Electronic supplementary information for

Remarkable enhancement of Cu catalyst activity in hydrogenation of dimethyl oxalate to ethylene glycol using gold

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Experimental details

Catalyst preparation

The SBA-15 supported Cu-Au nanocatalyst was prepared using a modified two-step approach described in literature.[1,2] The surface of the support SBA-15 was first functionalized with APTES ($H_2N(CH_2)_3Si(OEt)_3$) to prepare the SBA-15 supported Cu-Au alloy nanoparticles. Briefly, 1.0 g SBA-15 and 2.5 g APTES were dissolved in 50 mL ethanol, followed by reflux for 24 h. After filtration, washing and drying, the functionalized SBA-15 was obtained and denoted as NH_2-SBA-15. Subsequently, the NH_2-SBA-15 support was dissolved in a defined amount of tetrachloroaurate ($HAuCl_4$) solution followed by reduction with $NaBH_4$. After continuous stirring at room temperature for 30 min, filtration, and washing, the obtained solid was added to the 50 mL copper nitrate ($Cu(NO_3)_2$) solution. The mixture was again reduced with $NaBH_4$, followed by continuous stirring, filtration, and thorough washing. The discovered solid was air-calcined at 873 K for 6 h to obtain the catalyst precursor. Then, it was reduced under 5% H_2–95% N_2 atmosphere at 623 K for 4 h, affording the *x*Cu*y*Au/SBA-15 catalysts, where *x* and *y* denote the weight loadings of Cu and Au, respectively. During the preparation, Cu loading was kept constant at 6 wt%. The Au/Cu atomic ratio was varied accordingly.

Catalyst characterizations

A Panalytical X'pert Pro Super X-ray diffractometer equipped with a monochrometer and Cu K_α radiation (λ=0.15418 nm) was used for XRD patterns. The tube voltage was 40 kV and the current was 30 mA. For the *in situ* XRD measurement, a catalyst precursor was placed in a stainless steel holder and covered with a 0.1 mm thick beryllium plate. Afterward, 5% H_2-95% N_2 mixture was introduced at a flow rate of 40 cm^3 min^{-1}. Temperature ramping programs were performed from room temperature to 323, 373, 423, 473, 523, 573, 623 and 673 K at a rate of 2 K min^{-1}. The XRD patterns were collected after the samples reached the preset temperatures for 30 min. The diffraction pattern was identified by matching them with reference patterns in the JCPDS data base.

Nitrogen adsorption-desorption isotherms were measured using static N_2 physisorption on a Micromeritics TriStar II 3020 at 77 K. Before the measurement of the N_2 physisorption, all samples were outgassed at 473 K for 2 h and then evacuated at 573 K for 3 h to remove physically adsorbed impurities. The specific surface area (S_{BET}) was calculated by Brunauer–Emmett–Teller (BET) method. The total pore volume (V_p) was derived from the adsorbed N_2 volume at a relative pressure of approximately 0.99. Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distributions according to the desorption branch of the isotherms.

UV-Vis DRS were taken on a UV-VIS-NIR Spectrophotometer CARY 5000 with a scanning wavelength ranging from 200 nm to 1200 nm. Before the UV-Vis DRS measurement, all catalyst precursors were freshly reduced in 5% H_2-95% N_2 atmosphere at 623 K. The as-reduced samples were directly used for the UV-Vis DRS measurement.

TEM and HRTEM images were obtained using a Tecnai F30 apparatus operated at a voltage of 300 kV. The catalyst samples were ultrasonically dispersed in ethanol at room temperature for 30 min. The as-obtained solution was dropped onto the Cu grid for measurement.

FT-IR spectroscopy was recorded on a Nicolet 6700 spectrometer with a spectral resolution of 2 cm^{-1}. Self-supported wafers were prepared from the pure catalyst powder. The samples were placed in an IR cell, together with a high-vacuum turbo pump with a residual pressure below 10^5 Pa. All samples were reduced under an H_2 flow at 623 K for 4 h in the cell. The cell was then evacuated for 30 min to remove the chemisorbed hydrogen species. Afterward, the sample was cooled to room temperature and pure CO (10^5 Pa) was admitted into the cell for 30 min at 298 K. The spectra were then collected after evacuation for different times at 298 K.

XPS and XAES were carried out on a JEOL JPC-9010MC instrument equipped with an Mg

K_α X-ray radiation source (1253.6 eV) under a pressure of 1.0×10^{-7} Pa. To obtain the surface states of the catalysts ready for the reaction, the samples were collected through the following procedure. The catalyst precursor powder was pressed into thin disk and then transferred to an analysis chamber to determine the surface state of the catalysts before reduction. The sample was then *in-situ* reduced in a flow of 5% H_2-95% Ar at 623 K for 4 h under 90 kPa. Subsequently, XPS and XAES measurements for the hydrogenation-active catalyst were carried out. All spectra were recorded at room temperature and the binding energy (BE) was referred to 284.6 eV for C 1s. Peak deconvolution and fitting were performed using the peak-fitting software "SPECSURF, JEOL" with spin-orbit splitting and with relative intensities of the spin-orbit components fixed.

Catalytic reaction

A continuous flow mode equipped with a stainless steel tubular reactor and a computer-controlled auto-sampling system was built to evaluate the activity of $CuAu_x$/SBA-15 catalysts in the DMO hydrogenation. Typically, 200 mg catalyst precursor (40 to 60 meshes) was loaded into the center of the reactor with both sides of the catalyst bed packed with quartz powders (40 to 60 meshes). The catalyst precursor was pre-reduced at 623 K for 4 h under 5% H_2–95% N_2 atmosphere, and then cooled to the reaction temperature in preparation for the evaluation of its catalytic performance. Pure H_2 was fed into the reactor, keeping the reaction pressure at 3.0 MPa with the help of a back-pressure regulator. A 10 wt% DMO methanol solution was pumped into the reactor with varying weight liquid hourly space velocity ($WLHSV_{DMO}$) using a Series III digital HPLC pump (Scientific Systems, Inc.). The products were analyzed by an Aglient 7890 gas chromatograph with a flame ionization detector.

The thermal stability of the catalyst was measured using the changes of the steady space time yield (STY) of EG before and after heat treatment. Typically, the as-reduced catalyst was evaluated under the condition of 453 K and 0.6 h^{-1} $WLHSV_{DMO}$, giving a steady STY_F of EG. The reaction temperature was then raised and maintained at 623 K for 24 h. Afterward, the reactor was cooled to the previous temperature for measuring another steady STY_T of EG. The ratio of STY_T/STY_F was used to evaluate the thermal stability of the catalyst.

TOF was based on the number of surface metal atoms estimated by metal dispersion according to the equation in previous literature.[3]

For a bimetallic catalyst, the metal dispersion can be defined as following. In two existing metals, m and n, the total metal dispersion ($D_{m,n}$) can be calculated according to:

$$D_{m,n} = X_{(T)m} D_m + X_{(T)n} D_n$$

where $X_{(T)m}$ and $X_{(T)n}$ are the mol percentages of m and n, respectively and D_m and D_n are the value for metal dispersion determined by

$$D_m = 6\left(\frac{M_w}{\rho N_0 a_M}\right) / \bar{d}_{V_A}$$

where M_w is the molecular weight of the metal, ρ is the density of the metal, N_o is Avogadro constant, a_m is the efficient average area of one atom on the surface, $a_{Au}=8.7\times10^{-20}$, $a_{Cu}=6.8\times10^{-20}$ as referred to literature,[3] and $\overline{d}_v$ is the average metal particle diameter determined by TEM.

TOF indicates the moles of DMO converted per hour by per mol metal at the catalyst surface (mol-DMO mol-metal$_\mathrm{surf}^{-1}$ h^{-1}, for short h^{-1}). The DMO conversion for the TOF calculation was lower than 30% by adjusting the WLHSV$_\mathrm{DMO}$.

References:

1 X. Y. Liu, A. Q. Wang, T. Zhang, D. S. Su, C. Y. Mou, *Catal. Today*, 2011, **160**, 103.

2 X. Y. Liu, A. Q. Wang, X. D. Wang, C. Y. Mou, T. Zhang, *Chem. Commun.*, 2008, **27**, 3187.

3 J. R. Anderson, *Structure of metallic catalysts*, Academic Press, New York, **1975**.

Table 1S Physicochemical properties of the catalysts Physicochemical properties of the catalysts

Catalyst	Cu loading[a] [wt %]	Nominal Au/Cu [atomic ratio]	Actual Au/Cu[a] [atomic ratio]	S_{BET}[b] [m^2g^{-1}]	V_{pore}[b] [cm^3g^{-1}]	D_{pore}[b] [nm]	Particle size[c] [nm]	D_m[d]
SBA-15				783	0.85	4.8		0
NH_2-SBA-15				423	0.51	4.7		0
6Cu/SBA-15	5.8	0	0	357	0.56	6.0	2.6	0.40
6Cu0.9Au/SBA-15	5.6	0.05	0.02	359	0.68	6.1	2.8	0.37
6Cu1.4Au/SBA-15	5.7	0.075	0.05	373	0.67	5.8	3.2	0.33
6Cu1.9Au/SBA-15	5.6	0.1	0.08	386	0.66	6.1	3.4	0.32
6Cu3.7Au/SBA-15	6.1	0.2	0.16	388	0.51	5.1	3.7	0.29
6Au/SBA-15		∞	∞	545	0.87	6.0	4.9	0.23

[a] Determined by ICP-OES; [b] BET specific surface area; [c] Determined by TEM; [d] Metal dispersions.

Table 2S Space time yield (STY) of EG over several catalysts before and after heat treatment

Catalyst	STY_F [mg·(g-cat.·h)$^{-1}$]	STY_T [mg·(g-cat.·h)$^{-1}$]	Ratio of STY_T/STY_F
6Cu1.9Au/SBA-15	313	296	0.95
6Cu/SBA-15	86	57	0.66
10Cu/SBA-15	200	64	0.32

Reaction conditions: $WLHSV_{DMO}$ =0.6 h^{-1}, P (H_2) =3.0 MPa, H_2/DMO = 80.

Table 3S Deconvolution results of Cu LMM XAES

Catalyst	KE [eV][a]		AP [eV][b]		Cu 2p3/2 BE [eV]	X_{Cu+}[c] [%]
	Cu^+	Cu^0	Cu^+	Cu^0		
6Cu/SBA-15	914.0	918.1	1846.4	1850.5	932.4	36.9
6Cu1.4Au/SBA-15	914.0	918.3	1846.4	1850.7	932.4	45.0
6Cu1.9Au/SBA-15	914.0	918.3	1846.4	1850.7	932.4	40.9
6Cu3.7Au/SBA-15	914.0	918.3	1846.4	1850.7	932.4	31.5

[a] Kinetic energy; [b] Auger parameter; [c] Intensity ratio between Cu^+ and (Cu^+ + Cu^0) by deconvolution of Cu LMM XAES spectra.

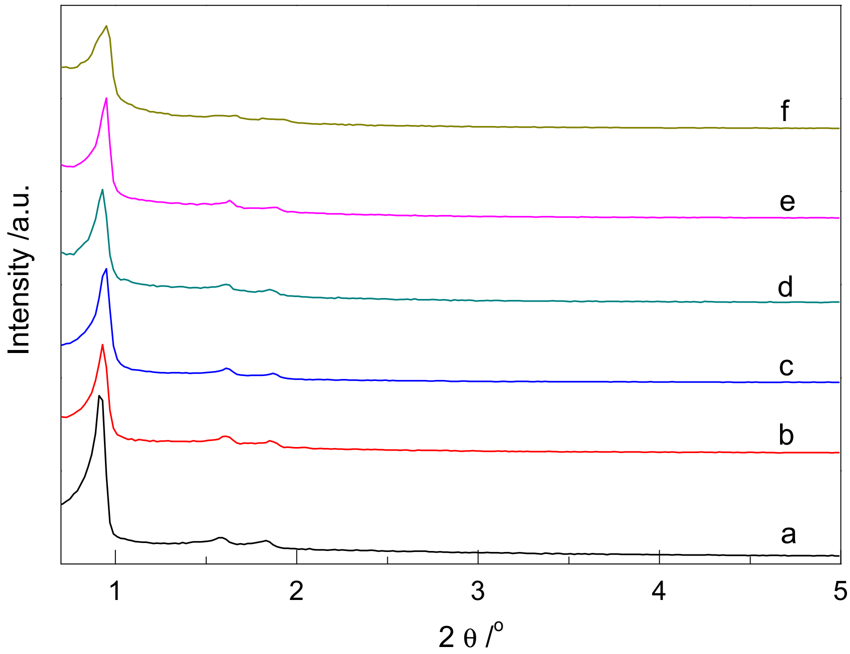

Figure 1S Small-angle XRD patterns of (a) SBA-15; (b) 6Cu/SBA-15; (c) 6Cu0.9Au/SBA-15; (d) 6Cu1.9Au/SBA-15; (e) 6Cu3.7Au/SBA-15; (f) 6Au/SBA-15.

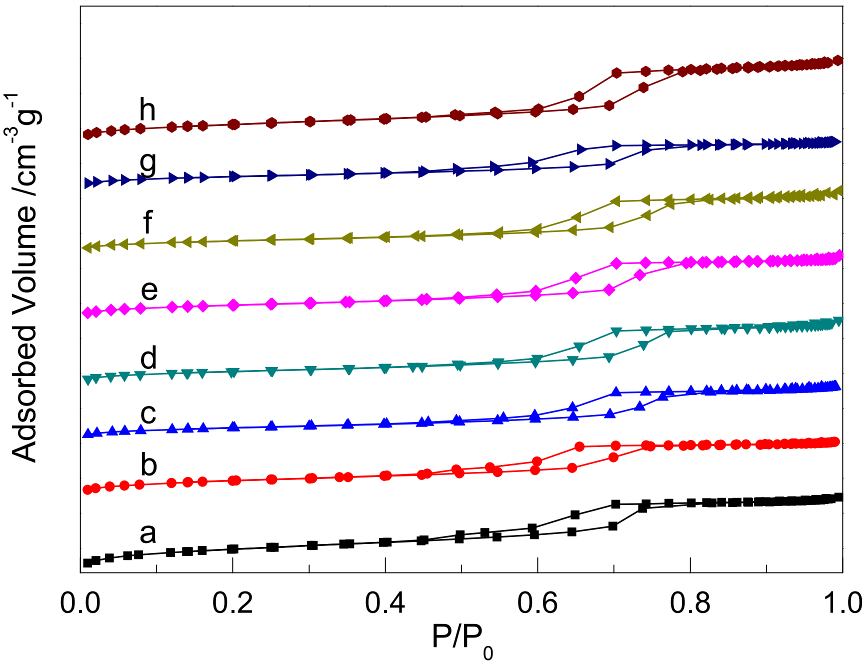

Figure 2S N_2 adsorption–desorption isotherms of (a) SBA-15, (b) NH_2-SBA-15, (c) 6Cu/SBA-15; (d) 6Cu0.9Au/SBA-15; (e) 6Cu1.4Au/SBA-15; (f) 6Cu1.9Au/SBA-15; (g) 6Cu3.7Au/SBA-15; (h) 6Au/SBA-15.

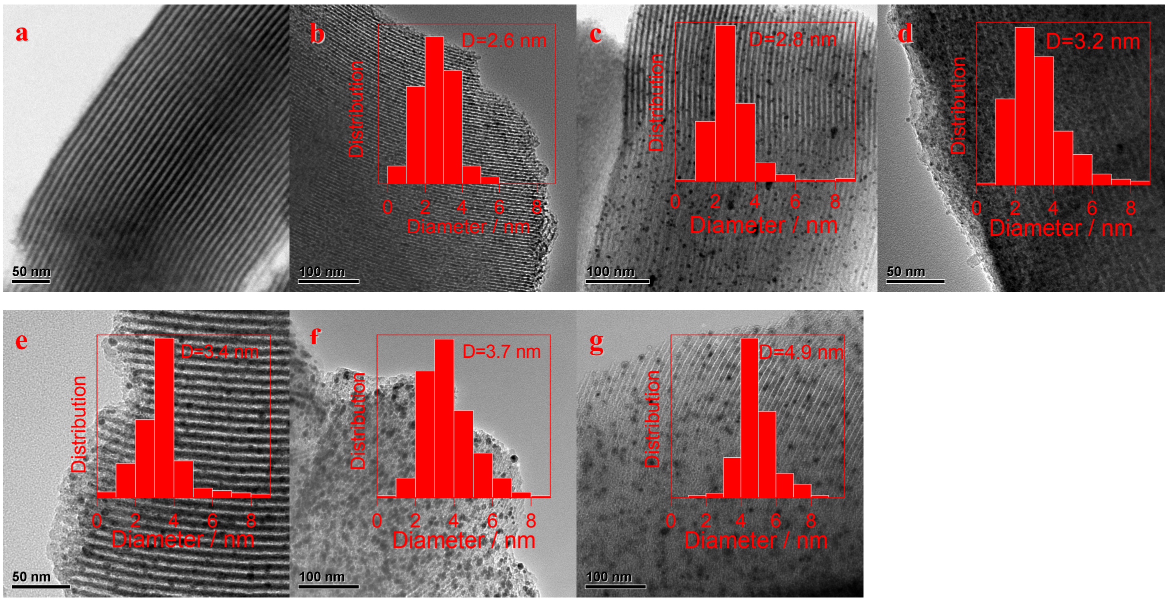

Figure 3S TEM images of (a) SBA-15, (b) 6Cu/SBA-15; (c) 6Cu0.9Au/SBA-15; (d) 6Cu1.4Au/SBA-15; (e) 6Cu1.9Au/SBA-15; (f) 6Cu3.7Au/SBA-15; (g) 6Au/SBA-15, and their metal particle size distributions.

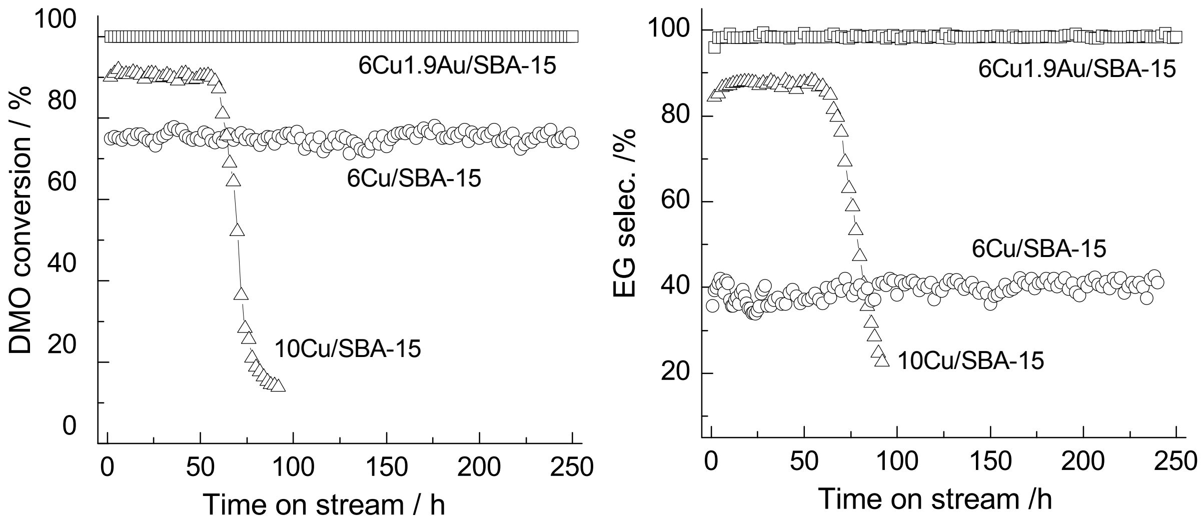

Figure 4S Catalytic performance of 6Cu1.9Au/SBA-15, 6Cu/SBA-15 and 10Cu/SBA-15 at 453 K as a function of time on stream. Reaction conditions: T=453 K, $WLHSV_{DMO}$=0.6 h^{-1}, P (H_2)=3.0 MPa, H_2/DMO=80.

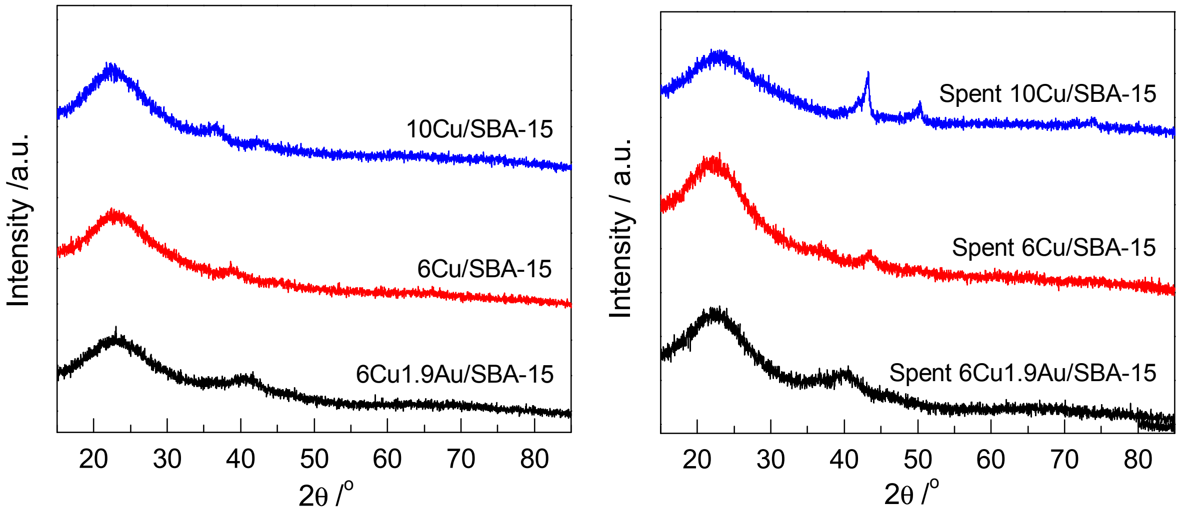

Figure 5S XRD patterns of catalysts before (left) and after (right) reaction.

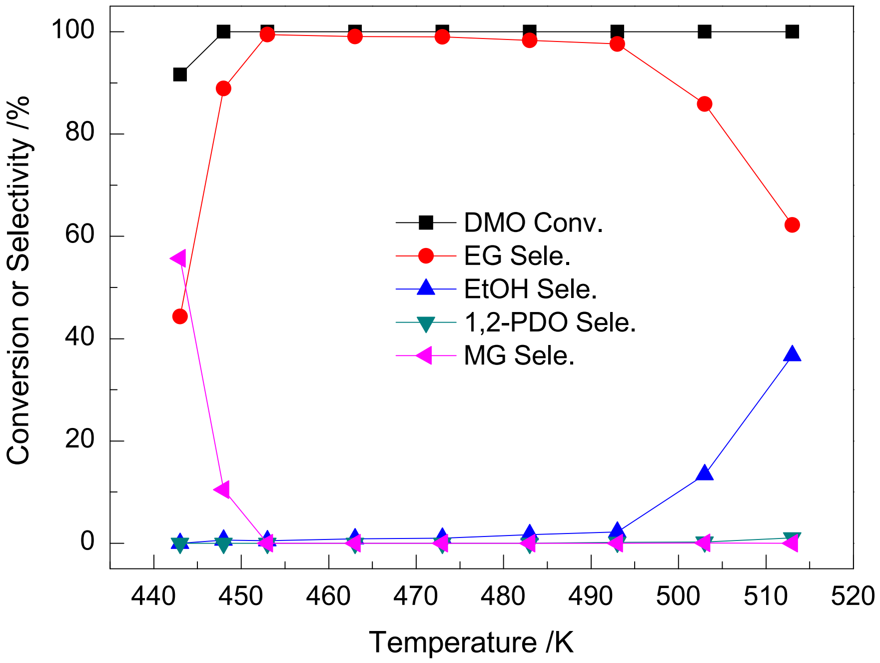

Figure 6S Hydrogenation of DMO over 6Cu1.9Au/SBA-15 catalyst as a function of temperature. Reaction conditions: $WLHSV_{DMO}$ =0.6 h^{-1}, P (H_2) =3.0 MPa, H_2/DMO=80.

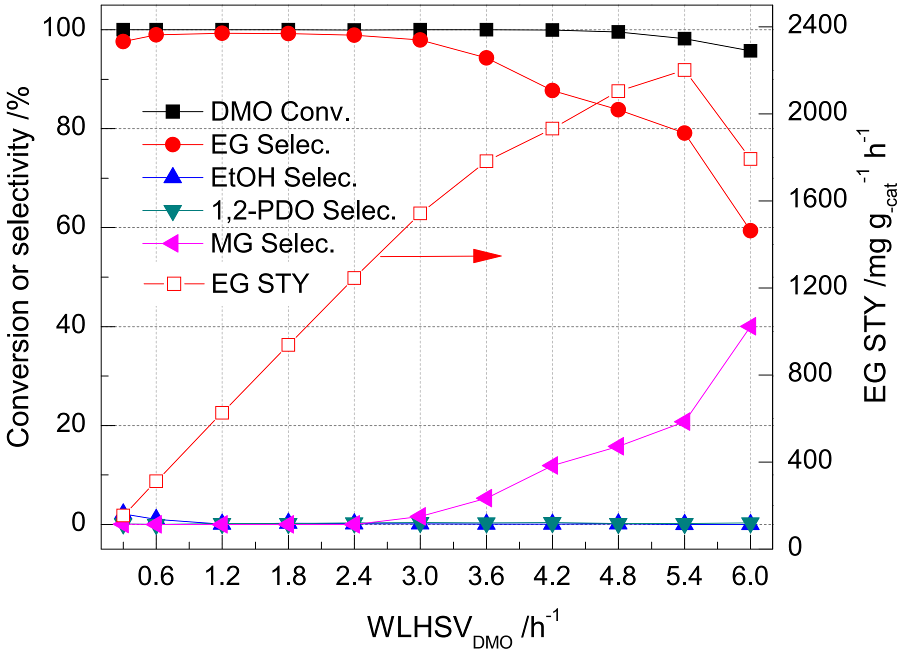

Figure 7S Hydrogenation of DMO over 6Cu1.9Au/SBA-15 as a function of $WLHSV_{DMO}$. Reaction conditions: T=473 K, P (H_2) =3.0 MPa, H_2/DMO = 80.

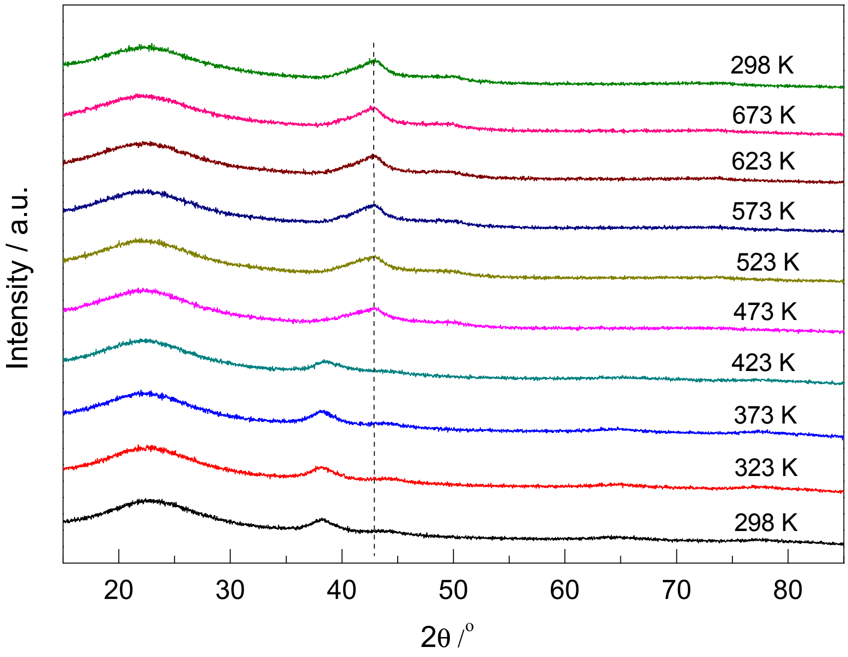

Figure 8S *In situ* XRD patterns of as-calcined 6Cu1.9Au/SBA-15 sample as a function of reduction temperature under 5%H_2-95%N_2.

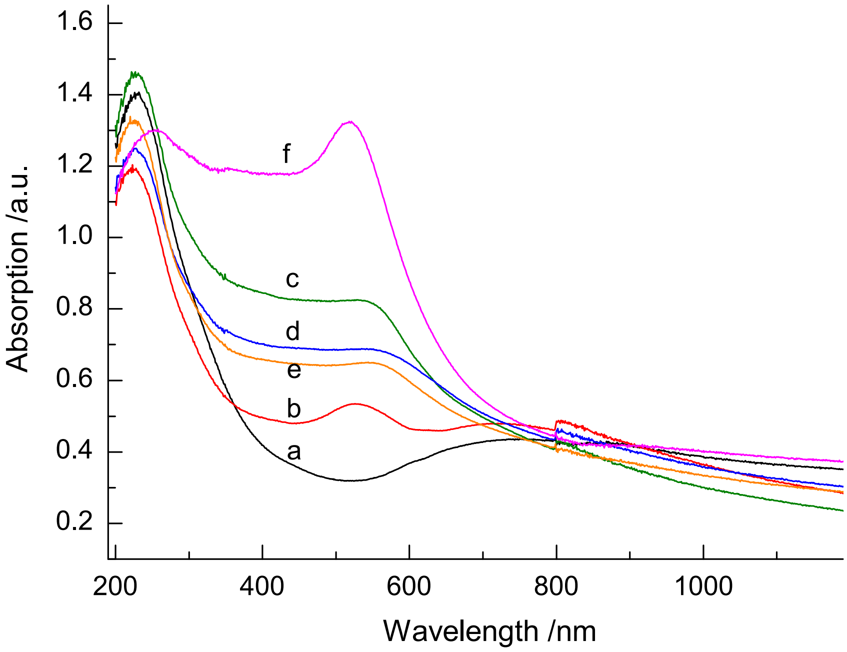

Figure 9S UV-Vis diffuse reflection spectroscopy of as-reduced *x*Cu*y*Au/SBA-15 catalysts. (a) 6Cu/SBA-15; (b) 6Cu0.9Au/SBA-15; (c) 6Cu1.4Au/SBA-15; (d) 6Cu1.9Au/SBA-15; (e) 6Cu3.7Au/SBA-15; (f) 6Au/SBA-15.

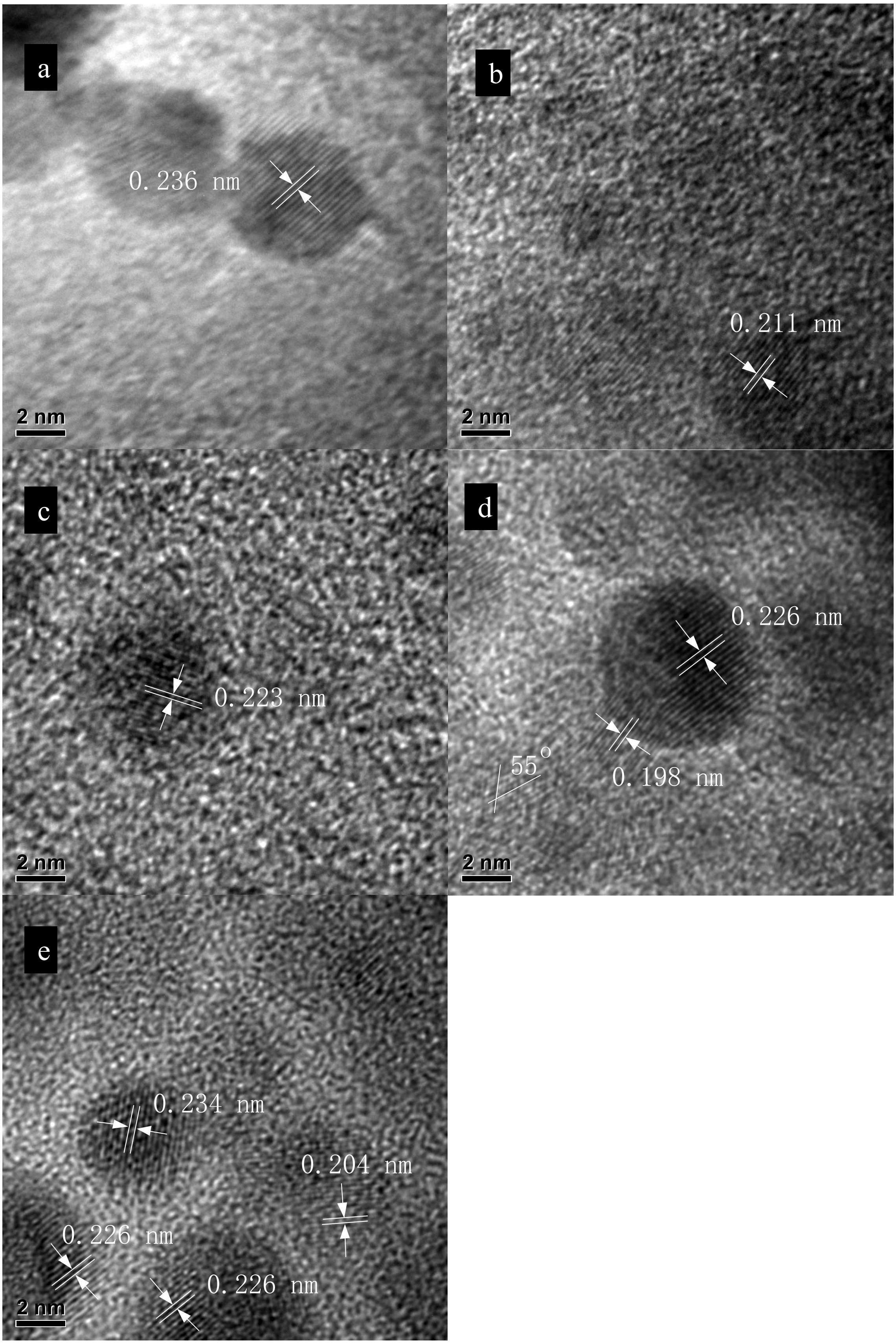

Figure 10S HRTEM images of (a) 6Au/SBA-15; (b) 6Cu/SBA-15; (c) 6Cu0.9Au/SBA-15; (d) 6Cu1.4Au/SBA-15; (e) 6Cu3.7Au/SBA-15.

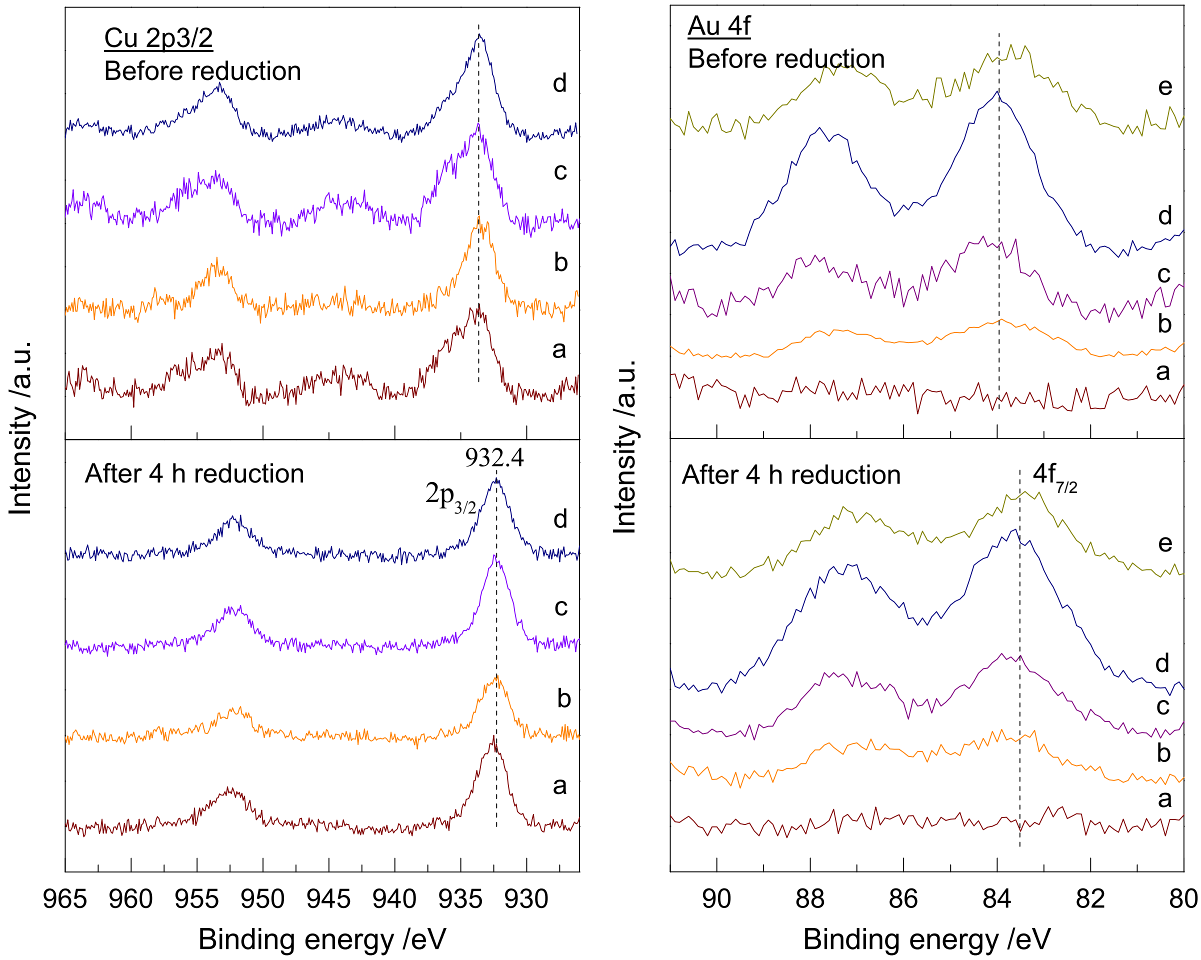

Figure 11S Cu 2p and Au 4f XP spectra of *x*Cu*y*Au/SBA-15 catalysts before (up) and after (down) 4 h reduction at 623 K under 5% H_2-95% Ar atmosphere.

(a) 6Cu/SBA-15; (b) 6Cu1.4Au/SBA-15; (c) 6Cu1.9Au/SBA-15; (d) 6Cu3.7Au/SBA-15; (e) 1.9Au/SBA-15.

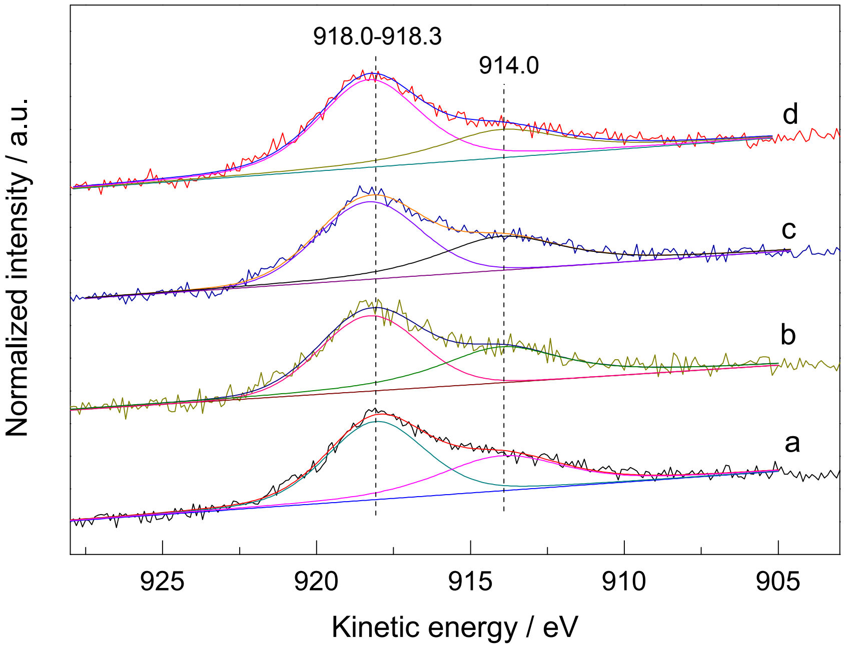

Figure 12S Cu LMM XAES spectra of the *x*Cu*y*Au/SBA-15 catalysts after 4 h reduction at 623 K under H_2 (5%)/Ar (95%) atmosphere.

a: 6Cu/SBA-15, b: 6Cu1.4Au/SBA-15, c: 6Cu1.9Au/SBA-15, d: 6Cu3.7Au/SBA-15.