

Supporting information for

**The Rise of Calcination Temperature Enhances the Performance
of Cu Catalysts: Contributions of Support**

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S1 Experimental details

S1.1 Materials

The chemicals (copper nitrate, zirconium nitrate, NH_4HCO_3) were purchased from Sino-Pharm Chemical Reagent Co., Ltd.. The acidic silica sol was purchased from Qingdao Ocean Chemical Reagent Co., Ltd.. All the chemicals were used as received without further purification.

S1.2 Preparation

The catalysts (CuSi-T, CuZr-T, CuSiZrx-T, CuO Ref and ZrO_2) were prepared by co-precipitation method as follows. The copper nitrate and/or support precursors (zirconium nitrate and/or acidic silica sol) were mixed and solved in water. Then, the solution was introduced into a 2 L precipitation vessel at 70 °C. In the meantime, an aqueous solution of NH_4HCO_3 was dripped into this vessel to maintain the pH at 5 ± 0.2 . After precipitation, the suspension was aged, washed, filtered and dried at 110 °C. The as-prepared samples were first heated to object temperatures at a heating rate of 1.5 °C/min, and then held for 5 h. The calcinations were performed in air. Cu/ SiO_2 , Cu/ ZrO_2 and Cu/ $\text{SiO}_2/\text{ZrO}_2$ catalysts were denoted as CuSi-T, CuZr-T and CuSiZrx-T respectively; T is the calcination temperature, x is the mass ratio of $\text{SiO}_2/\text{ZrO}_2$.

S1.3 Catalytic tests

The tests were performed in a stainless steel fixed-bed reactor after the catalysts were activated by in-situ reduction with diluted H_2 flow at 250 °C. In all tests, the products were condensed in a cold trap, then analyzed using a gas chromatography instrument. The conversion and selectivity of products were calculated based on the following general equations:

$$\text{Conversion(\%)} = 100 - \frac{\text{Amount of feeds after reaction (mol)}}{\text{Total amount feeds (mol)}} \times 100$$
$$\text{Selectivity (\%)} = \frac{\text{Amount of a product (mol)}}{\text{Total amount of feeds converted (mol)}} \times 100$$

To obtain the intrinsic activities, the yields of ethylene glycol were kept below 10% and the DMO conversions were kept below 50% at high liquid hour space velocities. The intrinsic activities were evaluated by turnover frequencies which were calculated via dividing the catalytic activities by the Cu surface areas. To form MG, one ester group of DMO needs to be hydrogenated. To form EG, both the ester groups of DMO need to be hydrogenated. Thus, in this paper, we presented two forms of turnover frequencies. The turnover frequencies based on the

converted ester groups (TOF¹) and the turnover frequencies based on the converted DMO (TOF²) were given as follows:

$$\begin{aligned} \text{TOF}^1 &= \frac{\text{Rate of converted ester groups (mol g}_{\text{cat}}^{-1} \text{ h}^{-1})}{\text{Numbers of Cu sites (mol g}_{\text{cat}}^{-1})} \\ &= \frac{(\frac{\text{DMO Conv.} \times \text{MG Sel.} \times 1}{\text{Molecular weight of DMO}} + \frac{\text{DMO Conv.} \times \text{EG Sel.} \times 2}{\text{Molecular weight of DMO}}) \times \text{WHSV (mol g}_{\text{cat}}^{-1} \text{ h}^{-1})}{\text{Numbers of Cu sites (mol g}_{\text{cat}}^{-1})} \\ \text{TOF}^2 &= \frac{\text{DMO conversion rate (mol g}_{\text{cat}}^{-1} \text{ h}^{-1})}{\text{Numbers of Cu sites (mol g}_{\text{cat}}^{-1})} \\ &= \frac{\text{DMO Conv.} \times \text{WHSV} \div \text{Molecular weight of DMO (mol g}_{\text{cat}}^{-1} \text{ h}^{-1})}{\text{Numbers of Cu sites (mol g}_{\text{cat}}^{-1})} \end{aligned}$$

The weight hourly space velocity (WHSV) is defined as the grams of DMO per hour per gram of catalyst. The numbers of Cu sites were determined by N₂O titration.

S1.4 Characterizations

ICP-OES (ICP optical emission spectroscopy)

The composition of catalysts was determined by Optima2100DV, PerkinElmer.

Brunauer-Emmett-Teller (BET)

BET surface areas were tested by N₂ physical adsorption at -196 °C using a Micromeritics ASAP 2420 instrument. Before tests, the samples were degassed at 90 °C for 1 h and 350 °C for 8 h.

N₂O titration

Cu dispersion and specific Cu surface area were measured using N₂O titration method. The experiments were conducted in Auto Chem. II 2920 equipment (Micromeritics, USA). First, the sample (placed into a U-shaped quartz tube) was reduced at 300 °C in a 10 vol. % H₂/Ar gas flow using a heating rate of 5 °C/min. Then, it was exposed to 10 vol. % N₂O/Ar flow for 1 h at 60 °C to oxidize the surface Cu species to Cu₂O. After that, the sample was flushed with Ar flow and cooled to 40 °C to start a temperature programmed reduction. Cu dispersion was calculated by dividing the amount of chemisorption sites into total Cu atoms; Cu surface area was calculated by assuming spherical shape of Cu particles and 1.47×10¹⁹ atoms/m².¹

Temperature programmed desorption of NH₃ (NH₃-TPD)

NH₃-TPD was employed to measure the acidity of catalysts. Prior to the tests, 200 mg catalysts were pretreated in He flow at 300 °C for 4 h. After cooling to 100 °C, the samples were adsorbed with NH₃ until saturation. Then, the samples were flushed with He at 100 °C to remove the physisorbed NH₃. The TPD analysis was carried out at a heating rate of 10 °C/min with a mass spectrometer as detector. The fragment of m/z = 16 was drawn as the characteristic patterns of NH₃.

XRD analysis and Rietveld refinement

Powder X-ray diffraction (XRD) patterns in the 2θ range of 10-80° were measured with a X-ray diffractometer (D8 Advance, Cu Kα radiation, 0.02 °/step, counting time 1 s, slit 1 mm) equipped with a reactor chamber (XRK 900). The in situ reduction was performed at 250 °C (heating rate of 2 °C/min) in diluted H₂ (5 vol.%).

The fraction of t-ZrO₂ (V_t) was determined by the equations²:

$$X_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(111) + I_m(11\bar{1}) + I_t(011)}$$

$$V_t = 1 - \frac{1.311X_m}{1 + 0.311X_m}$$

The I_m(111) and I_m(11 $\bar{1}$) in the equation are the peak intensities of (111) and (11 $\bar{1}$) planes of m-ZrO₂ respectively; the I_t(011) is the peak intensity of (011) plane of t-ZrO₂. The crystal structures were refined with the Pawley method by using TOPAS software (Bruker, Germany, 2010). The background was modeled using a fourth order Chebychev polynomial. Some technical details are listed in Table S3.

Raman analysis

The Raman spectra of the catalysts were measured with a LabRAM HR800 system equipped with a CCD detector at room temperature in the range of 100-1000 cm⁻¹. The 532 nm of the He-Cd laser was used as the exciting source with a power of 30 MW. The samples were checked with a microscopy after experiments to make sure they are not damaged.

XPS analysis

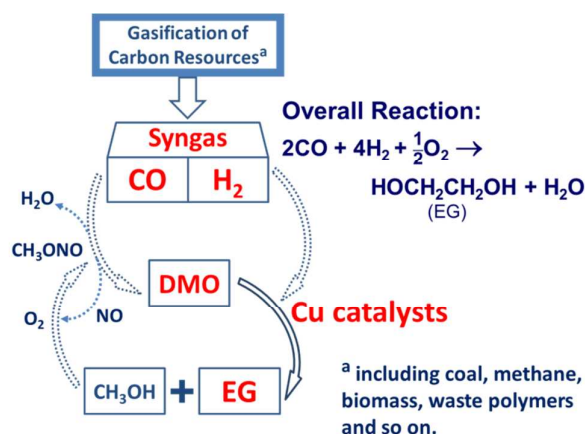
The XPS experiments were measured on a VG MultiLab 2000 spectrometer with Al Kα radiation (1486.6 eV) and a multichannel detector. The obtained binding energies were calibrated using the C1s peak as the reference. The experiment error reported in this study is within ±0.1 eV. The XPS experiments of reduced samples were measured on the same instrument. Prior to the

tests, the samples were in-situ reduced in diluted H₂ flow at 250 °C for 2 h.

TEM analysis

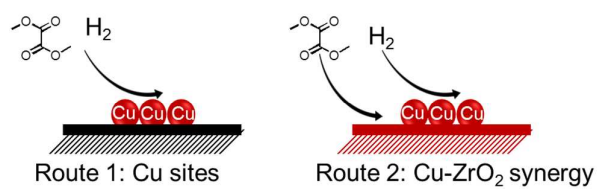
The transmission electron microscopy was done with a JEM-2100F high-resolution transmission operated at 200 keV. Before tests, the samples were reduced and uniformly dispersing in ethanol, and then placing onto copper grids.

S2 Details of dimethyl oxalate hydrogenation



Scheme S1 Alternative approach for EG synthesis.

The hydrogenation of dimethyl oxalate (DMO) is a highly exothermic reaction and an excellent example to study the deactivation of metal catalysts by metal particle growth. On the theoretical side, DMO as the simplest di-ester containing C=O, C-O and C-C bonds, provides the opportunity to understand the hydrogenation of these bonds over heterogeneous catalysts. Moreover, the hydrogenated product, ethylene glycol (EG), is a platform chemical for polymer industry and automotive antifreeze with a consumption of 20 million tons/year.³ It is industrially produced from petroleum based ethylene via multiple steps despite the dwindling oil and soaring demands. DMO hydrogenation to EG as an alternative syngas-based route holds great promises and bridges the non-renewable and cleaner resource utilization.⁴ This technology consists of carbon resources gasification, CO oxidative coupling to DMO and DMO hydrogenation to EG (Scheme S1), among which the first two have been commercialized.⁵ The hydrogenation of DMO to EG still has many problems that hinder the commercial applications, including the low efficiency and deactivation by sintering of Cu catalysts.



Scheme S2. Possible routes of DMO hydrogenation over Cu-ZrO₂ catalysts.

Table S1. Details of the Rietveld refinement of XRD results.

Catalysts	R _{Bragg}	R _{wp}	R _{wp} '	GOF
CuSiZr1-450 (unreduced)	0.120	3.10	2.62	1.08
CuSiZr1-450 (reduced)	0.051	3.14	2.42	1.05
CuSiZr1-550 (unreduced)	0.061	3.05	2.62	1.14
CuSiZr1-550 (reduced)	0.088	3.11	2.55	1.05
CuSiZr1-650 (unreduced)	0.034	3.30	2.48	1.04
CuSiZr1-650 (reduced)	0.084	3.12	2.74	1.06
CuSiZr1-750 (unreduced)	0.057	3.26	2.41	1.04
CuSiZr1-750 (reduced)	0.080	3.12	2.36	1.02
CuSiZr1-850 (unreduced)	0.075	3.32	2.86	1.08
CuSiZr1-850 (reduced)	0.072	3.12	2.50	1.03

Table S2. MG hydrogenation over CuO, Cu+t-ZrO₂ and Cu+m-ZrO₂ catalysts.^a

Catalyst	Conv. (%)	Sel. (%)		
		EG	EtOH	Others
CuO	23.9	97.0	2.7	0.3
CuO+t-ZrO ₂	31.6	95.7	2.1	2.2
CuO+m-ZrO ₂	45.1	92.5	2.6	4.9

^a Reaction conditions: 190 °C, 3 MPa, 0.3 h⁻¹, H₂/MG = 150 mol/mol. t-ZrO₂: tetragonal zirconia. m-ZrO₂: monoclinic zirconia. Others mainly comprise 2-methoxyethanol, 1,2-propanediol and 1,2-butanediol.

Table S3. DMO hydrogenation over CuO, CuO+t-ZrO₂ and CuO+m-ZrO₂ catalysts.^a

Catalyst	Conv. (%)	Sel. (%)			
		EG	MG	EtOH	Others
CuO	10.5	1.3	98.7	0	0
CuO+t-ZrO ₂	26.9	6.3	92.0	0.8	0.9
CuO+m-ZrO ₂	35.8	11.8	87.5	0.4	0.3

^a Reaction conditions: 190 °C, 3 MPa, 0.3 h⁻¹, H₂/DMO = 150 mol/mol. t-ZrO₂: tetragonal zirconia. m-ZrO₂: monoclinic zirconia. Others mainly comprise 2-methoxyethanol, 1,2-propanediol and 1,2-butanediol.

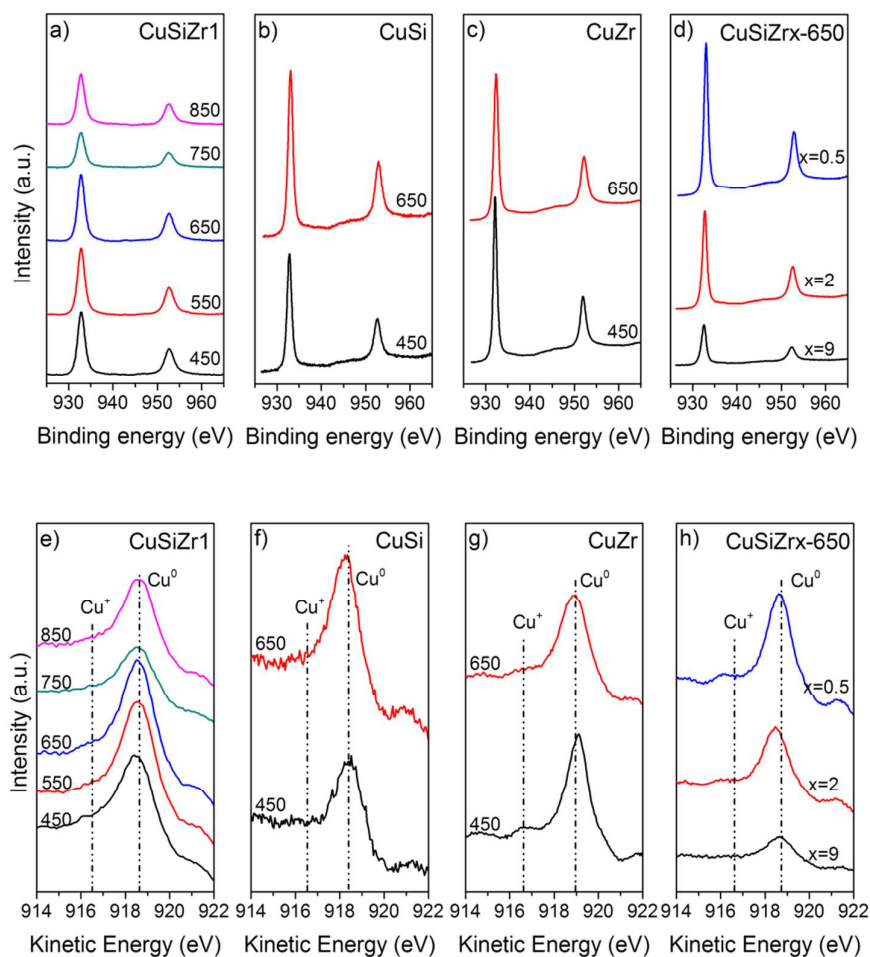


Figure S1. Cu 2p spectra and Cu LMM XAES spectra of reduced CuSiZr1-T (a, e), CuSi-T (b, f), CuZr-T (c, g) and CuSiZrx-650 (d, h) (number (T) above the line of a, b, c, e, f, g means relative calcination temperature).

As shown in Cu 2p spectra, two peaks at ~933 and 953 eV were observed for all the reduced catalysts, which could be attributed to Cu 2p_{3/2} and Cu 2p_{1/2}. However, the satellite peaks in the range of 935-950 eV were unobservable. The absence of satellite peaks indicated that the Cu²⁺ species were reduced to Cu⁰ and/or Cu⁺ species. The Cu LMM XAES spectra exhibited evident peak at ~918.8 eV (Cu⁰) and negligible peak at ~916.5 eV (Cu⁺). Thus, the Cu species over the surface existed mainly in metallic state.

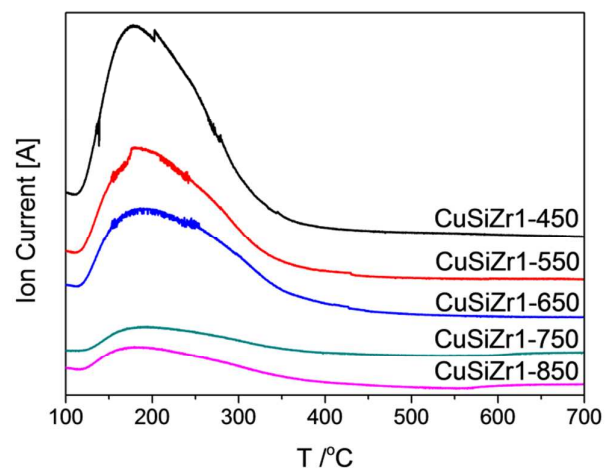


Figure S2. NH₃-TPD profiles of CuSiZr1-T catalysts.

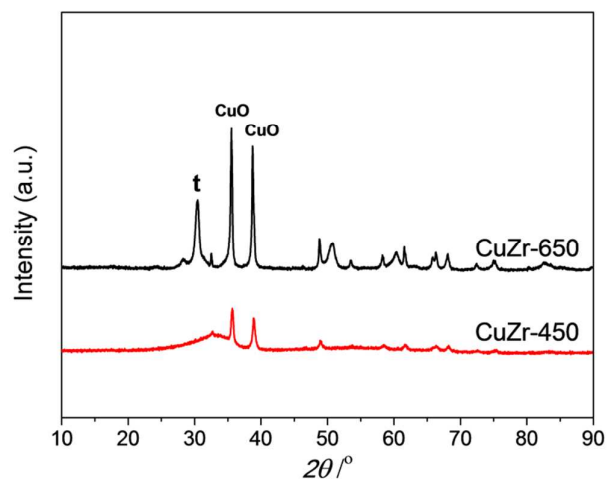


Figure S3. XRD spectra of CuZr catalysts (t: t-ZrO₂).

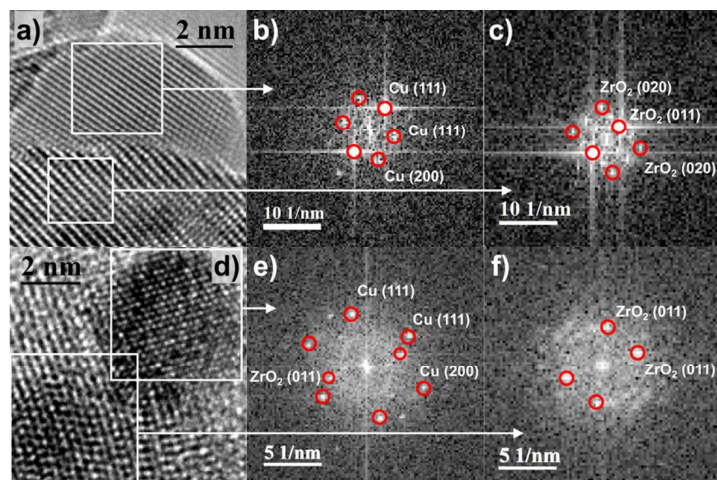


Figure S4. Selected area electron diffraction (SAED) patterns of reduced CuZr-650 (a, b, c) and CuSiZr-650 (d, e, f) catalysts.

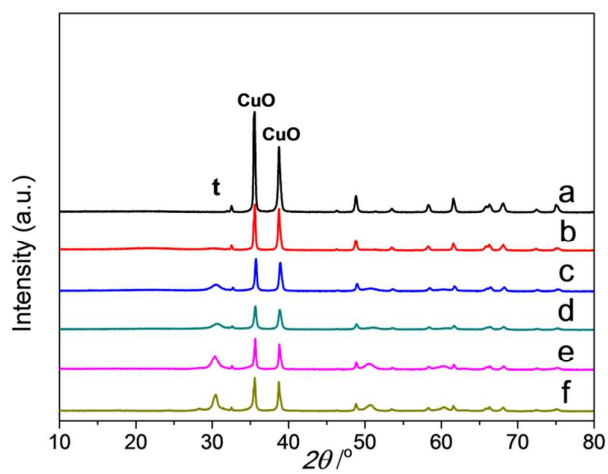


Figure S5. XRD results of calcined catalysts with different SiO₂/ZrO₂ ratios (t: t-ZrO₂; a: CuSi-650; b: CuSiZr9-650; c: CuSiZr2-650; d: CuSiZr1-650; e: CuSiZr0.5-650; f: CuZr-650).

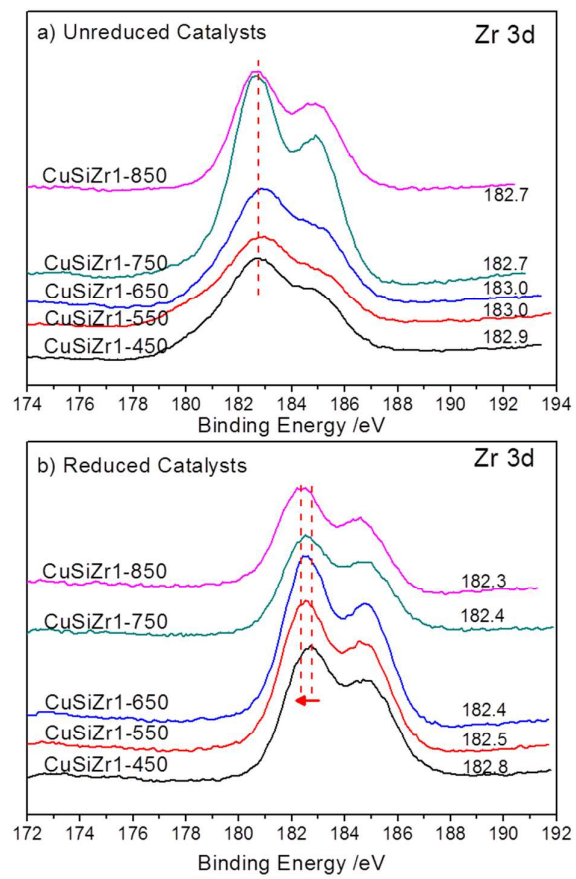


Figure S6. The Zr 3d spectra of unreduced (a) and reduced (b) CuSiZr1 catalysts.

References

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