

Supplementary Information

Efficient synthesis of glycerol carbonate by doping metallic copper in palladium-catalyzed glycerol system for carbonylation reaction

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Section 1. Experimental Procedures

Characterization: Scanning electron microscope (SEM) images were taken on a Hitachi S-4800 Scanning electron microscope. Transmission electron microscopy (TEM) images were taken on a Talos F200X G2 transmission electron microscope. The high-resolution TEM, HAADF-STEM images, and the corresponding energy-dispersive X-ray (EDX) mapping were recorded by Talos F200X G2 transmission electron microscope operating at 200 kV. optical emission spectroscopy (ICP-OES) was measured by Thermo Fisher iCAP PRO. N₂ adsorption and desorption isotherms were obtained at 298K using a Quantachrome Autosorb-IQ instrument. Powder X-ray diffraction patterns were measured with a Bruker D8 with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). FT-IR spectroscopy was performed on a Nicolet iS50 FT-IR infrared spectrometer. The chemical valence states and elements present in the catalyst surface were analyzed through X-ray photoelectron spectrometry (XPS) equipped with Al/K α radiation (Thermo, ESCALAB250XI). The obtained binding energies were referenced to the C 1s peak at 284.8 eV.

Synthesis of Cu_x-ZIF-8. 3.972 g of Zn(NO₃)₂·6H₂O and (0.27 g-2.16 g) Cu(NO₃)₂·3H₂O were dissolved in 45 ml of methanol, and another 9.72 g of 2-methylimidazole was dissolved in 45 ml of methanol, after which the ligand solution (2-methylimidazole) was rapidly poured into the metal solution, and the reaction solution was placed in a hydrothermal reactor, and the reaction solution was heated by using a programmable oven with a programmable temperature rise at 5 °C/min for 24h. The reaction solution was placed in a hydrothermal reactor and heated to 140°C for 24h using a programmable oven at 5°C/min, then cooled down to room temperature at 2°C/min, filtered and dried at 80°C for 24h to obtain the target product.¹

Synthesis of Cu_x-NC. The obtained Cu_x-ZIF-8 was calcined at 950 °C under nitrogen for 4h to obtain the target product.²

Synthesis of Pd/Cu_x-NC. Take 0.0346g Cu_x-NC dispersed in 30ml of methanol, weigh 0.01g PdCl₂ dissolved in 6ml of H₂O and 3ml of NH₃·H₂O, poured into the carrier solution and stirred for 2h (25°C,500rpm), then poured into the NaBH₄ solution (0.001g/ml) to continue the reaction for 24h, pumping filtration, 80°C drying for 24h, to get the target product. The target product was obtained.

Synthesis of Pd/ZIF-8, Pd/NC. 1.4 g of Zn(NO₃)₂·6H₂O and 0.4024 g of 2-methylimidazole were dissolved in 100 ml of DMF, and the reaction solution was placed in a hydrothermal reactor, which was heated with a programmable temperature-raising oven at 5 °C/min up to 140 °C for 24 h, and then cooled down to room temperature at 2 °C/min with DMF, washed with chloroform, filtered by pumping, and dried at 80 °C for 24 h, to obtain the target product.³ NC was obtained. The synthesis of NC was referred to Synthesis of Cu_x-NC, and the loading of Pd was referred to Synthesis of Pd/Cu_x-NC.

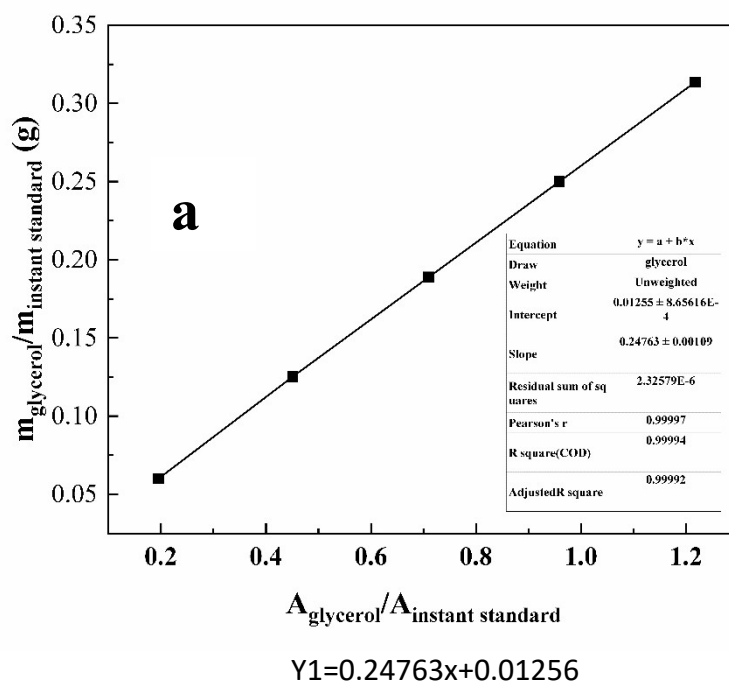
Synthesis of Pd/Cu(Im)₂. 0.483 g of Cu(NO₃)₂·3H₂O and 0.4024 g of 2-

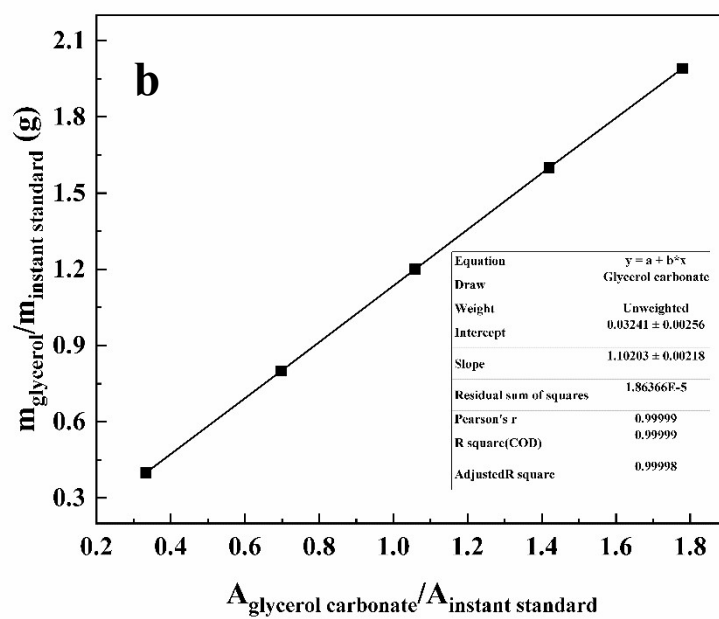
methylimidazole were dissolved in 100 ml of DMF, and the reaction solution was placed in a hydrothermal reactor and heated at 5 °C/min to 140 °C for 24 h using a programmable oven and then cooled down to room temperature at 2 °C/min, DMF, washed with chloroform, filtered, and dried at 80 °C for 24 h to obtain the target. The loading of Pd was referred to Synthesis of Pd/Cux-NC.

Synthesis of Metal ball milling. Weighing 0.188 g of ZIF-8, 0.5163 g of Cu (NO₃)₂·3H₂O, and 0.0116 g of PdCl₂ into put into a ball mill for two hours, followed by calcination of the obtained product under nitrogen at 950°C for 4h to obtain the target product.

Section2. Details of Catalytic performance test.

In order to obtain reproducible and distinguishable peaks, this experiment was carried out using gas chromatography for performance testing by the method of silanization. A certain amount of reaction solution was weighed with an excess of silanization reagent. The reaction solution: hexamethyldisilazane: trimethylchlorosilane 1:9:3 by weight ratio was processed into a 10 mL centrifuge tube. The tube was closed, stirred for 5 min, and the NH_4Cl was allowed to precipitate as a white solid after 30 min at room temperature. Then, 0.5 ml (251.08 g/L) of tritiated tetra ethylene glycol internal standard solution was added to the mixture. centrifugation was performed at 2500 rpm for 5 min, and the supernatant was taken for gas chromatographic analysis. The reaction products were analyzed by gas chromatography using a Nexis GC-2030. The chromatographic conditions were as follows: the column was a KB-Wax capillary column (30 m*0.32 mm*0.50 μm), with N_2 as carrier gas and a separation ratio of 1/20; the column temperature was programmed to 80 $^\circ\text{C}$ for 2 min, and then the temperature was increased to 260 $^\circ\text{C}$ at a rate of 30 $^\circ\text{C}/\text{min}$; the temperature of the vaporization chamber was 280 $^\circ\text{C}$, and the temperature of the detector was 300 $^\circ\text{C}$. The internal standard of tetraethyleneglycol tris(3-acetonitriloethylene) was chosen as the internal standard, and the internal standard of tetraethyleneglycol tris(3-acetonitriloethylene) was chosen as the internal standard. Tetraethylene glycol was used as the internal standard, and the quantitative analysis was carried out by the internal standard method. The yield and selectivity were evaluated based on the peak areas of the silylated derivatives of unreacted glycerol and generated carbonates. The standard curve of the internal standard method is shown in Figure S1 (a-b).





$$Y2 = 1.10203x + 0.03241$$

Figure. S1 (a-b) Internal standard curve.

$$Yield\% = \frac{Y2 \times m_{Internal\ standard}}{m_{Theoretical\ yield}}$$

$$Selective\% = \frac{Y2 \times m_{Internal\ standard} \times m_{glycerol}}{m_{Theoretical\ yield} (m_{glycerol} - Y1 \times m_{Internal\ standard})}$$

Section3. Catalyst characterization.

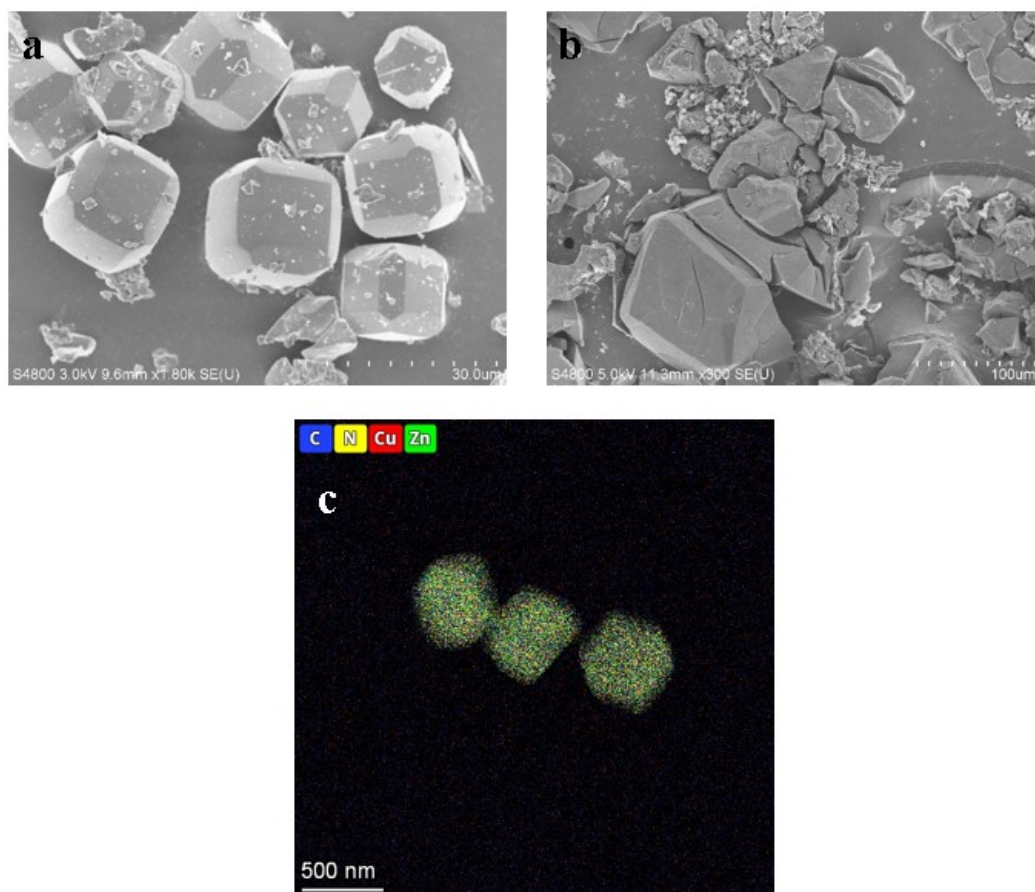


Figure. S2 (a) SEM image of ZIF-8 (b) SEM image of NC (c) HAADF-STEM image of Cu-ZIF-8.

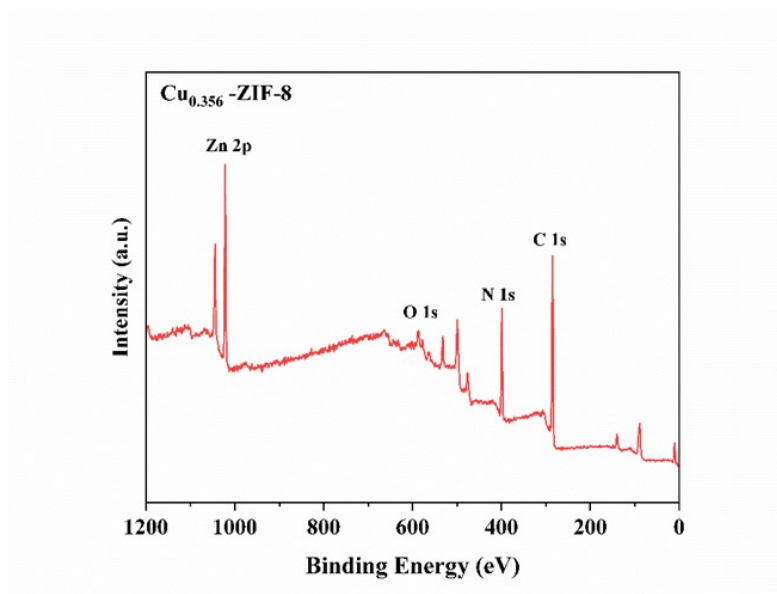


Figure. S3 wide spectra for (a) $\text{Cu}_{0.356}\text{-ZIF-8}$. (b) XPS spectra of Zn 2p for $\text{Cu}_{0.356}\text{-ZIF-8}$.

Section4. Computational methods.

All quantum chemical calculations were performed by using the Gaussian 16 program and use the way of DFT(B3LYP).⁴ For geometry optimization and frequency calculations, genecp basis set was used. 6-31g(d) was used for C H O N elements, and LANL2DZ was used for Pd I Cu elements. The optimal geometry for each compound was determined. The singlet point energy calculations were performed with a larger basis set 6-311G (d, p) and LANL2DZ basis set. For TS optimization and frequency calculations, the way of B3LYP and genecp basis set were used. 6-311G (d, p) was used for C H O N elements, and LanL2DZ was used for Pd I and Cu elements. The IRC analysis calculations were performed with basis set 6-311G (d, p) and LANL2DZ basis set(N=50).

The DFT-D3 with BJ-damping was applied to correct the weak interaction to improve the calculation accuracy.

The visualization of the ESP images were achieved using GaussView 6.0 software.⁵

Section5. Catalyst stability test.

Catalyst Activity Test Reaction In a 50 mL autoclave, 0.007 g of catalyst, 1.446 g of glycerol, 0.0018 g of KI, and 10 mL DMA were added and reacted at 140 °C for two

hours. At the end of the screening, the reaction solution was centrifuged, the catalyst was separated and the experiment was repeated doing five times following the above reaction steps.

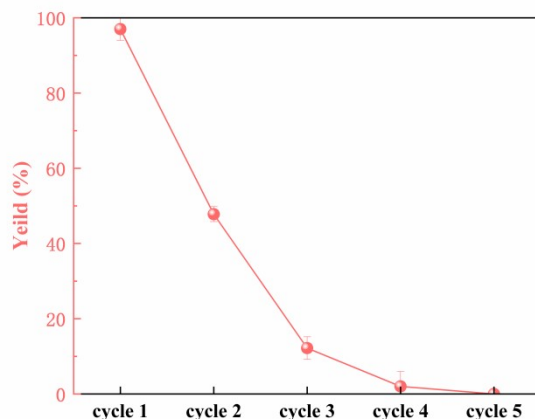


Figure S4 Catalyst stability test diagram.

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