Supporting information

CoZn-ZIF derived $ZnCo_2O_4$-framework for the synthesis of alcohols from glycerol

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Preparation of reference catalysts

Preparation of Co/ZnO-CP

$Co(NO_3)_2{\cdot}6H_2O$ (10 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (10 mmol) were dissolved in 200 mL distilled water under stirring, and this solution was referred as Solution A. Solution B was an aqueous of Na_2CO_3(250ml, 0.1 mol/L). Then solution B was added slowly to Solution A under vigorously stirring at room temperature. Then the suspension was filtrated and washed thoroughly with distilled water until the pH of effluent reached 7.0. Precipitate was then dried at 60 °C for 12 h, which was denoted as CoZn-CP, and calcinated at 400 °C in a flow of air for 3 h. Catalysts prepared according to this method were denoted as CoZnO-CP. At last, CoZnO-CP was further reduced in hydrogen flow (80 mL/min) at 450 °C for 1 h before the hydrogenolysis reaction, and the reduced catalyst was denoted as Co/ZnO-CP.

Preparation of Co/ZnO-IM

10 mmol $Co(NO_3)_2{\cdot}6H_2O$ was solved in small amount of water and added into 10 mmol ZnO. After ultrasonic processing for 30 min, the sample was dried at room temperature and grinded into powder which was denoted as CoZn-IM. Following calcination at 400 °C in a flow of air for 3 h, the prepared catalyst was denoted as CoZnO-IM. After hydrogen reduction (80 mL/min) at 450 °C for 1 h, the catalyst was denoted as Co/ZnO-IM.

Preparation of Co/ZnO-SF[1]

$Co(NO_3)_2·6H_2O$ (10 mmol) and $Zn(NO_3)_2·6H_2O$ (10 mmol) were mixed together in mortar, followed by the addition of NaOH (80 mmol) and Na_2CO_3 (25 mmol), and continued to grind for 15 min. Then, the mixture was sealed and heat to 120 °C for 24h. After that, the resulting powder was washed thoroughly with deionized water until the pH of effluent reached 7.0 and dried at 60 °C overnight which was denoted as CoZn-SF. Following calcination at 400 °C in a flow of air for 3h, the prepared catalyst was denoted as CoZnO-SF. At last, CuZnO-SF was further reduced in hydrogen flow (80 mL/min) at 450 °C for 1 h and the reduced catalyst was denoted as Co/ZnO-SF.

Appendix data

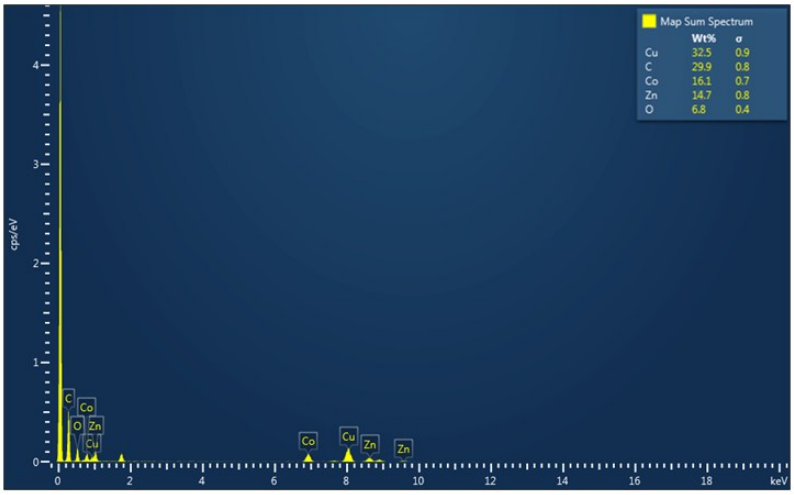

Fig. S1 The corresponding EDS spectra (of Fig. 4E).

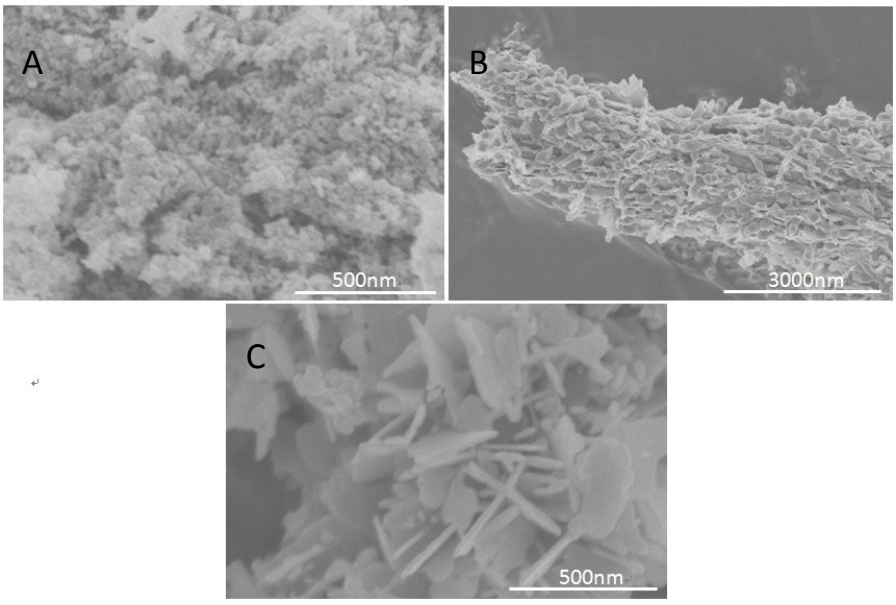

Fig. S2 SEM images of CoZnO-CP (A), CoZnO-IM (B) and CoZnO-SF (C).

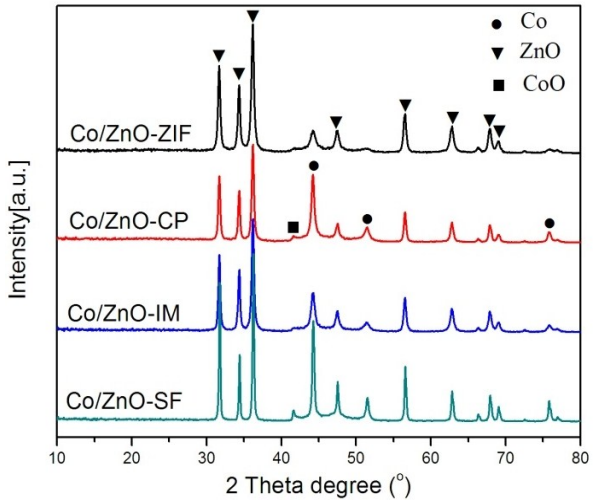

Fig. S3 The XRD patterns of Co/ZnO samples.

After reduction, all samples were consisted with Co and ZnO, which indicated cobalt ions could be reduced to Co metal under H_2 atmosphere at 450℃. There was a small peak at 42.4° which was belong to CoO (200) and it might be attributed to small amount of surface Co atoms were oxidized during XRD measurement.

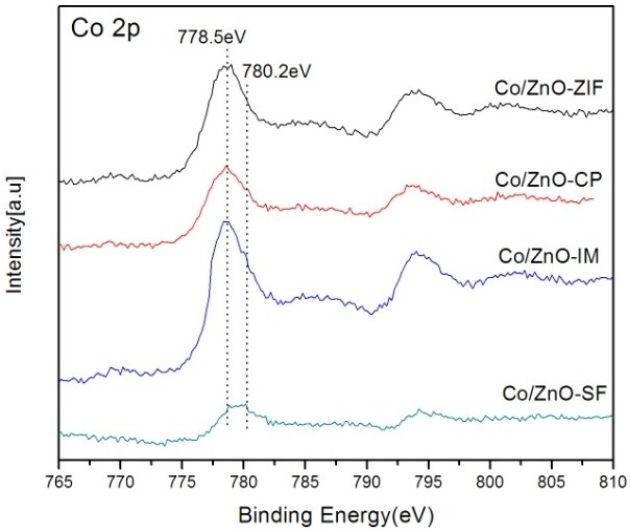

Fig. S4 The binding energy of Co2p in Co/ZnO samples.

After reduction, there were two peaks with band energy of 778.5[2] and 780.2 eV,[3] respectively. The former is readily assignable to metallic Co, and the latter was assigned to CoO which was generated from the oxidization of surface Co atoms during XPS measurement.

Table S1. Products distribution over different Co/ZnO with equivalent catalyst surface area.

Catalyst	Conversion	Production Selectivity in liquid phase (mol%)				Carbon
	(%)	1,2-PDO	Ethanol	PO	Others [a]	balance (%)[b]
Co/ZnO-ZIF	98.8	4.8	57.9	36.0	1.3	93.5
Co/ZnO-CP	97.2	17.9	43.4	34.1	4.6	94.4
Co/ZnO-IM	98.0	11.6	51.5	32.5	4.4	93.9
Co/ZnO-SF	92.5	42.9	29.5	16.5	11.1	96.2

Reaction conditions: catalyst surface area with ~9.77m^2; 2.0 MPa, 210 °C； 40 wt.% of glycerol aqueous solution 0.02 mL/min, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2h. [a] Including methanol, ethylene glycol, acrolein, acetol and acetaldehyde etc. [b] (All carbon atoms detected in liquid products)/(All carbon atoms in feed) × 100%.

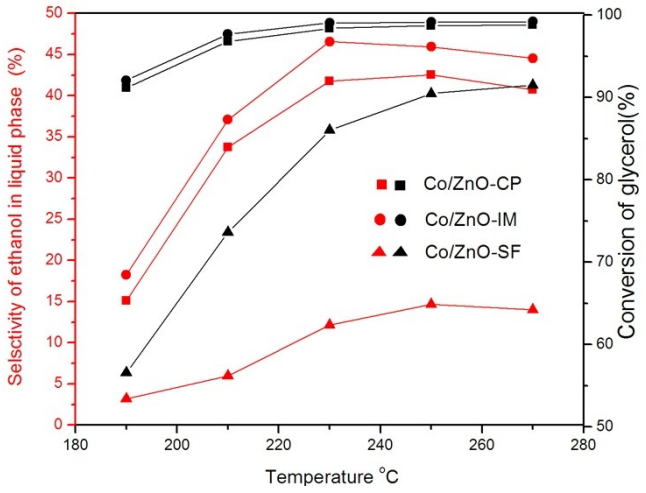

Fig. S5 Hydrogenolysis of glycerol at different temperature over Co/ZnO-CP, Co/ZnO-IM and Co/ZnO-SF. Reaction conditions: catalyst 0.10 g; 2.0 MPa; 40 wt.% of glycerol aqueous solution, 0.02 mL/min, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2h.

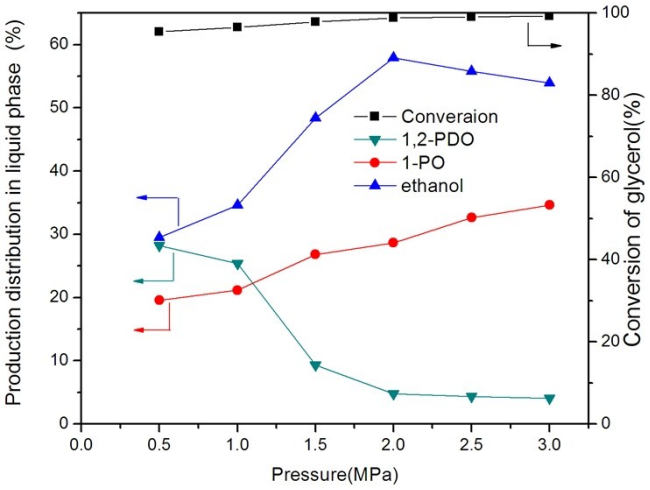

Fig. S6 Hydrogenolysis of glycerol under different **hydrogen pressure** over Co/ZnO-ZIF. Reaction conditions: catalyst 0.10 g; 210 °C; 40 wt.% of glycerol aqueous solution, 0.02 mL/min, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2h.

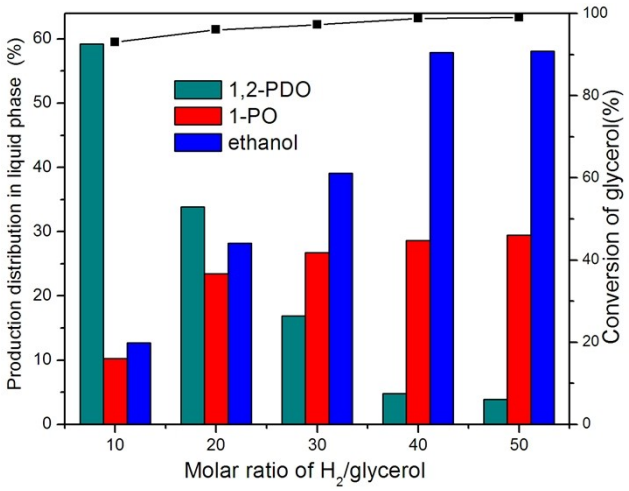

Fig. S7 Hydrogenolysis of glycerol with various molar ratio of H_2/glycerol in feed over Co/ZnO-ZIF. Reaction conditions: catalyst 0.10 g; 2 MPa, 210 °C; 40 wt.% of glycerol aqueous solution, 0.02 mL/min; data acquisition after steady operation for 2h.

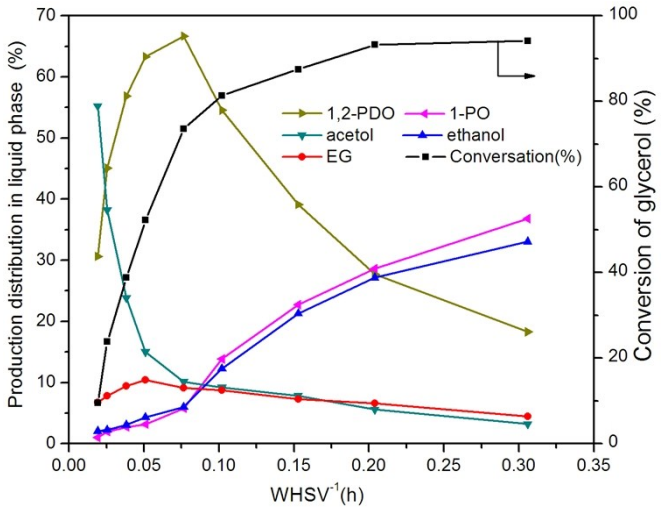

Fig. S8 Hydrogenolysis of glycerol over Co/ZnO-SF at various WHSV.

Reaction conditions: catalyst 0.10 g; 2.0 MPa; 210 °C; 40 wt.% of glycerol aqueous solution with the feed of 0.005-0.08 mL/min, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2 h.

Table S2 Product distribution over Co/ZnO-ZIF and Co/ZnO-SF under iso-conversion of glycerol.

Catalyst	$WHSV^{-1}$ (h)	Conversion (%)	Production Selectivity in liquid phase (mol%)				Carbon balance (%)[a]
			1,2-PDO	Ethanol	1-PO	acetol	
Co/ZnO-ZIF	0.015	24.9	39.1	1.3	0.4	47.8	98.9
	0.019	52.1	55.1	2.2	1.9	24.2	98.2
	0.038	88.5	47.0	20.3	11.6	2.7	97.7
Co/ZnO-SF	0.025	23.8	45.1	2.2	2.0	38.2	99.0
	0.051	52.3	63.3	4.3	3.2	15.0	98.3
	0.153	87.5	39.1	21.3	22.7	7.8	97.1

Reaction conditions: catalyst 0.10 g; 2.0 MPa, 210 °C; 40 wt.% of glycerol aqueous solution, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2h.

[a] (All carbon atoms detected in liquid products)/(All carbon atoms in feed) × 100%.

Table S3. Products distribution over different Co/ZnO catalysts under similar conversion of glycerol

Catalyst	Temperature (°C)	Conversion (%)	Production Selectivity in liquid phase (mol%)				Carbon balance (%)[b]
			1,2-PDO	Ethanol	PO	Others[a]	
Co/ZnO-ZIF	190	92.7	40.7	21.9	21.8	15.6	97.5
Co/ZnO-CP	190	91.2	53.9	15.1	16.4	14.6	98.4
Co/ZnO-IM	190	92.0	47.2	18.2	17.9	16.7	97.9
Co/ZnO-SF	270	91.5	42.9	14.0	16.6	26.5	98.2

Reaction conditions: catalyst 0.10 g; 2.0 MPa； 40 wt.% of glycerol aqueous solution 0.02 mL/min, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2h.

[a]Including methanol, ethylene glycol, acrolein, acetol and acetaldehyde etc. [b](All carbon atoms detected in liquid products)/(All carbon atoms in feed) × 100%.

Table S4. Products distribution of different raw materials over Co/ZnO-ZIF.

Raw material	Conversation (%)	Production Selectivity in liquid phase (mol%)					
		1-PO	2-PO	EG	EtOH	CH3OH	others[a]
1,2-PDO	87.3	29.7	8.0	2.1	56.0	1.2	3.0
EG	89.9				83.5	12.2	4.3
1-PO	3.3				70.9	23.7	5.4
2-PO	4.2				82.3	9.2	8.5
EtOH	6.6					90.1	9.9

Reaction conditions: catalyst, 0.10 g; 2.0 MPa, 210 °C, 40 wt.% of glycerol aqueous solution 0.02 mL/min, and H_2/glycerol = 40 (mol) in feed; data acquisition after steady operation for 2 h.

[a] Including acrolein, acetol and acetaldehyde etc.

References

1. W. Du, L. Zheng, X. Li, J. Fu, X. Lu, Z. Hou, *Appl. Clay. Sci.*, 2016, **123**, 166-172.
2. A.B. Mandale, S. Badrinarayanan, S.K. Date, A.P.B. Sinha, *J. Electron.Spectrosc.*,**1984**,33, 61-72.
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