Electronic Supplementary Material (ESI) for Green Chemistry.
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Supporting information

Selective hydrogenation of levulinate esters to 1,4-pentanediol using a ternary skeletal CuAlZn

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1. Experimental

1.1 Experimental materials

CuAlZn alloy, Cu, CuO, NaOH, ethyl levulinate and other organic solvents were all purchased from Sinopharm Chemical Reagent (China). 1,4-pentanediol was obtained from Sigma-Aldrich Co., Ltd. Pd/C (5 wt%) was purchased from Aladdin Chemical Reagent. CuAl alloy, Raney Ni, Raney Co, Raney Fe were purchased from Dalian Tongyong Chemical Co., Ltd.

1.2 Catalyst preparation and characterization

CuAlZn alloy powder (80-100 mesh) obtained by milling was treated with 20 wt% NaOH aqueous solution. Leaching process was conducted in an ice bath under the temperature range from 5-10 ^{o}C with vigorous stirring. After the desired leaching time, the powder was washed with deionized water until the pH was neutral and stored in ethanol.

XRD analysis was conducted in LabX XRD-6100 (Shimadzu) using a CuKα radiation source, the scanning speed was 6^{o} min^{-1} and 2θ ranges from 10-80^{o}. The surface area of catalyst was measured from N_2 adsorption-desorption isotherms by using automated gas sorption analyzer (Autosorb-iQ-TPX, Quantachrome, USA) with BET (Brunauer–Emmett–Teller) method. The element composition of alloy was analyzed by ICP-AES (inductively coupled plasma atomic emission spectroscopy, ICP-PS3500DD, HITACHI) after the alloy catalysts were digested with concentrated hydrochloric acid and nitric acid at first.

1.3 Typical experiment and product analysis

All the experiments were conducted into a high pressure reactor with a 100 mL Teflon liner (PARR instrument company, USA). Desired amount of skeletal catalysts were taken out from ethanol and blow-dried with nitrogen gas. After feedstock, catalyst and solvent were loaded. The reactor was sealed and purged 5 times with hydrogen, and then desired hydrogen pressure was filled. After reaction, the reactor was cooled to room temperature. The liquid sample was collected, filtered with a 0.45 μm membrane and analyzed by GC-FID (gas chromatography with flame ionization detector, Agilent GC7890A), GC-MS (gas chromatography with mass spectrometer, Agilent GC7890A- MS5975C), which equipped with HP-Innowax column (30 m × 0.25 mm × 0.25 μm). The solid catalysts were recovered and washed with water and ethanol for several times, then kept into ethanol.

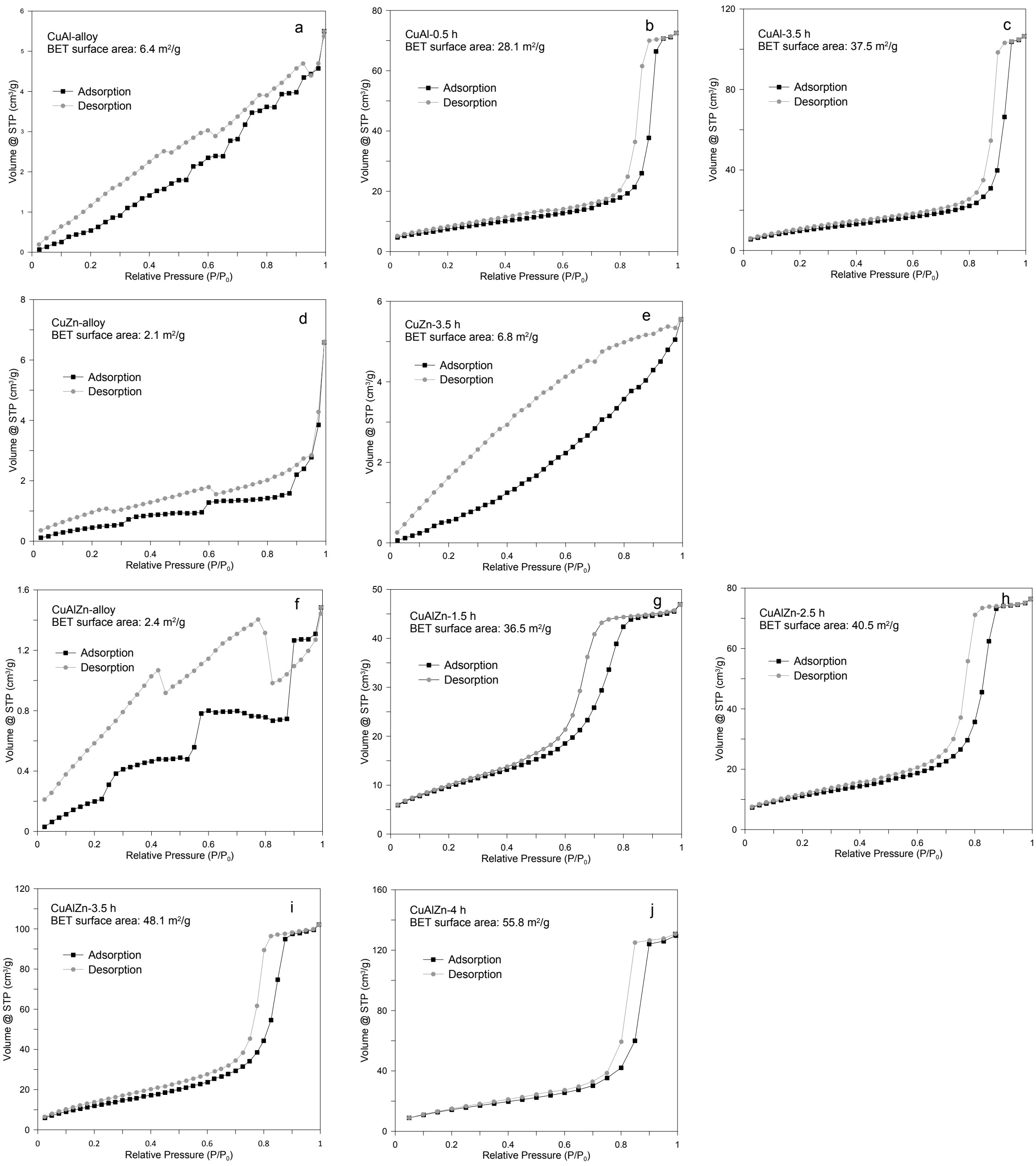

Figure SI-1. a) Nitrogen isotherms of CuAl alloy; b) Nitrogen isotherms of CuAl-0.5 h; c) Nitrogen isotherms of CuAl-3.5 h; d) Nitrogen isotherms of CuZn alloy; e) Nitrogen isotherms of CuZn-3.5 h; f) Nitrogen isotherms of CuAlZn alloy; g) Nitrogen isotherms of CuAlZn-1.5 h; h) Nitrogen isotherms of CuAlZn-2.5 h; i) Nitrogen isotherms of CuAlZn-3.5 h; j) Nitrogen isotherms of CuAlZn-4 h.

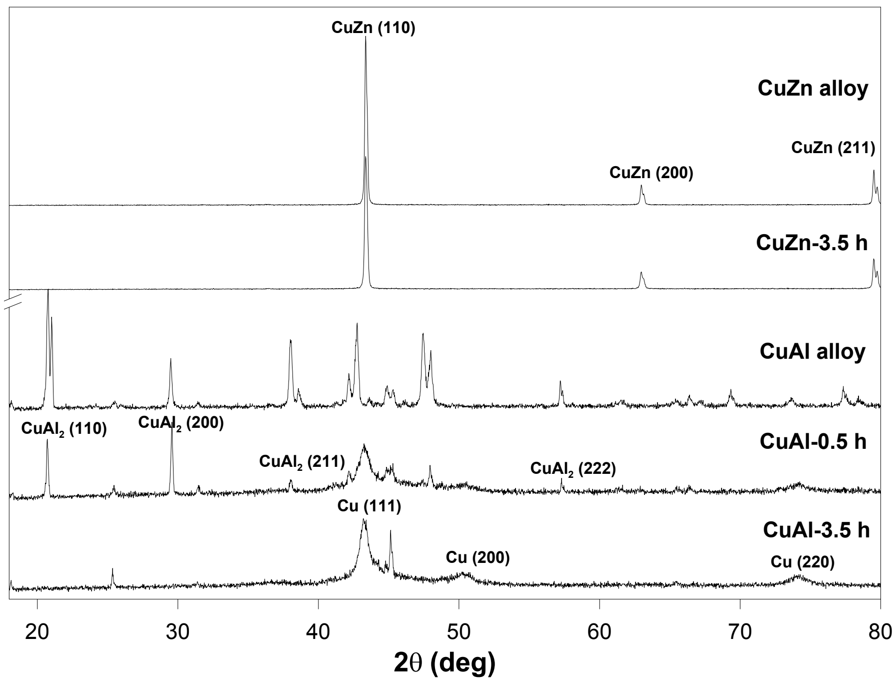

Figure SI-2. XRD patterns for leaching process of CuAl and CuZn alloys.

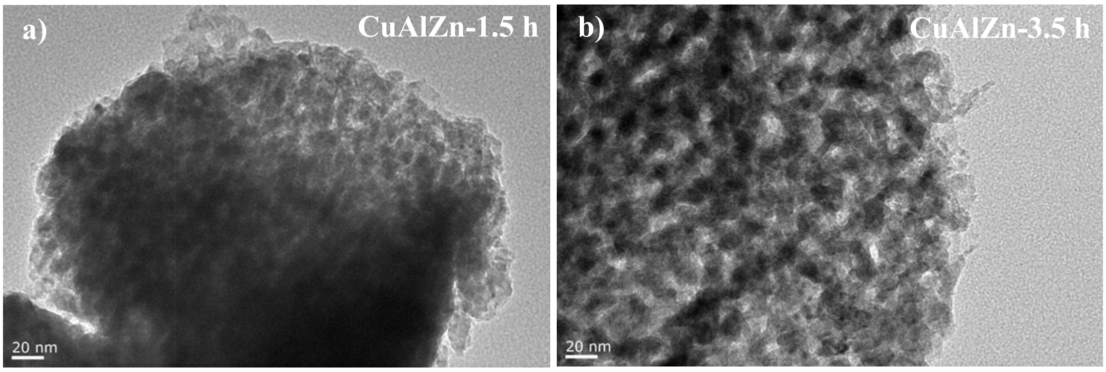

Figure SI-3. a) TEM image of CuAlZn-1.5 h; b) TEM image of CuAlZn-3.5 h.

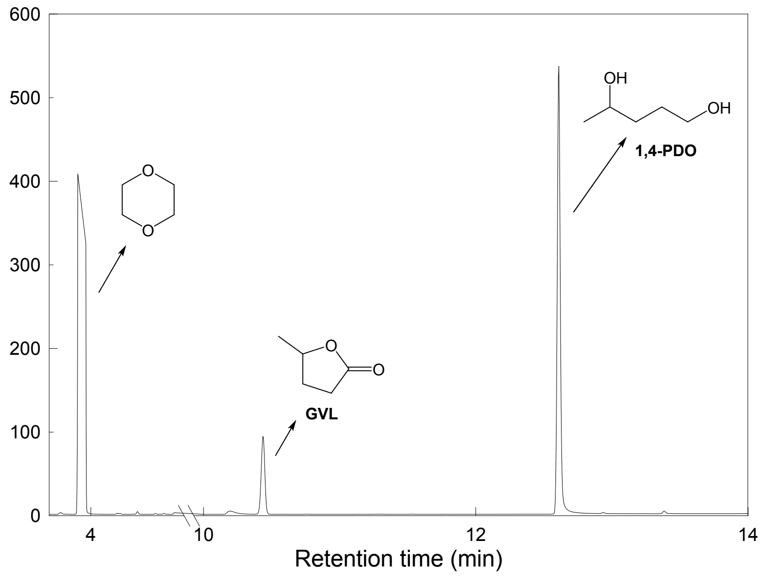

Figure SI-4. GC-FID for hydrogenation of EL (1 mmol EL, 50 mg CuAlZn-3.5 h, 10 mL dioxane, 160 °C, 4 MPa H_2, 10 h).

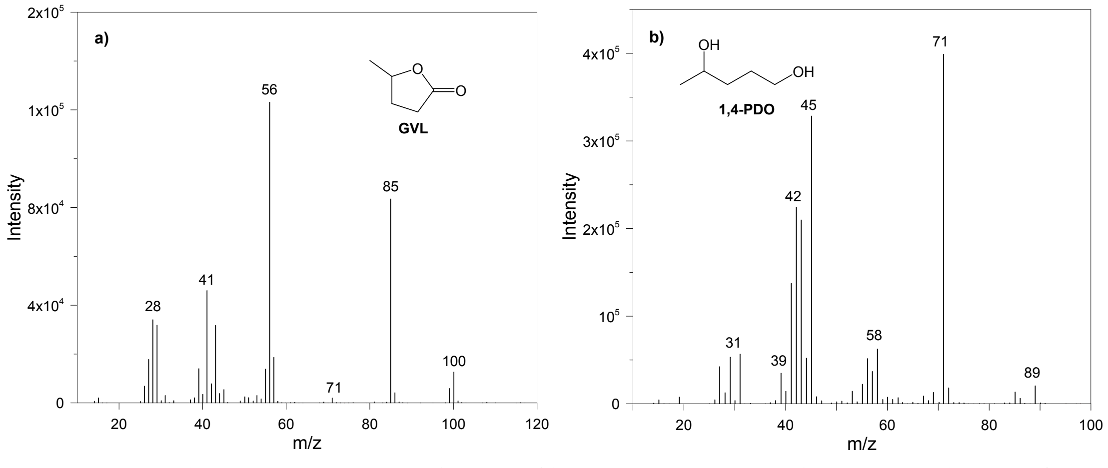

Figure SI-5. a) Mass spectrum of GVL; b) Mass spectrum of 1,4-PDO (1 mmol EL, 50 mg CuAlZn-3.5 h, 10 mL dioxane, 160 °C, 4 MPa H_2, 10 h).

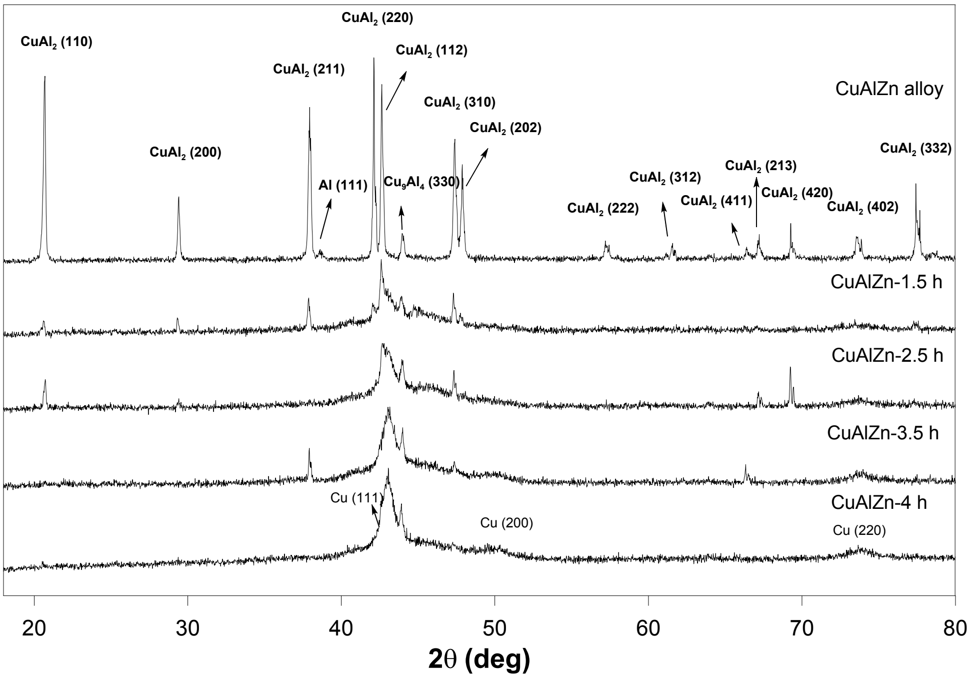

Figure SI-6. XRD patterns for leaching process of CuAlZn alloy.

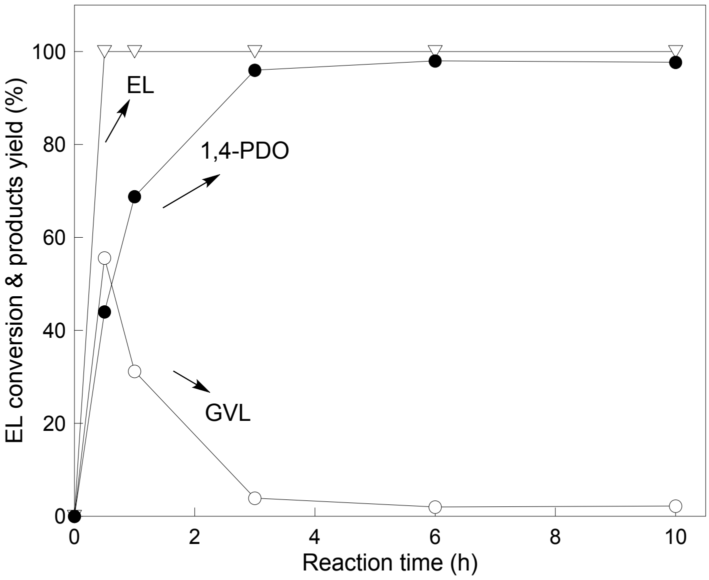

Figure SI-7. The time course of conversion of EL. (1 mmol EL, 70 mg CuAlZn-3.5 h, 10 mL 1,4-dioxane, 160 ^{o}C, 6 MPa H_2).

Table SI-1. Characteristic of skeletal copper-based catalysts.

Entry	Catalyst	BET surface area (m^2 g^{-1})	Elementary Composition Cu/Al/Zn (wt%)
1	CuAl-alloy	6.4	46.5 / 53.5 / 0
2	CuAl-0.5 h	28.1	77.5 / 22.5 / 0
3	CuAl-3.5 h	37.5	91.0 / 8.9 / 0
4	CuZn-alloy	2.1	53.0 / 0 / 47.0
5	CuZn-3.5 h	6.8	53.9 / 0 / 46.2
6	CuAlZn-alloy	2.4	52.3 / 46.0 / 1.6
7	CuAlZn-1.5 h	36.5	77.4 / 20.5 / 2.1
8	CuAlZn-2.5 h	40.5	83.8 / 13.9 / 2.2
9	CuAlZn-3.5 h	48.1	89.0 / 8.6 / 2.3
10	CuAlZn-4 h	55.8	91.0 / 7.0 / 2.0

Table SI-2. Hydrogenation of EL into 1,4-PDO with various catalysts[a].

Entry	Catalyst	Conv. (%)	Yield (%)	
			GVL	1,4-PDO
1	Cu	17.9	17.9	0
2	CuO	26.6	25.5	0
3	Raney Ni	92.0	84.2	3.8
4	Raney Co	100	97.2	2.4
5	Raney Fe	21.4	21.3	0
6	Pd/C	16.5	16.5	0

[a] Reaction condition: 1 mmol EL, 50 mg catalysts, 10 mL dioxane, 160 °C, 4 MPa H_2, 10 h.

Table SI-3. The effect of reaction temperature for hydrogenation of EL [a].

Entry	Temp (°C)	Conv. (%)	Yield (%)	
			GVL	1,4-PDO
1	120	100	75.4	24.5
2	160	100	2.2	97.7
3	180	100	4.5	95.5
4	200	100	8.2	91.5

[a] Reaction condition: 1 mmol EL, 70 mg CuAlZn-3.5 h, 10 mL 1,4-dioxane, 6 MPa H_2, 10 h.