

Support information for

**Selective conversion of furfural to cyclopentanone and
cyclopentanol by different preparation methods of Cu-Co
catalysts**

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1. Experimental

Catalyst characterization

X-ray power diffraction (XRD) patterns of Cu-Co-CP-500 and Cu-Co-OG-500 catalysts were obtained on X'pert (PANalytical) diffractometer with Ni-filtered Cu-K α radiation, at 40 kV and 40 mA. 2θ range was 20°~ 80°.

Transmission electron microscopy (TEM) microphotographs were operated on JEOL-2010 electron microscope at 200 kV. The samples were suspended in ethanol.

X-ray photoelectron spectra (XPS) data were obtained with a Thermo Scientific Escalab 250-X-ray photoelectron spectrometer which equipped a hemispherical electron analyzer and an Al K α X-ray source. All binding energies were referenced to C 1s line at 284.7 eV.

The content of Cu and Co was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo-Jarrell ASH-Atom Scan Advantage). The samples were dissolved with concentrated nitric acid and diluted with pure water.

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

2. Results

Table S1. Different catalysts for the hydrogenation conversion of CPO

Catalyst	C-CPO/% ^a	Yield/%				
		THFOL	FOL	2-CPEO	CPO ^b	CPL
5% Cu-Co-OG-500	98	0	0	0	2	88
5% Cu-Co-CP-500	39	0	0	0	61	38

(Reaction conditions: 0.2 g CPO, 50 mg catalyst, 10 mL H₂O, 443 K, 1 h, 2 MPa H₂, mole yield. [a] The conversion of CPO. [b] The proportion of residual CPO.)

Table S2. Monometallic Cu or Co as catalyst for the hydrogenation conversion of FFA

Catalyst	C-FFA/%	Yield/%				
		THFOL	FOL	2-CPEO	CPO	CPL
Cu ^a	53	0	3	13	3	0
Co ^b	100	0	0	0	51	25

(Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H₂O, 443 K, 1 h, 2 MPa H₂, mole yield. [a] Reduced CuO at 553 K for 2 h; [b] Reduced Co₃O₄ at 673 K for 2 h. ¹)

Table S3. Different additives and conditions for the hydrogenation conversion reaction

Entry	Catalyst	Additives	Conv./%	Yield/%				
				THFOL	FOL	2-CPEO	CPO	CPL
1	5% Cu-Co-OG-500 ^a	None.	99	0	-	0	5	64
2	5% Cu-Co-OG-300	10 mg H ₃ PO ₄	100	0	0	0	1	52
3	5% Cu-Co-OG-600	20 mg AcOH	100	0	0	0	14	46
4	5% Cu-Co-OG-300	15 mg NaOH	100	9	3	0	0	2
5	5% Cu-Co-OG-500 ^b	None.	15	-	0.3	0	0	0
6	None. ^c	None.	65	0	0	0	0	0
7	5% Cu-Co-OG-600 ^d	None.	82.5	0	3	21	31	1
8	5% Cu-Co-OG-600 ^e	None.	100	0	0	0	12	54
9	5% Cu-Co-OG-500 ^f	None.	100	0	3	0	16	46
10	5% Cu-Co-OG-600 ^g	None.	100	0	0	0	17	40
11	5% Cu-Co-OG-600 ^h	None.	100	0	0	0	48	7

(Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H₂O, 443 K, 1 h, 2 MPa H₂, mole yield. [a] Substrate was FOL; [b] Substrate was THFOL; [c] Without catalyst; [d] 10 mg catalyst; [e] 10 mg catalyst, 6h; [f] 40mg catalyst; [g] 493 K; [h] 523 K.)

Table S4. Physical properties of catalysts

Catalyst	BET Surface Area	Pore Volume	Average pore diameter
	[m ² /g]	[cm ³ /g] ^a	[Å] ^b
5% Cu-Co-CP-500	36.6	0.16	180
5% Cu-Co-OG-500	9.4	0.05	480.5

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

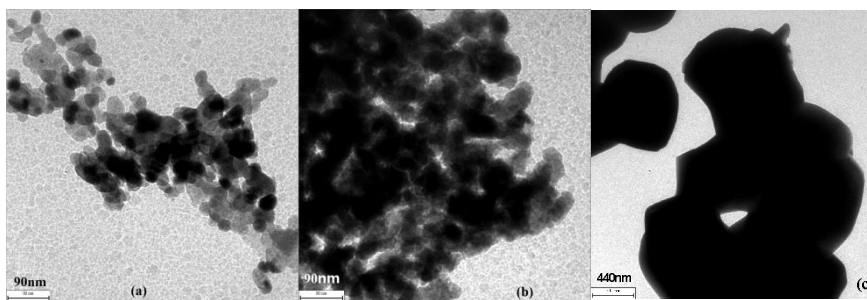


Fig S1. TEM microphotographs for (a. 5% Cu-Co-OG-500; b. 10% Cu-Co-OG-400; c. 5% Cu-Co-OG-800)

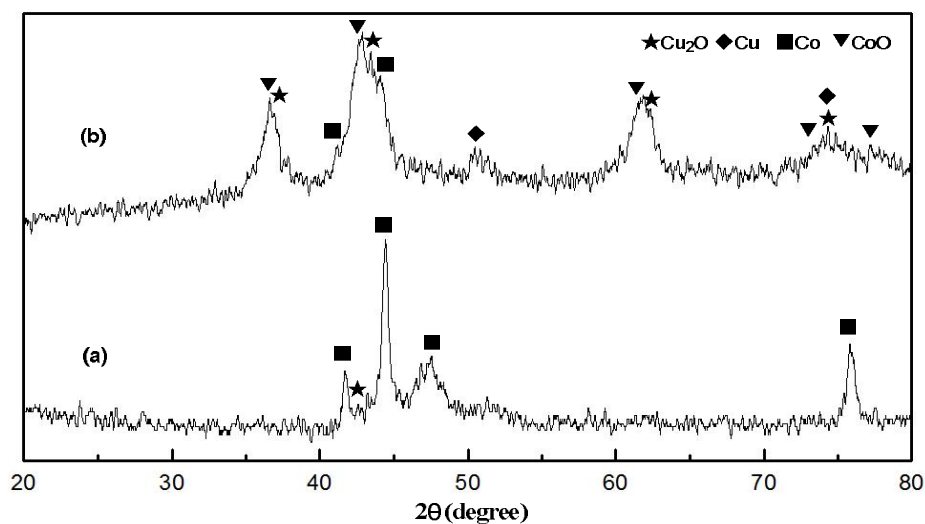


Fig S2. XRD diffraction peaks for (a. 5% Cu-Co-OG-500 reused five times; b. fresh 30% Cu-Co-OG-500)

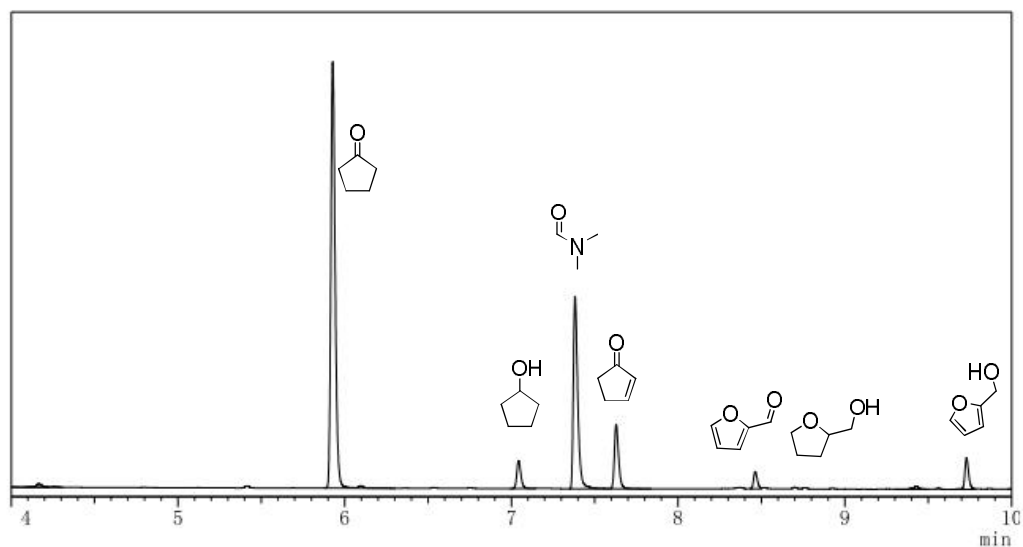


Fig S3. The GC peak position of major compounds during the hydrogenation conversion of FFA to CPO and CPL. N,N-dimethylformamide (DMF) was used as an internal standard substance. The GC retention time for major compounds: 5.9 min (CPO), 7.0 min (CPL), 7.4 min (DMF), 7.6 min (2-CPEO), 8.5 min (FFA), 8.7 min (THFOL), 9.7 min (FOL).

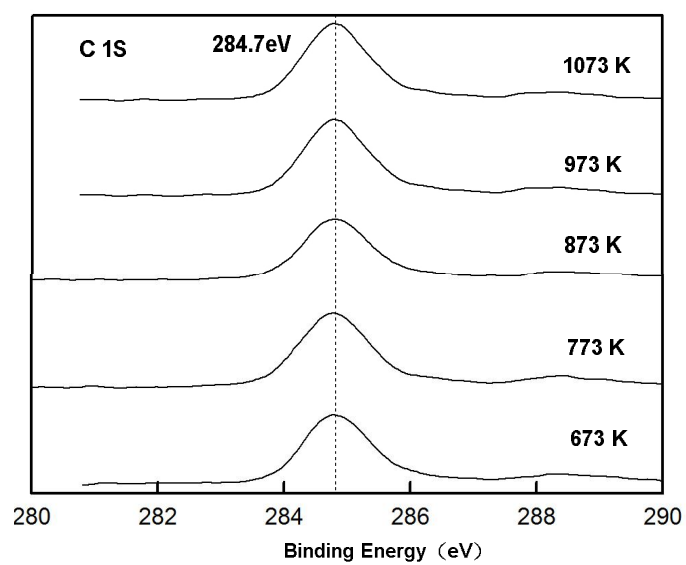


Fig S4. C1S XPS spectra for 5% Cu-Co-OG catalysts under different calcination temperature

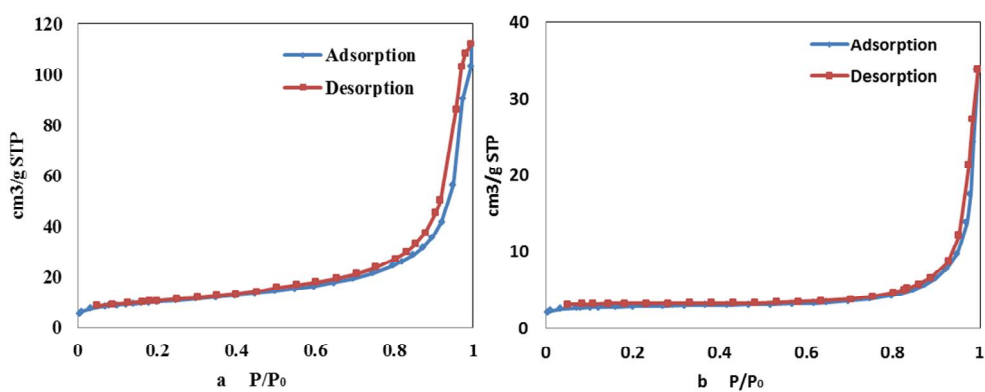


Fig S5. N₂ isotherms at 77 K for (a. 5% Cu-Co-CP-500; b. 5% Cu-Co-OG-500)



Fig S6. The reaction equipment

3. Discussion

The reused catalyst was washed with ethanol several times then used after dried.

The monometallic Cu and Co were prepared by sol-gel method (Table S2).

Table S3 showed the effects of different substrates and conditions for the hydrogenation of FFA. Results indicated that rearrangement reaction was unfavorable under acidic or alkaline conditions (Entry 2-4).

Under the reaction conditions, the reaction rate was very low and a few intermediates were obtained by using lower amounts of catalyst (Table S3 Entry 7, 9). The effect of prolonging the reaction time was similar to the increased amounts of catalyst (Table S3 Entry 8, 9). Based on the above results, we employed 25 wt. % of catalyst in the reaction.

Results showed that the high temperature could reduce catalyst activity and cause greater carbon-loss (Table S3 Entry 10, 11).

Fig. S2 (b) was the XRD spectra data for fresh 30% Cu-Co-OG-500 catalyst. The ratio of active phases was changed with the increased Cu loadings. The diffraction peaks of Cu_2O and Cu^0 increased and the diffraction peaks of Co^0 decreased. Reflecting on the product distribution, the yield of CPO increased and the yield of CPL decreased. It also illustrated that the different content of the two phases and the different interaction between Cu and Co had significant impact on the selectivity of products.

Due to the lower Cu loadings, the dispersion of copper was high and no obvious diffraction peaks of copper were observed for OG catalysts (Fig. 3b). The dispersion of copper was declined and the obvious diffraction peaks of copper were observed along with the increased Cu loadings (Fig. S2b). For CP catalysts, the diffraction peaks of copper were remarkable (Fig. 3a).

The increased binding energy of cobalt indicated that electrons were transferred from cobalt to copper (Fig. 7c).

Fig. S6 was the reaction equipment used for our rearrangement reactions.

The experiment at constant hydrogen pressure was operated as follows. In a typical experiment, we purged the autoclave with H_2 four times, and then pressurized with H_2 to a required pressure. But at constant hydrogen pressure, we purged the autoclave with H_2 four times and then closed the inlet valve and purge valve. Inside the autoclave is filled with hydrogen, and the pressure is atmospheric pressure. Then the following steps of constant hydrogen pressure conditions were the same to other experimental conditions.

The presence of cobalt showed that the reduction temperature of cobalt reduced because of the existence of copper.¹ This also indicated the strong interaction between Cu and Co.

4. References

1. H. C. Zhou, J. L. Song, H. L. Fan, B. B. Zhang, Y. Y. Yang, J. Y. Hu, Q. G. Zhu and B. X. Han, *Green Chem.*, 2014, **16**, 3870-3875.