Supporting Information

Efficient hydrogenolysis of biomass-derived furfuryl alcohol to 1,2- and 1,5-pentanediols over nonprecious Cu-Mg$_3$AlO$_{4.5}$ bifunctional catalyst

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1. Experimental details

1.1 Catalyst preparation and characterization

The CuO-Mg$_3$AlO$_x$ samples with Cu loadings from 2 to 30 wt% were prepared by co-precipitation method (CP). A mixed solution of Cu(NO$_3$)$_2$ (0.1 M), Mg(NO$_3$)$_2$ and Al(NO$_3$)$_3$ (Mg^{2+} : Al^{3+} = 3:1) and the solution of NaOH (8.0 M) were dropped concurrently into 100 mL Na$_2$CO$_3$ solution (Al^{3+} : CO$_3^{2-}$ = 2:1) and the pH and reaction temperature were maintained at ~10 and 303 K, respectively. After aging at 353 K for 24 h, the obtained precipitates were filtered and washed with deionized water until pH~7, and then, dried at 393 K overnight and calcined at 773 K for 3 h in air. Similarly, the Mg$_3$AlO$_x$ supported 10 wt% Ni, 10 wt% Co, 2 wt% Pt, 2 wt% Rh and 2 wt% Ru were also prepared by CP method mentioned above. The precursors for Pt, Rh and Ru were PtCl$_4$, RhCl$_3$·3H$_2$O and RuCl$_3$·xH$_2$O, respectively, and all purchased from Beijing HWRK Chem. Co., LTD. The calcined samples were marked as ωMO-LDO (M = Cu, Co, Ni, Ru, Pt, Rh), and the corresponding reduced catalysts were marked as ωM-LDO, where ω represents the nominal metal loading.

The 10Cu/LDO-IM catalyst was prepared by incipient wetness impregnation (IM) method of Mg$_3$AlO$_x$ (prepared by CP method mentioned above) with an aqueous solution containing the calculated amount of Cu(NO$_3$)$_2$ at room temperature, followed by drying at 393 K overnight and calcined at 773 K for 3 h in air.Meanwhile, 10Cu/LDO-PM catalyst was prepared by physical mixture of CuO (prepared by precipitating Cu(NO$_3$)$_2$ solution with NaOH and dried, calcined as above) and Mg$_3$AlO$_{4.5}$ by grinding for 30 min.

1.2 Catalysts characterization

The X-ray powder diffraction (XRD) was conducted on a PANalyticalX'pert Pro Diffractometer with nickel filtered Cu Kα radiation at a voltage and current of 40 kV and 30 mA, respectively. The measurements of BET surface area were performed on a Micromeritics TristarⅡ 3020 instrument at liquid nitrogen temperature. Prior to measurements, the samples were degassed at 573 K for 4 h. The scanning electron microscopic (SEM) investigations were carried out using a SU8020 electron microscope at 1 kV.

CO$_2$-TPD was carried out on a unit DAX-7000 instrument (Huasi Technology Co., Ltd, China)[1]. Before each CO$_2$-TPD measurement, the catalyst samples were pretreated at 473 K under He flow for 1 h and reduced at 623 K with 5% H$_2$-Ar for 2 h. Then CO$_2$ (99.99%) was adsorbed at 313 K for 1 h, after that, the adsorbed CO$_2$ was desorbed with He at a flow rate of 40 mL min^{-1} and a ramping rate of 10 K min^{-1} from 313 Kto 973 K. The desorbed CO$_2$ was continuously monitored by a thermal conductivity detector (TCD), and the TCD signals were calibrated by a given volume of CO$_2$.

The Cu dispersion was determined by dissociative N$_2$O chemisorptions–H$_2$-TPR reverse titration[2]. After pretreated in a He flow at 473 K, the samples (containing about 10 mg Cu) were reduced with 5% H$_2$-Ar at a flow rate of 40 mL min^{-1} and the temperature was increased from room temperature to 773 K at a ramping rate of 5 K min^{-1} (denoted as bulk TPR). After cooling to 323 K, the reduced samples were exposed to 5% N$_2$O-N$_2$ (40 mL min^{-1}) for 30 min. Afterwards, the resulting surface oxidized samples underwent the second TPR run at the ramping rate of 5 K min^{-1} from 323 to 623 K (denoted as surface TPR). The H$_2$ consumption was monitored by a thermal conductor detector (TCD). The specific exposed Cu surface area, average Cu particle size and dispersion were calculated by assuming 1.46×10^{19} Cu atoms per m^2 and a molar stoichiometry N$_2$O/Cu$_s$ = 0.5, where the symbol Cu$_s$ means the Cu atoms on the surface.

1.3 Catalytic test and product analysis

The FFA hydrogenolysis reaction was carried out in a stainless steel autoclave reactor (100 mL) at a stirring speed of 800 rpm. Prior to the reaction, the calcined Cu and noble metal samples were reduced at 623 K in 20% H$_2$-N$_2$ at a flow of 40 mL min^{-1}for 3 h, while the 10NiO-LDO and 10Co$_3$O$_4$-LDO samples were reduced at 723 K for 3 h. In a typical experiment, 40 g of 10 wt% FFA in ethanol solution and the reduced catalyst were added into the reactor. After flushing with H$_2$ for 3 times, the reactor was initially pressurized with H$_2$ to 6.0 MPa (after heating to reaction temperature, the pressure was raised to around 8.0 MPa and maintained during the reaction), and then heated to 413 K, which was kept steady during the reaction. The reactant and liquid products were analyzed by gas chromatograph (Agilent 7890A GC) with a PONA capillary column (50 m × 0.20mm × 0.50 μm). Products were also identified on an Agilent 7890A/5975C GC–MS with a HP-5MS column. The detected liquid products were 1,2-pentanediol (1,2-PeD), 1,5-pentanediol

(1,5-PeD), 2-methyl furan (2-MF), 2-methyl tetrahydrofuran, 1-pentanol, 2-pentanol, tetrahydrofurfuryl alcohol (THFA) and n-Pentane.

$$\text{Conversion (\%)} = \frac{\text{mol of reactant charged - mol of reactant left}}{\text{mol of reactant charged}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{mol of a product generated}}{\text{mol of reactant charged - mol of reactant left}} \times 100\%$$

2. **Complementary reaction and catalyst characterization data.**

Table S1. The detailed results for catalytic properties of various catalysts for the selective hydrogenolysis of FFA. [a]

| Entry | Catalysts | Conversion (%) | Selectivity (%) | | | | | |
			1,2-PeD	1,5-PeD	2-MF	1-Pentanol	THFA	Others [e]
1	2Cu-LDO [b]	40.3	35.2	23.5	3.3	9.8	3.6	24.6
2	5Cu-LDO	47.6	43.4	24.0	4.0	10.5	3.2	14.9
3	10Cu-LDO	63.1	50.0	30.5	3.8	11.5	3.9	0.3
4	10Cu-LDO [c]	>99	51.2	28.8	8.1	8.1	1.8	4.0
5	10Cu-LDO [c, d]	>99	45.2	25.5	8.9	7.5	3.1	9.8
6	20Cu-LDO	53.4	44.6	29.5	5.2	13.4	4.3	3.0
7	30Cu-LDO	31.9	32.1	21.4	9.8	18.4	4.8	13.6
8	2Pt-LDO [b]	28.5	23.1	10.8	0.2	1.6	63.0	1.3
9	2Rh-LDO [b]	>99	13.6	-	0.6	-	79.7	5.9
10	2Ru-LDO [b]	>99	0.1	0.1	0.7	-	95.7	3.3
11	10Ni-LDO	3.2	2.9	-	1.2	-	81.2	14.7
12	10Co-LDO	5.0	2.6	-	1.2	-	55.7	40.5
13	10Cu/LDO-IM	27.3	16.0	10.3	3.1	9.6	40.8	17.4
14	10Cu/LDO-PM	16.7	13.7	8.8	6.0	8.9	35.4	27.3
15	Pure Cu	7.9	2.1	1.4	3.1	0.2	6.4	85.8
16	LDO	N.R.	-	-	-	-	-	-
17	$CuCr_2O_4$	24.4	34.1	15.6	10.0	12.1	3.6	24.5

[a] Reaction conditions: 40 g 10 wt% FFA in ethanol solution, FFA : active metal = 20 :1 (wt%), reaction temperature 413 K, 6 MPa H_2, 8 h. PeD = pentanediol, THFA = tetrahydrofurfuryl alcohol.

[b] 40 g 2.5 wt% FFA in ethanol solution.

[c] 0.40 g Cu, reaction time: 24 h.

[d] 40 g 10 wt% FA in ethanol solution.

[e] Others including n-pentane, 2-methyl tetrahydrofuran, 2-pentanol and some undetermined products.
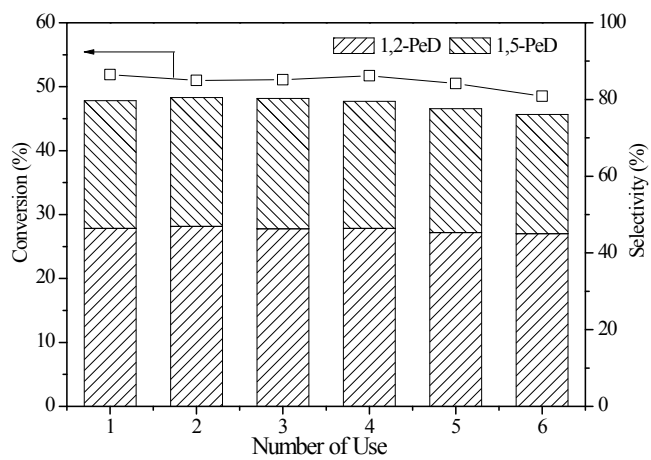
Fig. S1. Reusability in FFA hydrogenolysis of the 10Cu-LDO catalyst

Reaction conditions: 0.20 g Cu, 40 g 10 wt% FFA in ethanol solution, 413 K, 6 MPa H_2, 8 h.
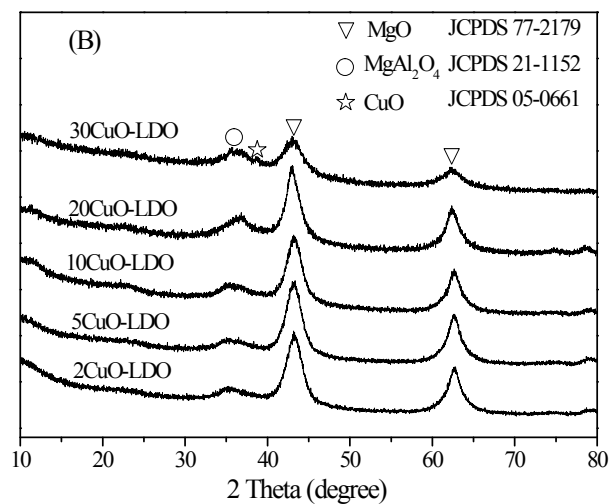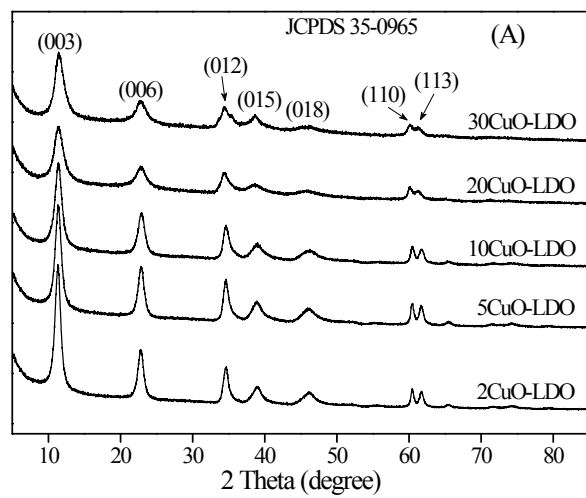
Fig. S2. XRD patterns of CuO-LDO samples before (A) and after (B) calcination with different Cu loadings.
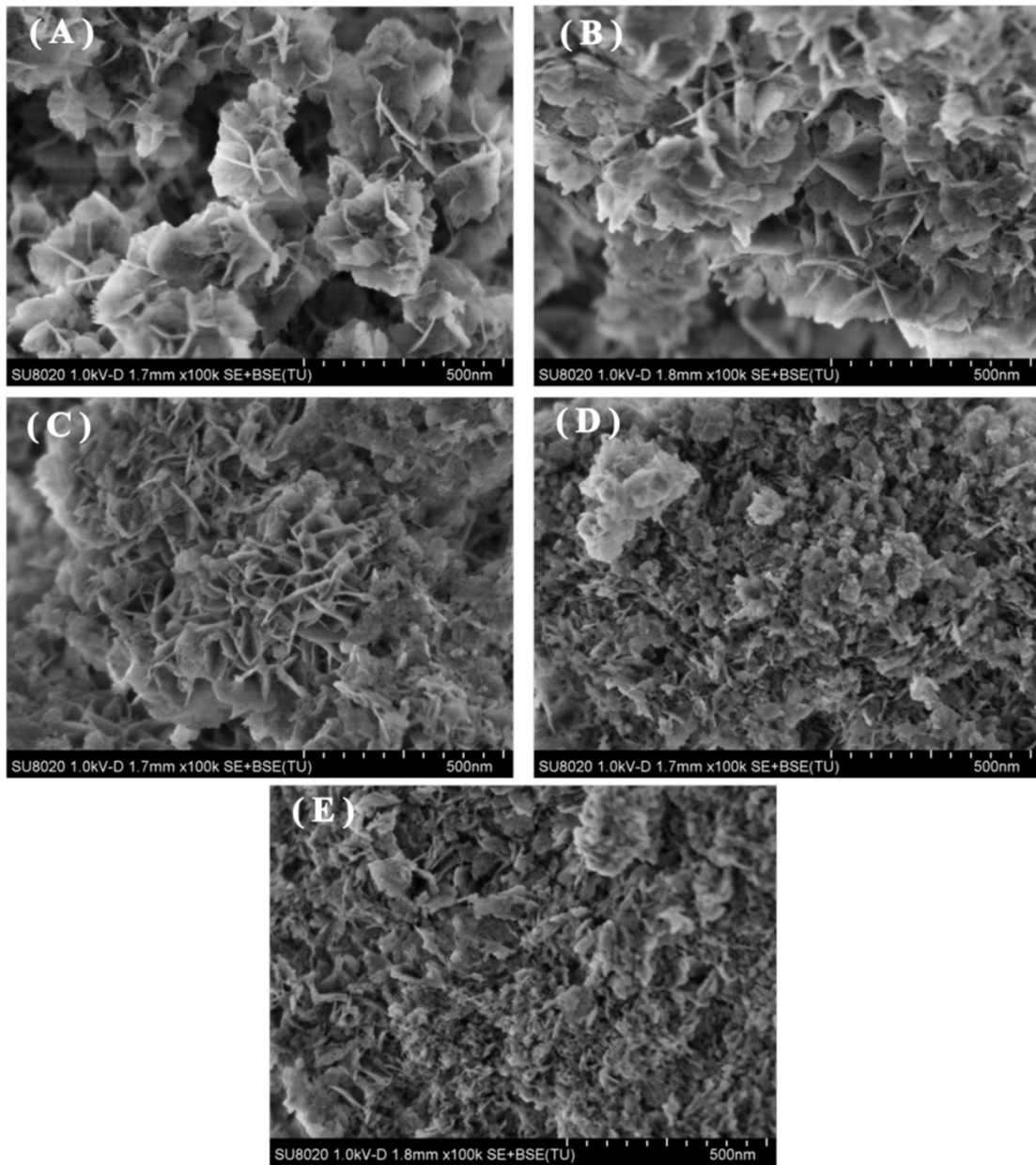
Fig. S3. The SEM photos of (A) 2CuO-LDO; (B) 5CuO-LDO; (C) 10CuO-LDO; (D) 20CuO-LDO; (E) 30CuO-LDO.

Table S2. The textural properties of CuO-LDO samples with different Cu loadings prepared by CP method and the reference of 10CuO/LDO-IM, 10CuO/LDO-PM, pure Cu and the LDO support.

Catalysts	Cu Content (wt%)[a]	S_{BET} (m^2 g^{-1})[b]	d_{pore} (nm)[b]	Dispersion (%)[c]	Cu surface area (m^2 g^{-1})[d]	Cu particle size (nm)[e]
2CuO-LDO	1.9	212.4	10.0	93.9	609.8	1.2
5CuO-LDO	4.8	191.2	10.2	75.1	487.8	1.5
10CuO-LDO	9.6	173.2	10.6	64.2	416.6	1.7
20CuO-LDO	19.4	158.9	10.7	45.1	292.7	2.4
30CuO-LDO	28.9	149.2	10.0	32.8	213.2	3.4
10CuO/LDO-IM	10.0	173.8	8.9	5.8	37.5	19.0
10CuO/LDO-PM	10.0	125.6	10.3	3.3	21.4	33.3
Pure Cu	100	20.1	19.2	2.8	18.2	39.3
LDO	-	152.3	10.2	-	-	-

[a] Cu content determined by ICP analysis.

[b] BET method.

[c] Cu dispersion obtained from dissociative N_2O adsorption.

[d] Cu^0 surface area obtained from dissociative N_2O adsorption.

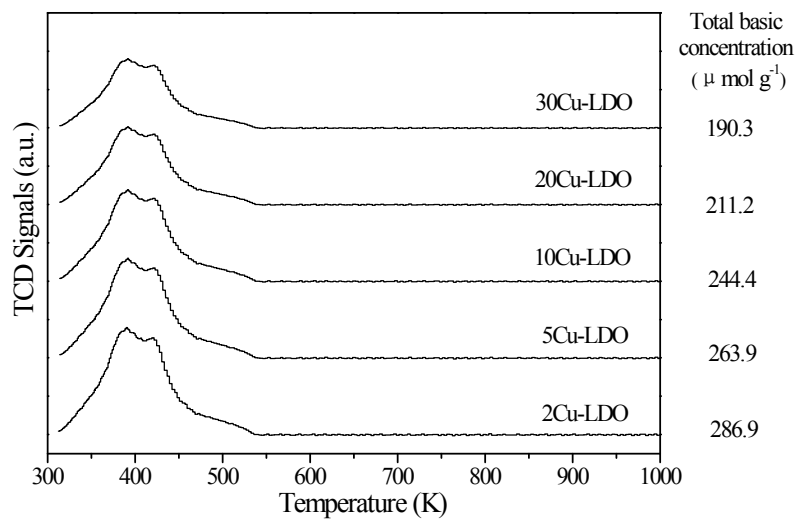[e] Mean Cu particle size calculated from dissociative N_2O adsorption.

Fig. S4. CO$_2$-TPD patterns of Cu-LDO catalysts with different Cu loadings.
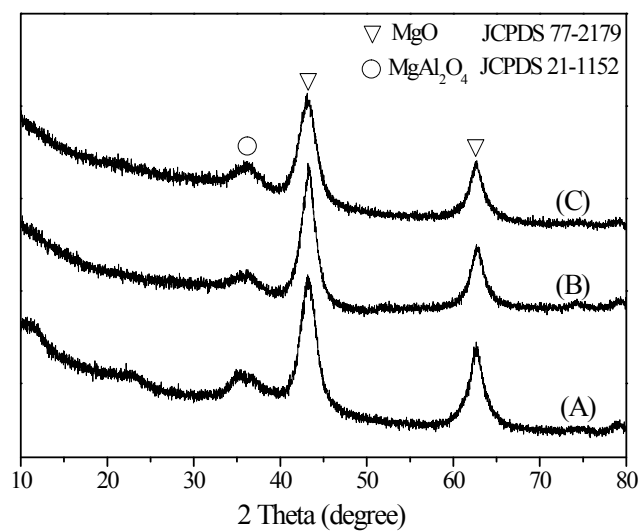
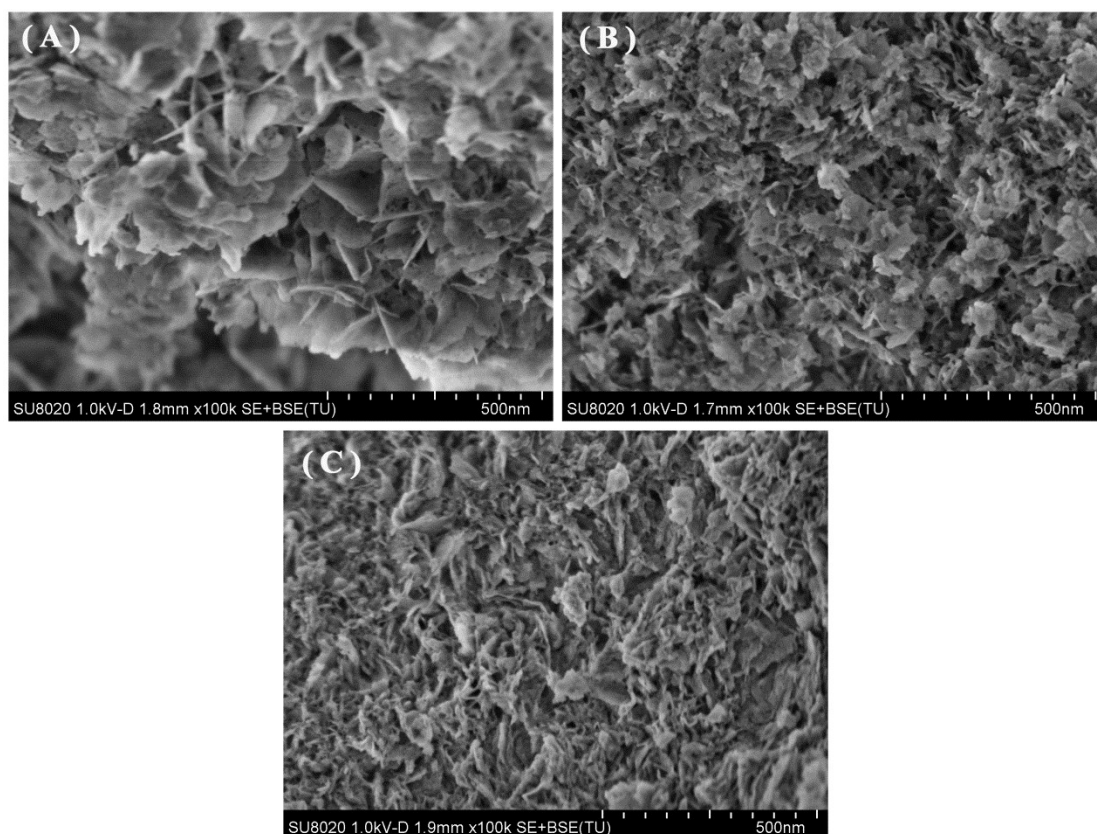Fig. S5. The XRD profiles of (A) calcined 10CuO-LDO; (B) fresh 10Cu-LDO; (C) used 10Cu-LDO after 6 runs.

Figure S6. The SEM photos of (A) calcined 10CuO-LDO; (B) fresh 10Cu-LDO; (C) used 10Cu-LDO after 6 runs.

Reference:

1. H. Liu, Z. Huang, Z. Han, K. Ding, H. Liu, C. Xia, J. Chen, *Green Chem.*, 2015, 17, 4281-4290.

2. (a) C. Van Der Grift, A. Wielers, B. Jogh, J. Van Beunum, M. De Boer, M. Versluijs-Helder, J. Geus, *J. Catal.*, 1991, **131**, 178; (b) H. Liu, Z. Huang, C. Xia, Y. Jia, J. Chen, H. Liu, *ChemCatChem*, 2014, **6**, 2918.