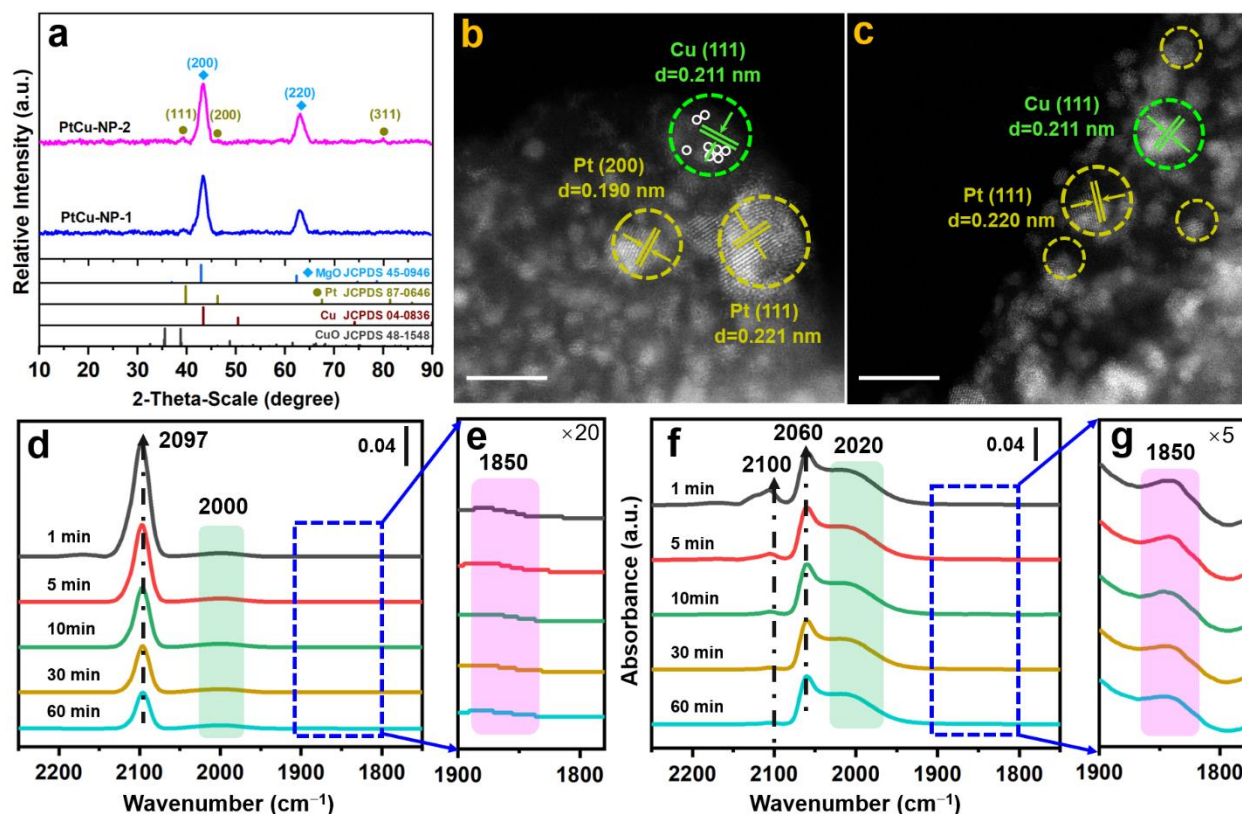


Supplementary Information

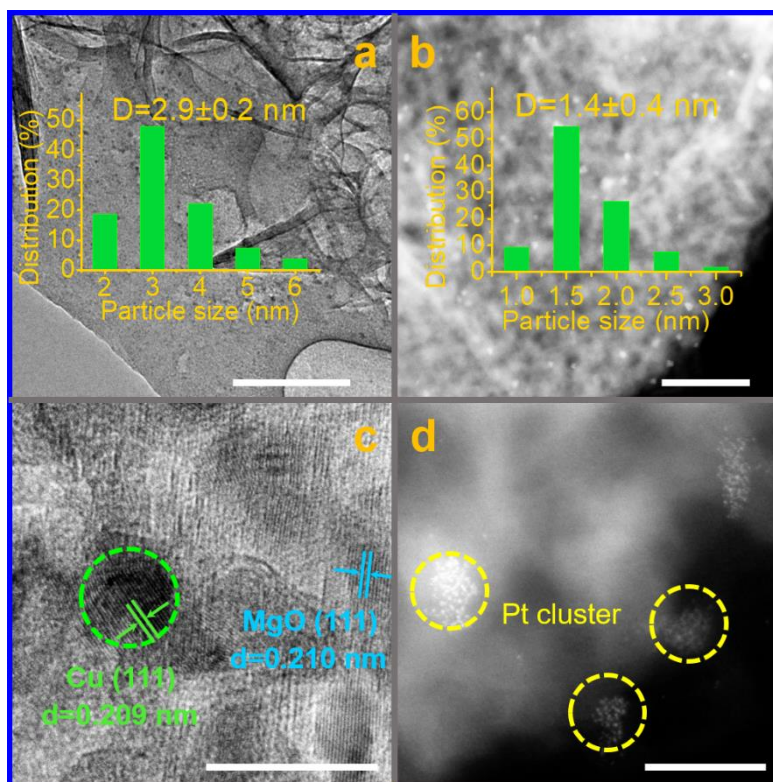
Platinum–copper single atom alloy catalysts with high performance towards glycerol hydrogenolysis

Zhang et al.

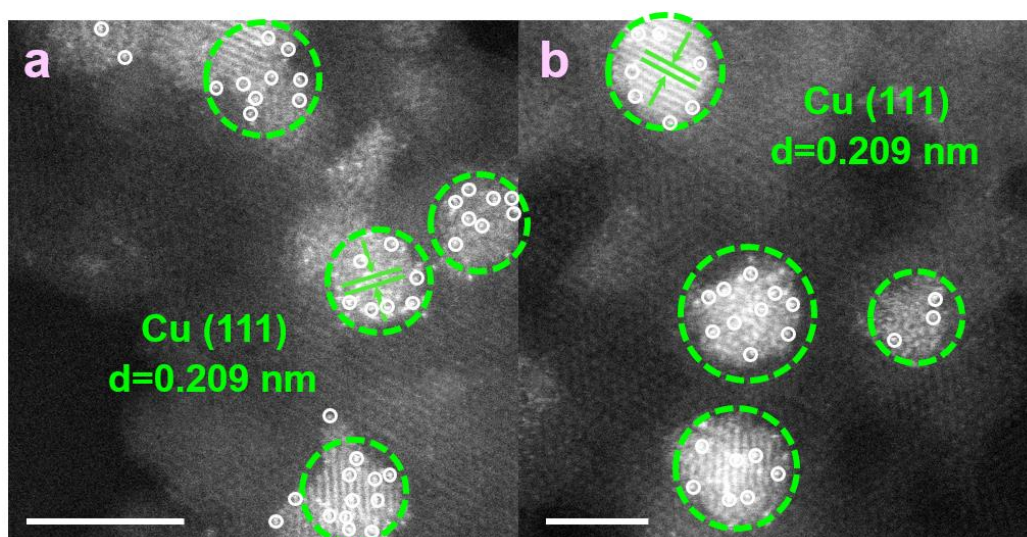
Supplementary Figures



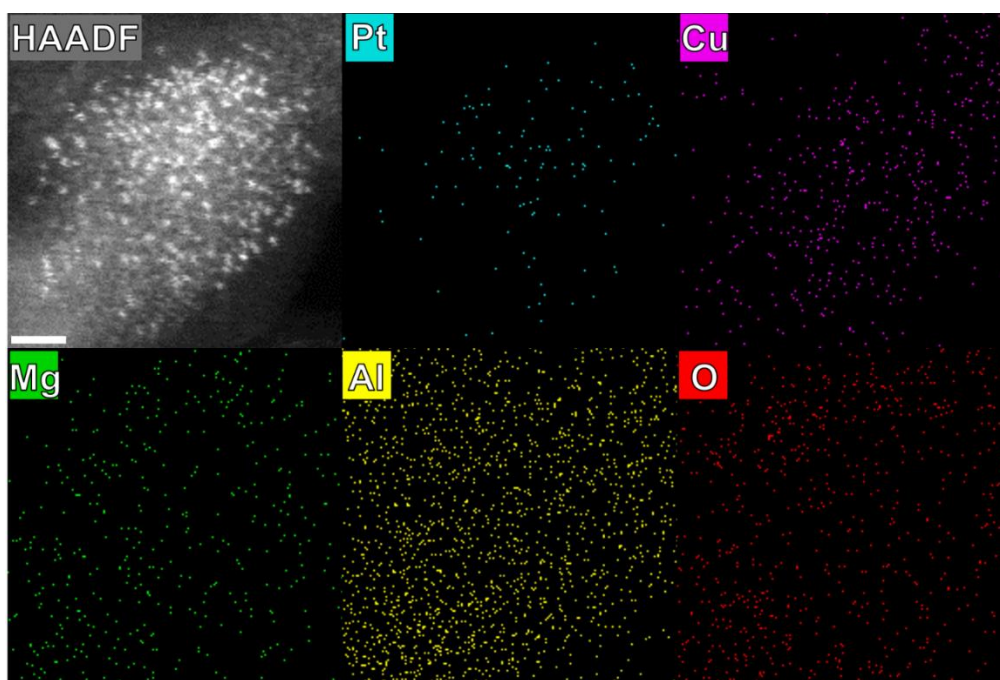
Supplementary Figure 1 | Structural characterization of PtCu-NPs. (a) The XRD patterns of PtCu-NP-1 and PtCu-NP-2 samples; AC-HAADF-STEM image of (b) PtCu-NP-1 and (c) PtCu-NP-2; *in situ* CO-DRIFTS spectra of (d, e) PtCu-NP-1 and (f, g) PtCu-NP-2 sample purging with helium as a function of time. Scale bars: a and b 5 nm



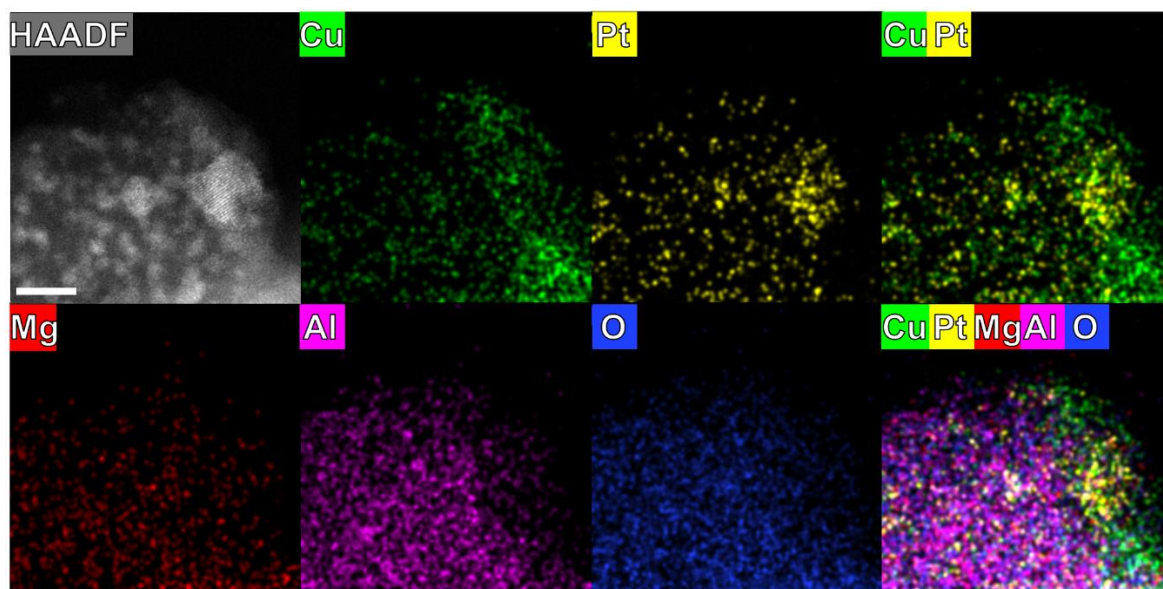
Supplementary Figure 2 | Structural characterization of Cu/MMO and Pt/MMO. (a) and (c): HRTEM images of Cu/MMO; (b) and (d): AC-HAADF-STEM images of Pt/MMO sample. Scale bars: a 100 nm; b 20 nm; c 10 nm; d 5 nm



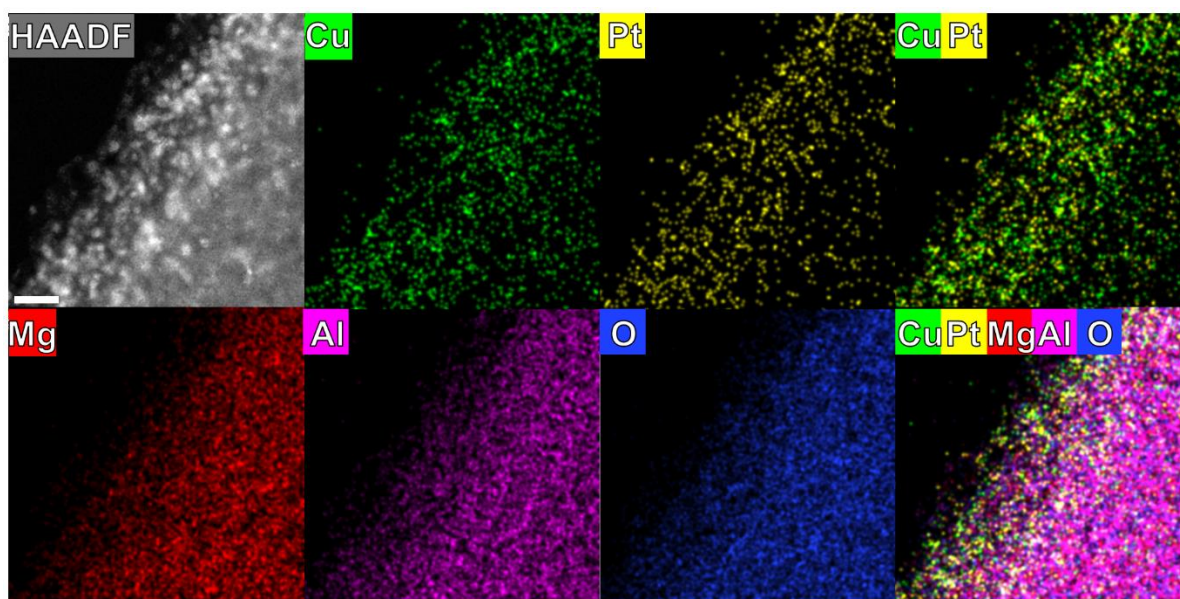
Supplementary Figure 3 | Structural characterization of PtCu-SAA. (a) and (b) The typical AC-HAADF-STEM images of PtCu-SAA sample in different regions; the atomically dispersed Pt atoms (white circles) are clearly observed on the Cu surface. Scale bars: a 5 nm; b 2 nm



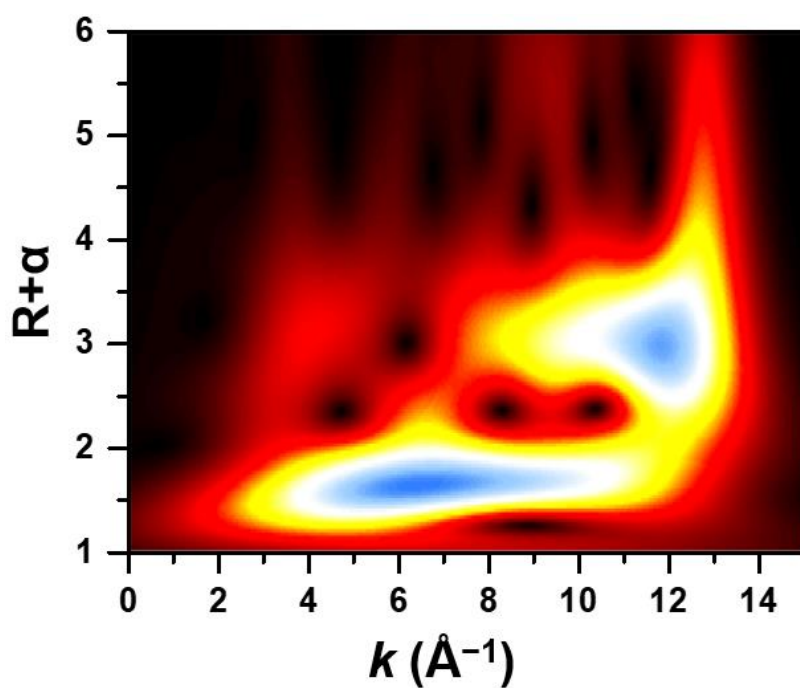
Supplementary Figure 4 | Element mapping images of PtCu-SAA. AC-HAADF-STEM images of PtCu-SAA sample and corresponding element EDS mapping of Pt, Cu, Mg, Al and O, respectively. Scale bar: 1 nm



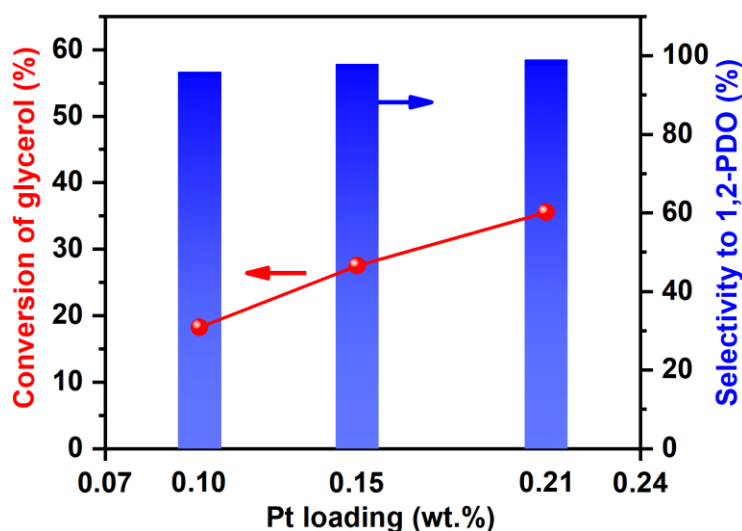
Supplementary Figure 5 | Element mapping images of PtCu-NP-1 sample. AC-HAADF-STEM images of PtCu-NP-1 sample and corresponding element EDS mapping of Pt, Cu, Mg, Al and O, respectively. Scale bar: 5 nm



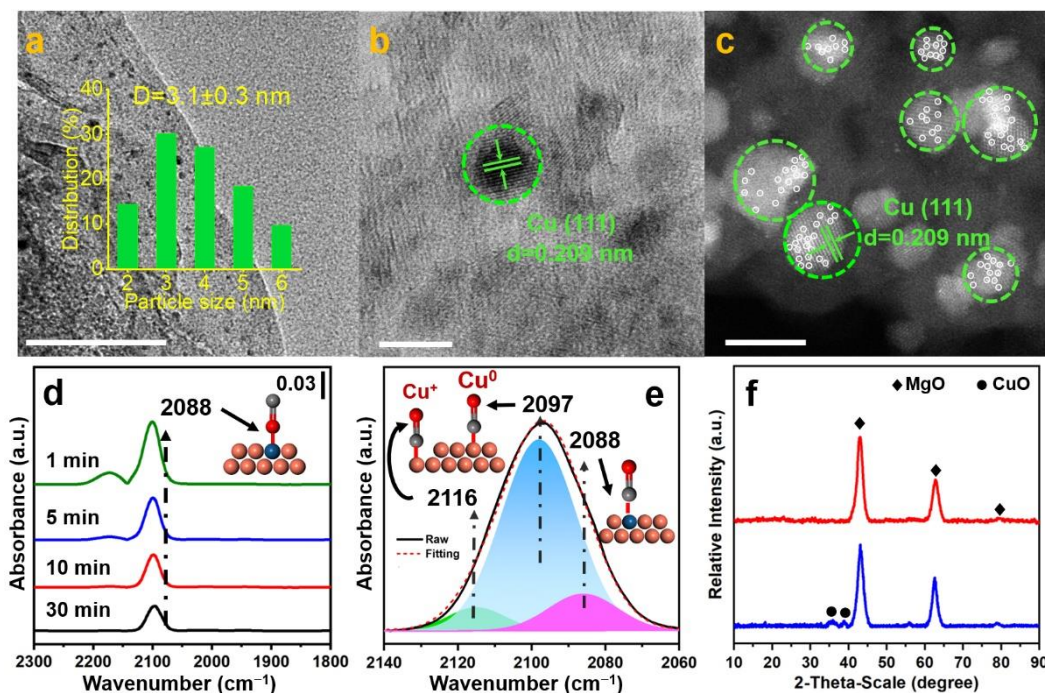
Supplementary Figure 6 | Element mapping images of PtCu-NP-2 sample. AC-HAADF-STEM images of PtCu-NP-2 sample and corresponding elemental EDS mapping of Pt, Cu, Mg, Al and O, respectively. Scale bar: 10 nm



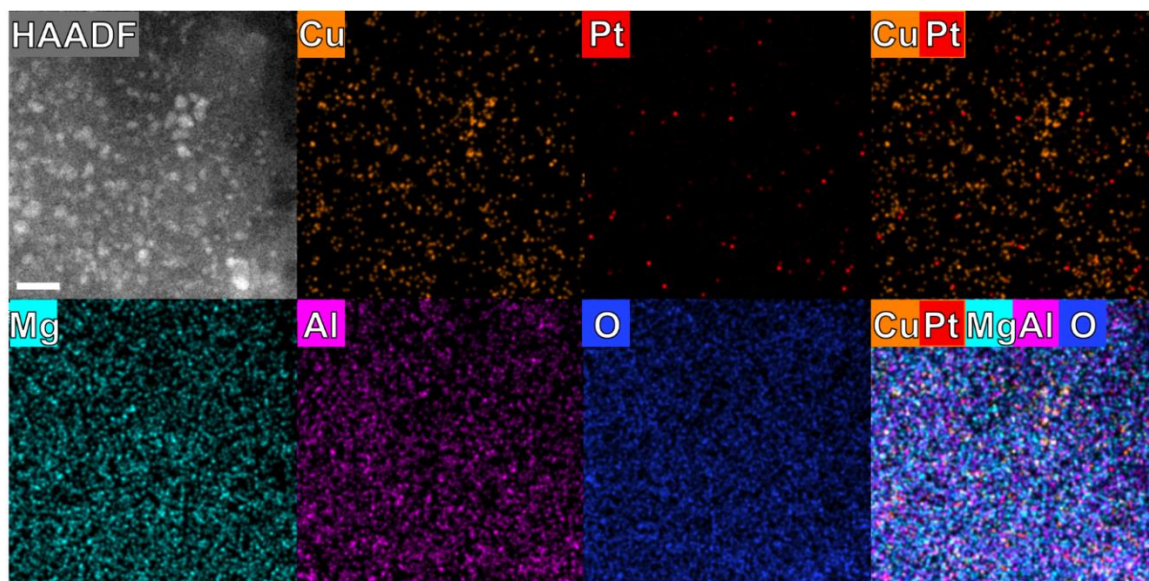
Supplementary Figure 7 | Structure characterization of PtO₂ standard sample. *In situ* Pt L3-edge EXAFS wavelet transforms spectra of PtO₂ standard sample



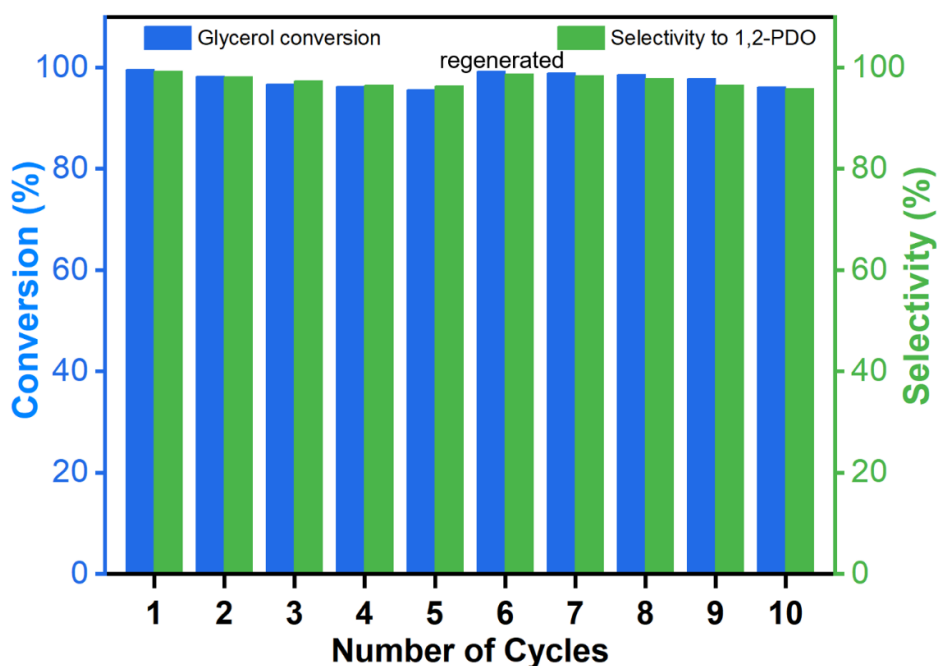
Supplementary Figure 8 | Identification for the active sites of PtCu–SAA catalyst. Catalytic evaluations of PtCu–SAA samples with various Pt loading toward glycerol hydrogenolysis to 1,2-PDO. Reaction conditions: 10 mL of glycerol alcoholic solution (0.283 g of glycerol), 0.014 g catalyst, 2.0 MPa of H₂ pressure, 200 °C



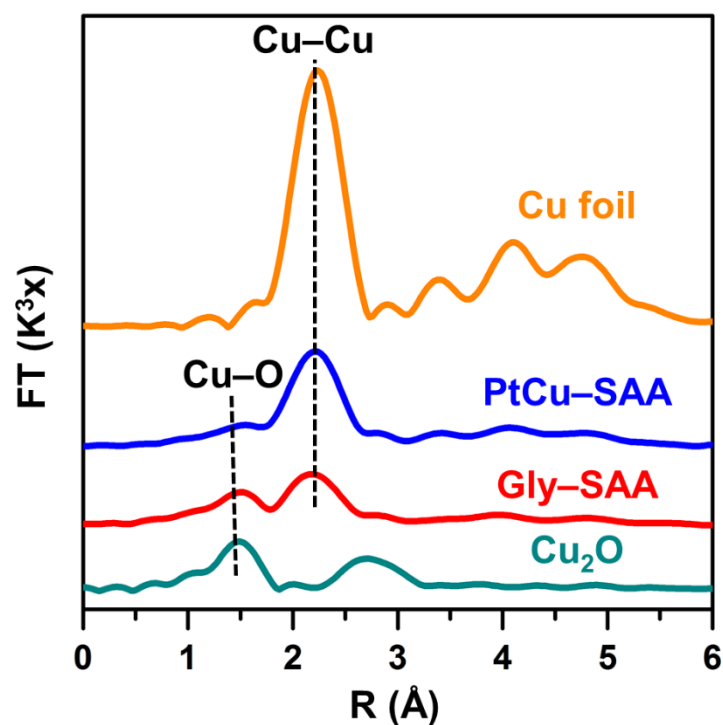
Supplementary Figure 9. | Characterization of the used PtCu–SAA catalyst. (a) TEM image, (b) HRTEM image, (c) AC–HAADF–STEM image, (d) and (e) CO–DRIFTS spectrum of the used PtCu–SAA catalyst after five cycles, (f) XRD patterns of the used catalyst (red line) and the regenerated catalyst (blue line). Scale bars: a 100 nm; b and c 5 nm



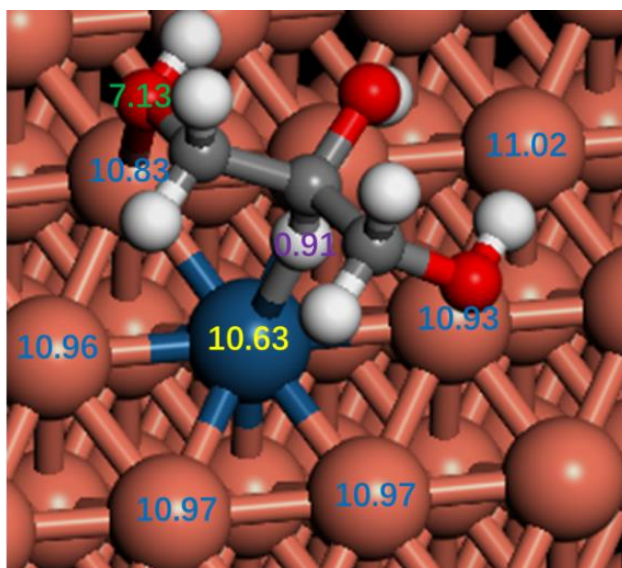
Supplementary Figure 10 | Element mapping images of the used PtCu-SAA catalyst. AC-HAADF-STEM images of the used PtCu-SAA catalyst after five cycles and corresponding elemental EDS mapping of Pt, Cu, Mg, Al and O, respectively. Scale bar: 20 nm



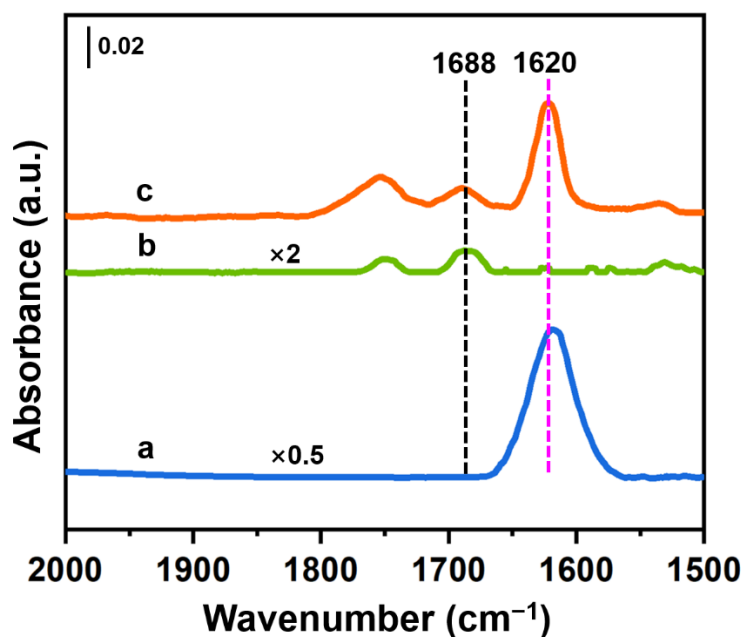
Supplementary Figure 11 | Catalytic reusability of PtCu-SAA sample. Catalytic performance of PtCu-SAA catalyst for glycerol hydrogenolysis over five cycles and another five cycles after regeneration



Supplementary Figure 12 | Structure characterization of various samples at Cu K edge. *In situ* fourier-transform EXAFS spectra at Cu K-edge for: Cu₂O, PtCu-SAA exposed to glycerol (shorten for Gly-SAA), PtCu-SAA, and Cu foil, respectively

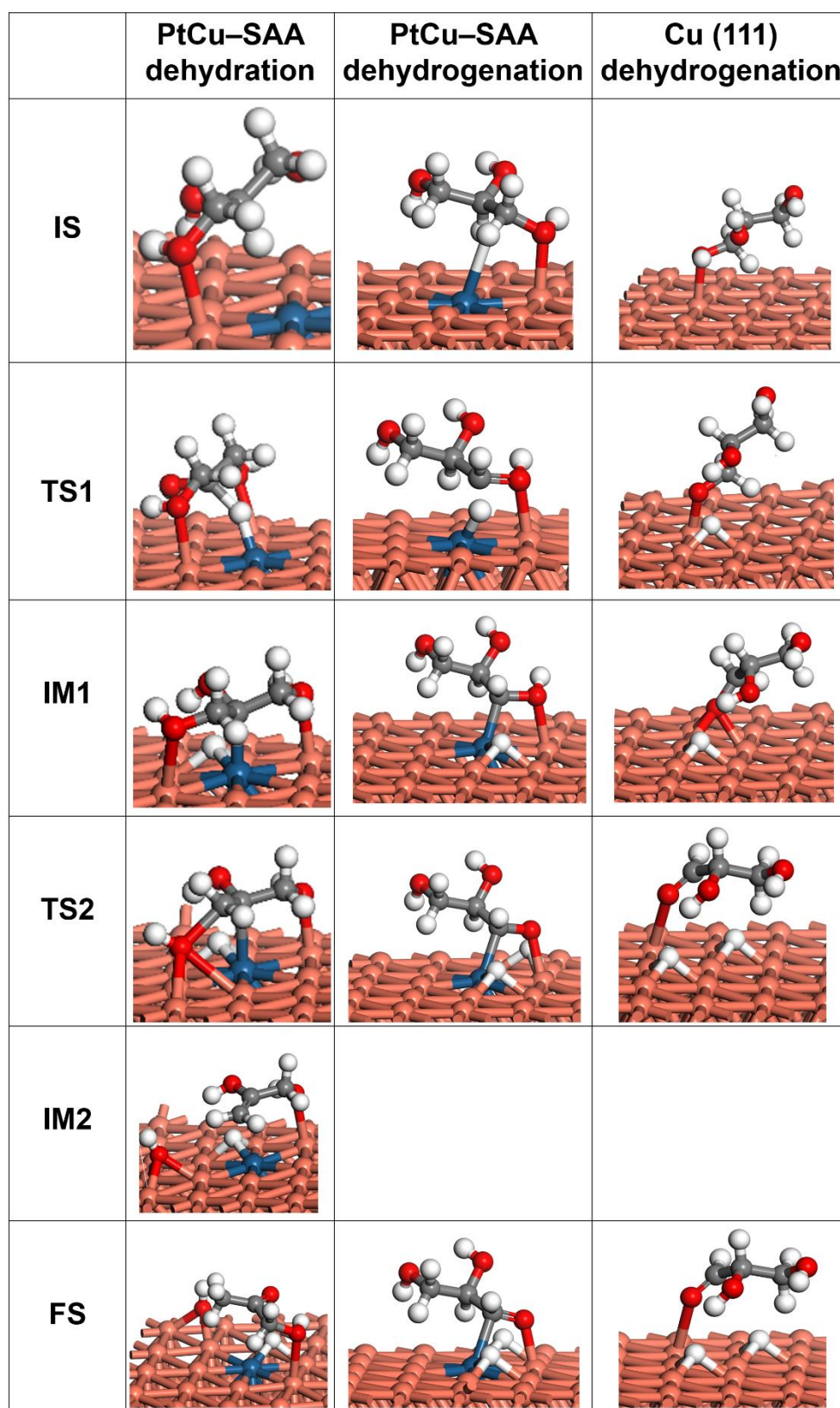


Supplementary Figure 13 | Surface electronic structure of PtCu-SAA. Bader charge analysis of glycerol molecule adsorbed on the PtCu-SAA surface



Supplementary Figure 14 | Determination of the characteristic peak for acetol. *In situ* DRIFTS spectra of (a) water, (b) glycerol and (c) glycerol aqueous solution in the presence of PtCu–SAA catalyst, respectively

The FTIR spectrum of pure water in the presence of catalyst was measured as a reference sample (Supplementary Figure 14, curve a), which displayed an obvious absorption band centered at about 1620 cm^{-1} . This band is usually assigned to the bending vibration of H_2O molecule in agreement with previous report⁸. For purpose of identifying the IR band at around 1688 cm^{-1} , *in situ* DRIFTS was conducted on PtCu–SAA by introducing a mixture of water and glycerol as a control sample. Compared with the IR spectrum of pristine gaseous glycerol on PtCu–SAA (Supplementary Figure 14, curve b and c), a new band at about 1620 cm^{-1} is observed, which is assigned to the bending vibration of adsorbed H_2O molecule. These comparative experiments verify that the IR band at around 1680 cm^{-1} is not derived from adsorbed water but really from acetol.



Supplementary Figure 15 | Geometric structures for the elementary step. Initial states (IS), transition states (TS), intermediates (IM), and final states (FS) for glycerol dissociation on various pathway of Cu (111) and PtCu-SAA (111) surface, respectively

Supplementary Tables

Supplementary Table 1. EXAFS fitting parameters at the Cu K-edge and Pt L₃-edge for various samples

Sample	Shell	N ^a	R (Å) ^b	σ^2 (10 ⁻³ Å ²) ^c	ΔE_0 (eV) ^d	R-factor (%) ^e
Pt-foil	Pt–Pt (metallic Pt)	12 ^f	2.77(±0.02)	5.6	2.9	0.11
PtO ₂	Pt–O	6	2.05(±0.01)	4.4	–3.6	0.24
	Pt–Pt	6	3.09(±0.02)	5.1	–6.6	
PtCu-SAA	Pt–Cu (Pt L ₃)	7.4	2.57(±0.01)	7.2	5.7	0.21
PtCu-SAA	Cu–Cu (Cu K)	8.9	2.56(±0.02)	8.2	3.7	0.32
	Cu–O (Cu K)	0.8	1.86(±0.03)	9.4	–1.8	
Gly-SAA	Cu–Cu (Cu K)	4.2	2.54(±0.02)	9.2	2.4	0.41
	Cu–O (Cu K)	1.6	1.87(±0.03)	6.0	3.3	
Cu ₂ O	Cu–O	4	1.85(±0.01)	7.6	4.7	0.27
	Cu–Cu (O-bridged)	8	3.02(±0.01)	6.7	7.7	
Cu-foil	Cu–Cu (metallic Cu)	12	2.56(±0.01)	5.2	5.6	0.16

^a *N*: coordination number; ^b *R*: average distance between absorber and backscattered atoms; ^c σ^2 : Debye-Waller factor; ^d ΔE_0 : the inner potential correction; ^e *R*-factor: if *r* < 5%, consistent with broadly correct models. ^f This value was fixed during EXAFS fitting, based on the known structure of Pt foil. The accuracy of the above parameters was estimated as follows: *N*, σ^2 , ΔE_0 , ± 20%. The data ranges used for fitting in *R* space (ΔR) are 1.3–3.1 Å.

Supplementary Table 2. Catalytic evaluations on Cu/Pt catalysts with various atomic ratios

Catalyst	Pt/Cu ^a	Pt/Cu ^b	Pt species on Cu surface ^c	Con. (%)	Sel. _{1,2-PDO} (%)	Sel. _{Others} (%)
	(mol/mol)					
PtCu–SAA	0.03	0.022	Single atoms	99.6	99.2	0.8
PtCu–NP–1	0.15	0.12	Single atoms and clusters	89.5	90.4	9.6
PtCu–NP–2	0.5	0.39	Clusters and islands	58.8	71.2	28.8

^a The nominal atomic ratio. ^b The determined atomic ratio by ICP–AES. ^c Determined by in situ CO-DRIFTS, XAFS, AC–HAADF–STEM and EDS mapping. Reaction conditions: 10 mL of glycerol alcoholic solution (10 wt.%), 0.14 g of catalyst, 2.0 MPa of H₂ pressure, 8.0 h, 200 °C.

Supplementary Table 3. Comparison studies on catalytic performance toward glycerol hydrogenolysis over various catalysts

Num.	Catalyst	Tem.	P.	Content ^c	T.	Con.	Sel.	TOF ^e	TOF ^f	TOF ^g	Yield	Pro. ⁱ	Pro. ^j	Ref.
		°C	MPa	wt.%	h	%	%	h ⁻¹	h ⁻¹	h ⁻¹	%	h ⁻¹	h ⁻¹	
1	PtCu–SAA ^a	200	2	0.21; 3.2 ^d	1	11.4	98.2	2.3×10 ³	95	49	11.2	890	55	This work
2	PtCu–SAA ^b	200	2	0.21; 3.2 ^d	6	99.2	99.6	1.2×10 ^{3h} 5.2×10 ³ 2.6×10 ^{3h}	2.1×10 ²	1.1×10 ²	98.8	384	23.7	This work
3	PtCu–SAA ^b	200	2	0.21; 3.2 ^d	2	82	99.6				81.7	952	58.6	This work
4	Ru–Cu/ZrO ₂	180	2.5	2.5; 2.5 ^d	24	13.7	100	41.4	41.4	1.5	13.7	3.1	1.6	9
5	Ru–Cu/Al ₂ O ₃	200	2.5	2.5; 2.5 ^d	24	45	94	32.8	32.8	7.1	42.3	9.7	4.9	9
6	Ru–Cu/Al ₂ O ₃	180	2.5	2.5; 2.5 ^d	24	20.6	91.9	11.5	11.5	2.5	18.9	4.3	2.2	9
7	Ru–Cu/ MWCNTs	200	4	4.8; 28.4 ^d	6	99.8	86.5	14.0	11.8	6.5	86.3	49.5	7.2	10
8	PtRu/C	200	4	1.9; 4.7 ^d	5	42	24	180.0	180.0	54.0	10.1	3.4	3.4	11
9	IrNi ₂	200	3.6	2; 1.2 ^d	12	22.3	80.8	46.8	46.8	6.1	18.0	3.9	2.4	12
11	Ru–Fe/CNT	200	4	5	12	86	52.3	147.5	147.5	36.1	45.0	9.9	9.9	13
12	5Pt–Re/CNT	170	4	5.3	8	55	52	51	51	15.3	28.6	2.2	2.16	14
13	Ru/ZrO ₂	180	2.5	2.5	24	30.1	69.8	289.8	289.8	10.1	21.0	4.8	4.8	9
14	Ru/Al ₂ O ₃	180	2.5	2.5	24	32.8	41.7	18.4	18.4	11.4	13.7	3.1	3.1	9
15	Pt/C	200	4	3	5	13	79	21.6	21.6	9.3	10.3	2.4	2.4	15
16	Ru/MWCNTs	200	4	5	6	65.5	71.2	198.7	198.7	53.7	46.6	25.7	25.7	10
17	Pd/m–ZrO ₂ +ZnO	220	6	4.3	4	40	94.1	324.7	324.7	63.6	37.6	38.9	38.9	16
18	ZnPd/ZnO @Al ₂ O ₃	230	3	4.3	1.5	24.4	90.9	63.7	63.7	7.8	22.2	34.0	34.0	17
19	ZnPd/ZnO	230	3	4.3	6	8.7	86.3	48.9	48.9	0.9	7.5	2.4	2.4	17
20	Cu/MWCNTs	200	4	37.6	6	31.3	91.1	6.5	6.5	1.9	28.5	–	2.1	10
21	Cu _{0.4} /Zn _{0.6} Mg _{5.0} Al ₂ O _{8.6}	200	2	5.3	10	85.5	98.6	18.6	18.6	9.2	84.3	–	19.7	18

^a Reaction conditions: 10 mL of glycerol alcoholic solution (0.283 g glycerol), 0.014 g of PtCu–SAA catalyst. ^b 10 mL of glycerol alcoholic solution (0.83 g glycerol), 0.14 g of catalyst. ^{c-d} The content of active metal species (^dthe former is noble metal and the latter means the non-noble metal). ^{e-h} The TOF value was evaluated by moles of initial glycerol converted per mole of exposed active site atoms per hour (including the surface noble metal atoms ^e, the whole surface metal atoms ^f, the overall metal atoms ^g and the active sites of SAA atoms ^h). ^{i-j} The 1,2-PDO productivity (Pro.) was defined as the mass of obtained 1,2-PDO per the overall^j (nobleⁱ) metal mass per hour.

Supplementary Table 4. Catalytic performance of PtCu–SAA and other reported catalysts at low reaction temperature

N	Catalyst	T	P	T.	Con	Sel	R1 ^a	R2 ^b	TOF ^c	Pro. ^f	Ref
		°C	MPa	h	%	%	mmol·h ⁻¹ ·g ⁻¹ -cat		h ⁻¹	h ⁻¹	
1	PtCu–SAA	120	4.0	6	34	97.3	2.5	2.3	2.3×10 ² (Pt) ^d 1.1×10 ² (SAA) ^e 9.3 (Cu+Pt) ^d	86.2	This work
2	Ru/C+A70(H ⁺)	120	8	10	8	68	23.1	15.7 1		24.0	19
3	Rh-ReO _x /SiO ₂	120	8	5	79	41	47.4	18.7 8		35.7	20
4	Ir-ReO _x /SiO ₂	120	8	1	7	9;69 ^g	50.7	4.6	284 ^d	34.7	21
5	Ir-ReO _x /SiO ₂	120	8	1	38	7;58 ^g	69.4	4.86	–	14.7	21
6	Pt-Re/SiO ₂	120	4	1	8.3	40	5.1	2.03	32.5 ^d	1.93	22
7	Pt/SBA-15	150	4	30	4	10.6	0.04	0.00 5	2.8 ^d	0.01	23
8	CuO/SiO ₂ -PG	160	9	12	19	98	2.8	2.70	1.9 ^d	0.7	24
9	CuO/SiO ₂ -IM	160	9	12	2	99	0.3	0.29	1.0 ^d	0.07	24
10	Cu/3Ce/Mg	160	6	10	19	94	2.0	1.86	14.6 ^d	1.8	25

Reaction conditions: 10 mL of glycerol alcoholic solution (10 wt.%), 0.21 g of catalyst. ^a The average reaction rate of glycerol conversion based on the mol of glycerol converted per catalysts mass and per hour. ^b The average formation rate of 1,2-PDO based on the mol of 1,2-PDO obtained per catalysts mass and per hour. ^{c-e} The TOF value was evaluated by the number of glycerol converted per hour per catalytic site (including of the surface metal atoms ^d and the active sites atoms ^e). ^f The 1,2-PDO productivity (Pro.) was defined as the mass of obtained 1,2-PDO per the overall active metal mass per hour. ^g The former is the selectivity of 1,2-PDO while the latter means that of 1,3-propanediol.

As shown in Supplementary Table 4, the PtCu–SAA catalyst displays a rather low glycerol conversion and TOF value at 120 °C than that at 200 °C; while the selectivity of 1,2-PDO maintains ~97.3% at 120 °C, close to 99.2% at 200 °C. The average reaction rate of glycerol and TOF value based on surface (active sites) metal atom of PtCu–SAA is lower than that of 4%Rh-ReO_x and 20%Ir-ReO_x catalysts (entry 3–5) at 120 °C and 8.0 MPa. It should be noted that the catalytic performance, TOF value and the 1,2-PDO productivity based on the overall active metal of PtCu–SAA are much higher than most Pt and/or Cu based catalysts at ~120 °C.

Supplementary Table 5. Catalytic performance toward glycerol hydrogenolysis over MgAl–MMO sample

Catalyst	Tem. (°C)	P. (MPa)	Time (h)	Con. _{Gly} (%)
MgAl–MMO	200	2.0	8.0	1.3

Reaction conditions: 10 mL of glycerol alcoholic solution (10 wt. %), 0.2 g of catalyst.

Supplementary Table 6. Catalytic performance of PtCu–SAA catalyst by using a fixed bed

Number	Catalyst	Gas	Con. _{GLY}	Sel. _{1,2-PDO}	Sel. _{acetol}	Sel. _{others}
			(%)	(%)	(%)	(%)
1	PtCu–SAA	H ₂	12.5	15.6	79.7	4.7
2	PtCu–SAA	N ₂	10.2	1.8	92.4	5.8

Reaction conditions: Temperature: 200 °C; Pressure: 0.1 MPa; WHSV: 2.0 g_{cat}^{−1}·h^{−1}; catalysts: 50 mg; H₂/Gly molar ratio: 80.

Supplementary Table 7. Born–Oppenheimer electronic energies for PtCu–SAA *via* dehydration pathway

Reaction	ΔE (eV)
CH ₂ OH-CHOH-CH ₂ OH (g) + * → CH ₂ OH-CHOH-CH ₂ OH* (1)	−1.02
CH ₂ OH-CHOH-CH ₂ OH* (1) → CH ₂ OH-COH-CH ₂ OH* + H* (2)	0.47
CH ₂ OH-COH-CH ₂ OH* + H* (2) → CH ₂ OH-COH-CH ₂ * + H* + OH* (3)	−0.18
CH ₂ OH-COH-CH ₂ * + H* + OH* (3) → CH ₂ OH-CO-CH ₃ * + H* + OH* (4)	−0.53

Supplementary Table 8. Born–Oppenheimer electronic energies for PtCu–SAA *via* dehydrogenation pathway

Reaction	ΔE (eV)
CH ₂ OH-CHOH-CH ₂ OH (g) + * → CH ₂ OH-CHOH-CH ₂ OH* (1)	−1.09
CH ₂ OH-CHOH-CH ₂ OH* (1) → CH ₂ OH-COH-CH ₂ OH* + H* (2)	0.62
CH ₂ OH-COH-CH ₂ OH* + H* (2) → CH ₂ OH-COH-CH ₂ O* + 2H* (3)	0.62

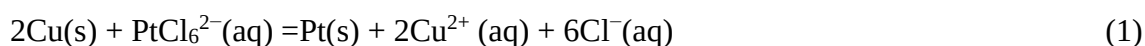
Supplementary Table 9. Born–Oppenheimer electronic energies for Cu (111) *via* dehydrogenation pathway

Reaction	ΔE (eV)
CH ₂ OH-CHOH-CH ₂ OH (g) + * → CH ₂ OH-CHOH-CH ₂ OH* (1)	−0.89
CH ₂ OH-CHOH-CH ₂ OH* (1) → CH ₂ OH-CHOH-CH ₂ O* + H* (2)	0.28
CH ₂ OH-CHOH-CH ₂ O* + H* (2) → CH ₂ OH-COH-CH ₂ O* + 2H* (3)	0.25

Supplementary Methods

The details of galvanic replacement method.

As the standard reduction potential of $\text{PtCl}_6^{2-}/\text{Pt}$ redox pair (1.44 V vs. the standard hydrogen electrode (SHE)) is much higher than that of Cu^{2+}/Cu redox pair (0.34 V vs. SHE), the following thermodynamically-favorable redox reaction occurs:



The large potential difference (up to 0.76 V) guarantees the reaction feasibility and makes this replacement reaction occur rapidly at room temperature. Moreover, Muhler *et al.*¹ have addressed how this thermodynamically-favorable reaction occurs at $T = 0\text{ }^{\circ}\text{C}$.

In situ XRD experiments

The as-obtained sample was elaborately reduced in a H_2/N_2 (1/9, v/v) stream at $350\text{ }^{\circ}\text{C}$ (heating rate: $2\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$) for 4.0 h, followed by flushing ($100\text{ mL} \cdot \text{min}^{-1}$) with high purity N_2 for 1.0 h. The reduced sample was slowly cooled down to room temperature in a N_2 atmosphere, and then the XRD patterns were precisely recorded with a 2θ scan range from 5° and 90° at a low scanning rate of $5^{\circ} \cdot \text{min}^{-1}$.

Surface H_2 –TPR experiments

Surface hydrogen temperature programmed reduction (H_2 –TPR) after the N_2O –oxidation treatment was measured on a Micromeritics Chemi-Sorb 2920 equipped with a thermal conductivity detector (TCD). Typically, the sample (50 mg) was pre-reduced in a H_2/Ar (1/9, v/v, $100\text{ mL} \cdot \text{min}^{-1}$) atmosphere at a rate of $5\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ from room temperature to $350\text{ }^{\circ}\text{C}$, and then cooled down to $50\text{ }^{\circ}\text{C}$ in an Ar flow ($50\text{ mL} \cdot \text{min}^{-1}$). Subsequently, the $\text{N}_2\text{O}/\text{Ar}$ (1/9, v/v, $50\text{ mL} \cdot \text{min}^{-1}$) was introduced

to oxidize the sample for 2.0 h. And then the sample was heated to 150 °C at 5 °C·min⁻¹ and hold at 150 °C for 1.0 h in an Ar flow (50 mL·min⁻¹) to release residual N₂O. Finally, the sample was slowly cooled down from 150 °C to 50 °C, followed by purging H₂/Ar (1/9, v/v, 50 mL·min⁻¹) along with increasing temperature to 350 °C at a rate of 5 °C·min⁻¹. Meanwhile, the surface H₂-TPR profile was recorded by a TCD detector.

N₂O chemisorption experiments

The dispersion of Cu and specific surface area of metallic Cu were determined by N₂O chemisorption and hydrogen pulse reduction method on a Micromeritics Autochem II 2920 equipped with a TCD. Briefly, after the pretreatment with He flow at 200 °C for 2.0 h, the sample (100 mg) was reduced in a H₂/Ar flow (1/9, v/v; 50 mL·min⁻¹) at 300 °C for 2 h, and the corresponding hydrogen consumption (denoted as *X*) was detected. Afterwards, the sample was flushed with high purity Ar for 1.0 h and cooled down to 150 °C. Subsequently, a pure flow of N₂O was induced at a rate of 50 mL·min⁻¹ for 2.0 h, guaranteeing a complete oxidization of surface Cu atoms to Cu₂O. Then successive pulses of high-purity H₂ were introduced at 300 °C to reduce surface Cu₂O to metallic Cu, with Ar as carrier gas (50 mL·min⁻¹). The volume of consumed hydrogen was obtained by subtracting the sum of residual unsaturated hydrogen pulses from the total hydrogen injection volume (denoted as *Y*). The dispersion of metallic Cu (*D*%, eq. 1), was obtained according to N₂O chemisorption value:

$$D(\%) = \frac{2 \times Y}{X} \times 100 \quad (2)$$

Hydrogen oxygen (H₂-O₂) titration experiments

The Hydrogen-oxygen titration (HOT) experiments were carried out on a Micrometric Autochem II 2920 equipped with a thermal conductivity detector (TCD). Briefly, after the

pretreatment in a H₂/Ar flow (1/9, v/v; 50 mL·min⁻¹) at 300 °C for 2 h, the sample (100 mg) was exposed to a flow of pure Ar (50 mL·min⁻¹) until the baseline was stabilized at 150 °C. Subsequently, the O₂/Ar (1/9, v/v) pulses were introduced into the carrier gas (50 mL·min⁻¹) until total saturation was reached to 150 °C. Subsequently, the absorbed oxygen was titrated by introducing pulses of H₂/Ar flow (1/9, v/v) at 150 °C. Finally, the consumption of H₂ was monitored and recorded by the TCD detector. The Pt dispersion was calculated based on the relation of HT: OT: Pt = 1.5:0.75:1.

***In situ* XAS characterization**

In situ extended X-ray absorption fine structure spectroscopy (EXAFS) at the Cu *K*-edge and Pt *L*₃-edge was carried out at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The powdered sample was pressed into a thin round sheet with a diameter of 13 mm and carefully placed into a reaction microdevice equipped with polyimide windows. The detailed experiment procedure is described as follows: The Cu/MMO, CuPt-SAA and Pt/MMO were pre-reduced in a H₂/He flow (1/9, v/v; 50 mL·min⁻¹) at 350 °C, followed by purging He (50 mL·min⁻¹) for 1.0 h and then cooled to room temperature in a He stream. Finally, the EXAFS spectra of Cu *K*-edge or Pt *L*₃-edge was collected as *in situ* EXAFS results. As for the *in situ* glycerol-XAFS, based on the above pretreatment, a certain amount of glycerol was carefully evaporated and pulsed into the thin cell in He flow (50 mL·min⁻¹) for 10 min, followed by evacuation to remove weakly-adsorbed glycerol, and then XAFS spectra were collected until a signal was obtained. Data processing and analysis were performed using the IFEFFIT package². The amplitude reduction factor (*S*₀²) was obtained from the fitting results of experimental EXAFS data of Pt foil as follows²⁻⁵: the coordination number (CN) of experimental Pt foil was fixed during EXAFS fitting process leading to the *S*₀² value, based

on the known crystallographic structure value of Pt foil. And then, this S_0^2 value was fixed to all the samples.

***In situ* DRIFTS experiments**

In situ diffuse reflectance Fourier transform infrared spectroscopy (*in situ* DRIFTS) of CO and glycerol was performed on a TENSOR 27 (Bruker Company) spectrometer equipped with an MCT narrow-band detector and a modified *in situ* reaction cell with a drier device. The detailed pre-treatment and test conditions are given as follows. Firstly, about 50 mg of sample was carefully put into the support sheet of reaction cell. Afterwards, the sample was pre-reduced in a H₂/He flow (1/9, v/v; 50 mL · min⁻¹) at 350 °C with a heating rate of 5 °C min⁻¹, followed by purging He (50 mL · min⁻¹) for 1.0 h and cooled to 25 °C in a pure He stream. In this process, the background spectrum was collected at different temperatures (25, 50, 80, 100 °C). Subsequently, the CO/He or glycerol/He (1/19, v/v; 50 mL · min⁻¹) was introduced into the cell, and then DRIFTS spectra were collected until CO or glycerol/He adsorption signals kept unchanged. Finally, the gas flow was switched to a high purity He stream, along with an increase of temperatures (25, 50, 80, 100 °C) to collect desorption spectra.

Computational section

The periodic DFT calculations were implemented by the Vienna ab initio simulation package (VASP 5.4). General gradient approximation (GGA) of Perdew-Burke-Ernzerhoff (PBE) functional was used to solve Kohn-Sham equation, and the Grimme's DFT-D3 method was added to investigate the effect of van der Waals interaction⁶. The projector augmented wave (PAW) method was used to describe the core electrons. A $3 \times 3 \times 1$ Monkhorst-Pack k point mesh and a 400 eV cutoff energy

for the plane-wave basis were employed for the geometry optimizations. The convergence criterion for the total energy self-consistent iterations was 10^{-4} eV, and the geometry optimization stops when the total force on the system was less than 0.02 eV/Å. The energy barriers were determined by the climbing image nudged elastic band (CI-NEB) method⁷.

According to the HRTEM characterization, the Cu (111) surface was modeled with a four-layer-slab in a $p(4 \times 4)$ surface unit cell; the bottom two slabs are fixed while the top two slabs are relaxed. A vacuum space of 15 Å ensures no spurious interaction between the periodically repeated slabs or adsorbates in the direction normal to the slab. The CuPt (111) surface was built by substituting one Cu atom on the topmost layer with one Pt atom. It should be noted that all the samples (Cu/MMO, PtCu-SAA and Pt/MMO) were calculated based on the metal surface rather than the interface model, since they have the same mixed metal oxides support (MgO and Al₂O₃) and the effect of support can be neglected in calculating the relative energies (such as adsorption energy and reaction barrier).

The adsorption energies (E_{ads}) of reactants/products were obtained based on the equation:

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{surf}} + E_{\text{adsorbate}}) \quad (3)$$

where E_{total} , E_{surf} and $E_{\text{adsorbate}}$ represent the energy after adsorption, clean surface and free adsorbate (gas phase), respectively.

Catalytic Testing

Glycerol alcoholic solution (10 mL, 10 wt.%) and catalyst at a certain molar ratio were carefully placed into a stainless steel autoclave reactor (50 mL) at a constant stirring speed of 500 rpm. Afterwards, the reactor was purged with pure H₂ (99.999%, 2.0 MPa) for five times, and then heated to the reaction temperature (200 °C). After the reaction, the autoclave was placed in an ice water bath, and the pressure was released carefully. The obtained liquid-phase products were

separated by filtration and analyzed using a DB–WAX–UI capillary column (Agilent Technologies Company, 30m×0.25mm×0.25mm) and a flame ionization detector (FID). In addition, few of fresh catalysts were compensated to achieve the same ratio between glycerol and catalysts, due to the slight loss of used catalysts during the recycle test process. The conversion of glycerol and the selectivity of products were calculated by following equations:

$$X_{Gly} = \frac{[Glycerol]_{in} - [Glycerol]_{out}}{[Glycerol]_{in}} \times 100\% \quad (4)$$

$$\text{Selectivity}(\%) = \frac{\text{Molar amount of carbon in specific product}}{\text{Total molar amount of carbon in converted glycerol}} \times 100\% \quad (5)$$

The turnover frequency (TOF) was measured as moles of initial glycerol converted per mole of exposed active site atoms per hour ($\text{mol}_{\text{glycerol}} \cdot \text{mol}_M^{-1} \cdot \text{h}^{-1}$, M represent surface metal). It should be noted that the mole of exposed active site atoms of the PtCu–SAA catalysts was calculated based on Pt–Cu single atom alloy sites with two atoms while those of Cu/MMO and Pt/MMO catalysts was evaluated by the exposed surface metal atoms.

$$\text{TOF} = \frac{k \times \text{Molar amount of initial glycerol}}{\text{Molar amount of exposed active site atoms}} \times 100\% \quad (6)$$

The k means the calculated reaction rate constant from Fig. 5A and B.

Supplementary References

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