Supporting Information

Manipulating the Interfacial Integration mode of Bio-templated Porous ZSM-5 Platform with Au/CuZnO$_x$ Catalyst for Enhanced Efficiency and Recycling Stability in Glycerol Conversion to 1,3-dihydroxyacetone

Zhen Yuan[a,b,c], Yimin Wang[a,b,c], Weidong Xie[a,b,c], Yuewen Chen[a,b,c], Xiaoli Zhang[a,b,c], Xiya Zhang[a,b,c], Zhile Xiong[a,b,c], Li Cui[a,b,c],*, Hai Liu[a,b,c],*

[a]School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan 750021, PR China

[b]Key Laboratory for Chemical Engineering and Technology, State Ethnic Affairs Commission, North Minzu University, Yinchuan 750021, PR China

[c]Ningxia Key Laboratory of Solar Chemical Conversion Technology, North Minzu University, Yinchuan 750021, PR China

Table of contents

EXPERIMENTAL

Materials and reagents

$Cu(NO_3)_2 \cdot 3H_2O$ (purity ≥ 99.0%), $Zn(NO_3)_2 \cdot 6H_2O$ (purity ≥ 99.0%), sodium carbonate (purity ≥ 99.8%), Tetrapropyl ammonium hydroxide (TPAOH, 25%), and tetraethyl orthosilicate (TEOS, 98%) were purchased from Aladdin Industrial Inc (China). Glycerol (purity ≥ 99.0%), $HAuCl_4 \cdot 4H_2O$ (Au ≥47.8%), Glycerol (20% in water), urea (purity ≥ 99.0%), H_2SO_4, and CH_3OH were purchased from Sinopharm Chemical Reagent Co., Ltd (China). DHA (98.0%) was purchased from J&K Scientific Ltd (China). The above chemicals were used without further purification.

Corn stover collected from Ningxia Hui Autonomous Region (China) was thoroughly washed with distilled water to remove soil and dust and then dried at 50 °C overnight. The treated corn stover was cut into 1 cm² strips and dried at 80 °C for 2 h. The final sample was stored in a desiccator for further use.

Preparation of catalysts

Preparation of ZSM-5 with Corn Stover as a Template (bio-ZSM-5): First, 2.5 g of TEOS was mixed with 17.4 g of TPAOH solution and 3.92 g of sodium aluminate solution (0.5 wt %). The gel was stirred at room temperature for 1 hour (pH 13). Then, 5.01 g of treated corn stover was added and stirred for 12 h. The mixture was transferred to a 100 mL Teflon-lined autoclave for thermal treatment at 170 °C for 12 h. The resulting bio-ZSM-5@CS mixture was washed thoroughly with plenty of water, dried overnight at 90 °C, and then calcined at 550 °C for 5 hours to remove the corn stover template to obtain the pale yellow powdery substance bio-ZSM-5.

Preparation of CuZnO$_x$ Composite Metal Oxide Support: The deposition-precipitation method was used to prepare the CuZnO$_x$ support with varying Cu molar ratios. For Cu:Zn= 1:1, 0.048 mol of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.048 mol of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 320 mL of double-distilled water. After stirring for 30 minutes, the solution was rapidly heated to 70 °C. A 0.25 M Na_2CO_3 solution was added dropwise until the pH reached approximately 9.5. The addition of the precipitant was stopped, and the mixture was aged by stirring at 70 °C for 1.5 h, then allowed to cool to room temperature. The precipitate was filtered, washed thoroughly with deionised water until neutral, and dried overnight at 110 °C in a blast drying oven. The resulting

solid was ground and calcined in a muffle furnace at 400 °C for 4 h (heating rate of 5 °C/min), yielding the $CuZnO_x$ (Cu: Zn=1:1) sample. $CuZnO_x$ samples with molar ratios of 3:1, 1:3, 1:5, 1:7, and 1:9 were prepared similarly, with only the $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ ratios varied.

Synthesis of $Au/CuZnO_x$ Metallic Catalysts: Supported gold catalysts were prepared using the deposition-precipitation method. An aqueous solution (3.12 mL) of $CuZnO_x$ (1.00 g) and $HAuCl_4$ (0.0485 mol/L) and urea (3.95 g; urea/Au = 400 mol/mol) was added to deionised water (50 mL) under stirring at room temperature. The suspension was stirred continuously for 6 h at 80 °C, then aged for 16 h at room temperature. The solids were separated by filtration and washed repeatedly with deionized water to remove Cl^- ions. The resulting solids were dried at 110 °C for 4 h and then calcined at 200 °C in flowing air for 5 h.

Preparation of Composite Catalysts with Different Binding Modes: Synthesis of $Au/CuZnO_x@bZ$: The prepared catalyst $Au/CuZnO_x$ and bio-ZSM-5 zeolite were ground together in an agate grinding jar to ensure thorough mixing. **Synthesis of $Au/CuZnO_x/bZ$:** During the preparation of the $CuZnO_x$ bimetallic oxide support precursor, the calculated amount of bio-ZSM-5 zeolite was added to obtain the $CuZnO_x/bZ$ support. Subsequently, 3% Au was loaded onto this support to produce $Au/CuZnO_x/bZ$. **Synthesis of $(Au/CuZnO_x)$-in-bZ:** The catalyst $Au/CuZnO_x$ was incorporated into the bio-ZSM-5 zeolite precursor, resulting in $(Au/CuZnO_x)$-in-bZ. **Synthesis of $Au/(CuZnO_x$-in-bZ):** The $CuZnO_x$ bimetallic oxide was incorporated into the bio-ZSM-5 zeolite precursor to obtain $CuZnO_x$-in-bZ. This composite was loaded with 3% Au, resulting in the bifunctional catalyst $Au/(CuZnO_x$-in-bZ). In all the above four schemes for preparing composite catalysts, metal oxides, and zeolites were ready in a 1:1 mass ratio, and the reaction of catalysts with glycerol was made with glycerol/Au=100 mol/mol.

Characterizations

Powder X-ray diffraction (XRD) of the as-prepared samples was performed with a Rigaku SmartLab X-ray diffractometer (Japan) with a Cu Kα source. A Micromeritics ASAP 2020 M system (USA) was used to determine the samples' specific surface areas and pore size distributions. The Au particle sizes and distributions were determined by transmission electron microscopy (TEM) (JEOL JEM-2100, Japan), and a minimum of 200 particles were counted to obtain an average value. X-ray photoelectron spectroscopy (XPS) was performed with an AXIS Ultra spectrometer (Kratos Analytical Ltd, UK) with an Al Kα source (1486.6 eV). The binding

energy was calibrated against the C 1s peak (284.8 eV). H$_2$ temperature-programmed reduction (H$_2$-TPR) was performed with a Micromeritics AutoChem II-2920 instrument (USA). The surface acidity of samples was analysed by temperature-programmed desorption of NH$_3$ (NH$_3$-TPD, Micro-meristics Auto Chem II 2920 instrument coupled with an Omni Star 300 mass spectrometer).

Catalytic evaluation

Glycerol oxidation reactions were performed in a stainless steel autoclave reactor (35 mL) with a magnetic stirrer (Shame S1). Unless otherwise specified, the catalyst was suspended in 0.1 mol L^{-1} GLY aqueous solution (24 mL) at a molar GLY/Au ratio 100. The reactor was purged three times with oxygen and then pressurised to the desired pressure of 10 bar at room temperature. The autoclave was heated to the desired reaction temperature under a stirring rate of 500 rpm. At the end of the reaction, an ice-water bath was used to cool the autoclave. The samples were analysed with a Shimadzu LC-20AT high-performance liquid chromatography system equipped with a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm). The mobile phase was 0.005 mol L^{-1} H$_2$SO$_4$, and the flow rate was 0.5 mL min^{-1}.

The GLY conversion and selectivities for various products were calculated according to the following equations:

$$X(\%) = \frac{C_O - C_x}{C_O} \times 100\%$$

(1)

X is the conversion rate of the reactants; C_0 is the initial amount of glycerol (mol/L); and C_x is the amount of glycerol after the reaction (mol/L) obtained from the quantitative analysis by HPLC.

$$S(\%) = \frac{C_i}{C_1 + C_2 + C_3} \times 100\%$$

(2)

S is the reactant selectivity; C_i is the amount of target product (mol/L); and $C_1+C_2+C_3$ represents the sum of carbon products containing one, two, and three carbon atoms.
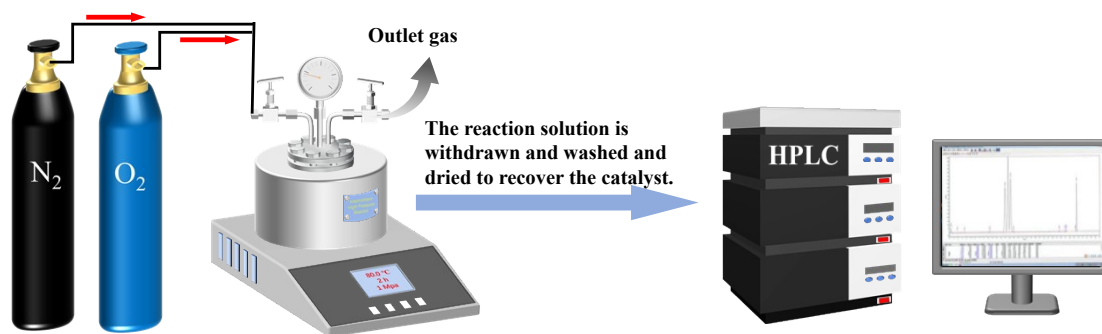
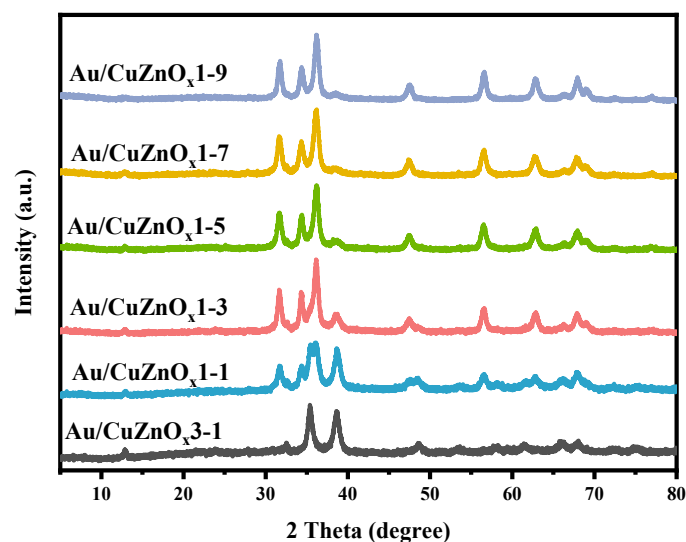**Schame S1.** Flow chart of experiments and evaluation of glycerol catalytic oxidation.
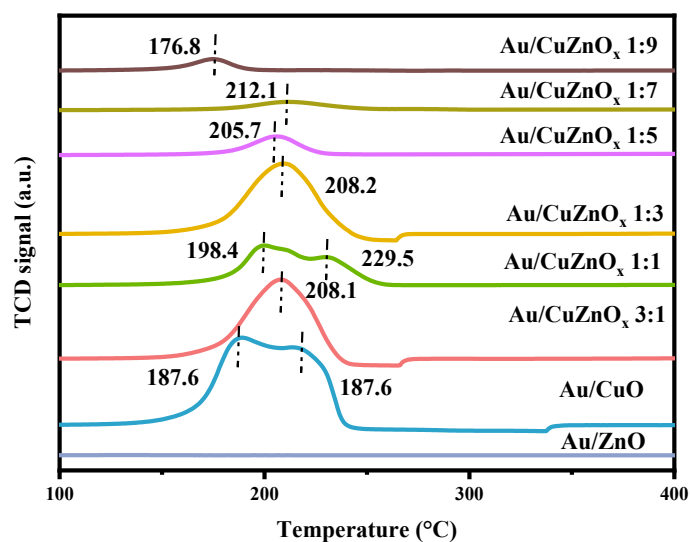
Figure S1. XRD patterns of the catalysts.

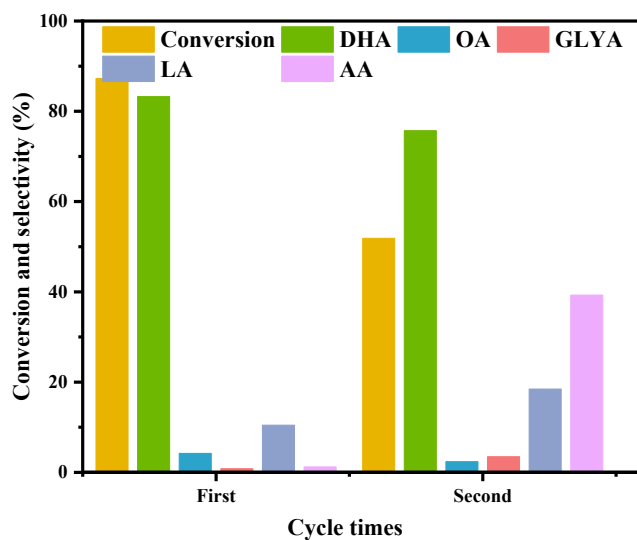**Figure S2.** H$_2$-TPD spectra of the catalysts.

Figure S3. Cycling experimental performance of the Au/CuZnO$_x$ (Cu:Zn=1:1).

In order to investigate whether the ratio of metal oxides has an effect on the crystal structure of zeolite-metal oxide catalysts prepared by physical milling method, the catalysts prepared by physical milling method with different ratios of $Au/CuZnO_x$ and bio-ZSM-5 were analysed by XRD (Figure S4), and it was found that the MFI characteristic peaks of the composite bio-ZSM-5 zeolite and the composite for the ratio of $Au/CuZnO_x$ metal oxide characteristic peaks both appeared simultaneously and coincided, so the effect of different metal ratios on its crystallinity was excluded for the physical milling method.
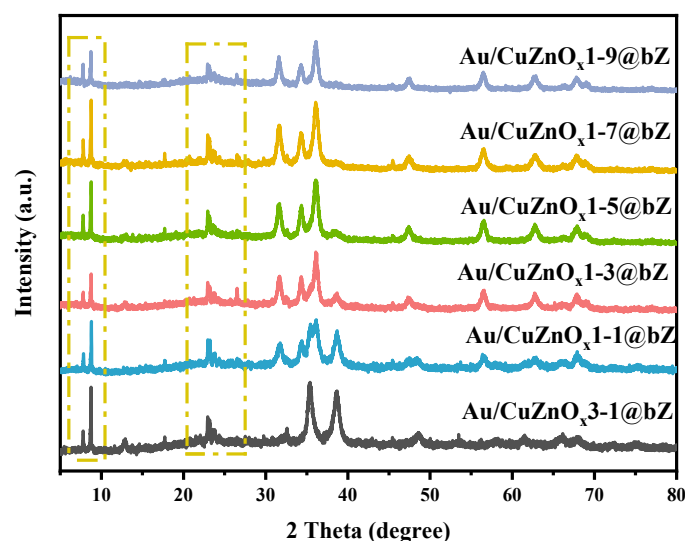

Figure S4. XRD spectra of the catalysts.

In order to study the pore structure and pore size of $CuZnO_x$ support (x=1:1), catalyst $Au/CuZnO_x$, catalyst $Au/CuZnO_x$ prepared by physical milling method and amorphous zeolite bio-ZSM-5, N_2 adsorption and desorption curves were analysed for the above materials as shown in Figures S4 and S5, and the specific data are shown in Table S1. The specific surface area of the support $CuZnO_x$ was found to be 41.12 m^2g^{-1}, which was slightly increased to 53.75 m^2g^{-1} after loading Au, and the specific surface area of amorphous zeolite bio-ZSM-5 was as high as 179.24 m^2g^{-1} with a large specific surface area, which was narrowed down to 119.54 m^2g^{-1} in combination with metal oxides and the volume of empty volume was reduced, the It indicates that some of the metal oxides filled with the inside of zeolite pores.

The pore structure of ZSM-5 was analyzed using 77 K N_2 physisorption isotherms (Figure S5) and pore size distribution (Figure S6). Bio-ZSM-5 exhibits a notable adsorption increase at $P/P_0 <$ 0.02, accompanied by typical type IV isotherms with H3 hysteresis loops at $P/P_0 = 0.8–1.0$. These

results indicate an irregular pore structure characterized by the coexistence of micropores and mesopores.
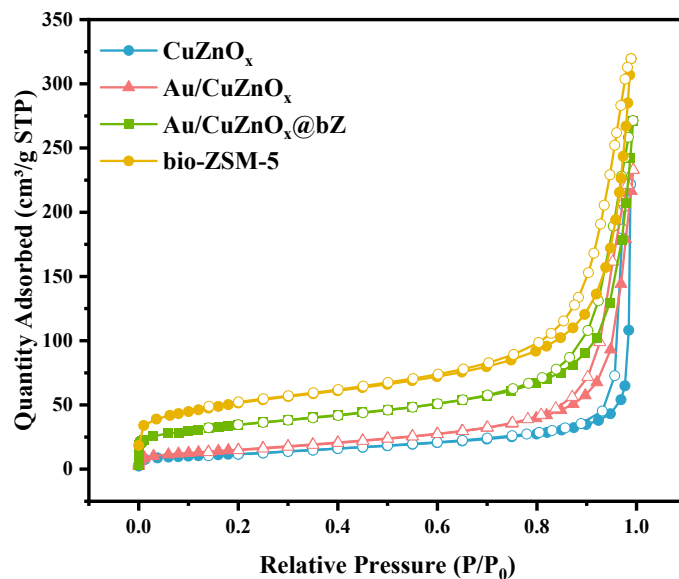

Figure S5. Nitrogen absorption−desorption isotherm curve of various catalysts and supports.
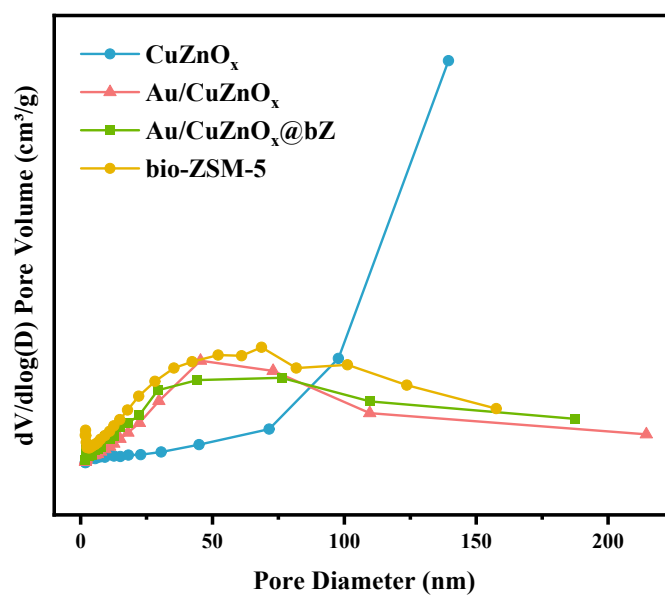

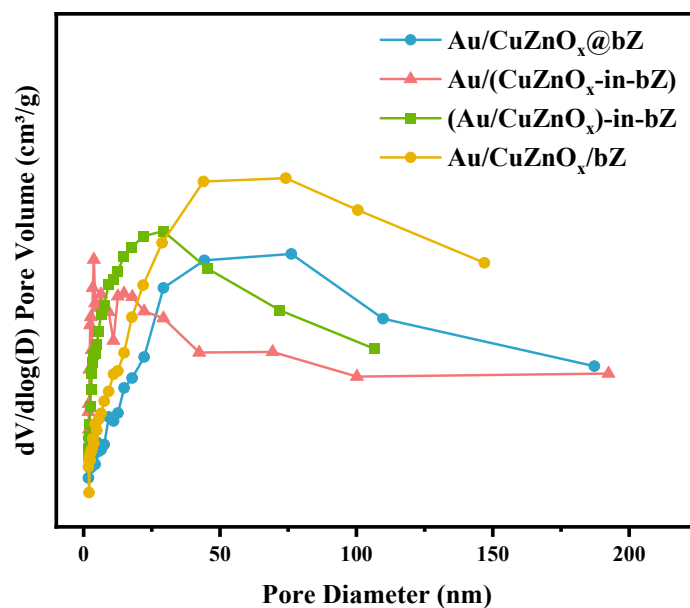**Figure S6.** Characterization of pore structure of various catalysts and supports.

Figure S7. Characterization of pore structure of various catalysts with different binding modes.
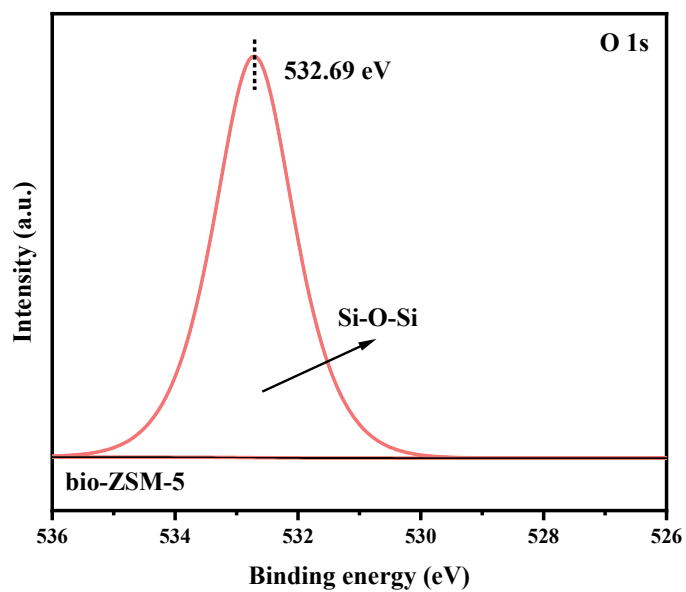

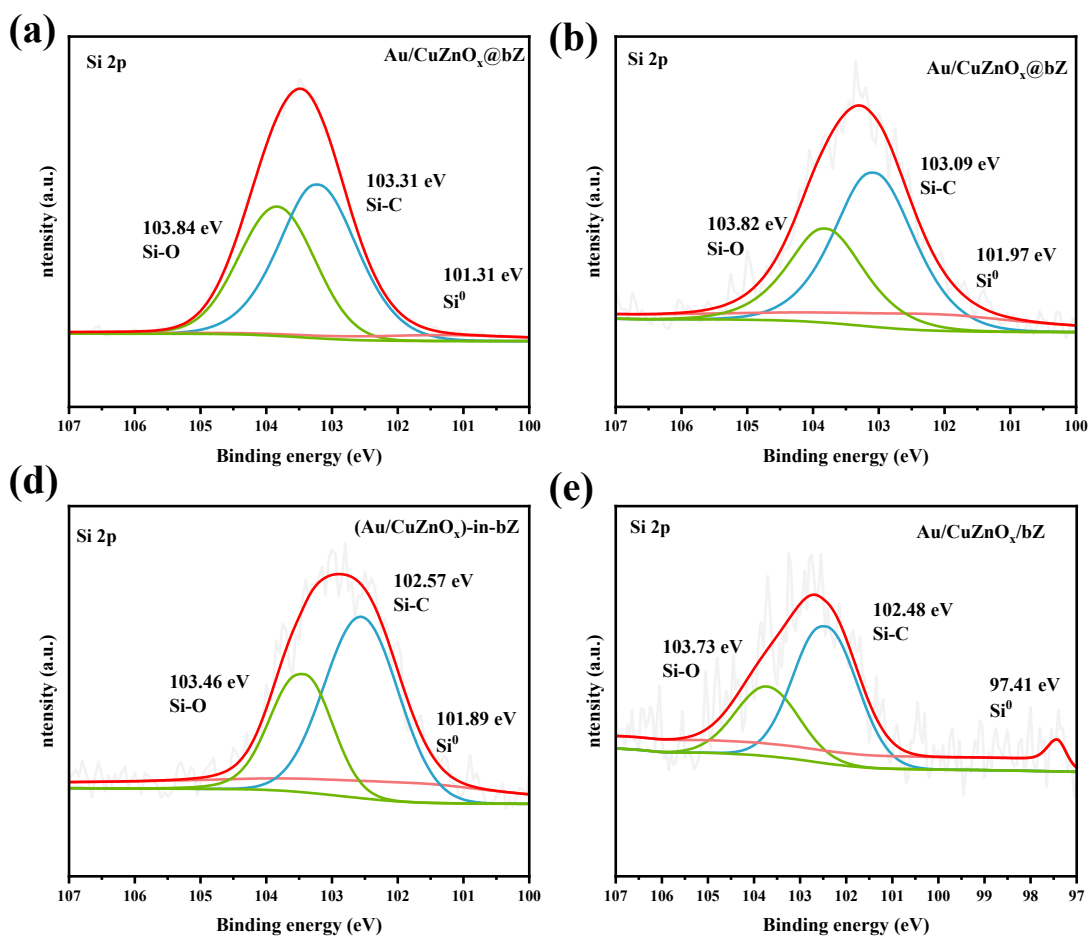**Figure S8.** O1s orbital analysis of bio-ZSM-5 XPS profiles.

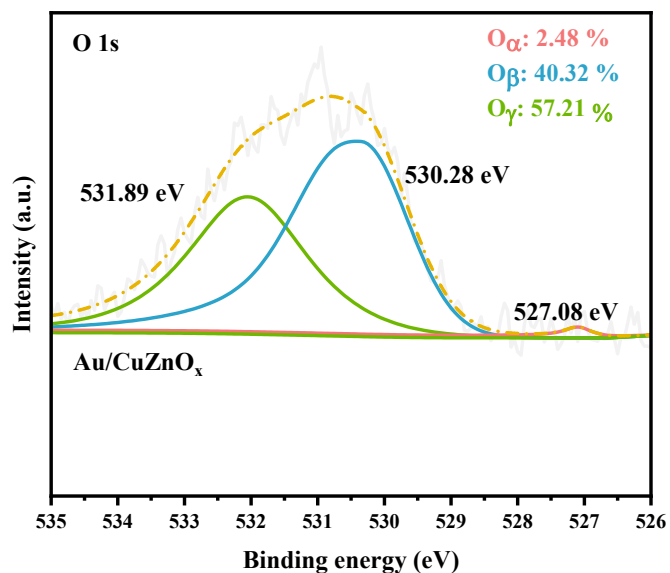**Figure S9.** XPS analysis of catalyst Si 2p prepared with different binding strategies
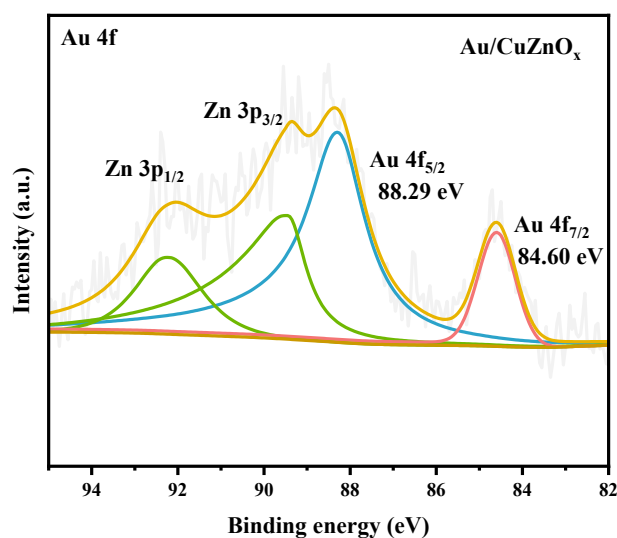

Figure S10. XPS O1s spectra of Au/CuZnO$_x$ catalysts

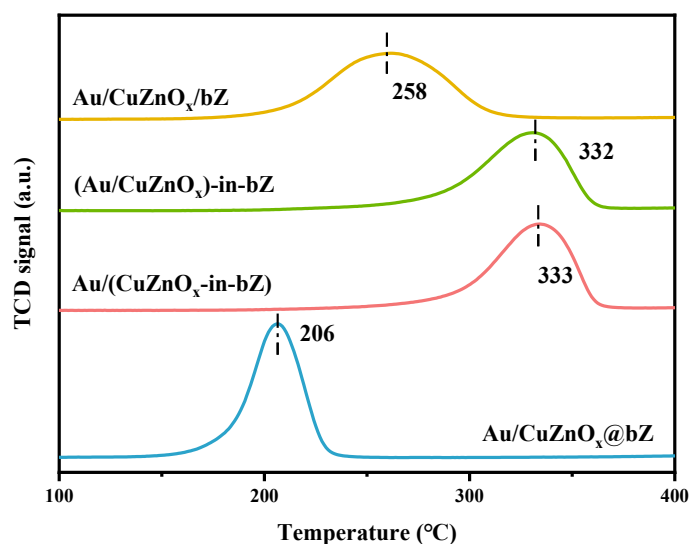**Figure S11.** XPS Au 4f spectra of Au/CuZnO$_x$ catalysts.

Figure S12. O$_2$-TPD spectra of catalysts and support.

In order to exclude the effect of zeolite composition on the catalytic oxidation performance of glycerol, glycerol catalytic oxidation experiments were carried out on the amorphous zeolite bio-ZSM-5 and Au/bio-ZSM-5 prepared by loading the same proportion of Au (3%) by urea reduction method as shown in Figure S13. Both zeolite and its Au-loaded yield were found to have less than 10% glycerol conversion and almost no successful conversion to DHA.
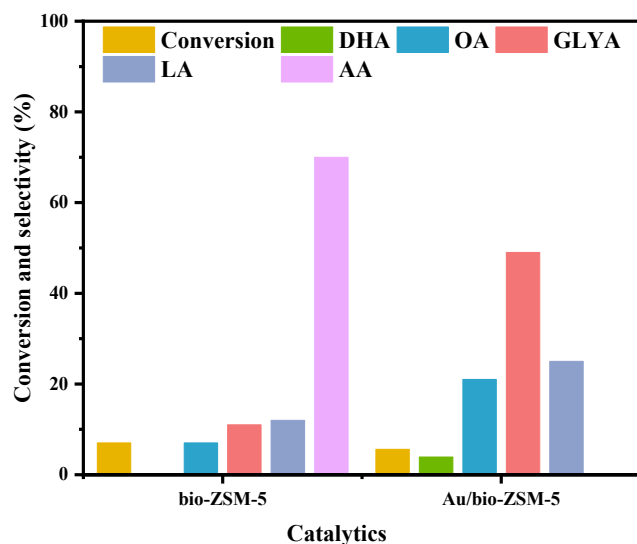
Figure S13. Amorphous zeolite and its selective oxidation data of glycerol after loading Au.
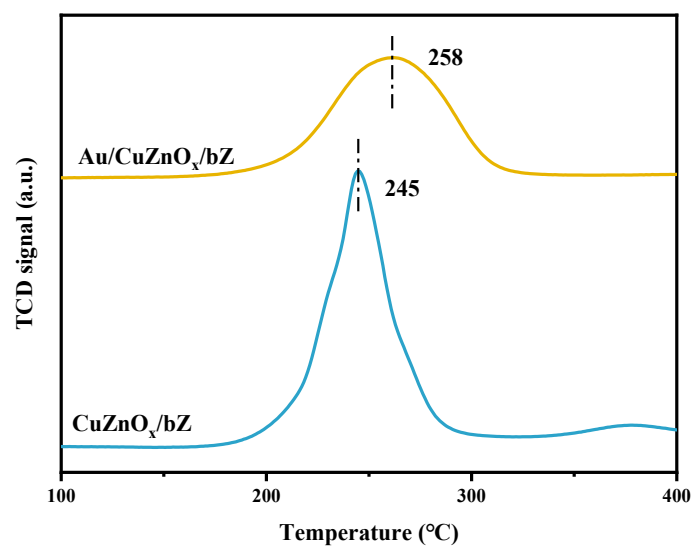

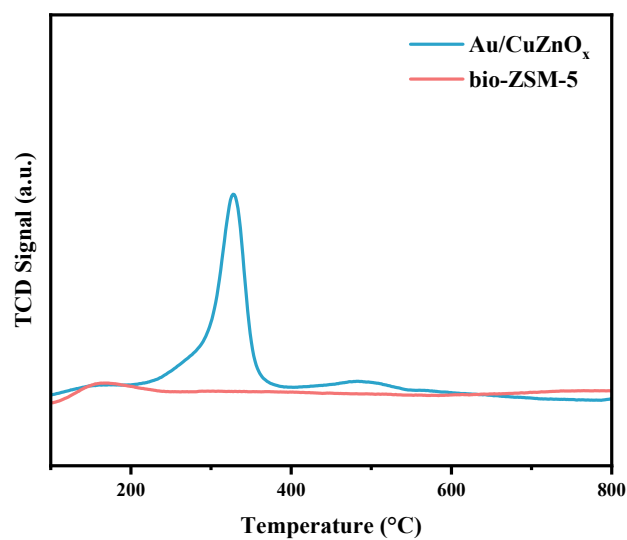**Figure S14.** H_2-TPR analysis of the $CuZnO_x/bZ$ support and $Au/CuZnO_x/bZ$ catalyst.

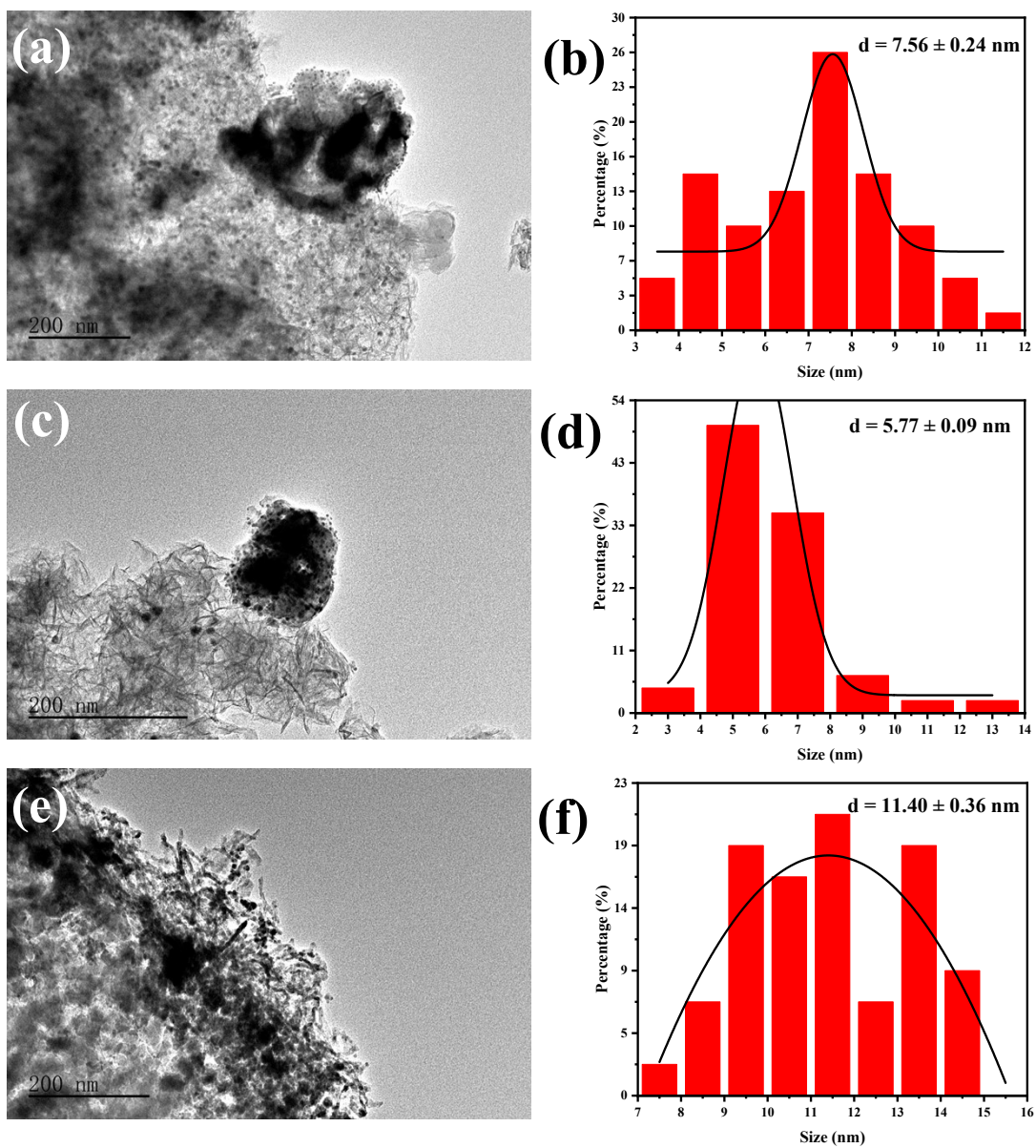**Figure S15.** NH_3-TPD analysis of catalysts.

Figure S16. TEM spectral analysis of catalysts (a) $Au/(CuZnO_x\text{-in-bZ})$, (c) $(Au/CuZnO_x)\text{-in-bZ}$, (e) $Au/CuZnO_x/bZ$. Catalysts surface Au NPs size statistics (b) $Au/(CuZnO_x\text{-in-bZ})$, (d) $(Au/CuZnO_x)\text{-in-bZ}$, (f) $Au/CuZnO_x/bZ$.

Table S1. BET analysis results of the catalysts and supports

Catalysts	S_{BET} (m^{2}g^{-1})	V_P (cm^{3}g^{-1})	D (nm)
CuZnO$_x$	41.12	0.34	32.70
Au/CuZnO$_x$	53.75	0.36	25.52
bio-ZSM-5	179.24	0.49	13.90
Au/CuZnO$_x$@bZ	119.54	0.42	13.79
Au/(CuZnO$_x$-in-bZ)	235.42	0.51	8.38
(Au/CuZnO$_x$)-in-bZ	188.46	0.57	11.63
Au/CuZnO$_x$/bZ	122.39	0.53	16.85

Table S2. XPS analysis results of the catalysts

Catalyst	Au^0 BE (eV)	Au^0 Fractions (%)	Au$^+$ BE (eV)	Au$^+$ Fractions (%)	Au^{3+} BE (eV)	Au^{3+} Fractions (%)
Au/CuZnO$_x$	84.5	56.7	85.1	19.1	86.2	24.2
Au/CuZnO$_x$@bZ	84.1	50.9	85.1	33.7	86.3	15.4
Au/(CuZnO$_x$-in-bZ)	84.6	59.7	85.6	18.8	86.5	21.6
(Au/CuZnO$_x$)-in-bZ	84.0	59.3	85.2	15.8	86.2	24.9
Au/CuZnO$_x$/bZ	84.4	77.8	85.7	11.2	86.4	11.1