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ELECTRONIC SUPPORTING INFORMATION (ESI)

Conversion of biomass-derived levulinate esters to γ-valerolactone with robust CuNi bimetallic catalyst

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Materials.

Levulinate acid (LA), ethyl levulinate (EL), butyl levulinate (BL), methyl levulinate (ML), γ-valerolactone, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $ZrOCl_2 \cdot 8H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, 2-butyl alcohol, 2-propanol (2-PrOH), methanol (MeOH), ethanol (EtOH), and *tert*-butyl alcohol (*tert*- BuOH) were gained from Huaxin Co., Ltd (Baoding, China) and used as received without further purification.

Characterization

The size and morphology of the samples were observed using transmission electron microscopy (TEM) using a JEOL model JEM-2011IJHR) at 200 kV. The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu Kα radiation (40 kV, 150 mA) in the range $2\theta = 5^o$-80^o. The surface area, total pore volume and pore size distribution of the samples were measured at 77 K using nitrogen adsorption with V-Sorb 2800P volumetric adsorption equipment (Jinaipu, China). The metal loading in the materials was analyzed by a T. J. A. ICP-9000 type inductively coupled plasma atomic emission spectroscopy (ICP-AES) instrument. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope using a Mg Kα X-ray source for excitation. GC analyses were carried out on a Shimadzu GC-2014-C series gas chromatograph (Shimadzu, Janpan) equipped with a flame ionization detector (FID) and a split/splitless injector. All the separations were performed on a HP-5 capillary column (30 m × 0.25mm i.d. × 0.25 μm film thickness) (WondaCap5) was employed to identify all reaction products. Ammonia-Temperature Programmed Desorption (NH_3-TPD) and Aarbon dioxide-Temperature Programmed Desorption (CO_2-TPD) were analyzed by an Auto Chemical 2920 chemisorption analyzer.

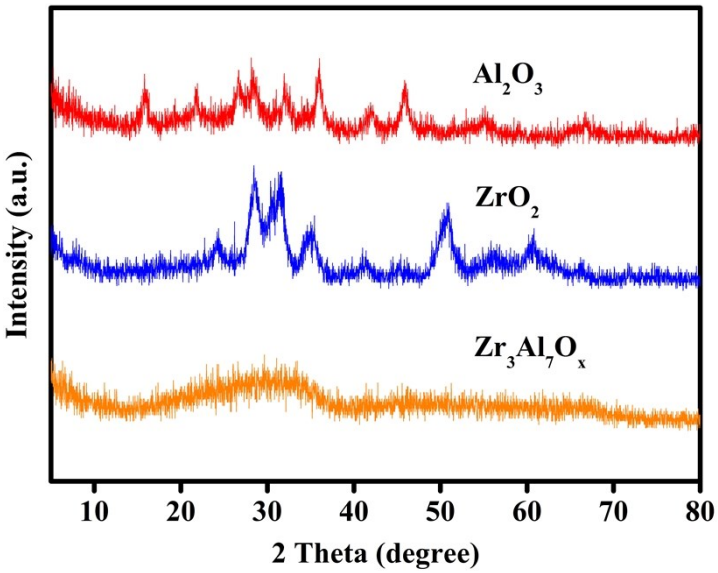

Fig. S1. The XRD images of different materials.

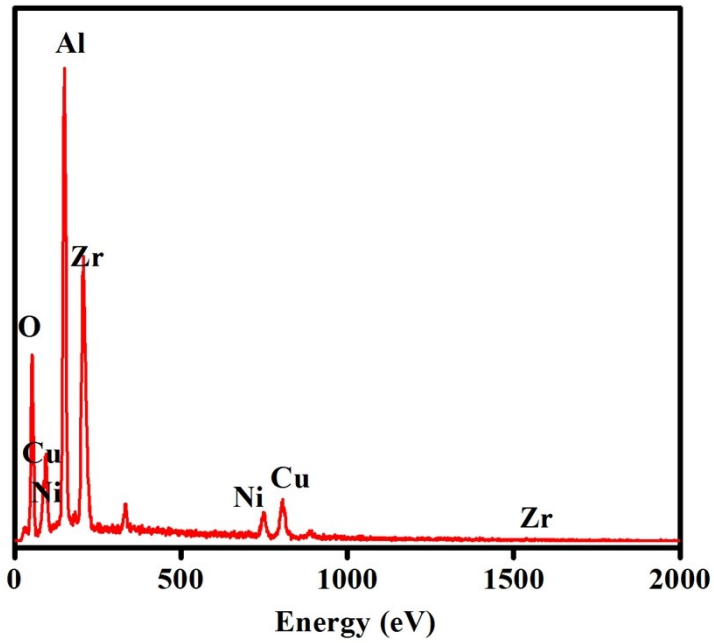

Fig. S2. The EDS elemental analysis of Cu_2Ni_1/Zr_3Al_7catalyst

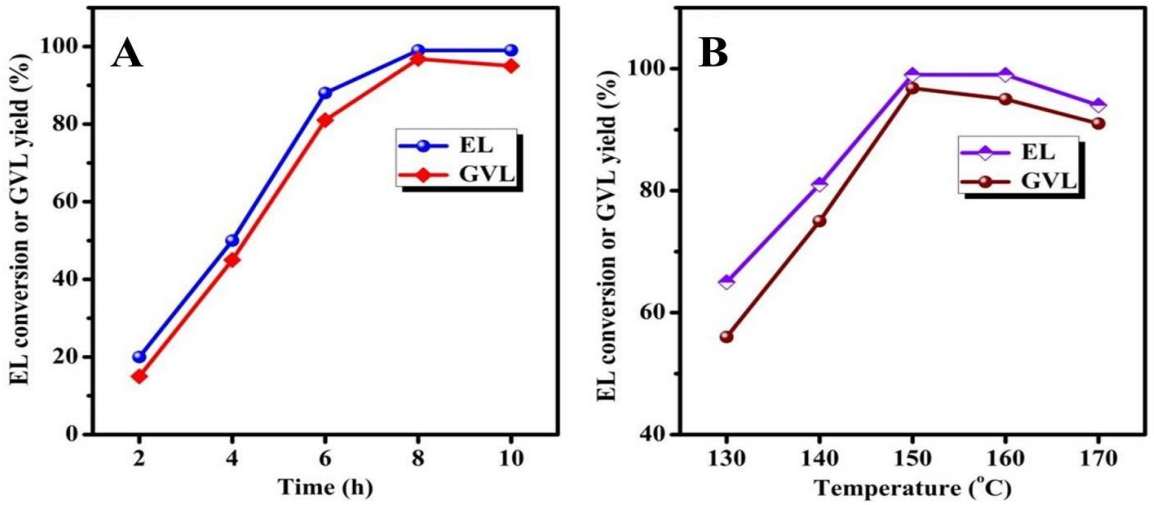

Fig. S3. Effect of reaction time (a) and reaction temperature (b) on the conversion of EL and yield of GVL. Reaction condition: EL 0.5 mmol, 50 mg $Cu_2Ni_1/Zr_3Al_7O_z$, 2-BuOH (3 mL); (a)150°C; (b)12 h.

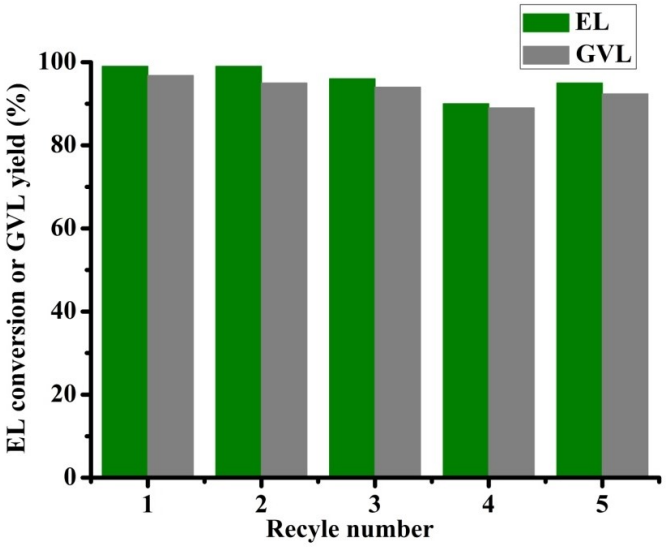

Fig. S4. Repetitiveness of $Cu_2Ni_1/Zr_3Al_7O_z$ for the CTH of EL to GVL.0.5 mmol, EL 3 mL, 2-BuOH, 50 mg $Cu_2Ni_1/Zr_3Al_7O_z$, T=150°C, t=8 h. The catalyst used for the fifth time was calcined at 400°C in H_2 flow.

Table S1 BET surface areas and acid strength of prepared catalyst.

Entry	Samples	BET (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)	<200ºC ($\mu molg^{-1}$)	300ºC-400ºC ($\mu molg^{-1}$)	Total acidity ($\mu molg^{-1}$)
1	Cu_2Ni_1/Al_2O_3	94	0.229	4.9	283.7	0	283.7
2	Cu_2Ni_1/ZrO_2	26	0.027	2.1	270.0	0	270.0
3	Cu_2Ni_1/Zr_7Al_3Oz	45	0.064	3.5	370.0	0	370.0
4	Cu_2Ni_1/Zr_5Al_5Oz	69	0.101	4.2	306.5	0	306.5
5	Cu_2Ni_1/Zr_3Al_7Oz	78	0.113	4.9	574.0	0	574.0
6	reused Cu_2Ni_1/Zr_3Al_7Oz	55	0.098	5.2	-	-	-
7	Zr_3Al_7Oz	110	0.214	5.3	-	-	-
8	Cu/Zr_3Al_7Oz	95	0.118	4.4	-	-	-
9	Ni/Zr_3Al_7Oz	81	0.104	4.6	-	-	-

Table S2 BET surface areas and base strength of prepared catalysts.

Entry	Sample	BET ($m^2\ g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)	Pore Size (nm)	<200ºC ($\mu molg^{-1}$)	300ºC-400ºC ($\mu molg^{-1}$)	Total Basicity ($\mu molg^{-1}$)
1	Cu_2Ni_1/Al_2O_3	95	0.229	4.7	268.9	0	268.9
2	Cu_2Ni_1/ZrO_2	26	0.027	0.97	0	53.7	53.7
3	Cu_2Ni_1/Zr_7Al_3Oz	45	45	0.064	24.1	46	70.1
4	Cu_2Ni_1/Al_5Zr_5Oz	69	69	0.101	30.5	0	30.5
5	Cu_2Ni_1/Zr_3Al_7Oz	78	0.113	4.9	615.8	0	615.8

Table S3 Various reported catalyst tested for the CTH toward GVL

Entry	Reactants	Catalysts	H donor	Temp (°C)	Time (h)	Conv (%)	Yield (%)	Ref
1	LA[a]	Ag-Ni/ZrO_2	FA	220	5	99	99	1
2	EL[b]	$Zr(OH)_4$	ethanol	200	1	93	95	2
3	LA	RuN/SiO_2	FA	150	12	92	89	3
4	LA	Ni_5Zr_5	2-propanol	200	3	96	94	4
5	ML[c]	ZrO_2/SBA-15 1.0 MpAr	2-propanol	150	6	>99	95	5
6	EL	Al_2O_3–ZrO_2	2-propanol	220	4	96	83	6
7	EL	10Cu-5Ni/Al_2O_3	2-BuOH	150	12	>99	97	7
8	EL	$Cu_2Ni_1/Zr_3Al_7O_x$	2-BuOH	150	8	>99	96.8	This work

[a] Levulinic acid, [b] Ethyl levulinate,[c] Methyl levulinate.

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