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**Structured Pd-Au/Cu-fiber catalyst for gas-phase
hydrogenolysis of dimethyl oxalate to ethylene glycol**

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Experimental

Catalyst preparation

The monolithic sinter-locked microfibrous structured supports with entirely open 3-dimension (3D) porous network, respectively consisting of Cu-fibers (8 μm in dia.), Al-fibers (60 μm in dia.), Ni-fibers (8 μm in dia.), and 316-L stainless-steel-fibers (SS-fiber, 20 μm in dia.), were utilized as substrates, which were prepared through wet layup paper making/sintering processes developed by our group.^{S1} Pd-Au/Cu-fiber catalyst was prepared using galvanic deposition method (named as ***GD method***) with aqueous solution containing appointed amount of palladium acetate and chloroauric acid (Sinopharm Chemical Reagent Co., Ltd., China) at room temperature. The resulting sample was dried overnight at 100 °C and calcined in air at 300 °C for 2 h. Similarly, the Pd-Au/SS-fiber, Pd-Au/Al-fiber, and Pd-Au/Ni-fiber catalysts were also prepared using the ***GD method*** with aqueous solution containing appointed amount of palladium acetate and chloroauric acid at room temperature. The resulting samples were dried overnight at 100 °C and calcined in air at 300 °C for 2 h. For reference, the pure Cu-fiber substrate calcined in air at 300 °C for 2 h was also tested for the titled reaction.

Catalyst characterization

The catalysts were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, FEI-Tecnai G2F30). Specific surface area was calculated using the standard Brunauer-Emmett-Teller (BET) theory based on the N_2 adsorption isotherm obtained on a Quantachrome apparatus (Autosorb-3B, USA) at -196 °C. H_2 temperature programmed reduction (H_2 -TPR) was performed on a Quantachrome chemisorption

apparatus (ChemBET 3000, USA) with a thermal conductivity detector (TCD) and an online Mass Spectrometer (Proline Dycor, AMETEK Process Instrument, USA). X-ray diffraction (XRD) was performed on a Rigaku Uitima IV diffractometer with Cu K α radiation (35 kV and 25 mA). Element analysis was performed using a Thermo Scientific iCAP 6300 inductively coupled plasma atomic emission spectrometry (ICP-AES) on a USA Thermo IRIS Intrepid II XSP ICP spectrometer. The X-ray photoelectron spectroscopy (XPS) was recorded on an Escalab 250xi spectrometer, using a standard Al K α X-ray source (300 W) and an analyzer pass energy of 20 eV. All binding energies were referenced to the adventitious C1s line at 284.6 eV.

Reactivity tests

The hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG) was performed in a fixed-bed stainless-steel reactor with 8 mm inner diameter. Firstly 0.5 g catalyst was loaded into reactor and heated to 270 °C, and then pure hydrogen was introduced to the reactor until the pressure was raised to 2.5 MPa and DMO methanol solution (13 wt%) was simultaneously introduced to the reactor. The DMO methanol solution was pumped using high-pressure advection pump and the liquid products was collected and analyzed using a Shimadzu 2014C gas chromatography-flame ionization detector (GC-FID) with a HP-INNOWax column. The DMO conversion and products selectivities were calculated as follows:

$$\text{DMO conversion (\%)} = (1 - A_{\text{DMO}}f_{\text{DMO}} / \sum A_i f_i) \times 100$$

$$S_i (\%) = (A_i f_i / \sum A_i f_i) \times 100$$

where A_i is the peak area of the individual component i and f_i is the mole correction factor of the individual component i .

TOF calculations

The turnover frequency (TOF) of all the catalysts was defined as the number of DMO converted per Cu⁺ site per time, and was calculated based on the following equation:

$$\text{TOF} = \text{DMO converted rate (mol g}_{\text{cat}}^{-1} \text{ h}^{-1}) / \text{Numbers of Cu}^+ \text{ sites (mol g}_{\text{cat}}^{-1})$$

The number of surface Cu⁺ sites was calculated based on the following equation:

$$n(\text{Cu}^+) \sum \left(\frac{X_i}{X_{\text{Cu}^+}} \pi r_i^2 \right) = S_{\text{BET}}$$

Here, $n(\text{Cu}^+)$ is the number of Cu⁺ sites, X_i is the mole fraction of individual atom i analyzed by XPS (i contains Cu⁰, Cu⁺, Au, Pd, C, and O), S_{BET} is the specific surface area of catalysts. In order to obtain the intrinsic activity of catalysts, the DMO conversion was kept below 30% at 210 °C and high WHSV of 9 h⁻¹.

The X_i (i contains Cu⁰ and Cu⁺, Au, Pd, C and O) was calculated on the basis of XPS spectra. Take the 0.1Pd-0.5Au/Cu-fiber catalyst as an example, the surface molar ratio of Cu: Au: Pd: C: O is provided from the XPS survey spectra. Firstly, the surface molar ratio of Cu: Au: Pd: C: O is supposed to be $X_{\text{Cu}}: X_{\text{Au}}: X_{\text{Pd}}: X_{\text{C}}: X_{\text{O}}$ ($X_{\text{Cu}} + X_{\text{Au}} + X_{\text{Pd}} + X_{\text{C}} + X_{\text{O}} = 1$). Because Cu 2p_{3/2} XPS spectra cannot differentiate between Cu⁺ and Cu⁰, Auger Cu LMM spectra were used to differentiate Cu⁺ and Cu⁰. Considering the extremely low Cu²⁺ percentage in all the Cu states, Cu²⁺ ratio was omitted from the total Cu states to calculate the “ X_i ”. Subsequently, the Cu⁺: Cu⁰ molar ratio can be determined using Auger Cu LMM spectra and supposed to be $\chi_{\text{Cu}^+}: \chi_{\text{Cu}^0}$ ($\chi_{\text{Cu}^+} + \chi_{\text{Cu}^0} = 1$). Finally, the surface molar ratio of Cu⁰: Cu⁺: Au: Pd: C: O can be determined to be $(X_{\text{Cu}} \times \chi_{\text{Cu}^0}): (X_{\text{Cu}} \times \chi_{\text{Cu}^+}): X_{\text{Au}}: X_{\text{Pd}}: X_{\text{C}}: X_{\text{O}}$.

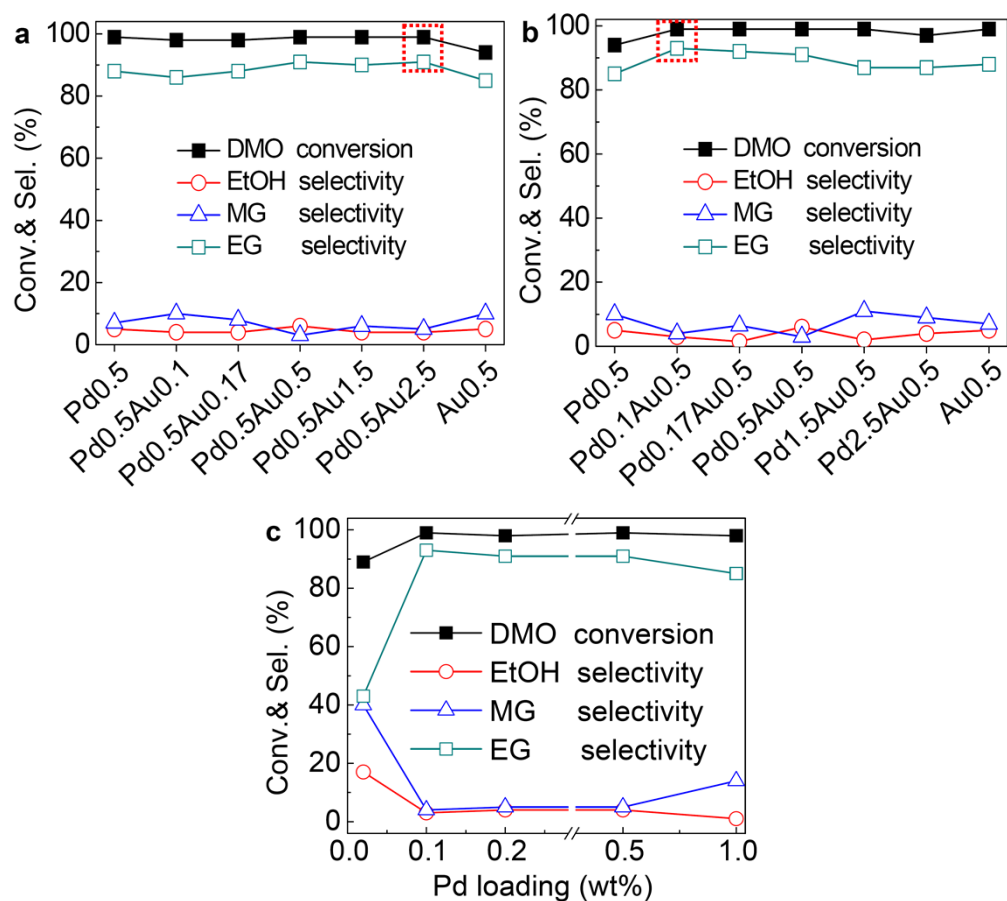


Fig. S1. (a) With constant Pd loading of 0.5 wt%, the effect of Au loadings. (b) With constant Au loading of 0.5 wt%, the effect of Pd loadings. The results in Figures S1a,S1b indicate the optimal Au-to-Pd weight ratio of 5. (c) The effect of Pd and Au loadings with Au-to-Pd weight ratio of 5. Reaction conditions: 270 °C, WHSV of total liquid feed of 5.3 h⁻¹ with 13 wt% DMO dissolved in methanol (MeOH), H₂ pressure of 2.5 MPa, molar ratio of H₂-to-DMO of 180.

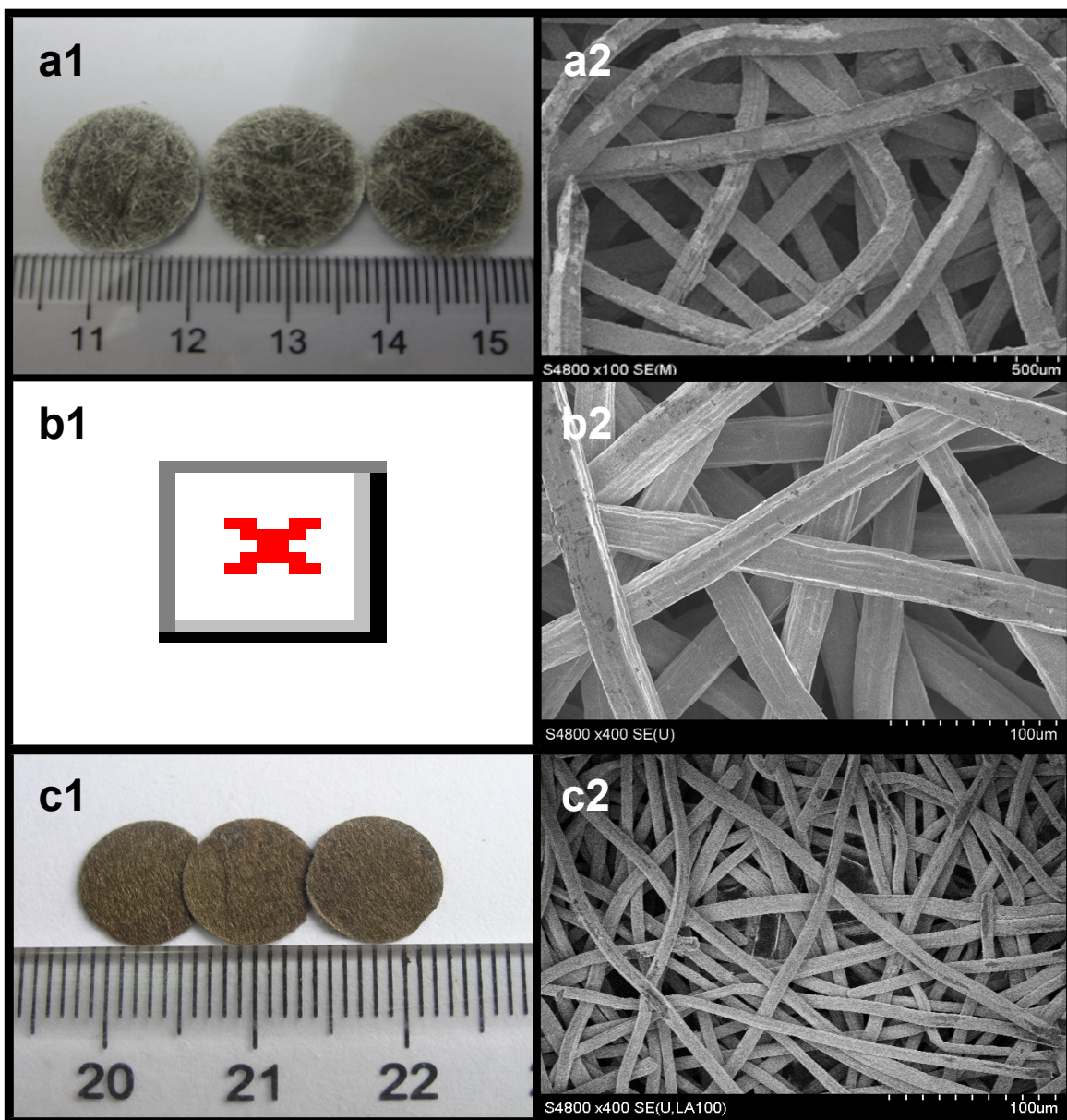


Fig. S2. Optical photographs and SEM images of the monolithic structured 0.1Pd-0.5Au/60 μ m-Al-fiber (a1,a2), 0.1Pd-0.5Au/20 μ m-SS-fiber (b1,b2) and 0.1Pd-0.5Au/8 μ m-Ni-fiber (c1,c2), showing entirely open 3D porous network.

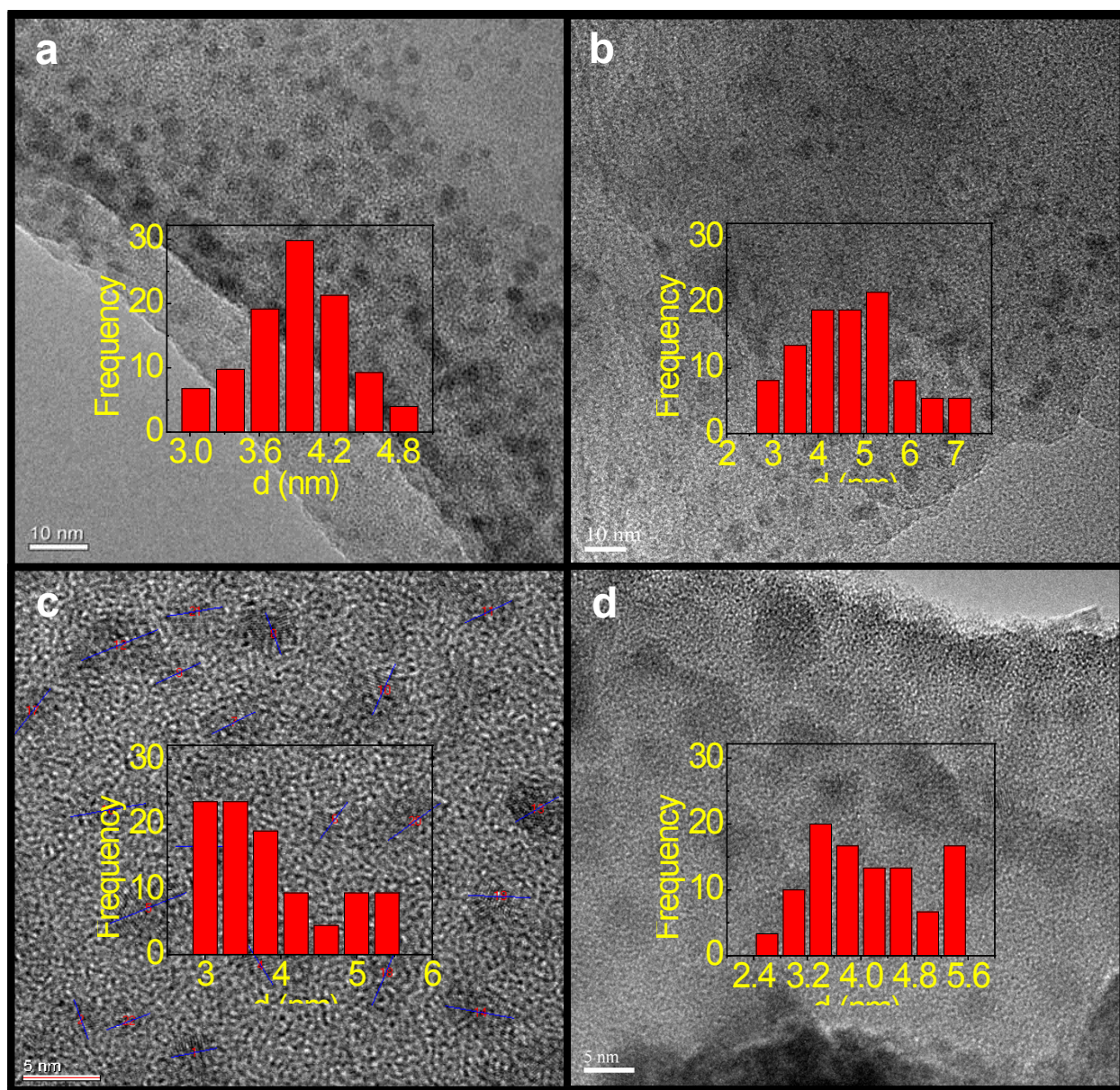


Fig. S3. TEM images of the (a) 0.1Pd-0.5Au/Cu-fiber, (b) 0.1Pd-0.5Au/Al-fiber, (c) 0.1Pd-0.5Au/SS-fiber, and (d) 0.1Pd-0.5Au/Ni-fiber catalysts.

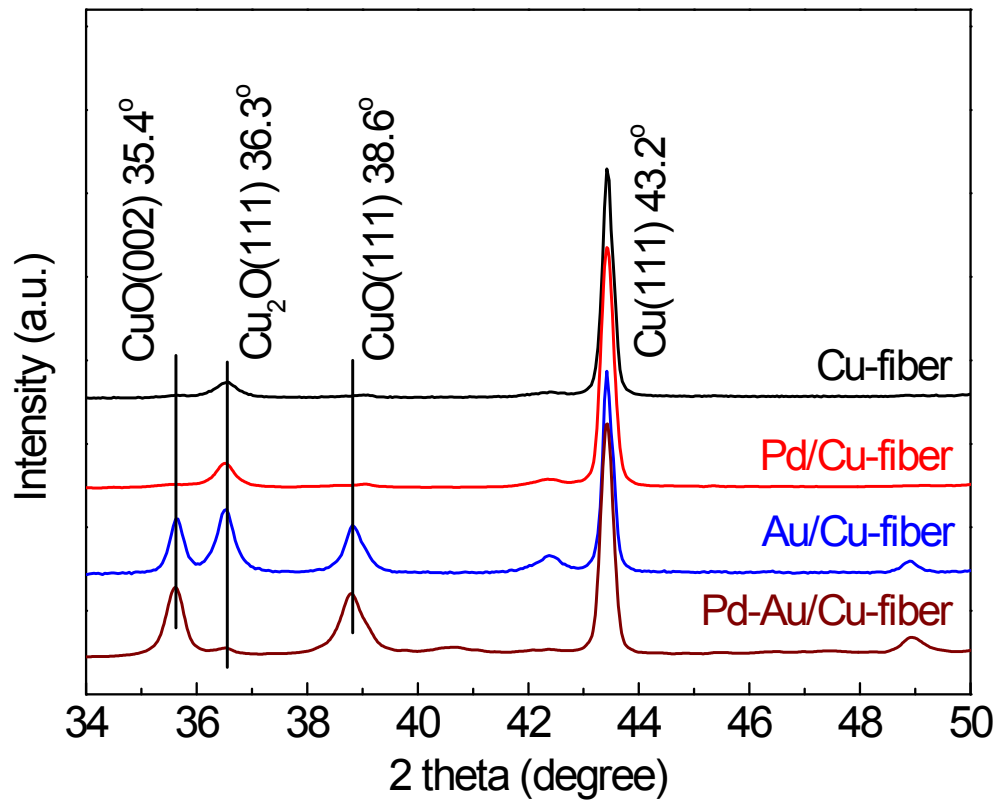


Fig. S4. XRD patterns of the Cu-fiber, 0.1Pd/Cu-fiber, 0.5Au/Cu-fiber, and 0.1Pd-0.5Au/Cu-fiber. All the samples are calcined in air at 300 °C for 2 h.

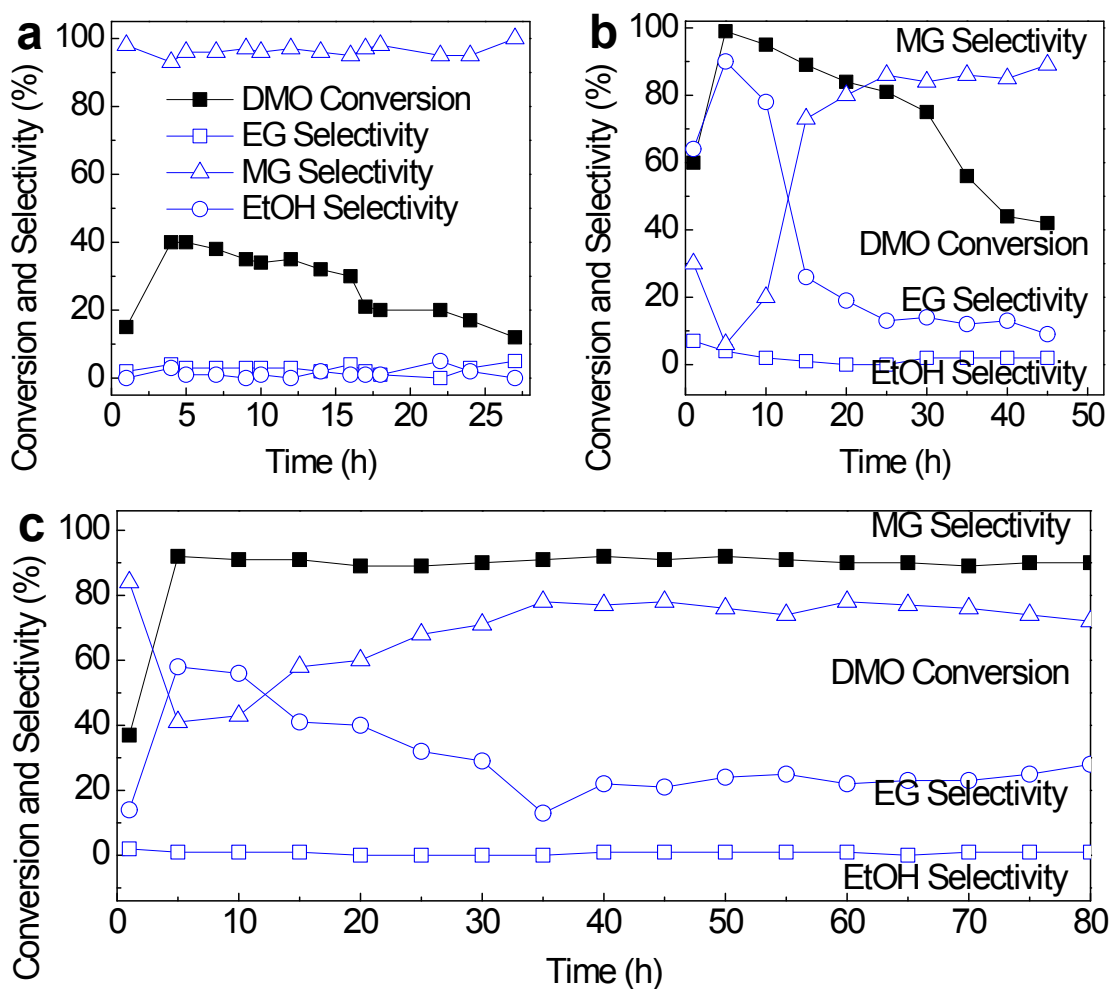


Fig. S5. DMO conversion and EG/MG/EtOH selectivities *vs* time on stream over the (a) Cu-fiber, (b) 0.1Pd/Cu-fiber, and (c) 0.5Au/Cu-fiber catalysts. Reaction conditions: 270 °C, WHSV of total liquid feed of 5.3 h⁻¹ with 13 wt% DMO dissolved in MeOH, H₂ pressure of 2.5 MPa, molar ratio of H₂ to DMO of 180.

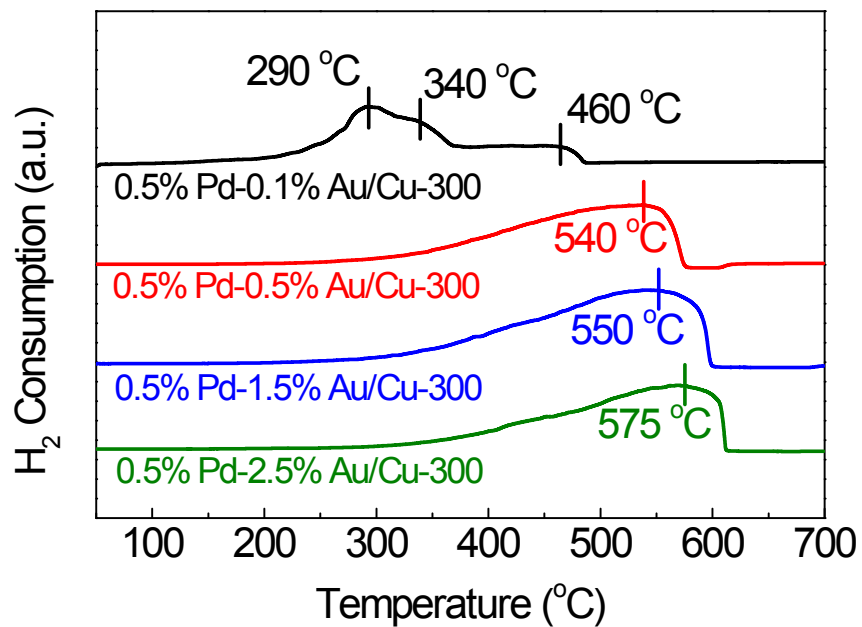


Fig. S6. TPR profiles of the Pd-Au/Cu-fiber catalysts with constant Pd loading of 0.5 wt% and different Au/Pd weight ratio.

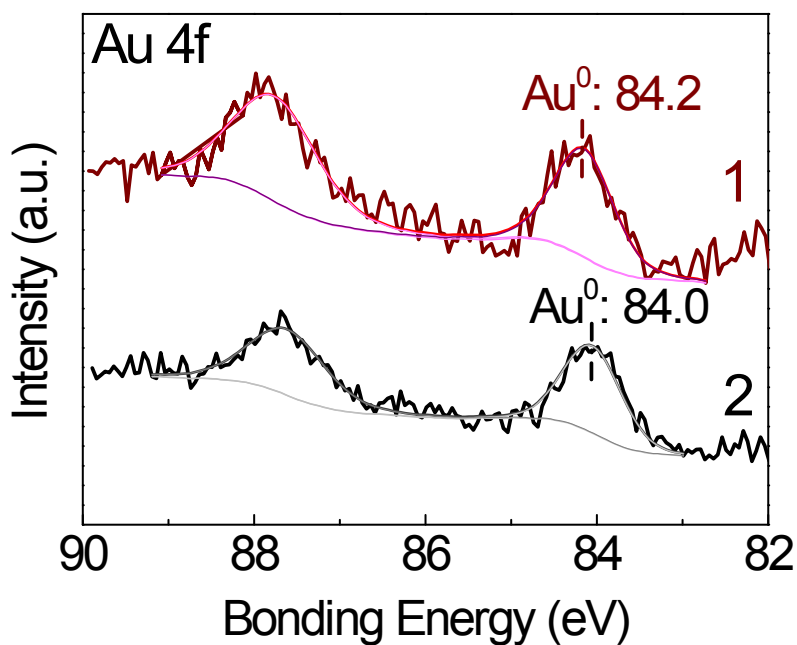
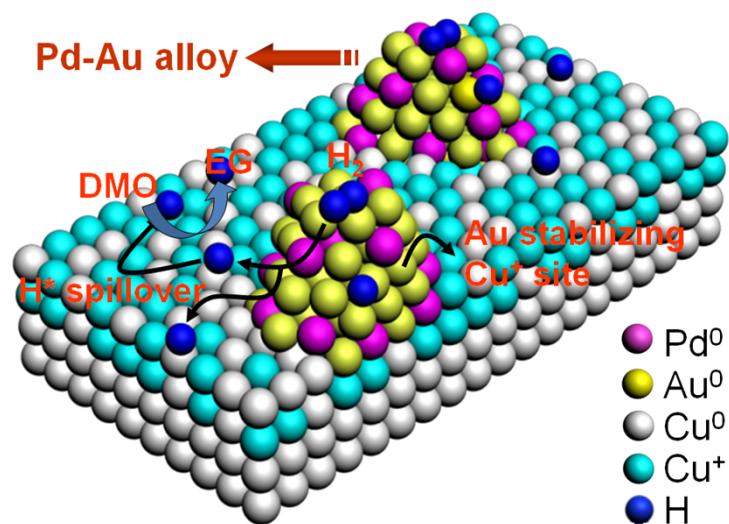


Fig. S7. XPS spectra of the catalysts: (1) 0.5Au/Cu-fiber after 10 h running and (2) 0.1Pd-0.5Au/Cu-fiber after 10 h running. Reaction conditions: 270 °C, WHSV of total liquid feed of 5.3 h⁻¹ with 13 wt% DMO dissolved in MeOH, H₂ pressure of 2.5 MPa, molar ratio of H₂ to DMO of 180.

Note: An obvious up-shifting of the metallic Pd 3d_{3/2} BE (binding energy) is observed from 335.0 eV for the 0.1Pd/Cu-fiber to 335.6 eV for the 0.1Pd-0.5Au/Cu-fiber (Figure 3b in manuscript). However, slight down-shifting of the metallic Au 4f_{7/2} BE is from 84.2 eV for the 0.5Au/Cu-fiber to 84.0 eV for the 0.1Pd-0.5Au/Cu-fiber, which is likely due to the very low Pd/Au weight ratio of only 1/5.



Scheme S1. The illustration of proposed ternary Pd-Au-Cu⁺ complex for DMO hydrogenolysis to EG.

Table S1. The reported catalysts and our Cu-fiber structured catalyst for DMO hydrogenolysis to EG process.

Catalyst	React. Temp. (°C)	LHSV (h ⁻¹)	DMO Conv. (%)	EG Sel. (%)	TOS* (h)	Ref.
Cu/SiO ₂	200	0.3	98	71	30	S2
Cu/TiO ₂ -SiO ₂	200	0.3	99	96	70	S2
B-Cu-SiO ₂	190	0.75	99.7	93	300	S3
Cu/SBA-15	200	0.6	100	99	---	S4
Cu/HAP	240	---	99	80	120	S5
Cu/HMS	200	0.2	100	92	---	S6
La-Cu/SiO ₂	180	1.5	98.5	80.3	200	S7
AuCu/SiO ₂	180	0.6	100	99.1		S4
0.1Pd-0.5Au/Cu-fiber	270	0.7	99	93	200	---
0.1Pd-0.5Au/Cu-fiber	240	0.7	99	90	---	---
0.1Pd-0.5Au/Cu-fiber	220	0.7	94	80	---	---

* TOS: time on stream.

Table S2. The Au, Pd and Cu loadings of the catalysts determined by ICP measurement.

Catalyst	Loadings (wt%)		
	Au	Pd	Cu
0.1Pd-0.5Au/Cu-fiber ^a	0.36	0.06	99.6
0.1Pd-0.5Au/Ni-fiber ^a	0.38	0.08	--
0.1Pd-0.5Au/Al-fiber ^a	0.35	0.07	--
0.1Pd-0.5Au/SS-fiber ^a	0.34	0.06	--
Cu-fiber	--	--	100
0.1Pd-0.5Au-30Cu/Ni-fiber ^{a,b}	0.42	0.09	21.6
0.1Pd-0.5Au-30Cu/Al-fiber ^{a,b}	0.31	0.07	23.1
0.1Pd-0.5Au-30Cu /SS-fiber ^{a,b}	0.32	0.07	22.5
0.1Pd/Cu-fiber ^a	--	0.07	99.9
0.5Au/Cu-fiber ^a	0.32	--	99.6

^a The numbers of “0.1” and “0.5” in these catalysts represent the nominal loadings of 0.1 wt% Pd and 0.5 wt% Au, respectively. ^b The number of “30” in these catalysts represents the nominal loading of 30 wt% Cu.

Table S3. The DMO conversion and products selectivities over the various catalysts.^a

Catalyst	DMO Conversion (%)	Selectivity (%)		
		EG	MG	EtOH
0.1Pd-0.5Au/Al-fiber	10	97	0	3
0.1Pd-0.5Au/SS-fiber	7	100	0	0
0.1Pd-0.5Au/Ni-fiber	8	100	0	0
0.1Pd-0.5Au/Cu-fiber	99	93	4	3
0.1Pd-0.5Au-30Cu/Al-fiber	96	85	13	2
0.1Pd-0.5Au-30Cu/SS-fiber	94	68	32	0
0.1Pd-0.5Au-30Cu/Ni-fiber	95	80	18	2
Cu-fiber	40	1	96	3
0.1Pd/Cu-fiber	98	85	12	3
0.5Au/Cu-fiber	92	58	41	1

^a Reaction conditions: 270 °C, WHSV of total liquid feed of 5.3 h⁻¹ with 13 wt% DMO dissolved in EtOH, H₂ pressure of 2.5 MPa, molar ratio of H₂ to DMO of 180.

Table S4. The DMO conversion and the corresponding TOF over the catalysts.^a

Catalyst	DMO Conversion (%)	Converted DMO ^b (mol g _{cat} ⁻¹ h ⁻¹)	Cu ⁺ sites ^c (mol g _{cat} ⁻¹)	TOF ^d (h ⁻¹)
0.1Pd-0.5Au/Cu-fiber	32.0	1.10×10^{-3}	1.80×10^{-6}	612
Cu-fiber	4.2	0.14×10^{-3}	8.46×10^{-6}	17
0.1Pd/Cu-fiber	6.4	0.22×10^{-3}	2.73×10^{-6}	80
0.5Au/Cu-fiber	18.3	0.63×10^{-3}	3.60×10^{-6}	174

^a In order to obtain the intrinsic activity of all the catalysts, DMO conversion is kept below 30% under the following reaction conditions: catalyst 0.5 g, 210 °C, WHSV of total liquid feed of 9 h⁻¹ with 13 wt% DMO dissolved in methanol, H₂ pressure of 2.5 MPa, molar ratio of H₂ to DMO of 180. ^b Take the 0.1Pd-0.5Au/Cu-fiber catalyst as an example, the molar amount of the converted DMO is calculated as the following: Converted DMO = DMO Conversion (32.0%) × Feedstock (0.00342 mol/h) = 0.00110 mol/h. ^c Take the 0.1Pd-0.5Au/Cu-fiber catalyst as an example, the molar amount of the Cu⁺ sites is calculated as the following: Cu⁺ sites = Surface area of 0.1Pd-0.5Au/Cu-fiber (0.48 m²/g) / Area occupied by one Cu⁺ site (0.444 nm², see the equation in “TOF” calculations in SI) = 1.08×10^{18} = 1.80×10^{-6} mol/g. ^d The TOF is calculated as the following: TOF = Converted DMO (1.10×10^{-3} mol g_{cat}⁻¹ h⁻¹) / Cu⁺ sites (1.80×10^{-6} mol g_{cat}⁻¹) = 612 h⁻¹.

Table S5. The molar percentage of Cu²⁺ : Cu⁺ : Cu⁰ on the surface of the catalysts.^a

Catalyst	Molar ratio of Cu ²⁺ : Cu ⁺ : Cu ⁰		
	Stage A ^b	Stage B ^c	Stage C ^d
Cu-fiber	2.5 : 70.6 : 26.9	0 : 43.0 : 57.0	---
0.1Pd/Cu-fiber	0 : 54.8 : 45.2	0 : 34.0 : 66.0	---
0.5Au/Cu-fiber	1.3 : 63.2 : 35.5	---	1.5 : 65.6 : 32.9
0.1Pd-0.5Au/Cu-fiber	1.8 : 61.6 : 36.6 ^e	---	0 : 62.5 : 37.5

^a The existence of Cu²⁺ is caused by the oxidation of Cu⁰ and Cu⁺ inevitably during the sample preparation. ^b All the catalysts undergo the reaction for 10 h. ^c The Cu-fiber undergoes the reaction for 30 h and Pd/Cu-fiber deactivates after 50 h. ^d The catalysts undergo the reaction for 60 h. ^e The molar percentage of Cu²⁺: Cu⁺: Cu⁰ on the surface of the catalysts was obtained based on Cu 2p_{3/2} and Cu LMM XPS spectra. Take the 0.1Pd-0.5Au/Cu-fiber catalyst at Stage A (undergoing the reaction for 10 h) as an example, the Cu²⁺: Cu⁺: Cu⁰ molar percentage of about 1.8%: 98.2% was determined using Cu 2p_{3/2} XPS spectra, and then Cu⁺: Cu⁰ molar percentage of about 62.7%: 37.3% was determined using Auger Cu LMM spectra. Finally, the molar percentage of Cu²⁺: Cu⁺: Cu⁰ on the surface of 0.1Pd-0.5Au/Cu-fiber at Stage A was determined as to be 1.8%: (0.627×98.2%): (0.373×98.2%) = 1.8%: 61.6%: 36.6%.

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