Tunable copper-catalyzed chemoselective hydrogenolysis of biomass-derived γ-valerolactone into 1,4-pentanediol or 2-methyltetrahydrofuran

Xian-Long Du, Qing-Yuan Bi, Yong-Mei Liu, Yong Cao,* He-Yong He and Kang-Nian Fan

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China.

Electronic Supplementary Information

1. Catalyst preparation

1.1 Preparation of CuO/ZrO_2-OG catalysts

A series of CuO/ZrO_2-OG catalysts (Cu loading ranging from 10 to 40 wt%) were prepared by an oxalate gel-coprecipitation method previously developed by our group.[S1] In brief, an alcoholic solution of 20% excess of oxalic acid was injected rapidly into an alcoholic solution of zirconium nitrate (0.1 M) containing the desired amount of copper nitrate at room temperature under vigorous stirring. After 4 h stirring at room temperature the resultant gel-like precipitates were separated by centrifuge followed by drying at 110 ^{o}C overnight. Then, calcination of the as-obtained materials was performed in a muffle oven at elevated temperatures ranging from 300 to 700 ^{o}C for 4 h.

1.2 Preparation of reference CuO/ZrO_2-CP catalyst

The CuO/ZrO_2-CP catalyst (Cu loading ~ 30 wt%) was prepared by a conventional carbonate co-precipitation method. Typically, a mixed aqueous solution of copper nitrate and zirconium nitrate (each 0.1 M) and a solution of sodium carbonate (0.1 M) were added slowly and simultaneously into 150 mL of deionized water at 80 ^{o}C with vigorous stirring. The pH was kept constant at 6.5–7.0. The precipitates were separated by centrifuge followed by drying at 110 ^{o}C overnight. Then, calcination of the as-obtained materials was performed in a muffle oven at temperature of 600 ^{o}C for 4 h.

1.3 Preparation of reference CuO/ZrO_2-IMP catalyst

The CuO/ZrO_2-IMP catalyst (Cu loading ~ 30 wt%) was prepared by an incipient wetness impregnation of the ZrO_2 support (prepared by aforementioned oxalate gel-precipitation followed by calcination in air at 600 ^{o}C), with aqueous solution of $Cu(NO_3)_2$ precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried at 100 ^{o}C overnight. Then, calcination of the as-obtained materials was performed in a muffle oven at temperature of 600 ^{o}C for 4 h.

1.4 Preparation of Ru/C, Ru/ZrO_2, Ru/ZnO and Ru/Al_2O_3 catalysts

5 wt% Ru/C, 5 wt% Ru/ZrO_2, 5 wt% Ru/ZnO and 5 wt% Ru/Al_2O_3 catalysts were prepared by incipient wetness impregnation of the supports (Actived carbon, ZrO_2, ZnO and Al_2O_3), with aqueous solution of $RuCl_3$ precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried at 100 ^{o}C for 5 h and then reduced in 5 vol.% H_2/Ar (flow rate 30

mL/min) at 450 °C for 2 h.

2. Catalyst characterization

2.1 X-ray diffraction (XRD) measurements

XRD analysis of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu Kα radiation with a scanning angle (2θ) of 20–80°, a scanning speed of 2°/min, and a voltage and current of 40 kV and 20 mA. The crystallite size of Cu corresponding to the broadening of each *hkl* line was determined from Scherrer equation: $d = k\lambda / \beta \cos\theta$, where $k = 0.89$, and $\lambda = 1.5406$ Å.

2.2 Temperature-programmed reduction (TPR)

TPR profiles were obtained on a homemade apparatus as described elsewhere.[S2] Approximate 50 mg of a freshly calcined catalyst was placed on top of glass wool in a quartz reactor. TPR experiments were carried out in 5 vol.% H_2/Ar flowing at 40 mL/min with a ramp rate of 10 °C/min to a final temperature of 500 °C. The H_2 consumption was monitored using a thermal conductivity detector (TCD). The water produced in TPR was trapped on a 5 Å molecular sieve.

2.3 X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg Kα (hv = 1253.6 eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C1s peak at 284.6 eV.

2.4 NH_3-Temperature-programmed desorption (NH_3-TPD)

NH_3-TPD characterization was conducted with a U-shape quartz reactor. The sample (100 mg) was pretreated at 300 °C for 2 h in 5 vol.% H_2/Ar and cooled to 25 °C in flowing Ar. At this temperature, sufficient pulses of NH_3 were injected until adsorption saturation, followed by purging with Ar (30 mL/min) at 100 °C for about 2 h. The temperature was then raised from 100 °C to 500 °C at a ramp rate of 10 °C/min to desorb NH_3. The desorbed NH_3 was monitored by a OmniStar mass spectrometer (QMS-200) with the signal of m/e = 16.

2.5 N_2O titration

The specific surface area of metallic copper and copper dispersion of the copper-zirconia catalysts were measured by N_2O titration.[S3] The N_2O chemisorption process consists of three sequential steps:

$$CuO + H_2 \rightarrow Cu + H_2O \qquad (1)$$

$$\text{hydrogen consumption} = A_1$$

$$2Cu + N_2O \rightarrow Cu_2O + N_2 \qquad (2)$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O \qquad (3)$$

$$\text{hydrogen consumption} = A_2$$

Step 1 represents reduction of CuO in the catalyst. In this step, a flow of 5 vol.% H_2/Ar (30 mL/min) was used as the reducing agent, and the temperature was raised from room temperature to 500 °C with a heating rate of 10 °C /min. Step 2 represents oxidation of surface Cu to Cu_2O by N_2O, which is a well-known method to evaluate the dispersion and crystallite size of Cu catalysts.[S4] This step was initiated after the reduced catalyst was cooled to 60 °C in He (30 mL/min) and purged with He for 30 min. Then, pure N_2O (40 mL/min) was introduced to the catalyst at 60 ^{o}C for 0.5 h. Subsequently, the catalyst was purged with He (30 mL/min) for 0.5 h to remove the residual N_2O. Step 3 represents reduction of Cu_2O surface species. In this step, a flow of 5 vol.% H_2/Ar (30 mL/min) was also used as the reducing agent, and the temperature was raised from room temperature to 500 ^{o}C with a heating rate of 10 ^{o}C /min. The dispersion (D) of Cu, was calculated as follows:

$$D = \frac{2A_2}{A_1} \times 100\%$$

which has extensively been used in literature.[S3] The specific area of metallic copper was calculated from the amount of H_2 consumption (A_2) with 1.46×10^{19} copper atoms per m^2.[S5]

3. Catalytic reaction

3.1 Hydrogenolysis of GVL

The hydrogenolysis of GVL was performed in a 50-mL high pressure Parr reactor. Prior to the reaction, the as-synthesized Cu-based catalyst was activated under 5 vol.% H_2/Ar at 300 ^{o}C for 2 h. The mixture of GVL (5 mmol) and the reduced catalyst (0.1 g, 80-100 mesh) were added into the autoclave pre-charged with ethanol or *n*-butanol (10 mL). After the introduction of H_2 with a certain pressure (6 MPa at room temperature), the reaction was started by heating the mixture to a desired temperature at a stirring speed of 800 rmp. The liquid products were analyzed by a gas chromatograph (Shimadzu GC-17A) equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and FID detector. The identification of the products was performed by using a GC-MS spectrometer.

3.2 Recovery and reuse of Cu/ZrO_2-OG catalyst

First, 0.3 g fresh Cu/ZrO_2-OG catalyst (Cu loading ~ 30 wt%) was used in a mixture containing 15 mmol GVL and 30 mL ethanol in 150 mL high pressure reactor. After the introduction of H_2 with a certain pressure (6 MPa at room temperature), the reaction was started by heating the mixture to 200 ^{o}C at a stirring speed of 800 rmp. After finishing the reaction, the catalyst was recovered, filtered and washed three times with ethanol. Then, they are dried under vacuum at room temperature for 12 h followed by reduction under 5 vol.% H_2/Ar to obtain the 1st re-use catalyst. Second, 0.2 g 1st re-use catalyst was used in a mixture containing 10 mmol GVL and 20 mL ethanol in 100 mL high pressure reactor. Repeat the recovery process to get the 2nd re-use bath. Then, 0.1 g 2nd re-use catalyst was used in a mixture containing 5 mmol GVL and 10 mL ethanol in 50 mL high pressure reactor. After three times (using the 2nd re-used catalyst for the third reaction), the Cu/ZrO_2-OG catalyst still remain highly active for production of 1,4-PDO (Table 1, entry 5). Moreover, XRD and XPS results show that no obvious changes in the mean diameters of the Cu nanoparticles and in the metallic state of Cu, respectively, after three successive runs.

Table S1 Physicochemical properties of Cu/ZrO_2 calcined at 600 °C with different Cu loadings and preparation methods.

Sample	Calcination temperature (°C)	Cu loading (%)	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	S_{Cu} [a] (m^2/g_{cat})	D_{Cu} (%)	d_{Cu} [b] (nm)	d_{ZrO2} [c] (nm)
Cu/ZrO_2-OG	600	10	24	0.11	5.4	38	-	T17.1
Cu/ZrO_2-OG	600	20	27	0.13	9.6	34	14.3	T16.4
Cu/ZrO_2-OG	600	30	30	0.18	13.5	32	15.2	T14.9
Cu/ZrO_2-OG	600	40	28	0.19	11.6	20	21.3	T15.6
Cu/ZrO_2-OG	700	30	7	0.10	10.3	24	27.8	M25.4/T26.5
Cu/ZrO_2-OG	500	30	37	0.18	12.5	29	14.6	T13.9
Cu/ZrO_2-OG	400	30	45	0.16	11.8	28	13.7	-
Cu/ZrO_2-OG	300	30	64	0.16	10.3	24	12.4	-
Cu/ZrO_2-CP	600	30	21	0.10	5.1	12	45.1	T15.6
Cu/ZrO_2-IMP	600	30	13	0.08	1.0	3	80.6	M17.5/T17.7

[a] Cu metal surface area determined by N_2O titration method. [b] Estimated by Scherrer equation from the diffraction peaks of Cu in the XRD patterns. [c] Average crystal size obtained with the Scherrer equation by using the $(\bar{1}11)$ diffraction ($2\theta = 28.4^o$) for monoclinic and the (111) diffraction ($2\theta = 30.3^o$) for tetragonal crystals; M and T represent the monoclinic and tetragonal phase, respectively.

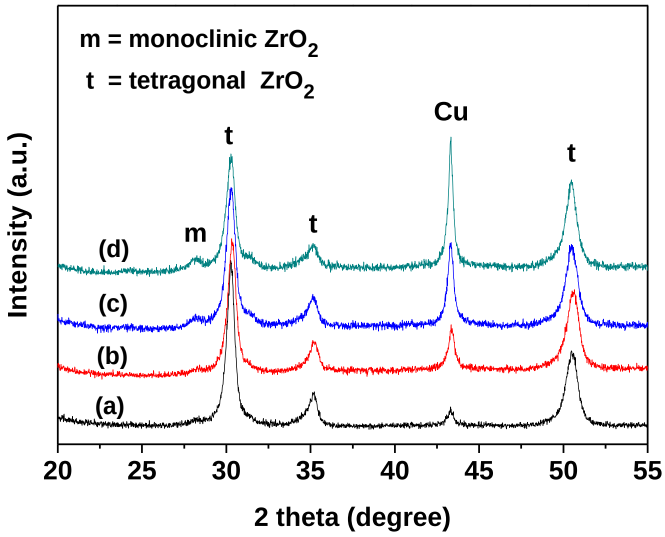

Fig. S1 XRD patterns of various reduced form of Cu/ZrO_2-OG catalysts obtained by calcination at 600 °C: (a) 10 wt% Cu/ZrO_2-OG, (b) 20 wt% Cu/ZrO_2-OG, (c) 30 wt% Cu/ZrO_2-OG, (d) 40 wt% Cu/ZrO_2-OG. (Sample pre-reduction procedure: activation in a 5 vol.% H_2/Ar stream at 300 °C for 2 h.)

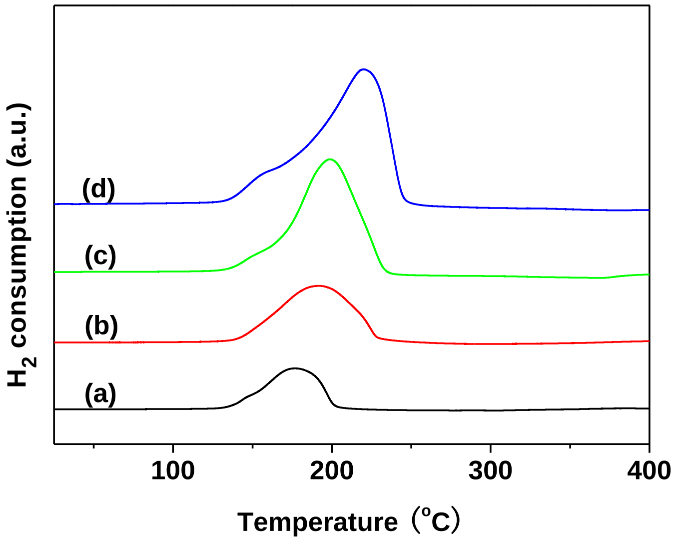

Fig. S2 TPR profiles of various 600 °C-calcination derived CuO/ZrO_2-OG catalysts with different Cu loadings: (a) 10 wt% Cu/ZrO_2-OG, (b) 20 wt% Cu/ZrO_2-OG, (c) 30 wt% Cu/ZrO_2-OG, (d) 40 wt% Cu/ZrO_2-OG.

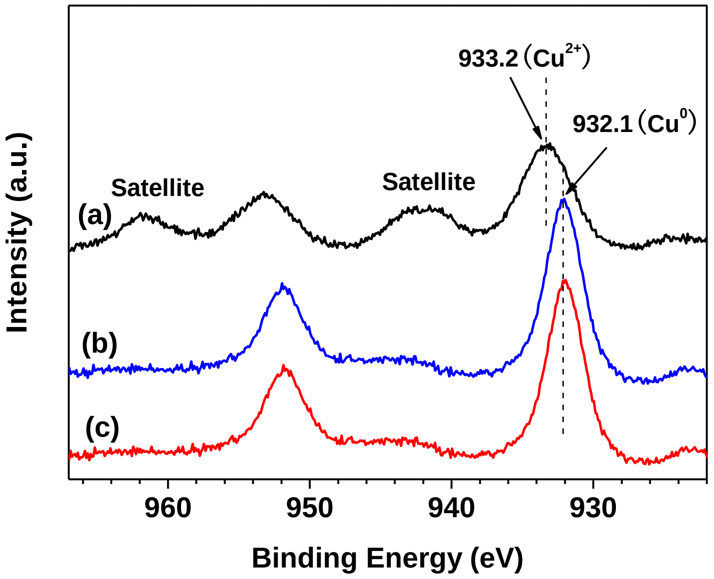

Fig. S3 XPS results of various 30 wt% Cu/ZrO_2-OG samples: (a) oxide precursor obtained by calcination at 600 °C; (b) reduced form of sample (a) obtained by pre-reduction at 300 °C in 5% H_2/Ar for 2 h; (c) after three runs of sample (b) under reaction conditions as described in Table 1, entry 5.

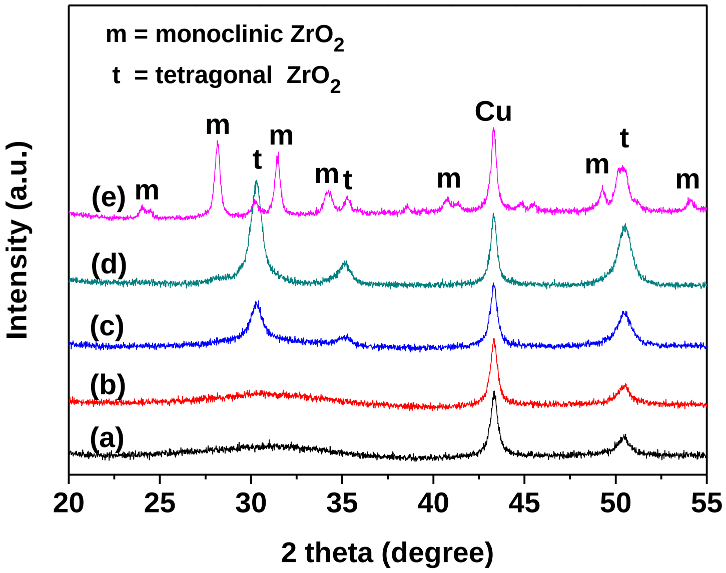

Fig. S4 XRD patterns of different reduced form of 30 wt% CuO/ZrO_2-OG catalysts obtained by calcination in air at various temperatures: (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C.

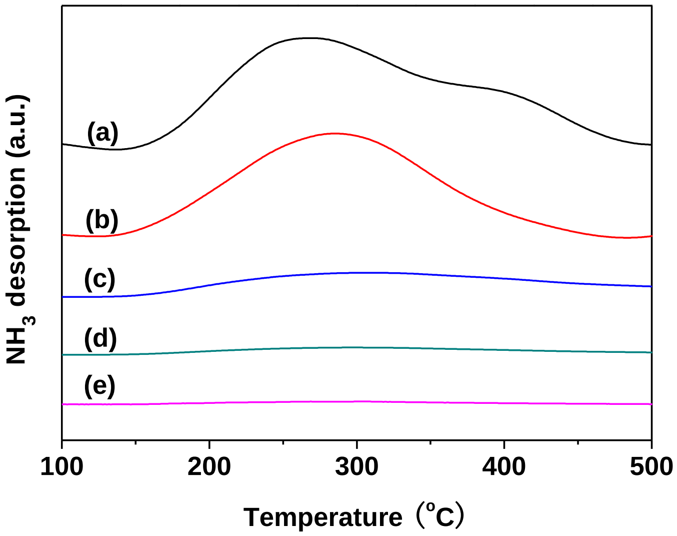

Fig. S5 NH_3-TPD profiles of various 30 wt% Cu/ZrO_2-OG catalysts obtained by different calcination at temperatures of: (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C.

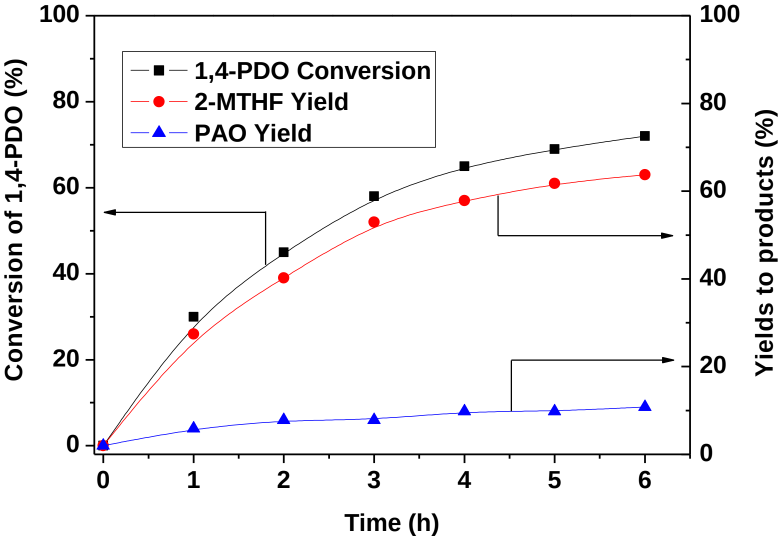

Fig. S6 Time course of the conversion of 1,4-PDO catalyzed by Cu/ZrO_2-OG obtained by 400 °C-calcination. Reaction conditions: 1,4-PDO (5 mmol), catalyst (0.1 g), ethanol (10 mL), P (H_2) = 6 MPa, temperature (240 °C). Note that PAO was produced from over hydrogenation of 1,4-PDO.

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