvent (acetone/methanol) followed by the addition of an internal standard (anisole is used in this study) prior to the analysis of product mixture by gas chromatograph-mass spectroscopy (GC-MS; QP5050A Shimadzu for the qualitative analysis) and gas chromatograph (GC; Agilent 7820 B GC equipped with HP-5 capillary column and FID detector for the quantitative analysis). The activity data presented in this work is

acquired after 6 h of continuous operation unless mentioned elsewhere. The carbon mass balance was found to be >98% based on inlet and outlet carbon unless otherwise stated. The conversion, selectivity, rate and productivity were calculated using standard equations which are given below:

$$\text{Conversion of LA} = \left(\frac{\text{LAc}_{\text{in}} - \text{LAc}_{\text{out}}}{\text{LAc}_{\text{in}}} \right) \times 100$$

$$\text{Selectivity of GVL} = \left(\frac{S_{\text{GVL}}}{S_{\text{GVL}} + S_{\text{AL}} + S_{\text{Others}}} \right) \times 100$$

$$\text{Selectivity} = \left[\frac{P_i}{\sum P_i} \right] \times 100 \text{ (where } i = \text{GVL, AL and Others; P is product)}$$

$$r_{\text{GVL}} = \frac{\text{GVL}_{\text{yield}} \times \text{LA}_{\text{flow rate}} (\text{mol s}^{-1})}{\text{Weight of the catalyst (g}_{\text{cat}})} ; r: \text{Rate}; \quad \text{TOF}_{\text{GVL}} (\text{s}^{-1}) = \frac{r_{\text{GVL}}}{\text{CO uptake}}$$

$$\text{Productivity} = \left(\frac{\text{Weight of LA pumped per hour} \times \text{Fractional yield of GVL}}{\text{Weight of the catalyst}} \right)$$

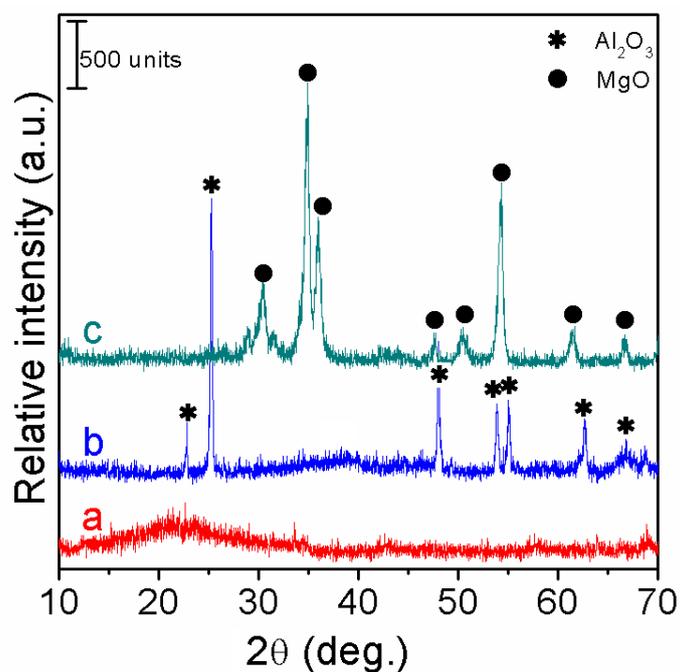
Table S1. CO pulse chemisorption of the supported Ru catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}_{\text{cat}}^{-1}$)	CO uptake ($\mu\text{mol/g}_{\text{cat}}$)	Dispersion (%)	MSA ($\text{m}^2/\text{g}_{\text{Ru}}$)	MCS (nm)
Ru/C	270.5	76.8	38.9	189.8	2.6
Ru/Al ₂ O ₃	135.2	63.1	31.9	156.0	3.1
Ru/MgO	62.7	60.9	30.7	150.6	3.2
Ni/C	254.6	64.9	19.1	126.8	5.3
Pt/C	287.6	60.1	58.6	144.6	2.0
Pd/C	280.3	75.8	40.4	178.0	2.8

^a Obtained from CO-chemisorption; ^{b, c, d} Calculated using CO-uptakes.

Table S2. Comparison of productivity values with reported catalysts in vapour phase.

Catalyst	Catalyst source/ Preparation method	Reaction conditions	Productivity ($\text{kg}_{\text{GVL}} \text{kg}_{\text{catalyst}}^{-1} \text{h}^{-1}$)	Ref.
2% Ru/C	Wet impregnation	Vapour phase 1 bar, 275 °C	1.18 (Substrate: LA in H ₂ O)	Present study
30% Ni/H-ZSM-5	Wet impregnation	Vapour phase 1 bar, 250 °C	0.90 (Substrate: Pure LA)	34
5% Ru/C	Sigma-Aldrich	Vapour phase 1 bar, 265 °C	0.45 (Substrate: LA in 1,4-dioxane)	35
5% Cu/SiO ₂	Precipitation– deposition method	Vapour phase 10 bar, 265 °C	0.44 (Substrate: LA in 1,4-dioxane)	36
5% Pt/C	Sigma-Aldrich	Vapour phase 1 bar, 265 °C	0.15 (Substrate: LA in 1,4-dioxane)	35

**Figure S1.** Powder XRD patterns of reduced a) Ru/C, b) Ru/Al₂O₃ and c) Ru/MgO catalysts.

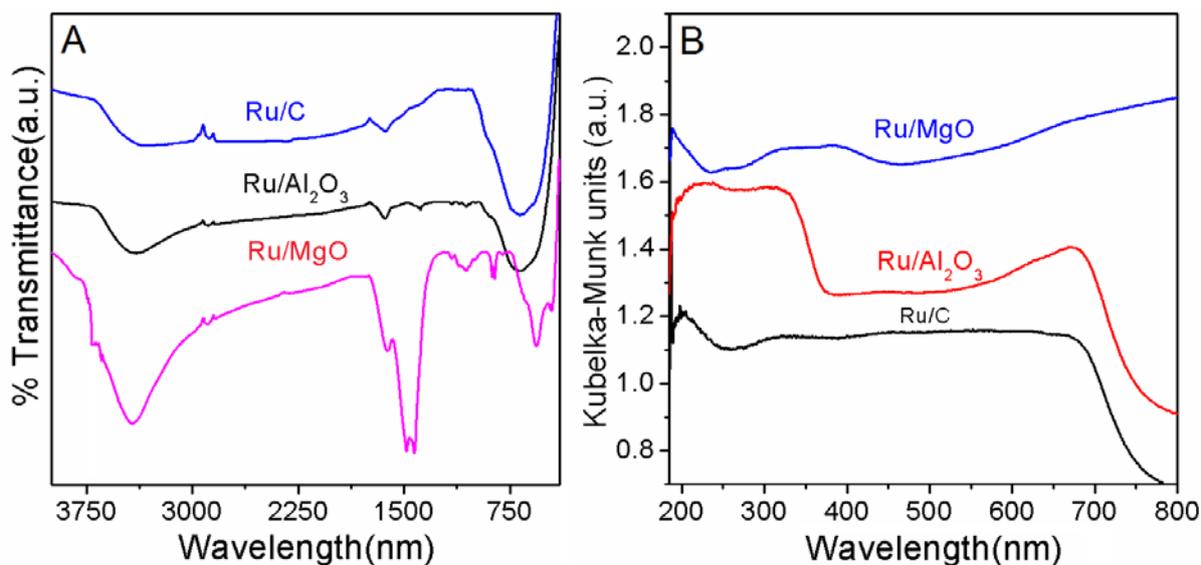


Figure S2. A) FT-IR and B) UV-DR spectra of calcined Ru/C, Ru/Al₂O₃ and Ru/MgO catalysts.

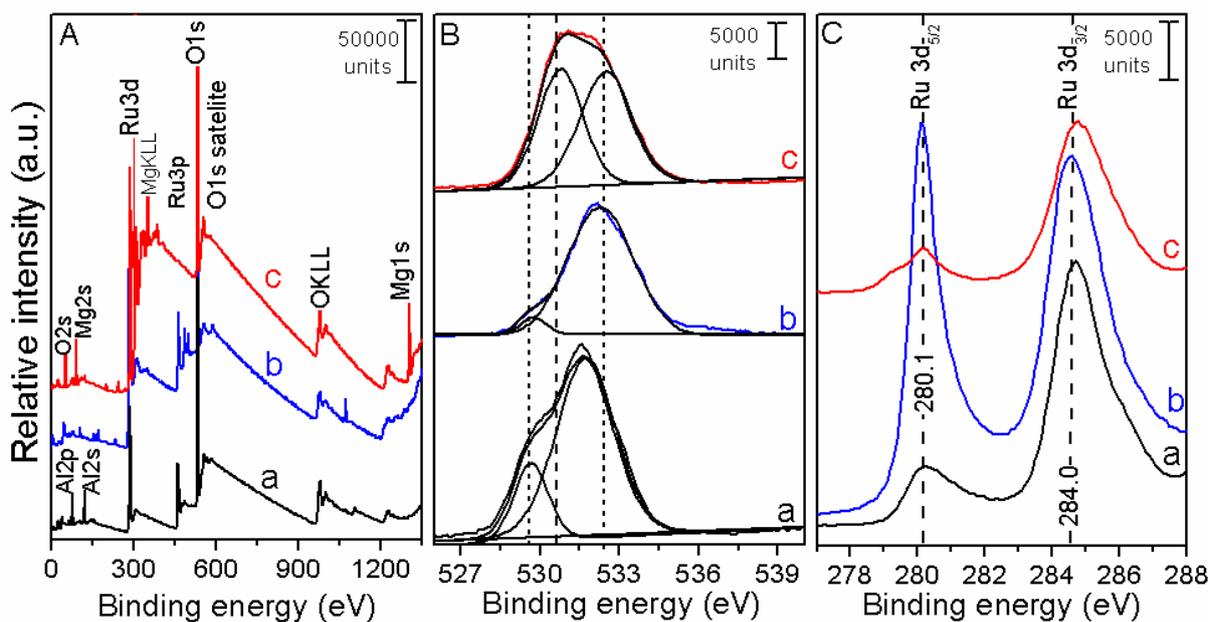


Figure S3. XPS analysis of the reduced samples (A) survey scan, (B) O 1s and (C) Ru 3d spectra of: a) Ru/Al₂O₃ b) Ru/C and c) Ru/MgO.

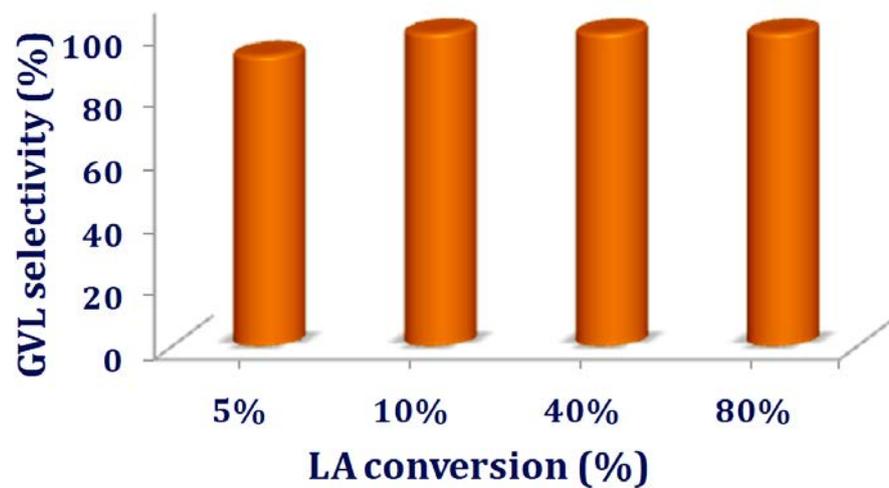


Figure S4. GVL selectivity at different LA conversions over Ru/C catalyst.