HOKKAIDO UNIVERSITY

Title	Remarkable enhancement of Cu catalyst activity in hydrogenation of dimethyl oxalate to ethylene glycol using gold
Author(s)	Wang, Ya-nan; Duan, Xinping; Zheng, Jianwei et al.
Citation	Catalysis Science & Technology, 2(8), 1637-1639 https://doi.org/10.1039/c2cy20154b
Issue Date	2012-08
Doc URL	https://hdl.handle.net/2115/52662
Rights	Catal. Sci. Technol., 2012,2, 1637-1639 - Reproduced by permission of The Royal Society of Chemistry (RSC)
Type	journal article
File Information	Supplementary_information.pdf, Supplementary information

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Electronic supplementary information for

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

Ya-nan Wang,[a] Xinping Duan,[a] Jianwei Zheng,[a] Haiqiang Lin,[a] Youzhu Yuan,*[a] Hiroko Ariga,[b] Satoru Takakusagi,[b] Kiyotaka Asakura*[b]

[a] *Department of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry for Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols–Ethers–Esters, Xiamen University, Xiamen 361005, China. E-mail: yzyuan@xmu.edu.cn; Fax: +86 592 2183047;Tel: 86 592 2181659*

[b] *Catalysis Research Center, Hokkaido University, Kita-ku N21W10, Sapporo, Hokkaido 001-0021, Japan.*

Experimental details

Catalyst preparation

The SBA-15 supported CuAu nanocatalyst was prepared using a modification of the two-step approach described in literature.[1,2] Typically, before the preparation of catalysts, the surface of the support SBA-15 was first functionalized with APTES ($H_2N(CH_2)_3Si(OEt)_3$) so as to prepare SBA-15 supported gold-copper alloy nanoparticles. Briefly, 1.0 g SBA-15 and 2.5 g APTES were dissolved into 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. After that, 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, and then filtration and washing, the obtained solid was added to the 50 ml of copper nitrate ($Cu(NO_3)_2$) solution. The mixture was again reduced by $NaBH_4$, followed by continuously stirring, filtration and thorough washing. The discovered solid was calcined at 873 K in air for 6 h to get catalyst precursor, and then reduced at 623 K in 5% H_2–95% N_2 atmosphere for 4 h to obtain the $CuAu_x$/SBA-15 (where x denotes atomic radio of Au to Cu) catalysts. In the synthesis, the Cu loading was kept constant at 6 wt% and 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 X-ray powder diffraction (XRD) patterns. The tube voltage was 40 kV and the current was 30 mA. For *in situ* XRD measurement, a catalyst precursor was placed in a stainless steel holder and then covered with a beryllium plate having a thickness of 0.1 mm. After that a 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 samples reached the preset temperatures for 30 min. The diffraction pattern was identified by matching them with reference patterns included 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 the 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, and the Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distributions according to the desorption branch of the isotherms.

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

The reducibility of the calcined sample was determined by H_2 temperature-programmed reduction (TPR) performed on a Micromeritics Autochem II 2920 instrument connected with a Hiden Qic-20 mass spectrometer (MS). Prior to the TPR test, the catalyst was pretreated in a quartz U-tube reactor at 523 K for 1 h under a gas flow of 20% O_2-80% Ar at a rate of 50 cm^3 min^{-1} to drive off physically adsorbed impurities. After the catalyst cooled to room temperature under argon, 5% H_2-95% Ar was introduced at a flow rate of 50 cm^3 min^{-1}, and then the temperature was ramped linearly from ambient temperature to 1073 K at a rate of 10 K min^{-1}. Hydrogen consumption was simultaneously monitored by a thermal conductivity detector and MS.

Transmission electron microscopy (TEM) and High-resolution TEM (HRTEM)

micrographs 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 copper grid for TEM.

The infrared (IR) spectra were 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 into a in situ 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.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (XAES) were carried out on a JEOL JPC-9010MC instrument equipped with an Mg Ka X-ray radiation source (1253.6eV) under the pressure of $1.0x10^{-7}$ Pa. To obtain the surface states of the catalysts ready for the reaction, the samples were collected by the following procedure. The catalyst precursor powder were pressed into thin disks, and then transferred to an analysis chamber to determine the surface state of the catalysts before reduction. And then the samples were In-situ reduced in a flow of 5% H_2-95% Ar at 623 K for 4 h under 90 kPa. After that, the XPS and XAES for the hydrogenation-active catalysts were carried out. All spectra were recorded at room temperature and the binding energy (BE) was set as 284.6 eV for C 1s. Peak deconvolution and fitting were performed using the peak-fitting software "SPECSURF, JEOL" with the spin-orbit splitting and the 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 build to evaluate the activity of $CuAu_x$/SBA-15 catalysts in DMO hydrogenation. Typically, 200 mg of catalyst precursor (40-60 meshes) was loaded into the center of the reactor with both sides of the catalyst bed packed with quartz powders (40-60 meshes). The catalyst precursors were pre-reduced at 623 K for 4 h in 5% H_2–95% N_2 atmosphere and then cooled to the reaction temperature to get ready to the evaluation of catalytic performance. Pure H_2 was fed into the reactor, keeping the reaction pressure at 3.0 MPa under the help of a back-pressure regulator. A 10 wt% DMO methanol solution was pumped into the reactor with varying the weight liquid hourly space

velocity ($WLHSV_{DMO}$) by using a Series III digital HPLC pump (Scientific Systems, Inc.). The products were analyzed by an Aglient 7890 gas chromatograph (GC) 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 a $WLHSV_{DMO}$ of 0.6 h^{-1}, giving a steady STY_F of EG. Then the reaction temperature was raised to 623 K and kept at that temperature for 24 h. After that the reactor was cooled to the previous temperature, measuring another steady STY_T of EG. The ratio of STY_T/STY_F was used to evaluate the thermal stability of the catalyst.

The turnover frequency (TOF) was based on the number of surface metal atoms estimated by metal dispersion according to the equation in literature.[3]

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

Where, D_m is the metal dispersion; M_w is the weighted average molecular weight of Au and Cu, ρ is the weighted average density of Au and Cu, N_o is Avogadro constant; a_m is the weighted average area of Au and Cu atoms on the surface, a_m = ??; $\bar{d}_v$ is the average metal particle diameter determined by TEM. The TOF value indicates the moles of glycerol converted by per mol metal at the catalyst surface per hour (mol-DMO mol-$metal_{surf}^{-1}$ h^{-1}, for short, h^{-1}). The DMO conversion for the TOF calculation was lower than 30% through adjusting the DMO WLHSV.

References:

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

[2] X. Liu, A. Wang, X. 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

Catalyst	Cu loading[a] / wt %)	Nominal Au/Cu / molar ratio	Actual Au/Cu[a] / molar 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
Cu/SBA-15	5.8	0	0	357	0.56	6.0	2.59	0.40
$CuAu_{0.05}$/SBA-15	5.6	0.05	0.02	359	0.68	6.1	2.80	0.37
$CuAu_{0.075}$/SBA-15	5.7	0.075	0.05	373	0.67	5.8	3.16	0.33
$CuAu_{0.1}$/SBA-15	5.6	0.1	0.08	386	0.66	6.1	3.35	0.32
$CuAu_{0.2}$/SBA-15	6.1	0.2	0.16	388	0.51	5.1	3.70	0.29
Au/SBA-15[e]		∞	∞	545	0.87	6.0	4.89	0.23

[a] Determined by ICP-OES; [b] BET specific surface area; [c] Determined by TEM; [d] Metal dispersions; [e] The loading of Au was 6 wt%.

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

Catalyst	STY_F / $mg\cdot(g\text{-}cat.\cdot h)^{-1}$	STY_T / $mg\cdot(g\text{-}cat.\cdot h)^{-1}$	Ratio of STY_T/STY_F
$CuAu_{0.1}$/SBA-15	313	296	0.95
Cu/SBA-15	86	57	0.66
Cu/SBA-15[a]	200	64	0.32

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

[a] The loading of Cu was 10 wt%.

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		
6wt% Cu/SBA-15	914.0	918.1	1846.4	1850.5	932.4	36.9
$CuAu_{0.075}$/SBA-15	914.0	918.3	1846.4	1850.7	932.4	45.0
$CuAu_{0.1}$/SBA-15	914.0	918.3	1846.4	1850.7	932.4	40.9
$CuAu_{0.2}$/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.

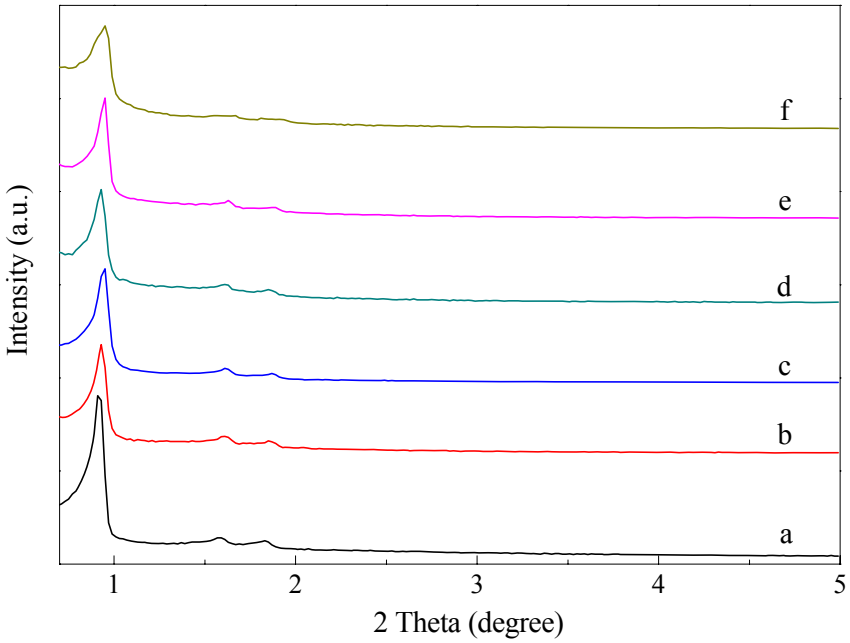

Figure 1s Small-angel XRD patterns of the (a) SBA-15; (b)-(e) for $CuAu_x$/SBA-15 with different x: (b) x=0; (c) x=0.05; (d) x=0.1; (e) x=0.2; (f) Au/ SBA-15, Au loading 6 wt%.

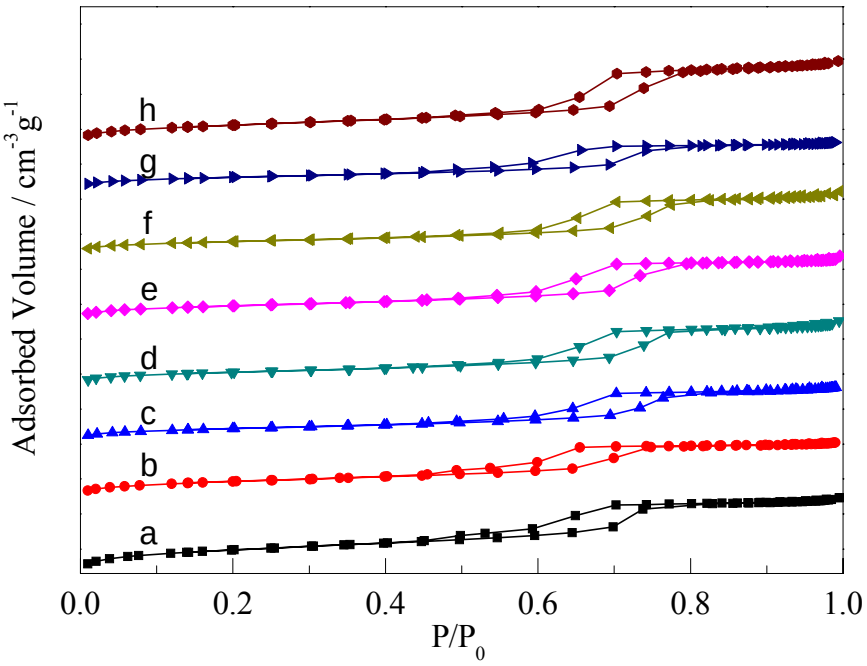

Figure 2s (a) SBA-15, (b) NH_2-SBA-15, $CuAu_x$/SBA-15 with X= (c) 0, (d) 0.05, (e) 0.1, (f) 0.2 and (g) Au/ SBA-15, Au loading 6 wt%.

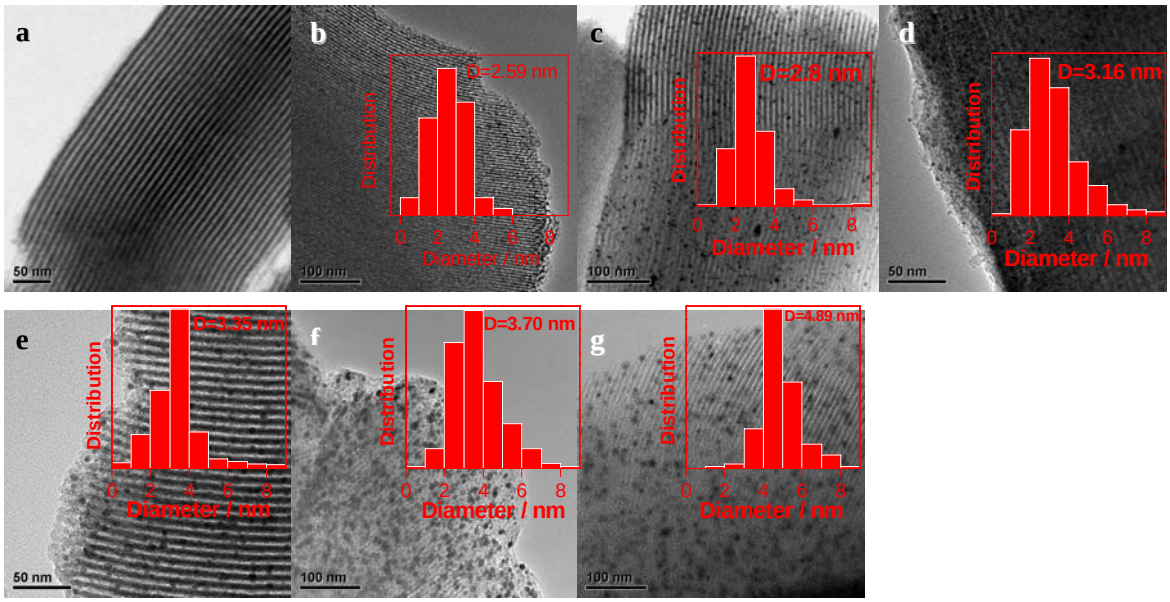

Figure 3s TEM images of (a) SBA-15, $CuAu_X$/SBA-15 with X= (b) 0; (c) 0.05; (d) 0.075; (e) 0.1; (f) 0.2 (g) ∞ and the size distributions.

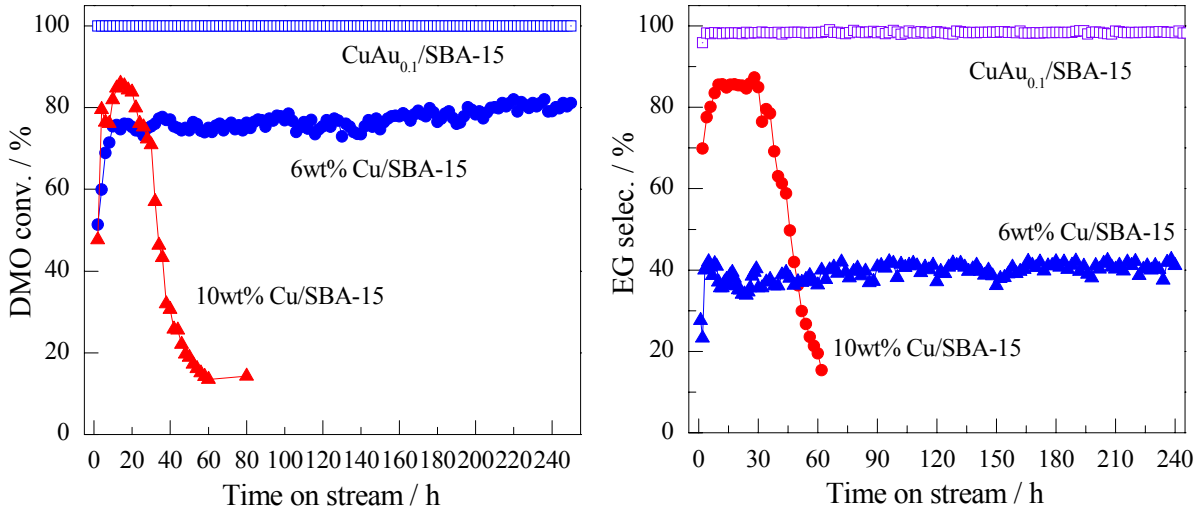

Figure 4s Catalytic performance of $CuAu_{0.1}$/SBA-15 and Cu/SBA-15 at 453 K as a function of time on stream. Reaction conditions: T = 453 K, $WLHSV_{DMO}$ = 0.6 h^{-1}, P (H_2) = 3.0 MPa, H_2/DMO = 80.

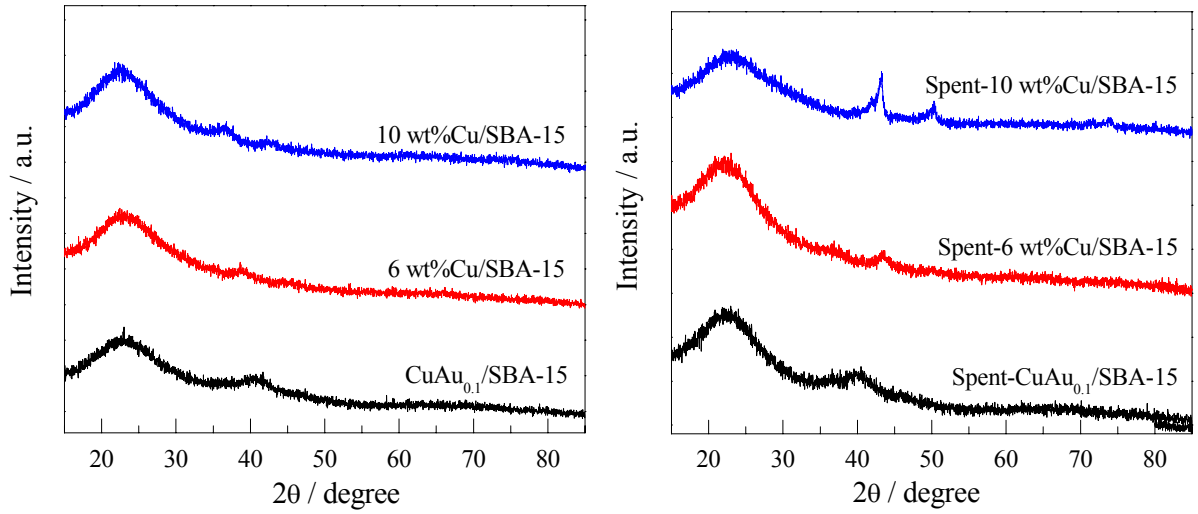

Figure 5s XRD patterns of catalysts before (left) and after (right) reaction

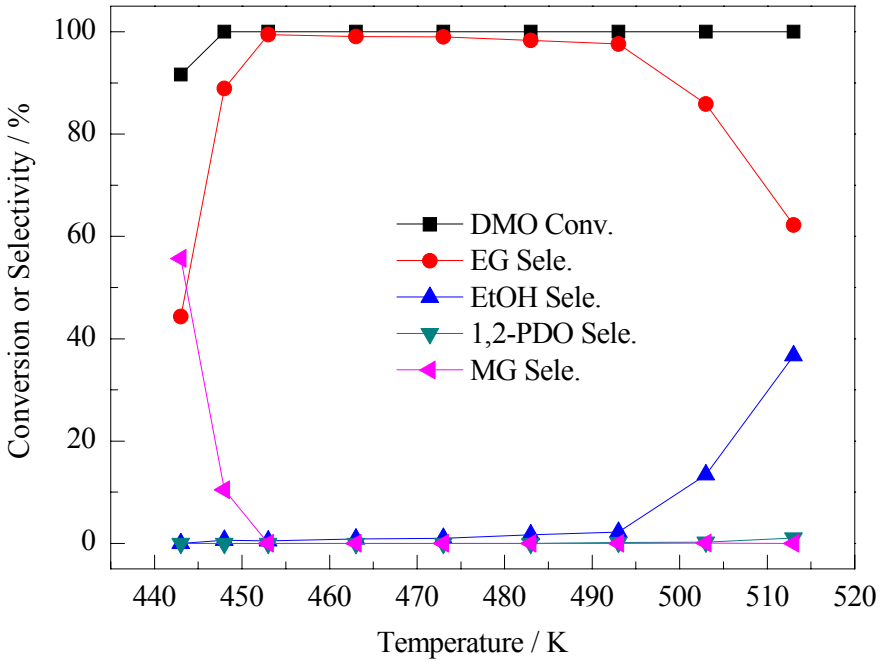

Figure 6s Hydrogenation of DMO over $CuAu_{0.1}$/SBA-15 catalyst as a function of temperature. Reaction conditions: $WLHSV_{DMO}$ =0.6 h^{-1}, P (H_2) =3.0 MPa, H_2/DMO=80.

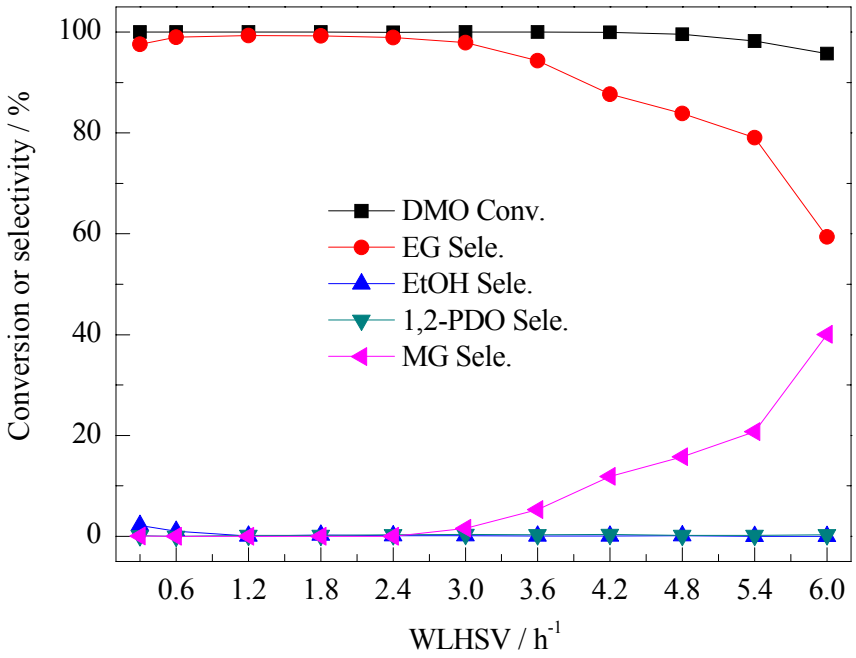

Figure 7s Hydrogenation of DMO over $CuAu_{0.1}$/SBA-15 as a function of $WLHSV_{DMO}$. Reaction conditions: T=473 K, P (H_2) =3.0 MPa, H_2/DMO = 80.

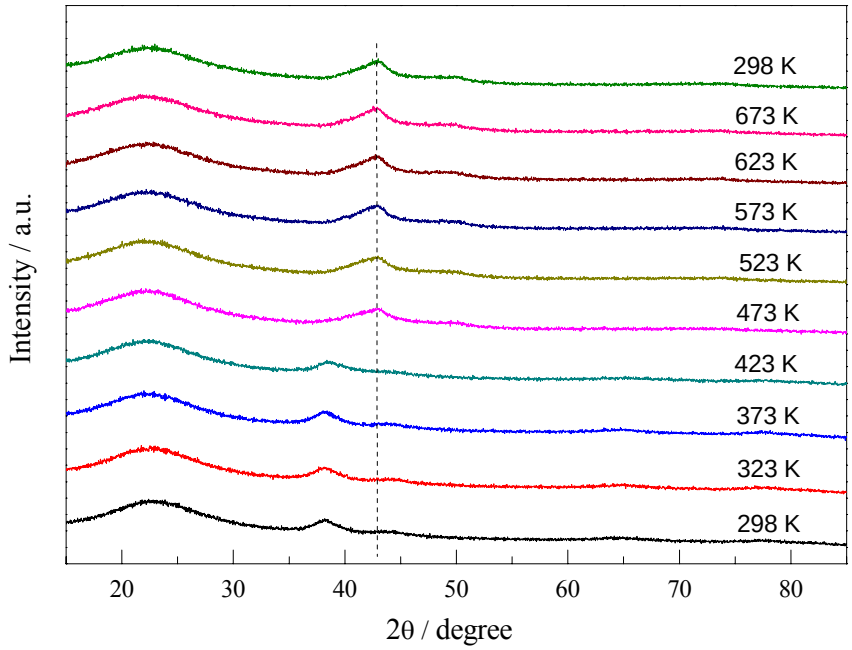

Figure 8s *In situ* XRD patterns of as-calcined $CuAu_{0.1}$/SBA-15 sample as a function of reduction temperature under 5%H_2-95%N_2.

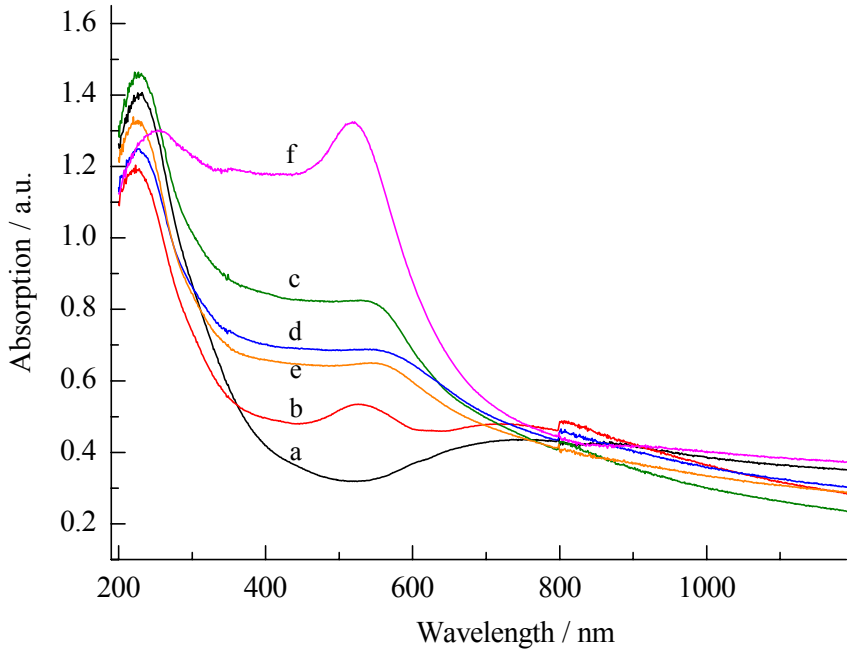

Figure 9s UV-Vis diffuse reflection spectroscopy of as-reduced $CuAu_x$/SBA-15 catalysts. (a) x=0; (b) x=0.05; (c) x=0.075; (d) x=0.1; (e) x=0.2; (f) x=∞.

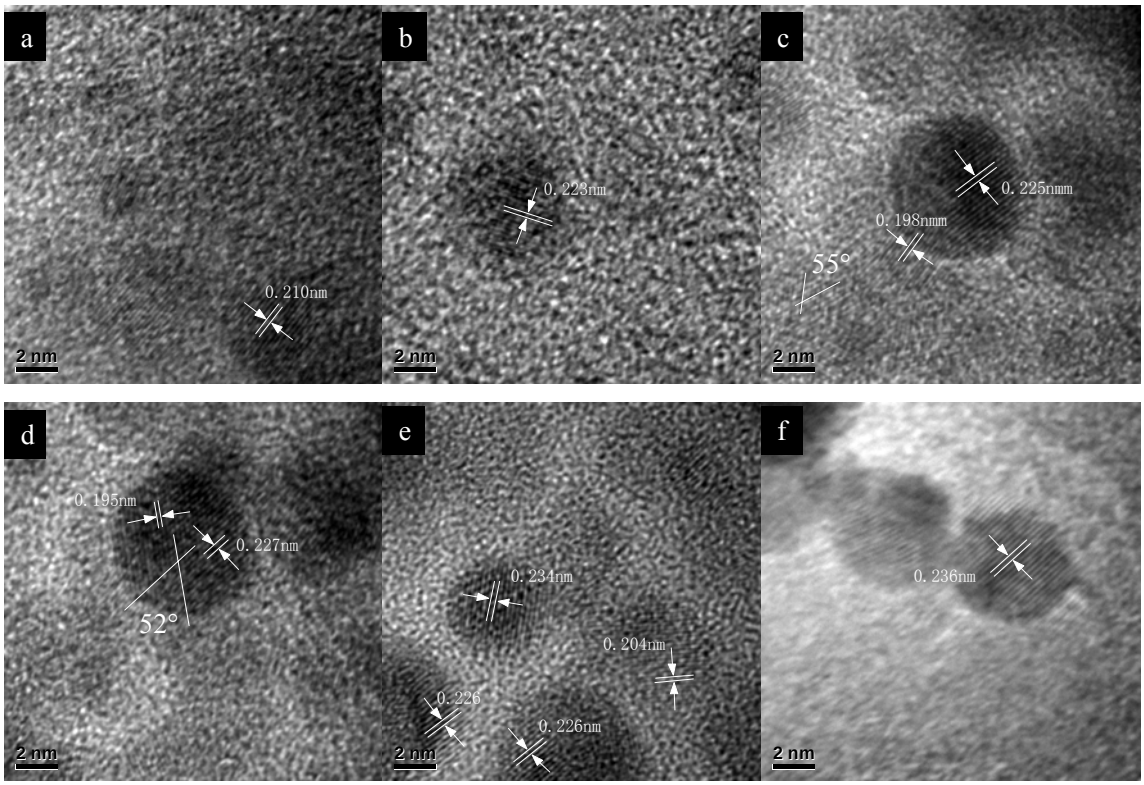

Figure 10s HRTEM images of (a) Cu/SBA-15; (b) $CuAu_{0.05}$/SBA-15; (c) $CuAu_{0.075}$/SBA-15; (d) $CuAu_{0.1}$/SBA-15; (e) $CuAu_{0.2}$/SBA-15; (f) Au/SBA-15.

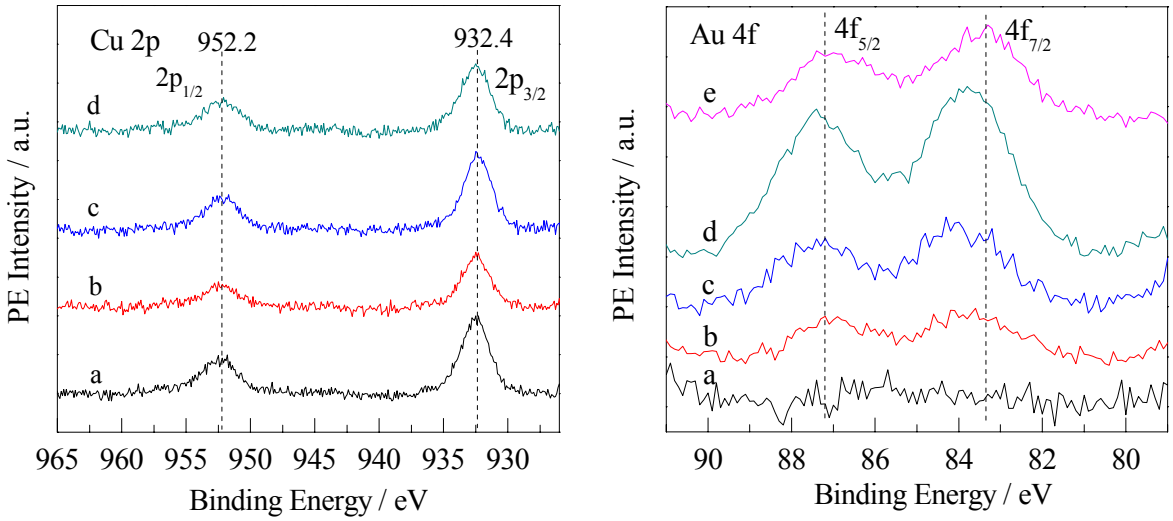

Figure 11s Cu 2p and Au 4f XP spectra of $CuAu_x$/SBA-15 catalysts with after 4 h reduction at 623 K under 5% H_2-95% Ar.

(a) Cu/SBA-15; (b) $CuAu_{0.075}$/SBA-15; (c) $CuAu_{0.1}$/SBA-15; (d) $CuAu_{0.2}$/SBA-15; (e) Au/SBA-15.

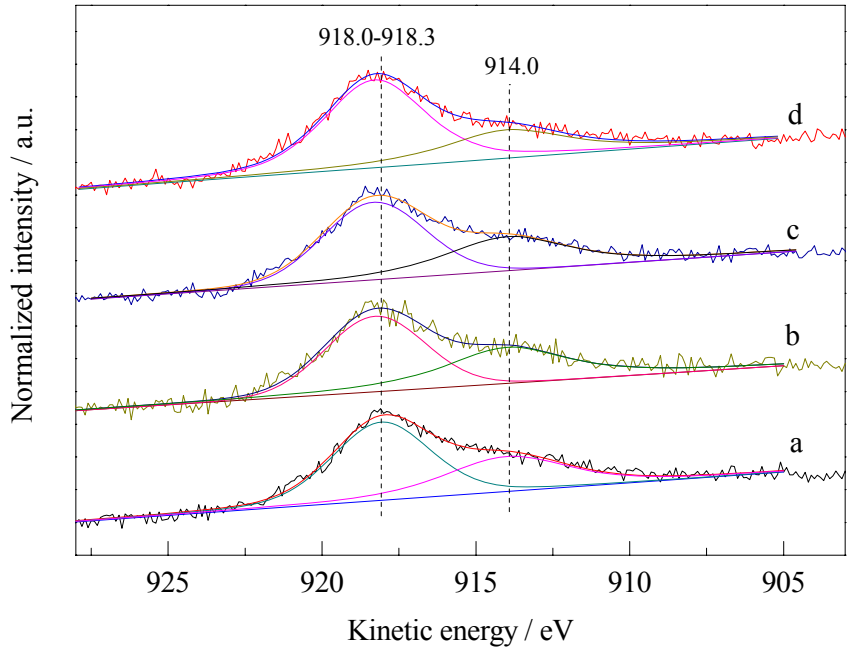

Figure 12s Cu LMM XAES spectra of the $CuAu_X$/SBA-15 catalysts after 4 h reduction on 623 K under H_2 (5%)/Ar (95%) atmosphere.

a: Cu/SBA-15, b: $CuAu_{0.075}$/SBA-15, c: $CuAu_{0.1}$/SBA-15, d: $CuAu_{0.2}$/SBA-15.