Supporting Information

for

Supported copper catalysts for highly efficient hydrogenation of biomass-derived levulinic acid and γ-valerolactone

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Experimental

Catalyst preparation

Cu/C: Cu/C catalyst was prepared by impregnation method. Activated carbon(1.4 g) were added to a 50 mL aqueous solution of copper nitrate(2.28 g) with vigorous stirred at room temperature. The resulting solution was dried at 363 K for 12 h, and calcined at 573 K for 4 h. The oxides were reduced at 553 K for 3 h with the heating rate 2 ^{o}C/min and the gas composition was H_2:N_2 (10:90), 100 mL/min. The Cu/HZSM-5、Cu/ZSM-5、Cu/SiO_2、 Cu/ZrO_2、Cu/Ta_2O_5、Cu/γ-Al_2O_3、Cu/SBA-15 catalysts were prepared similar as the Cu/C catalyst by impregnation method. And the Cu loading of these catalysts was 30%.

Catalyst characterization

X-ray power diffraction (XRD) patterns of supported copper catalysts were recorded on an X'pert (PANalytical) diffractometer at 40 kV and 40 mA, using Ni-filtered Cu-Kα radiation. 2θ range was 10^{o} ~ 70^{o}.

Transmission electron microscopy (TEM) microphotographs were performed on a JEOL-2010 electron microscope operating at 200 kV. The samples were suspended in methanol.

The amount of the copper loading were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo-Jarrell ASH-Atom Scan Advantage). The pretreatment of the samples were pretreated by alkali fusion or HF dissolution method.

The surface area was measured by Brunauer-Emmett-Teller (BET) method and the average pore size, pore volume and pore size distribution were measured by Barret-Joyner-Halenda(BJH) method.

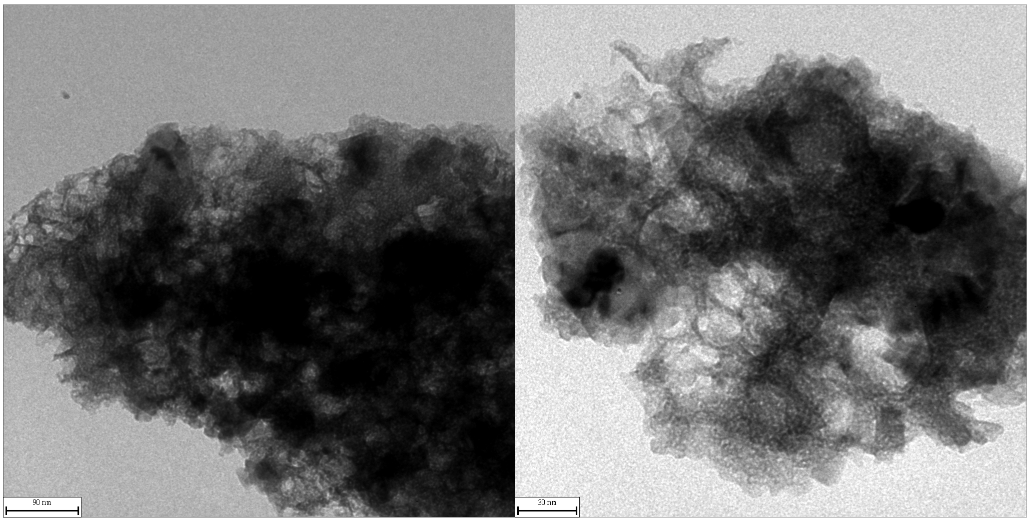

Fig. S1 TEM micrographs of Cu(30%)/ZrO_2-OG-300 (scale bar 90 nm (left) and 30 nm (right))

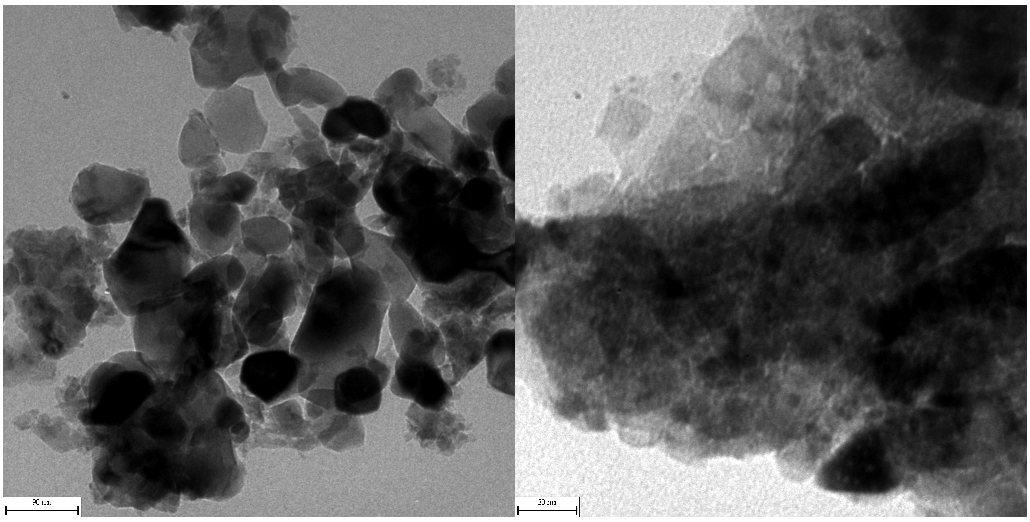

Fig. S2 TEM micrographs of Cu(30%)/ZrO_2-OG-600 (scale bar 90 nm (left) and 30 nm (right))

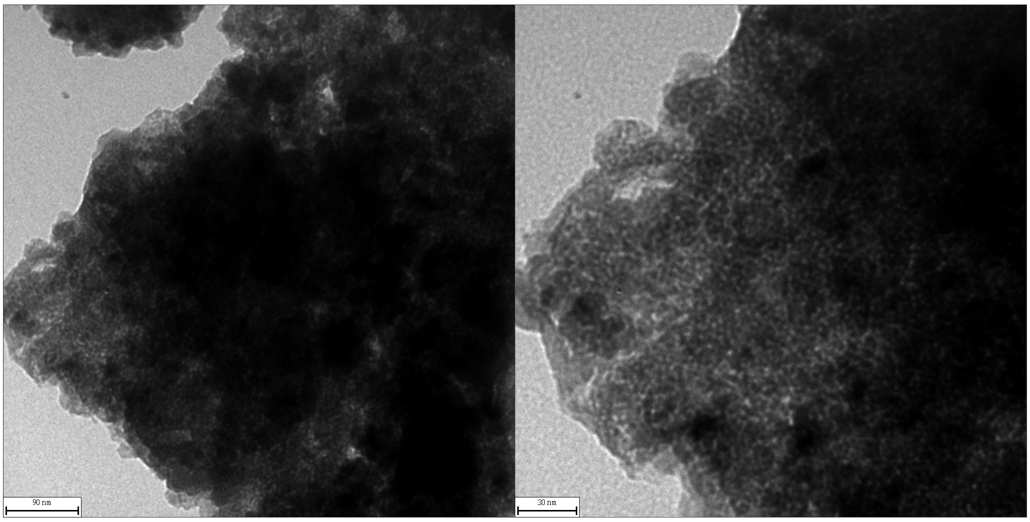

Fig. S3 TEM micrographs of Cu(30%)/ZrO_2-CP-300 (scale bar 90 nm (left) and 30 nm (right))

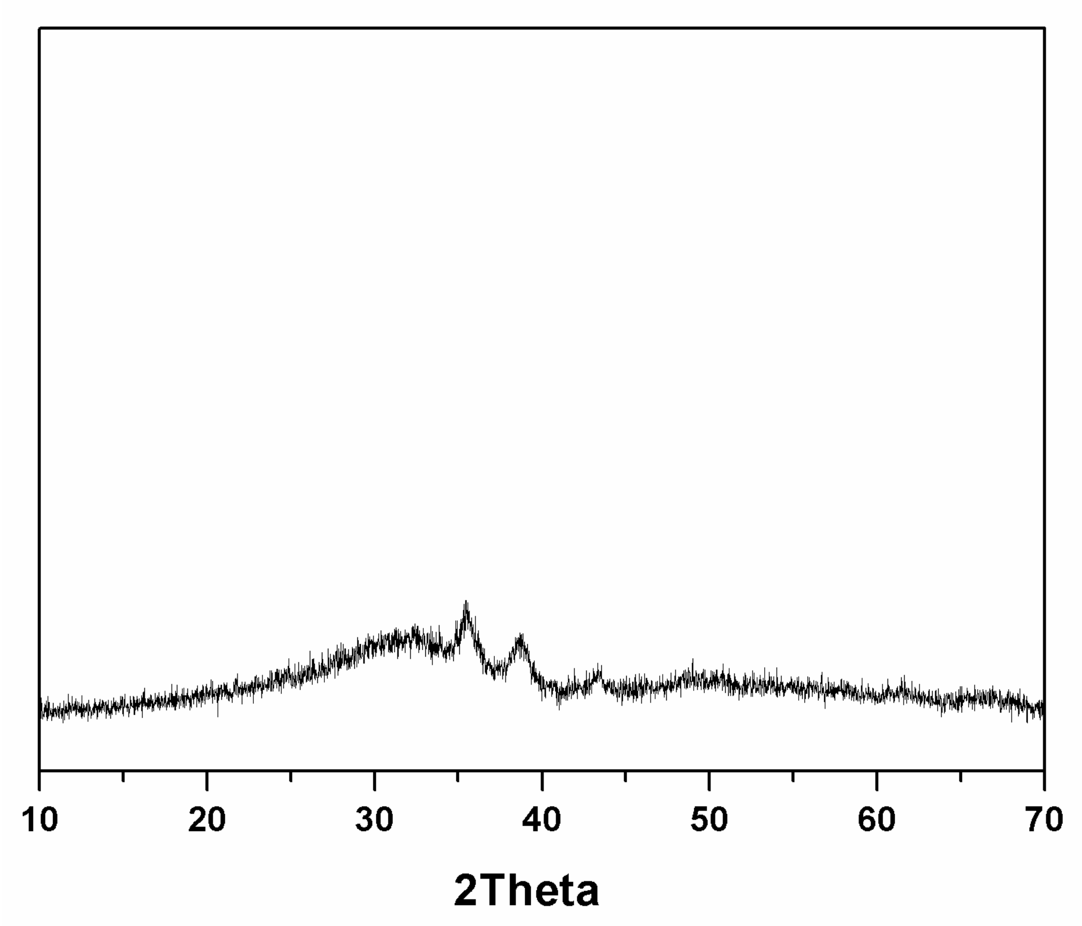

Fig. S4 X-ray diffraction patterns of Cu(30%)/ZrO_2-OG-300

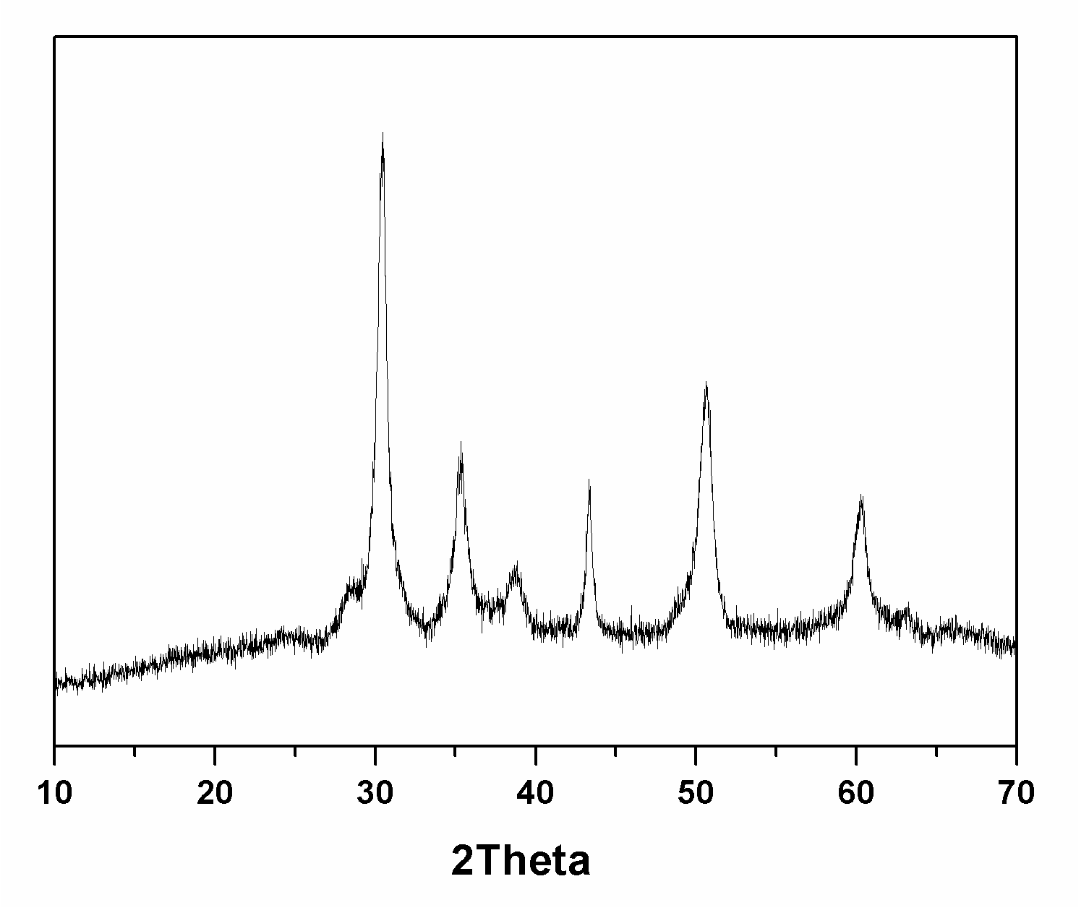

Fig. S5 X-ray diffraction patterns of Cu(30%)/ZrO_2-OG-600

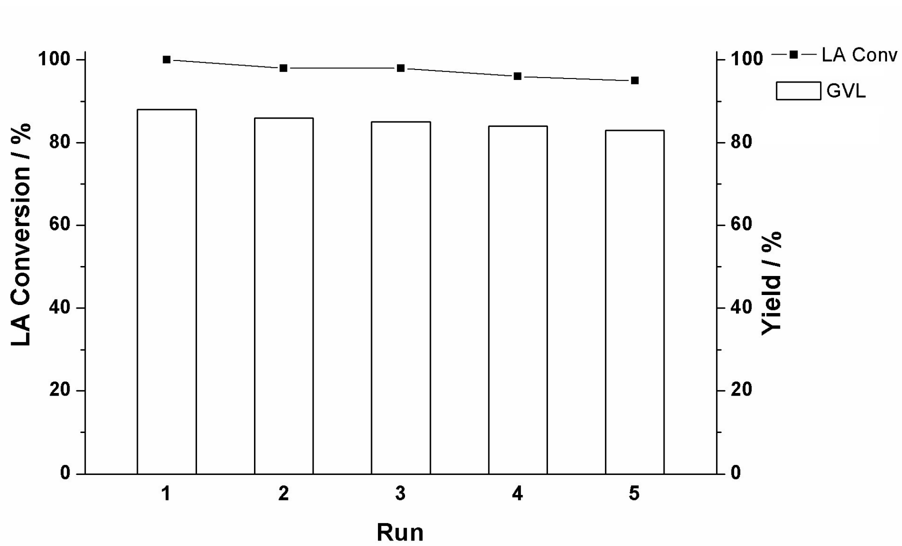

Fig. S6 The reuse of Cu(30%)/ZrO_2-OG-300 at the conversion of LA to GVL. Reaction conditions: LA 0.25 g, cat 0.1 g, 413 K, 6 h, 5 MPa H_2. Solvent: water 5 mL. GC Yield.

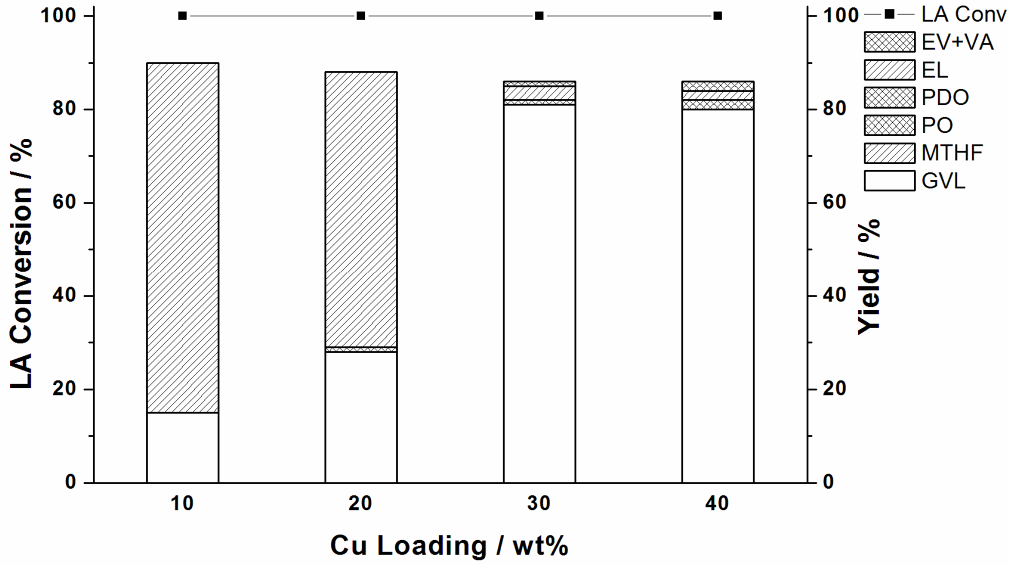

Fig S7. The effect of Cu loadings on the hydrogen conversion of LA in ethanol at 413 K. Reaction conditions: LA 0.25 g, Cu-WO_3(10%)/ZrO_2-CP-300 0.1 g, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield.

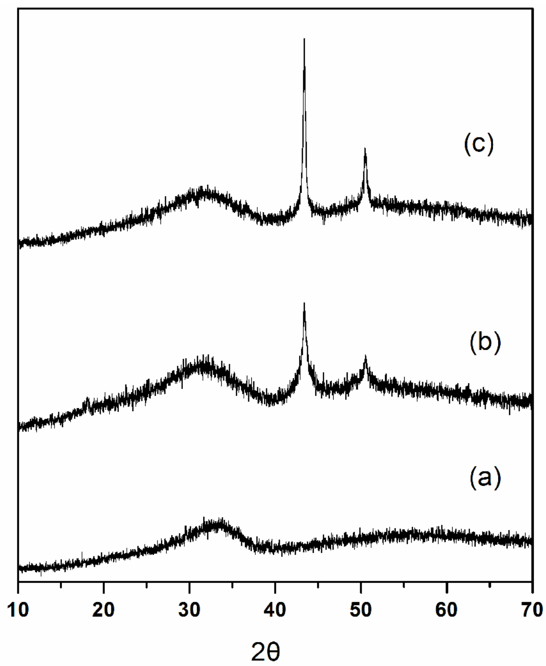

Fig S8. The XRD of Cu-WO_3(10%)/ZrO_2-CP-300 catalyst. [a] the fresh catalyst. [b] The used catalyst was obtained after reaction with ethanol as solvent. [c] The used catalyst was obtained after reaction with water as solvent.

Table S1. The leaching of Cu determined by ICP-AES.

$Cu(30\%)/ZrO_2$-OG-300	Cu (wt%)
Before reaction	30.5
After 5 runs	29.4

Reaction conditions: LA 0.25 g, $Cu(30\%)/ZrO_2$-OG-300 0.1 g, 6 h, 5 MPa H_2. Solvent: water 5 mL.

Table S2. The effect of temperature on the conversion of LA in ethanol.(the data of Fig. 1)

T/K	LA conversion/%	Yield/%					
		GVL	MTHF	PO	PDO	EL	EV+VA
373	35	9	0	0	0	23	1
393	54	25	0	0	0	18	0
413	100	81	0	0	1	3	1
433	100	89	0	0	0	2	0
453	100	90	0	0	3	1	4
473	100	94	0	0	2	0	0
493	100	81	1	0	1	1	6
513	100	71	1	0	1	1	8

Reaction conditions: LA 0.25 g, Cu (30%)-WO_3 (10%)/ ZrO_2-CP-300 0.1 g, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield.

Table S3. The effect of Cu loadings on the hydrogen conversion of LA. (the data of Fig. 2)

Cu Loading/%	LA Conversion/%	yield/%					
		GVL	MTHF	PO	PDO	EL	EV+VA
10	100	38	0	0	1	60	1
20	100	53	0	0	1	43	0
30	100	94	0	0	2	0	0
40	100	93	0	0	3	1	0

Reaction conditions: LA 0.25 g, Cu-WO_3(10%)/ZrO_2-CP-300 0.1 g, 473 K, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield.

Table S4. The effect of temperature on the conversion of LA in water. (the data of Fig. 3)

T/K	LA conversion /%	yield/%		
		GVL	MTHF	PDO
373	14	7	0	0
393	54	47	0	0
413	100	88	0	0
433	100	92	0	0
453	100	93	0	0
473	100	96	0	0
493	100	73	1	0
513	100	53	1	0

Reaction conditions: LA 0.25 g, Cu (30%)/ZrO_2-OG-300 0.1 g, 6 h, 5 MPa H_2. Solvent: water 5 mL. GC Yield.

Table S5. The leaching of Cu and W determined by ICP-AES

Catalyst	Solvent	Cu (wt%)	W (wt%)
Cu(30%)/WO3(10%)/ZrO_2-OG-300[a]	-	30.2	10.1
Cu(30%)/WO3(10%)/ZrO_2-OG-300[b]	ethanol	29.8	9.9
Cu(30%)/WO3(10%)/ZrO_2-OG-300[c]	water	25.3	8.6

Reaction conditions: LA 0.25 g, Cu(30%)/ZrO_2-OG-300 0.1 g, 6 h, 413 K, 5 MPa H_2. Solvent: 5 mL. [a] the fresh catalyst. [b] The used catalyst was obtained after reaction with ethanol as solvent. [c] The used catalyst was obtained after reaction with water as solvent.

Table S6. The effect of W loadings on the hydrogen conversion of LA in ethanol.

Entry	W	LA	yield/%					
	Loading/%	Conversion/%	GVL	MTHF	PO	PDO	EL	EV+VA
1	5	100	62	0	0	0	17	0
2	10	100	81	0	0	1	3	1
3	20	100	80	1	0	3	0	4

Reaction conditions: LA 0.25 g, Cu(30%)-WO_3/ZrO_2-CP-300 0.1 g, 413 K, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield.

Table S7. The study of pathway on the hydrogen conversion of substrate.[a]

Entry	Conversion/%	yield/%					
		GVL	MTHF	PO	PDO	EL	EV+VA
1[b]	100	95	0	0	1	1	0
2[c]	100	0	0	0	0	97	0
3[d]	2	0	0	0	0	0	0

Reaction conditions: [a] LA 0.25 g, Cu-WO_3(10%)/ZrO_2-CP-300 0.1 g, 473 K, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield. [b] the substrate is EL. [c] 5 MPa N_2. [d] 5 MPa N_2, solvent : water 5 mL.

Table S8. Physical properties of catalysts

Entry	Catalyst	BET Surface Area [m^2/g]	Pore Volume [cm^3/g] [a]	Average pore diameter [Å] [b]
1	Cu-WO3/ZrO2-CP-300	7.4	0.01	44.5
2	Cu-WO3/ZrO2-CP-600	21.3	0.06	82.1
3	Cu/ZrO2-OG-600	26.1	0.11	151.8
4	Cu/ZrO2-OG-300	60.7	0.13	76.3
5	Cu/ZSM-5	92.0	0.02	59.1

([a] BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameters; [b] BJH Adsorption average pore diameter.)