Supplementary Material (ESI)

Cu-ZrO_2 nanocomposite catalyst for selective hydrogenation of levulinic acid and its ester to γ- valerolactone

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Experimental

BET surface area and N2 adsorption full isotherm of the copper zirconia catalyst was measured at 77 K preformed on a Quantachrome Instruments (V 5.02).

The software program X-Pert High Score Plus was employed to subtract contribution of copper Kα2 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 x 140-8 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).

FTIR spectra was recorded on a Perkin-Elmer Spectrum one make instrument. The reaction liquid sample in chloroform as a solvent. FTIR spectra were recorded between 600 to 4000 cm-1 with accumulation of 20 scan and 4 cm-1 resolution.

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Characterization

Table 1. Textural properties of Cu-ZrO_2 catalyst

Catalyst	Surface Area m^2/g	Pore Volume cc/g	Pore Size (nm)
Cu-ZrO_2 (1:1)	22.1	0.061	2.7

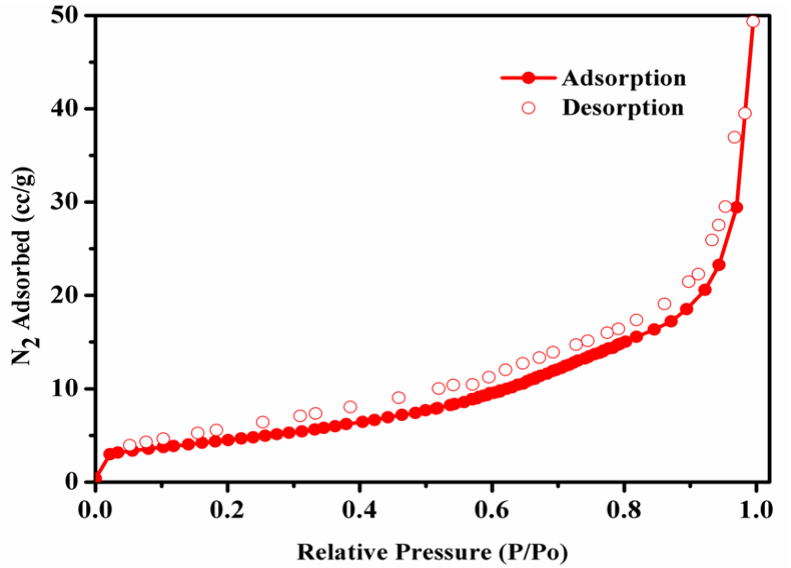


Fig. 1 Adsorption isotherm of Cu-ZrO_2 catalyst.

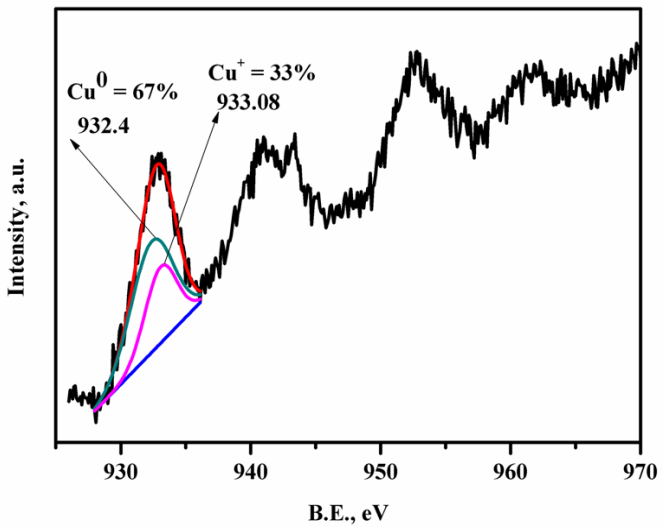


Fig. 2 XPS of Used Cu-ZrO_2 catalyst

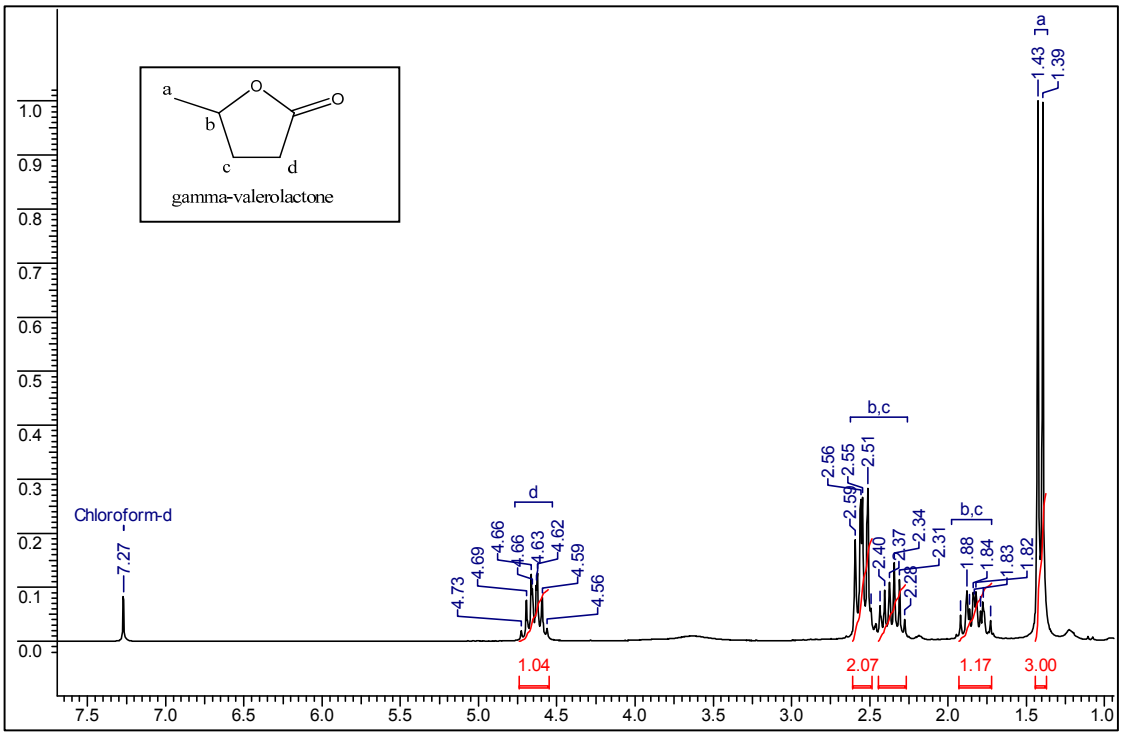


Fig. 3 NMR spectra of γ- valerolactone

^{1}H-NMR ($CDCl_3$ 200MHz) : δ 1.39-1.43 (d, 3H), 1.73-1.93 (m, 1H), 2.28-2.43 (m, 1H), 2.51-2.59 (m, 2H), 4.56-4.73 (m, 1H).

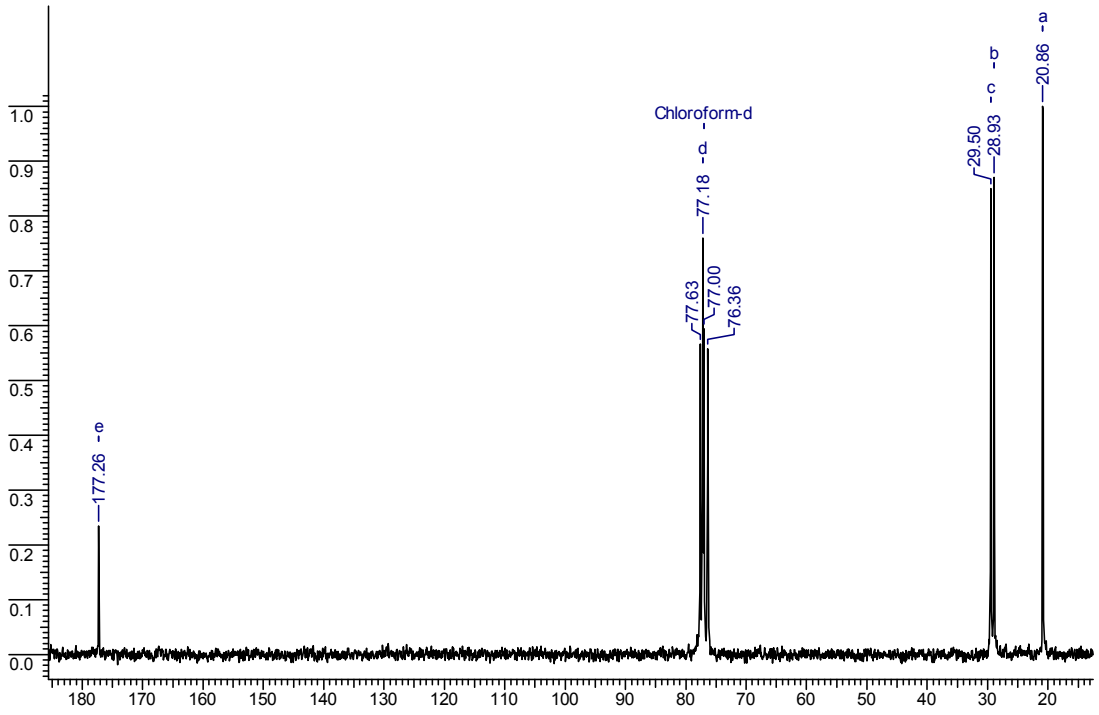


Fig. 4 C^{13} NMR spectra of γ- valerolactone

^{13}C NMR ($CDCl_3$, 50MHz) : δ 20.86, 28.93, 29.50, 77.18, 177.26.

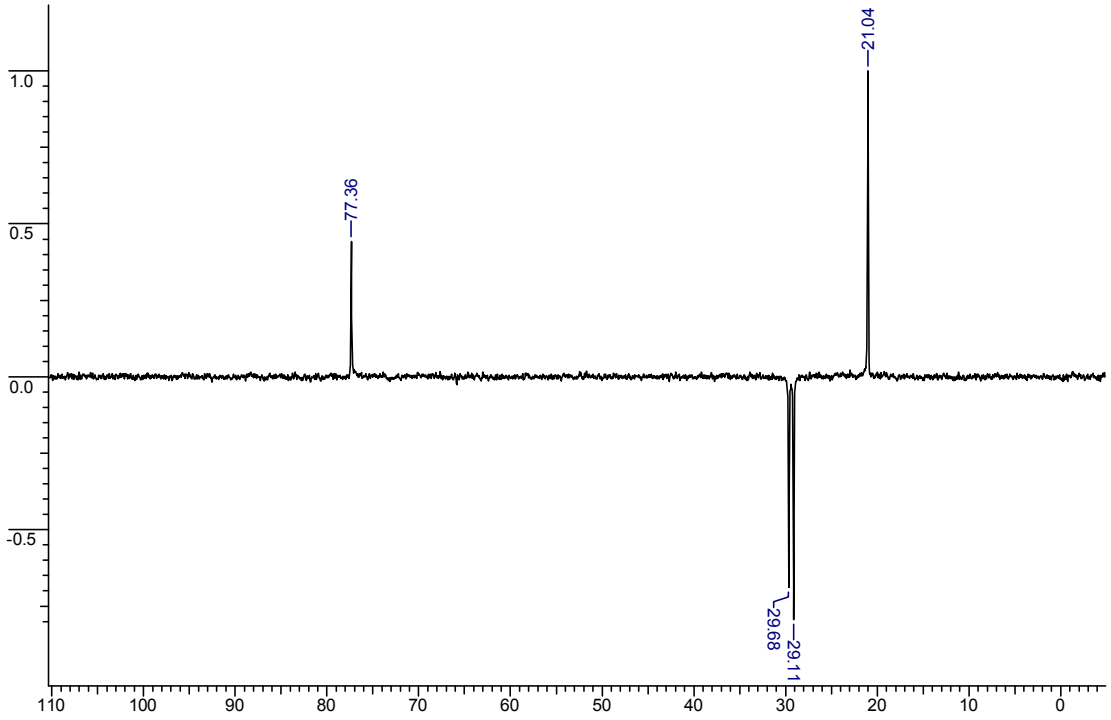
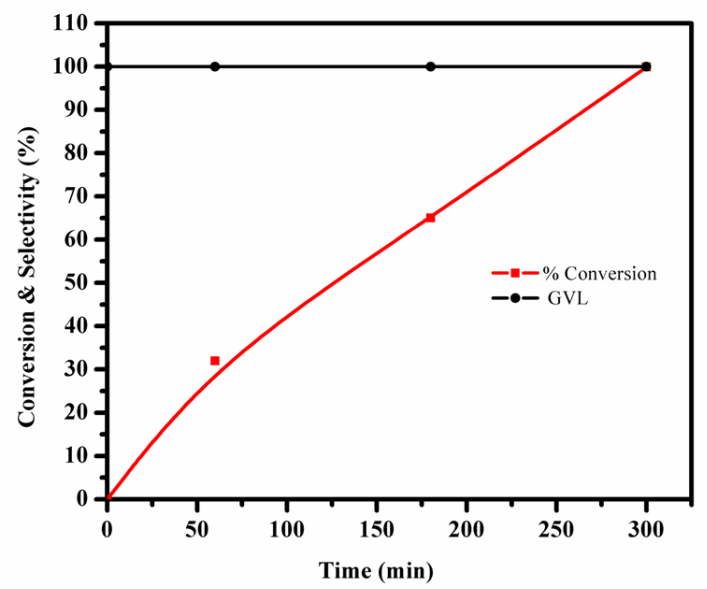


Fig. 5 DEPT C^{13} NMR spectra of γ- valerolactone



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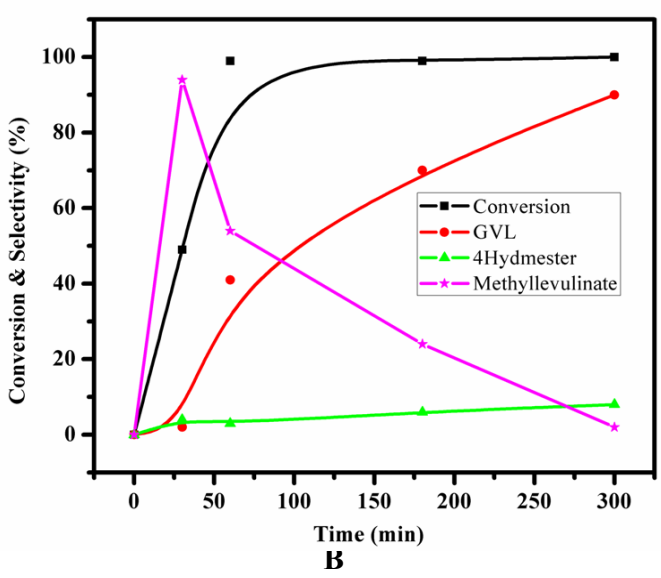
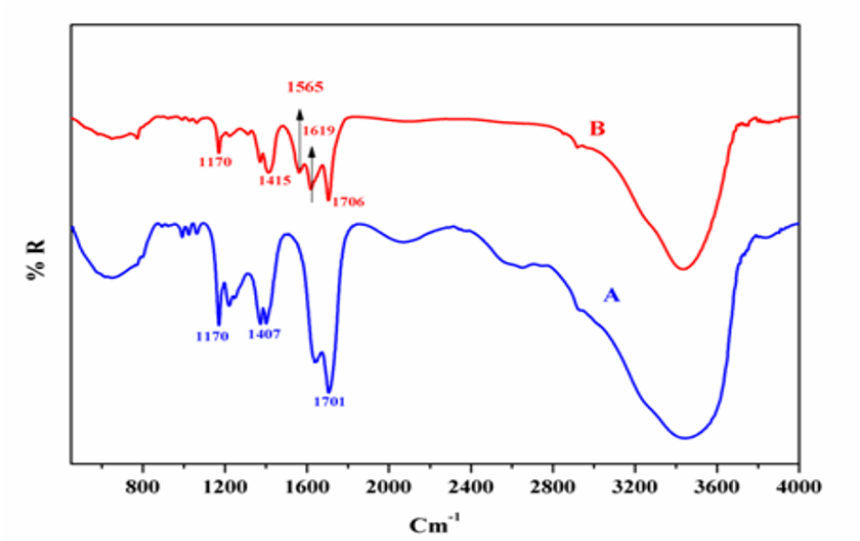


B

Fig 6. Conversion selectivity pattern of LA Hydrogenation (A) LA hydrogenation in water (B) LA hydrogenation in methanol



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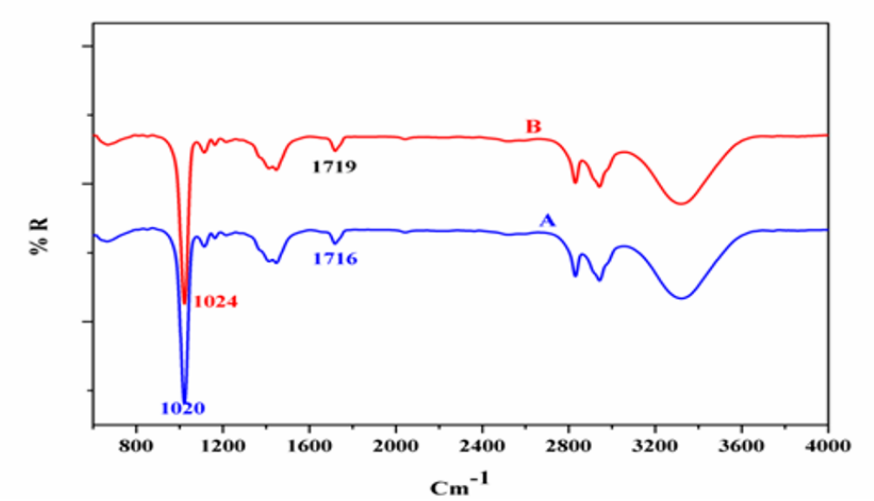

B

Fig. 7 FTIR study LA hydrogenation (A) LA hydrogenation in water (B) Methyl LA hydrogenation in methanol

Levulinic acid, Methyl Levulinate 5% (w/w); solvent, water, methanol (95 ml); Temp, 473K; Catalyst, 0.5 g; (Cu-Al_2O_3, Cu-ZrO_2)