Supporting Information

An investigation on the influence of support type for Ni catalysed vapour phase hydrogenation of aqueous levulinic acid to γ-valerolactone

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1 Experimental

The SiO_2 (**BET-SA: 395.0 m^2 g^{-1}**), γ-Al_2O_3 (**BET-SA: 230.5 m^2 g^{-1}**) ZrO_2 (**BET-SA: 52.8 m^2 g^{-1}**) $Ni(NO_3)_2 \cdot 6H_2O$, levulinic acid (98%), γ-valerolactone (99%) and angelica lactone (98%), valeric acid, methyl tetrahydrofuran (MTHF) were purchased from Sigma Aldrich and used as received. The α-Al_2O_3 received from NORPRO- R97655. All the catalyst samples were prepared by incipient wet impregnation method. Briefly, required amount of solid support (e.g. SiO_2, γ-Al_2O_3, ZrO_2) and in some case α-Al_2O_3 was added to an aqueous solution of $Ni(NO_3)_2$ $6H_2O$ (an amount required to obtain a 20wt% Ni loading) and the suspension was then stirred at 100 °C until the water had evaporated. The solid recovered was then oven dried at 120 °C overnight and calcined in static air at 500 °C for 5 h.

2 Characterization of the catalysts

The powder XRD analysis of the catalysts were recorded with an Ultima-IV X-ray diffractometer (M/s. Rigaku Corporation, Japan) using a Ni-filtered Cu K$_\alpha$ (λ = 0.15418 nm) radiation source and a scintillation counter detector. The diffraction patterns were recorded with a scan rate of 5° min^{-1} in the 2θ range of 10-70° at 40 kV and 20 mA. The surface areas of the reduced samples were measured by N_2 adsorption at -196 °C (Micromeritics ASAP 2010 surface area analyzer).

The nature of acid sites of the catalysts was examined by pyridine adsorbed FT-IR spectroscopy (Carry 660, Agilent Technologies). Spectra were obtained in the range of 1700-1400 cm^{-1} with a resolution of 2 cm^{-1} with 64 scans for each spectra collection. The experiments were performed in situ using a purpose-made IR cell connected to a vacuum adsorption set-up. In a typical method the reduced samples were pressed into self-supporting wafers (density ~ 40 mg cm^{-3}) under a pressure of 10^5 Pa. Subsequently the wafers were transferred in to the IR cell and were pre-treated in N_2 flow by heating at a rate of 10 °C min^{-1} up to 400 °C for 1 h. After cooling down to 150 °C the spectrum was collected in the drift

mode. Then the sample was exposed to pyridine until the surface saturation in successive pulse injections at 150 °C and subsequently the sample was purged for 30 min in N_2 flow before recording the spectra. The drift spectra after pyridine adsorption were subtracted from the spectra of the untreated catalyst to obtain the vibrational bands due to pyridine acid site interaction. Finally, the spectra were quantified with the Kubelka-Munk (K-M) function and the fitted curves were used to measure the relative ratios of Brønsted (BAS) and Lewis acid sites (LAS) for the corresponding spectral lines at full width at half maximum (FWHM).

The H_2-TPR analysis was carried out in a quartz micro-reactor interfaced to a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) unit. Prior to TPR analysis the catalyst was degassed at 300 °C in helium gas for 30 min and then cooled to room temperature. The helium gas was switched to 4.97% H_2 in argon with a flow rate of 30 mL min^{-1} and the temperature was increased to 900 °C at a ramping rate of 5 °C min^{-1}. The hydrogen uptakes of the samples were measured using a calibration curve of Ag_2O TPR under similar protocol. The calibrated mass flow controllers (Alicat Scientific, USA) were used to regulate the flow rates for all the gases used.

Carbon contents in the used samples were measured using a VARIO EL, CHNS analyzer. The elemental analysis of the fresh and used samples were analyzed by atomic absorption spectroscopy (AAS) Perkin-Elmer, Analyst-300. The AAS analysis of the fresh and used samples indicated no leaching of metal during the course reaction (Table S2). The CO pulse chemisorption experiments were carried out using a pulse titration procedure at 40 °C on an AUTOSORB-iQ automated gas sorption analyzer (M/s. Quantachrome Instruments, USA). In a typical method the sample was reductively pre-treated at 450 °C for 2 h in 4.97% H_2 balance Ar then the sample was flushed in helium gas for 30 min at 450 °C followed by titrated with 5.02% CO balance He at 40 °C. The Ni dispersion, Ni metal surface area and particle size of Ni was calculated using the following equations presented below:

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

$$\text{Metal area } = \text{Metal cross sectional area} \times \text{No. of metal atoms on surface (i. e. CO uptake)}$$

$$\text{Particle size (nm)} = \frac{6000}{\text{Ni metal surface area } (\frac{m^2}{g_{cat}}) \times \rho}; \ \rho: \text{metal density}$$

3 Activity measurements

The vapour phase hydrogenation of aqueous levulinic acid was carried out in a fixed bed quartz reactor (i.d. = 10 mm, length = 420 mm) in down flow mode. The experimental conditions and product analysis details were similar as reported by us earlier [1]. The carbon mass balance in all the experiments were >99% unless otherwise stated. The influence of both Brønsted and Lewis acid sites in the LA conversion was examined by carrying out two independent experiments (1) by using 2,6-dimethylpyridine (2,6-lutidine) as selective Brønsted acid site blocker and (2) pyridine (Py) as both Brønsted and Lewis acid site blocker.

In a typical method about 12.4 mmol of probe was injected successively in 4 pulses (3.1 mmol each) into the aqueous LA stream. After each pulse, the samples were collected and analyzed by GC-MS. After the dosage, the catalyst was regenerated at 450 °C in flowing air and subsequently reduced the catalysts at 450 °C with 4.97% H_2 balance Ar before the aqueous LA was being subjected on to the catalyst. The conversion, selectivity, rates and turnover frequency (TOF) on product formation was calculated using the equations given below:

$$Conversion\ of\ LA\ (X_{LA}) = \left(\frac{LAc_{in} - LAc_{out}}{LAc_{in}}\right) \times 100$$

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

$$Selectivity = \left[\frac{Pi}{\sum Pi}\right] \times 100\ (where\ i = GVL,\ AL\ and\ Others)$$

$$r_{GVL} = \frac{GVL_{yield} \times LA_{flow\ rate}\ (mol\ s^{-1})}{Weight\ of\ the\ catalyst\ (g_{cat})}$$

$$TOF = \frac{rate(mol\ s^{-1}g_{cat}^{-1})}{CO\ uptake\ (mol\ g_{cat}^{-1})}$$

4. Results and Discussion

4.1 Activity

4.2 Effect of support for Ru in the aqueous LA hydrogenation to γ-valerolactone

Catalyst Wt: ~ 0.25 g; Feed rate: 1mL h^{-1}; H$_2$ flow rate: 20 cm^3 min^{-1} Reduction: 450 ^{o}C/3h; Reaction Temp.: 275 °C; Reaction Mixture: 10wt% LA in H$_2$O Samples collected after 6 h.

Table S1 Aqueous LA hydrogenation over Ru supported on different metal oxides.

Sl. No.	Catalyst	LA conversion (%)	Selectivity (%)		
			GVL	AL	Others[a]
01	5wt% Ru/HAP	92.0	99.8	0.2	-
02	5wt% Ru/SiO$_2$	98.4	96.2	3.8	-
03	5wt% Ru/Al$_2$O$_3$	52	94.2	5.8	-
04	5wt% Ru/MgO	65	78.4	10.1	11.0
05	5wt% Ru/La$_2$O$_3$	54	92.0	80.7	-
06	5wt% Ru/TiO$_2$	26.0	24.0	57	19.0
07	5wt% Ru/ZnO	3.0	53.0	38.0	8.0
08	5wt% Ru/Al-HAP	66.5	87.3	11.4	-
09	5wt% Ru/Mg-HAP	45.0	92.3	-	7.7
10	5wt% Ru/SiO$_2$-Al$_2$O$_3$	56.9	91.8	6.2	-
11	5wt% Ru/C	100	100	-	-

[a] Others include VA, MTHF and etc.

Table S2: AAS Analysis of 20wt%Ni/SiO$_2$ catalyst

Catalyst	Ni content (wt.%)
Ni/SiO$_2$-Fresh	19.83
Ni/SiO$_2$-Used[a]	19.92

[a]Catalyst sample recovered after 15 h of use.

Table S3 Time on stream analysis over supported Ni catalysts. Reaction conditions: 10wt% LA in H$_2$O, 270 °C, GHSV = 19.5 mL s^{-1} g$_{cat}$$^{-1}$; H$_2$ = 20 cm^3 min^{-1}, Time = 15 h.

Catalyst	LA conversion (%)	GVL selectivity (%)	Carbon (%)[a]	**BET-SA[b]**
Ni/SiO$_2$	14.8	89.6	0.52	**157.4**
Ni/ZrO$_2$	3.6	61.0	2.57	**105.4**
Ni/Al$_2$O$_3$	10.2	72.5	2.28	**20.1**

[a] Obtanined from CHNS analysis;
[b] BET surface area of recycled catalysts

5 Catalyst poisoning studies

The influence of both Brønsted and Lewis acidity in the LA conversion was examined by carrying out two independent experiments (1) by using 2,6-dimethylpyridine (2,6-lutidine) as Brønsted acid site blocker and (2) pyridine (Py) as both Brønsted and Lewis acid site blocker. In a typical experiment about 12.4 mmol of probe was injected successively in 4 pulses into the aqueous LA stream. After each pulse, the samples were collected and the product mixture was analyzed by Gas Chromatograph (Varian CP-3800 GC) equipped with ZB wax column and Flame ionization detector (FID). After the dosage, the catalyst was regenerated at 400 °C in flowing air and subsequently reduced the catalysts at 500 °C with 4.97% H$_2$ (balanced Ar) before the aqueous LA was being subjected to the catalyst. From the catalysts poisoning results, it was observed that a drop in the activity was seen for the hydrogenation of LA after addition of pyridine. But, in case of 2,6-dimethyl pyridine no

considerable change in the activity was observed for both the catalysts. This in turn confirms the role of Lewis acidity in this transformation.

6 Characterization of catalysts

6.1 Transmission electron microscopy (TEM)

The TEM images of all the fresh Ni catalysts are presented in the Fig. S1. The images showed the different surface morphology in all the catalysts. In case of Ni/Al$_2$O$_3$, Ni/ZrO$_2$ and Ni/SiO$_2$ catalysts, there was a broad distribution of Ni particles. The Ni/SiO$_2$ catalyst also has shown a narrow distribution of Ni particles better than Ni/Al$_2$O$_3$ and Ni/ZrO$_2$ catalysts. A clear and relatively uniform distribution was seen in the Ni/SiO$_2$ catalyst and the particles were finely dispersed on the support.
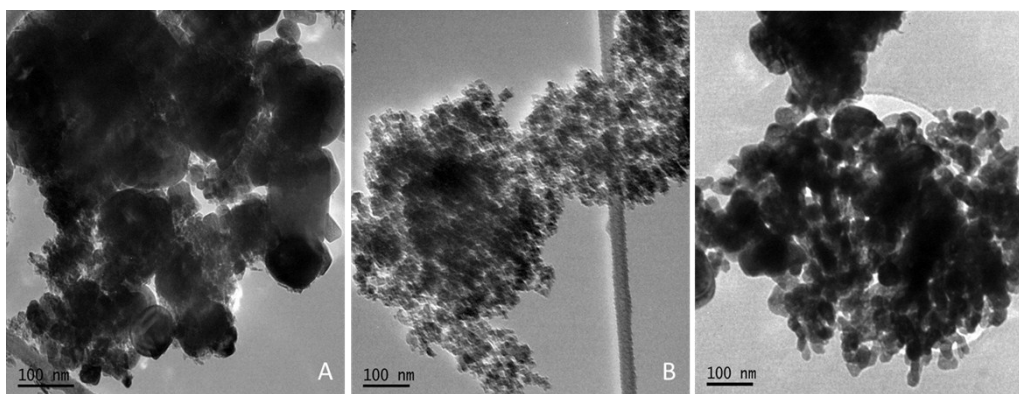
Fig. S1 TEM images of the 20wt%Ni supported on (A) Al$_2$O$_3$, (B) SiO$_2$ and (C) ZrO$_2$.
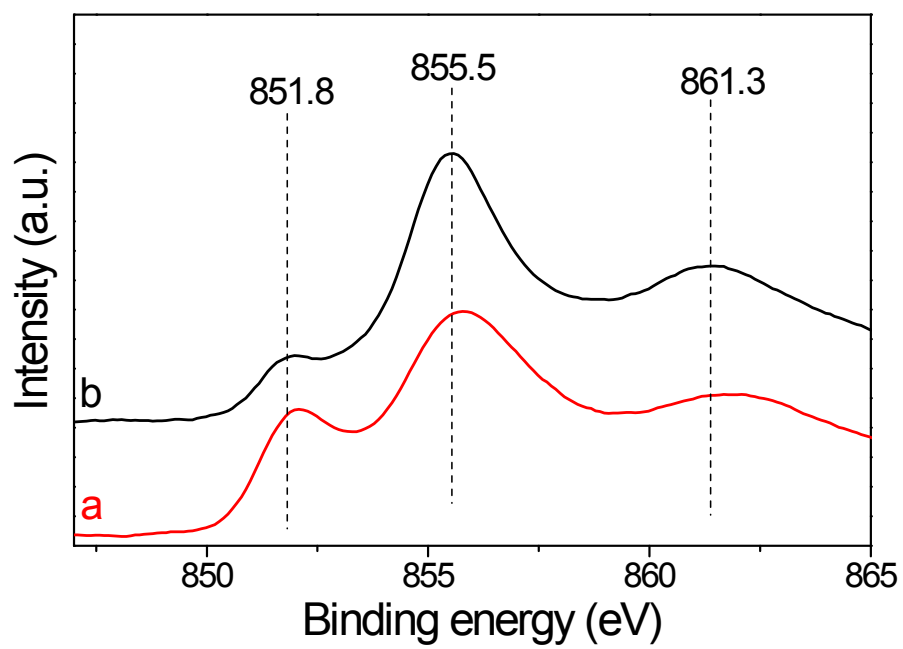
Fig. S2 XPS analysis of the 20wt%Ni supported on SiO_2 (a) Fresh (b) Recycled catalysts
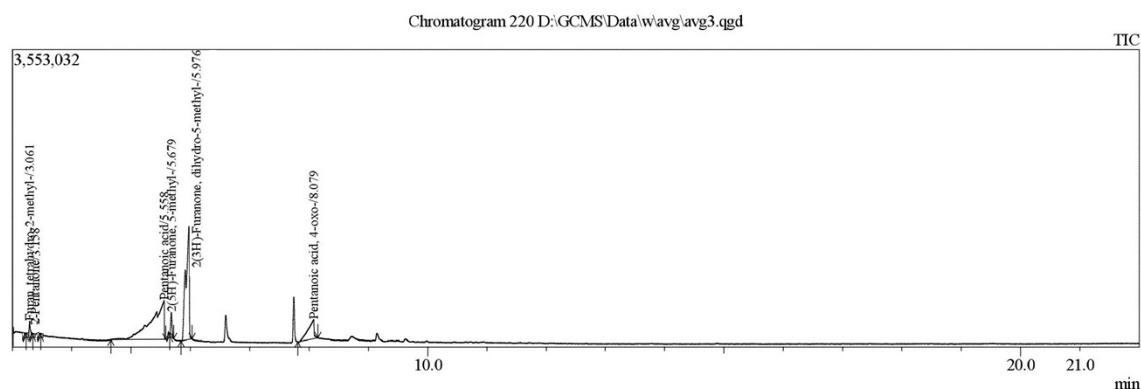
GCMS REPORT

Fig. S3 GC-MS report for aqueous LA hydrogenation over the 20wt% Ni/ZrO$_2$ catalyst
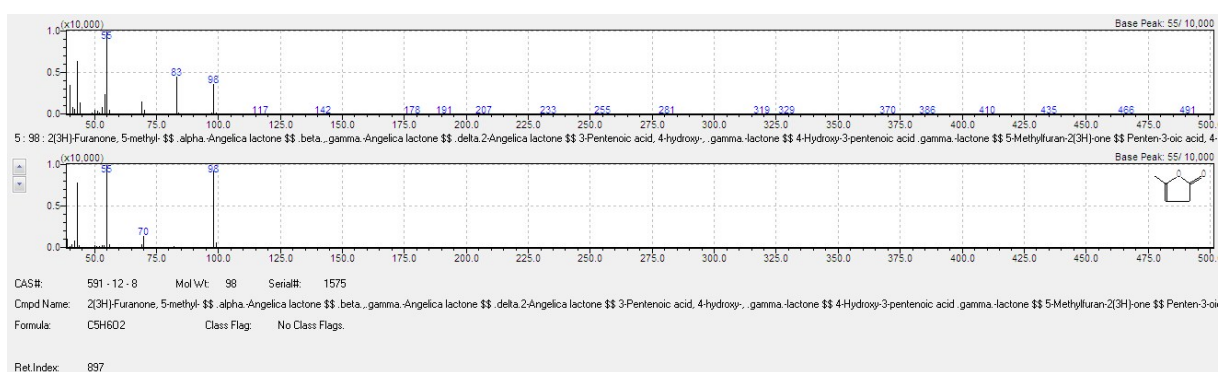

Fig. S4 Mass spectrum of the α-angelica lactone
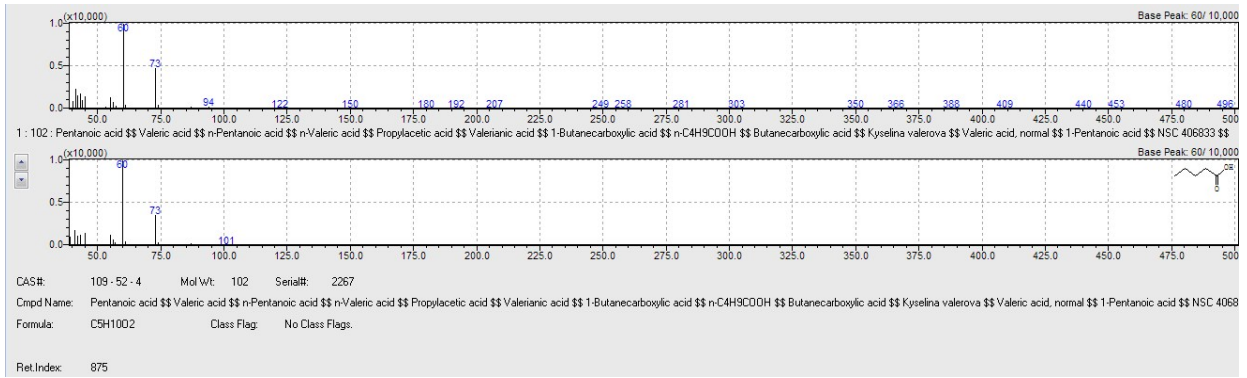
9

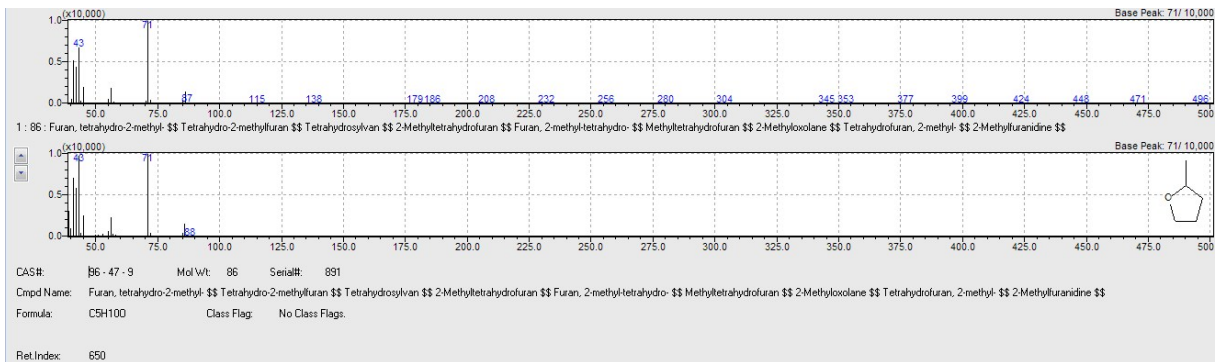**Fig. S5** Mass spectrum of the Pentanoic acid

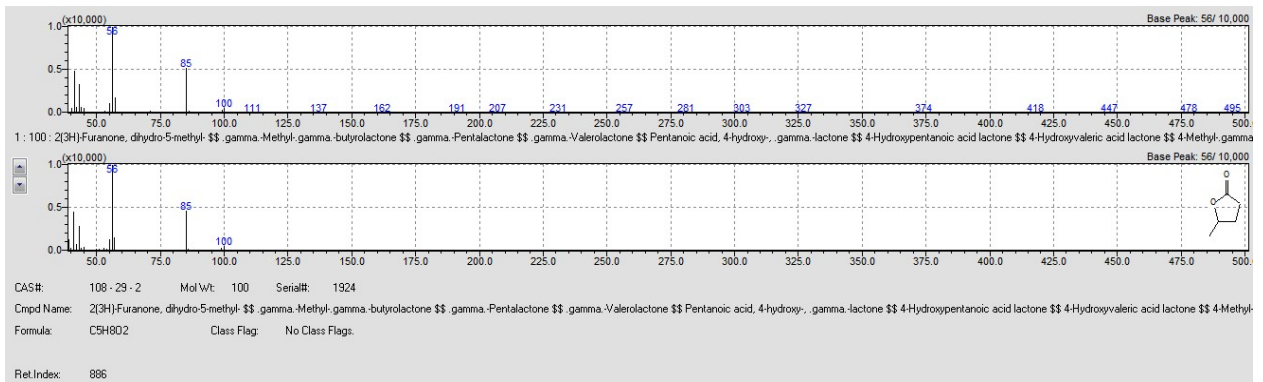**Fig. S6** Mass spectrum of the 2-methyltetrahydrofuran (MTHF)

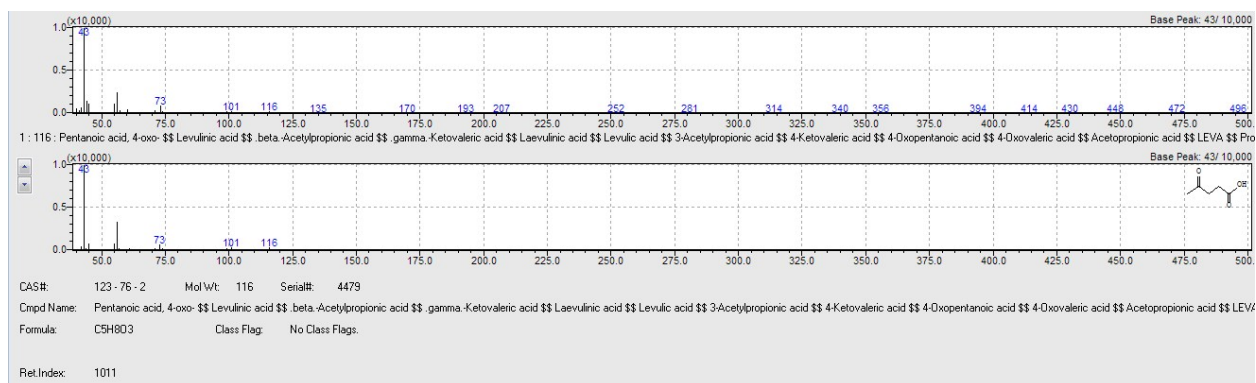**Fig. S7** Mass spectrum of the γ-Valerolactone (GVL)

Fig. S8 Mass spectrum of the Levulinic acid (LA)

References

[1] V.V. Kumar, G. Naresh, M. Sudhakar, James Tardio, S. K. Bhargava, A. Venugopal, App. Catal. A 505 (2015) 217-223.