

## Supporting Information

### Surface Deposition of 2D Covalent Organic Frameworks for Minimizing Nanocatalyst Sintering

Zhenqian Zheng<sup>a,b,#</sup>, Zheng Li<sup>a,#</sup>, Yuhao Yang<sup>b,#</sup>, Xuepeng Wang<sup>a</sup>, Song Wang<sup>b</sup>, Ziyang Zhang<sup>b</sup>, Ting Kang<sup>b</sup>, Xingkun Chen<sup>a,\*</sup>, Wen-Jun Wang<sup>b</sup>, Yunjie Ding<sup>a,c,d,\*</sup>, Pierre Braunstein<sup>e</sup>, Pingwei Liu<sup>b,\*</sup>

a Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou 311231, PR China

b State Key Lab of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang Province 310027, China

c Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

d The State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

e Université de Strasbourg, CNRS, CHIMIE UMR 7177, Laboratoire de Chimie de Coordination, Strasbourg, France

# Equal contribution

Corresponding Authors: liupingwei@zju.edu.cn; cxklned@zjnu.cn; dyj@dicp.ac.cn

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## Experimental

### Materials

1,4-Dioxane (99%), mesitylene (98%), ammonia solution ( $\text{NH}_4\text{OH}$ , 25~28 wt.%), dimethyloxalate (DMO, 99%), hydrochloric acid (HCl, 36~38%) and the solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , >99.0 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Benzaldehyde (98%), aniline (99.5%), scandium (III) trifluoromethanesulfonate ( $\text{Sc}(\text{OTf})_3$ , 98%) and 1,3,5-tris(4-aminophenyl)-benzene (TAPB, 98%), were purchased from J&K Scientific Co. 1,3,5-Benzenetricarbaldehyde (BTCA, 98%) was purchased from ATK Chemical Company Limited. NaOH solution (1.0 N Standardized Solution) was purchased from Afaesha (China) Chemical Co., Ltd. All reagents and solvents were used without further purification.

### Instrumentation

**Powder X-ray diffraction (PXRD).** PXRD diffraction spectra were obtained with a PANalytical X-pert Powder diffractometer (Cu anode) using a Scan step of  $0.0262606^\circ$  and step time of 97.983 s.

**High-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM).** Elemental mapping analysis was performed on a JSM-7800F field emission scanning electron microscope and (HAADF-STEM) equipped with energy dispersive spectroscopy (EDS).

**X-ray photoelectron spectroscopy (XPS).** XPS was performed on an Escalab 250Xi unit (Thermo Fisher) to record the carbon and nitrogen content with Mg  $K\alpha$  X-ray as excitation light source.

**Field emission scanning electron microscopy (FESEM).** FESEM images were collected on a Hitachi SU-8010 field emission scanning electron microscope with accelerating voltage of 3 kV. All the samples were sprayed by Pt for 60 s. Energy Dispersive X-ray Spectroscopy (EDS) mapping was combined with an accelerating voltage of 15 kV.

**Transmission electron microscope (TEM).** TEM images were obtained using a HT-7700 transmission electron microscope from HITACHI company, with an accelerating voltage of 100 kV. Energy Dispersive X-ray Spectroscopy (EDS) mapping was combined with a X-MAXn65 T from Oxford Instruments with an accelerating voltage of 100 kV.

**$\text{N}_2$  absorption-desorption analysis.** The absorption-desorption isotherms were collected by an

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AUTOSORB-IQ2-MP Surface Area and Porosimetry Analyzer. All the samples were kept at 120 °C for 12 h for dewatering. N<sub>2</sub> isotherms were measured at 77 K and analyzed by ASiQwin software.

**Fourier transform infrared (FT-IR) spectroscopy.** FT-IR spectra were recorded with a Nicolet5700 FT-IR spectrometer.

**Thermogravimetric Analysis (TGA).** A TA-Q500 thermogravimetric analyzer was used to collect the sample thermograms. The samples were stored at room temperature at a humidity of 50% prior to testing. Analysis involved heating to 900 °C at a rate of 5.00 °C/min.

## Experimental Methods

**Synthesis of Cu/SiO<sub>2</sub>.** The Cu/SiO<sub>2</sub> catalyst was prepared using the ammonia evaporation (AE) method. In a typical synthesis, an ammonia solution (12.6 mL) was mixed with a 0.3 M copper nitrate solution (70 mL) and stirred for 5 min. The pH of the complex was about 11. Then fumed silica (SiO<sub>2</sub>, AEROSIL 300) (11.52 g) was added to the copper ammonia complex solution and the mixture was stirred at 35 °C for another 4 h. The suspension was then heated to 90 °C to evaporate the ammonia until the pH decreased to 6-7. The solid was filtered, washed with deionized water (500 mL), dried at 120 °C for 10 h, and calcined in air at 450 °C (4 h, ramping rate 1°C/min).

**Synthesis of COF/Cu/SiO<sub>2</sub> with different weight ratios of monomers to Cu/SiO<sub>2</sub>.** Various ratios of COF precursors were employed. We detail COF/Cu/SiO<sub>2</sub>-I (2.5%) as an example. TAPB (17.6 mg), BTCA (8.1 mg), benzaldehyde (60.7 μL) and aniline (54.4 μL) were dissolved in a mixture dioxane/mesitylene (20 mL, 1/2 v/v). Cu/SiO<sub>2</sub> (1.0 g) was dispersed in the above solution under sonication. Then, Sc(OTf)<sub>3</sub> (0.73 mg, 1.5 μmol) in dioxane/mesitylene (0.1 mL, 2/1 v/v) was added to the mixture and stirring at room temperature was maintained for 3 days. The obtained COF/Cu/SiO<sub>2</sub> was collected by filtration and dried in vacuum at 40 °C.

Table S1. The weight ratios of monomers in production of COF/Cu/SiO<sub>2</sub> catalysts

|                              | Weight Ratio (%) | Feeding Amount (mg) |      |                     | Solvent dosage (ml) |
|------------------------------|------------------|---------------------|------|---------------------|---------------------|
|                              |                  | TAPB                | BTCA | Cu/SiO <sub>2</sub> |                     |
| Cu/SiO <sub>2</sub>          | 0.0              | /                   | /    | /                   | /                   |
| COF/Cu/SiO <sub>2</sub> -I   | 1.2              | 8.8                 | 4.1  | 1025.0              | 20.0                |
| COF/Cu/SiO <sub>2</sub> -II  | 2.5              | 17.6                | 8.1  | 1025.0              | 20.0                |
| COF/Cu/SiO <sub>2</sub> -III | 5.0              | 35.2                | 16.2 | 1025.0              | 20.0                |
| TAPB-BTCA COF                | /                | 35.2                | 16.2 | 0                   | 20.0                |

$$\text{*Weight Ratio} = (m_{\text{TAPB}} + m_{\text{BTCA}}) / m_{\text{Cu/SiO}_2}$$

**Synthesis of TAPB-BTCA COF.** TAPB (35.2 mg), BTCA (16.2 mg), benzaldehyde (121.4  $\mu\text{L}$ ) and aniline (108.8  $\mu\text{L}$ ) were dissolved in a mixture dioxane/mesitylene (20 mL, 1/2 v/v). Sc(OTf)<sub>3</sub> (0.73 m) in dioxane/mesitylene (0.1 mL, 2/1 v/v) was added to the mixture and stirring was maintained at room temperature for 3 days. The obtained COF was collected by filtration and dried in vacuum at 40 °C.

**Catalytic test of DMO hydrogenation.** The catalytic vapor-phase hydrogenation of DMO was performed in a stainless steel fixed-bed micro-reactor (inner diameter, 10.0 mm; length, 660 mm), equipped with a thermocouple and a mass flow controller. Typically, the catalyst (1.0 g) was placed in the center of the reactor and reduced in situ with H<sub>2</sub> (30 cm<sup>3</sup>/min, 230 °C, 0.1 MPa, 3 h). After cooling to the reaction temperature, the system pressure was increased to 1.5 MPa with a back-pressure regulator. Then, a DMO solution (20 wt.% DMO in methanol, 99%, Analytic Reagent) was admitted using a plunger pump (NP-KX-210, Nihon Seimitsu Kagaku Co., Ltd). The reaction products were collected by a cold trap and analyzed offline with an Agilent 7890B chromatograph equipped with an HP-FFAP capillary column (30 m $\times$ 0.32 mm $\times$ 0.25  $\mu\text{m}$ ) and a flame ionization detector (FID) using *n*-butanol as the internal standard.

**Etching experiment of COF/Cu/SiO<sub>2</sub>.** Etching off SiO<sub>2</sub> and Cu in COF/Cu/SiO<sub>2</sub>, then characterizing the residues to prove the existence of COF. The sample was watered and ultrasounded. 300 mg COF/Cu/SiO<sub>2</sub>

was placed in a 40 ml strain bottle. Then, 20 ml 1 mol/L NaOH solution was added to the bottle and stirring at 70 °C was maintained for 20 min. After placing for 10 min, removed 10 ml of upper liquid and added 10 ml 1 mol/L NaOH solution. Repeated above process 6 times, the obtained COF/Cu-Residue was collected by filtration and dried in vacuum at 40 °C. Took 5 mg COF/Cu in a centrifugal tube and 5 ml 2 mol/L hydrochloric acid was added to it. The obtained COF-Residue was collected by centrifuge and dried in vacuum at 40 °C.

**Etching experiment of Cu/SiO<sub>2</sub>.** The sample was watered and ultrasounded. 300 mg Cu/SiO<sub>2</sub> was placed in a 40 ml strain bottle. Then, 20 ml 1 mol/L NaOH solution was added to the bottle and stirring at 70 °C was maintained for 20 min. After placing for 10 min, removed 10 ml of upper liquid and added 10 ml 1 mol/L NaOH solution. Repeated above process 6 times, the obtained Cu-Residue was collected by filtration and dried in vacuum at 40 °C. Took 5 mg Cu in a centrifugal tube and 5 ml 2 mol/L hydrochloric acid was added to it. There was no residue after the reaction.

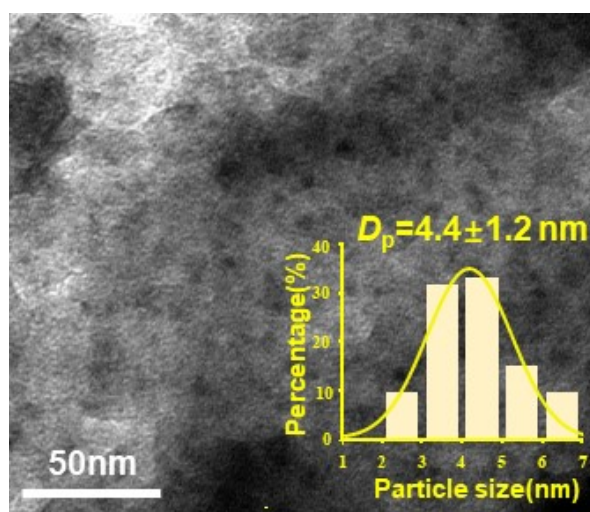


Fig. S1. TEM image of Cu/SiO<sub>2</sub> and Nanoparticle distribution of Cu/SiO<sub>2</sub>.

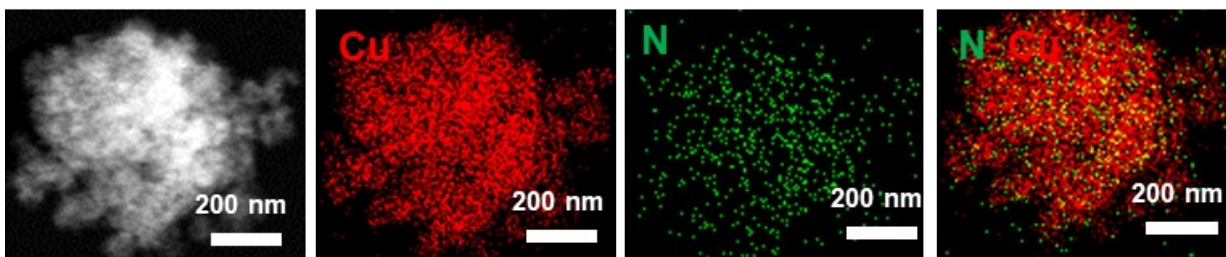


Fig. S2. HAADF-STEM images, and N and Cu elemental mapping of COF/Cu/SiO<sub>2</sub>.

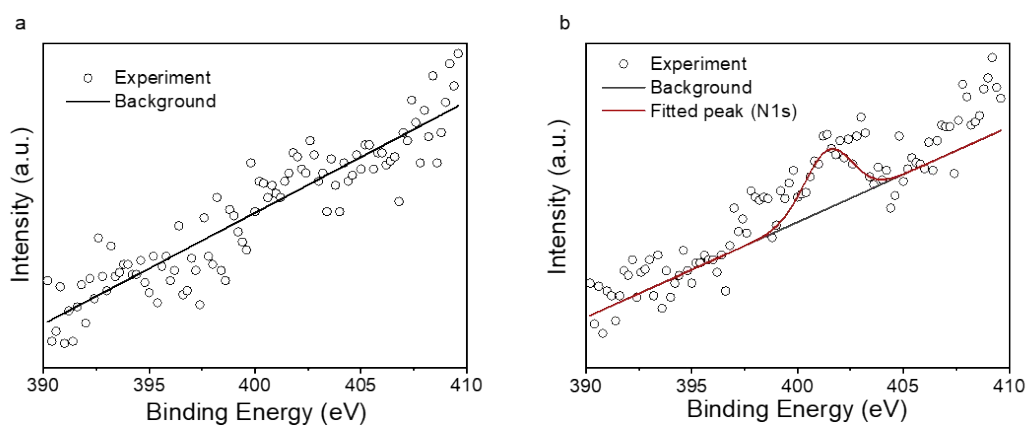


Fig. S3. XPS spectra of Cu/SiO<sub>2</sub> (a) and COF/Cu/SiO<sub>2</sub> (b).

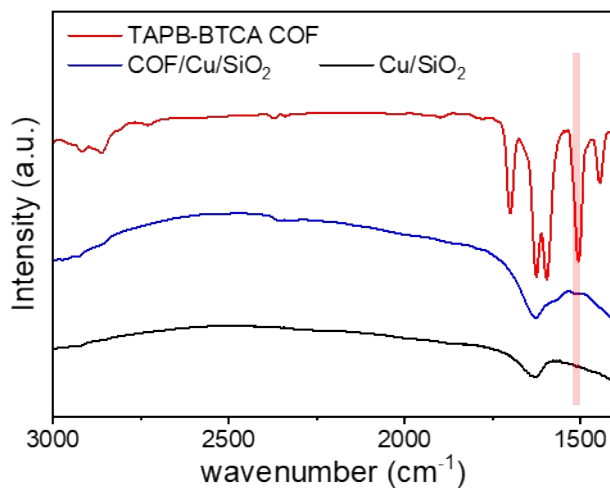


Fig. S4. FT-IR spectra of TAPB-BTCA COF, COF/Cu/SiO<sub>2</sub> and Cu/SiO<sub>2</sub>.

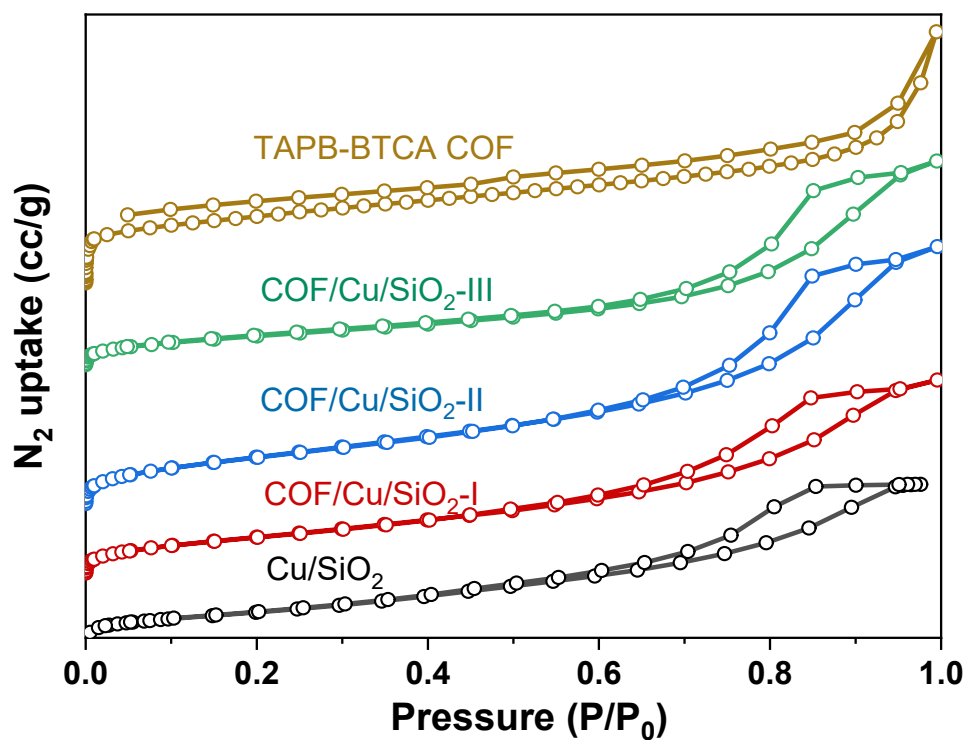


Fig. S5. Nitrogen isothermal adsorption and desorption curve of Cu/SiO<sub>2</sub>, COF/Cu/SiO<sub>2</sub>-I, COF/Cu/SiO<sub>2</sub>-II, COF/Cu/SiO<sub>2</sub>-III and TAPB-BTCA COF.

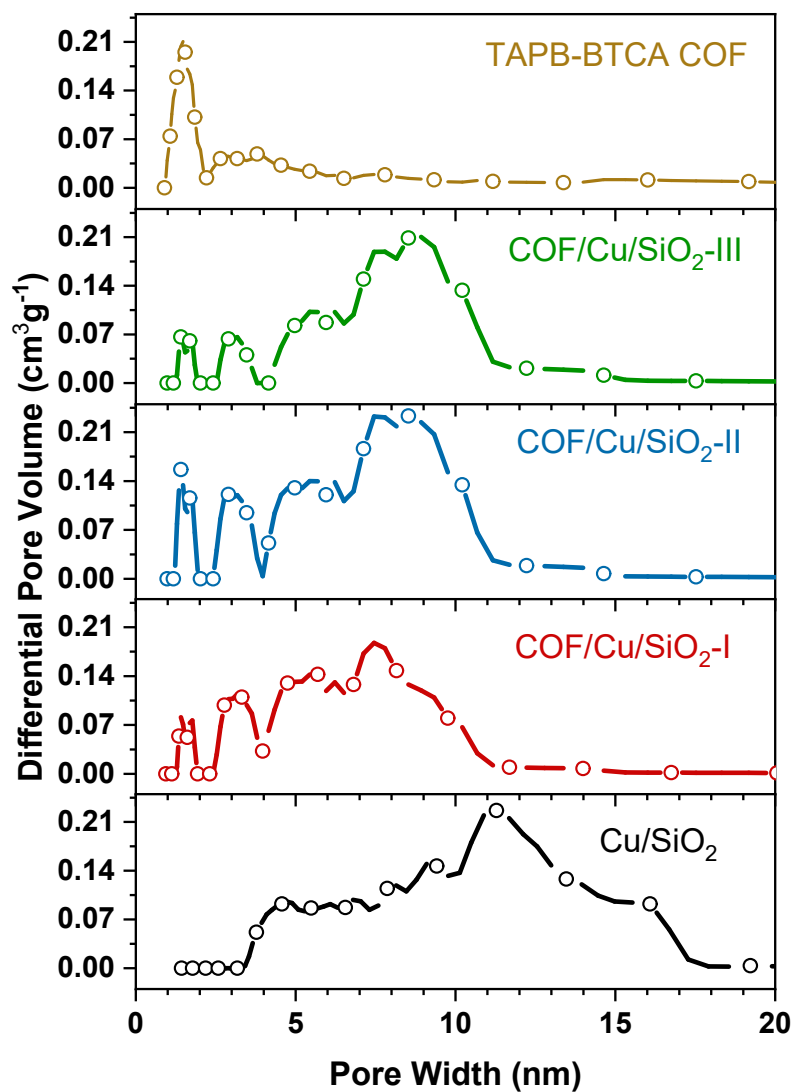


Fig. S6. Pore size distribution of Cu/SiO<sub>2</sub>, COF/Cu/SiO<sub>2</sub>-I, COF/Cu/SiO<sub>2</sub>-II, COF/Cu/SiO<sub>2</sub>-III and TAPB-BTCA COF.



Table S2. Specific surface area and pore size distribution of samples with different weight ratios.

|                              | Weight Ratio (%) | $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) | $D_{\text{pore}}$ (nm) | $V_{\text{total}}$ ( $\text{cm}^3 \text{g}^{-1}$ ) |      |         |
|------------------------------|------------------|---|------------------------|--|------|---------|
|                              |                  |   |                        | micro  | meso | Overall |
| Cu/SiO <sub>2</sub>          | 0.0              | 439   | 11.3                   | 0.00   | 0.90 | 0.90    |
| COF/Cu/SiO <sub>2</sub> -I   | 1.2              | 246   | 7.5                    | 0.04   | 0.58 | 0.62    |
| COF/Cu/SiO <sub>2</sub> -II  | 2.5              | 217   | 8.5                    | 0.04   | 0.51 | 0.55    |
| COF/Cu/SiO <sub>2</sub> -III | 5.0              | 232   | 8.9                    | 0.05   | 0.52 | 0.57    |
| TAPB-BTCA COF                | /                | 426   | 1.5                    | 0.24   | 0.22 | 0.46    |

Table S3. Standard deviation of dimethyl oxalate conversion and ethylene glycol selectivity.

|                              | Standard deviation of DMO conversion | Standard deviation of EG selectivity |
|------------------------------|--------------------------------------|--------------------------------------|
| Cu/SiO <sub>2</sub>          | 0.0022                               | 0.0065                               |
| COF/Cu/SiO <sub>2</sub> -I   | 0.0004                               | 0.0020                               |
| COF/Cu/SiO <sub>2</sub> -II  | 0.0049                               | 0.0048                               |
| COF/Cu/SiO <sub>2</sub> -III | 0.0041                               | 0.0090                               |

Table S4. For Fig. 2f the comparison between spent COF/Cu/SiO<sub>2</sub> and Cu/SiO<sub>2</sub>.

variance analysis

| source of difference | SS      | DF | MS     | F      | P-value  | F crit |
|----------------------|---------|----|--------|--------|----------|--------|
| Between groups       | 977.77  | 1  | 977.77 | 454.85 | 9.55E-23 | 4.10   |
| Within groups        | 81.69   | 38 | 2.15   |        |          |        |
| Total                | 1059.46 | 39 |        |        |          |        |

SS: sum of square

Df: degrees of freedom

MS: mean square

F: Test statistics

P-value: observed significance level

F crit: critical value

Since  $F (454.85) > F \text{ crit} (4.10)$ , a significant difference was present for Cu particles sizes distribution when inspection standard  $\alpha=0.05$ .

Table S5. For Fig. S16 the comparison between fresh and spent Pd/SiO<sub>2</sub> catalysts:

variance analysis

| source of difference | SS     | DF  | MS     | F      | P-value | F crit |
|----------------------|--------|-----|--------|--------|---------|--------|
| Between groups       | 484.74 | 1   | 484.74 | 242.73 | 3E-36   | 3.89   |
| Within groups        | 395.40 | 198 | 1.99   |        |         |        |
| Total                | 880.15 | 199 |        |        |         |        |

Since  $F (242.73) > F \text{ crit} (3.89)$ , a significant difference was present for Pd particles sizes distribution when inspection standard  $\alpha=0.05$ .

Table S6. For Fig. S16 the comparison between fresh and spent COF/Pd/SiO<sub>2</sub> catalysts:

variance analysis

| source of difference | SS     | DF  | MS    | F     | P-value | F crit |
|----------------------|--------|-----|-------|-------|---------|--------|
| Between groups       | 23.02  | 1   | 23.02 | 10.89 | 0.0011  | 3.89   |
| Within groups        | 418.39 | 198 | 2.11  |       |         |        |
| Total                | 441.42 | 199 |       |       |         |        |

Since  $F > F_{crit}$ , a significant difference was present for Pd particles sizes distribution when inspection standard  $\alpha=0.05$ .

Table S7. For Fig. S16 the comparison between the spent Pd/SiO<sub>2</sub> and COF/Pd/SiO<sub>2</sub> catalysts:

variance analysis

| source of difference | SS     | DF  | MS     | F     | P-value | F crit |
|----------------------|--------|-----|--------|-------|---------|--------|
| Between groups       | 130.5  | 1   | 130.05 | 48.06 | 5.7E-11 | 3.89   |
| Within groups        | 535.79 | 198 | 2.71   |       |         |        |
| Total                | 665.84 | 199 |        |       |         |        |

Since  $F > F_{crit}$ , a significant difference was present for Pd particles sizes distribution when inspection standard  $\alpha=0.05$ .

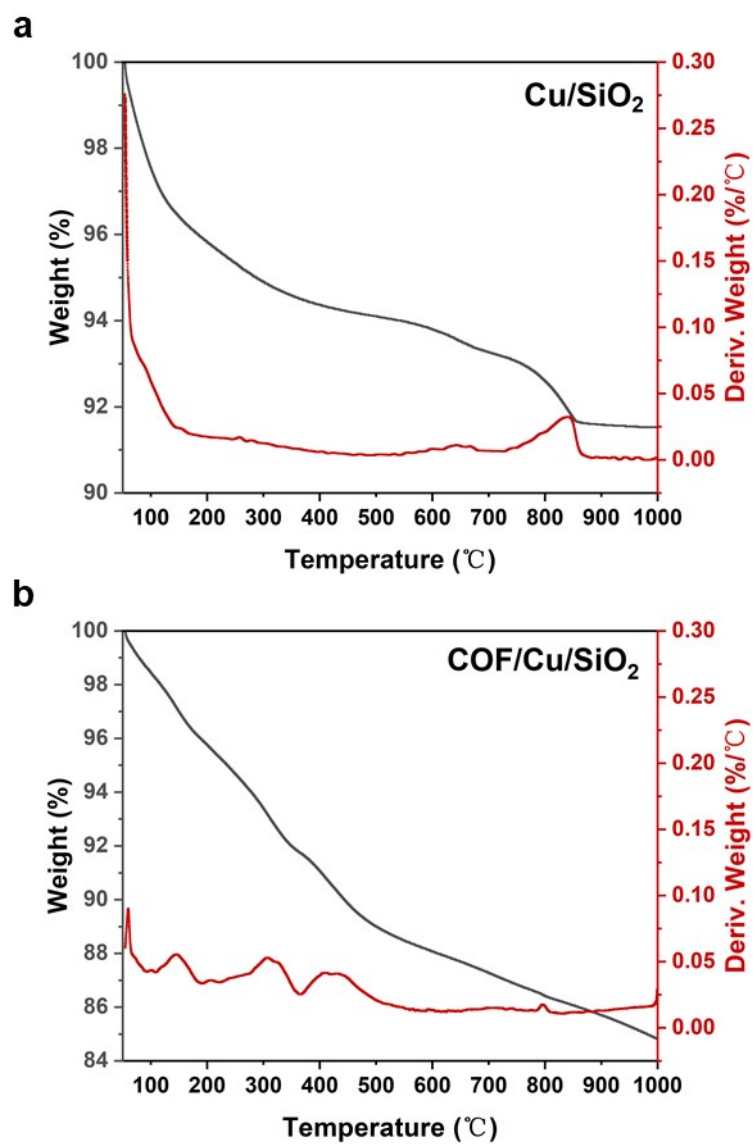
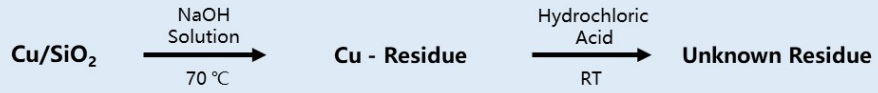


Fig. S7. TGA thermograms of Cu/SiO<sub>2</sub> (a), COF/Cu/SiO<sub>2</sub> (b).

**Two-step etching process removes SiO<sub>2</sub> and Cu from COF/Cu/SiO<sub>2</sub>:**



**Control group (Cu/SiO<sub>2</sub>):**



**After etching process:**

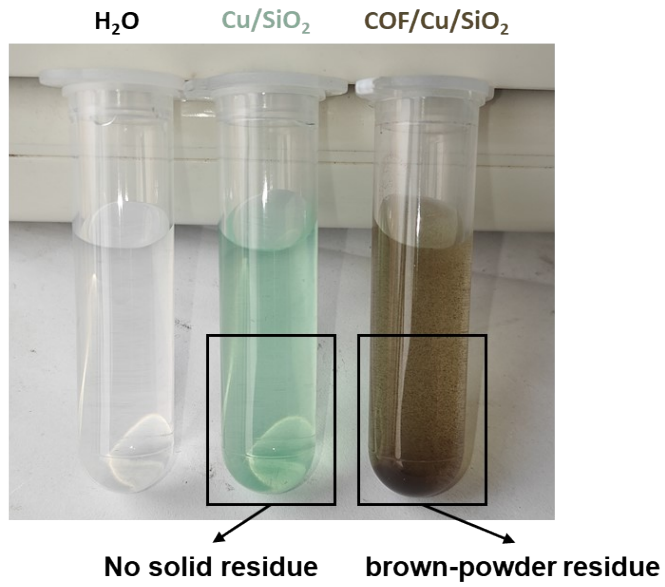


Fig. S8. Etching experiment of COF/Cu/SiO<sub>2</sub> and Cu/SiO<sub>2</sub>

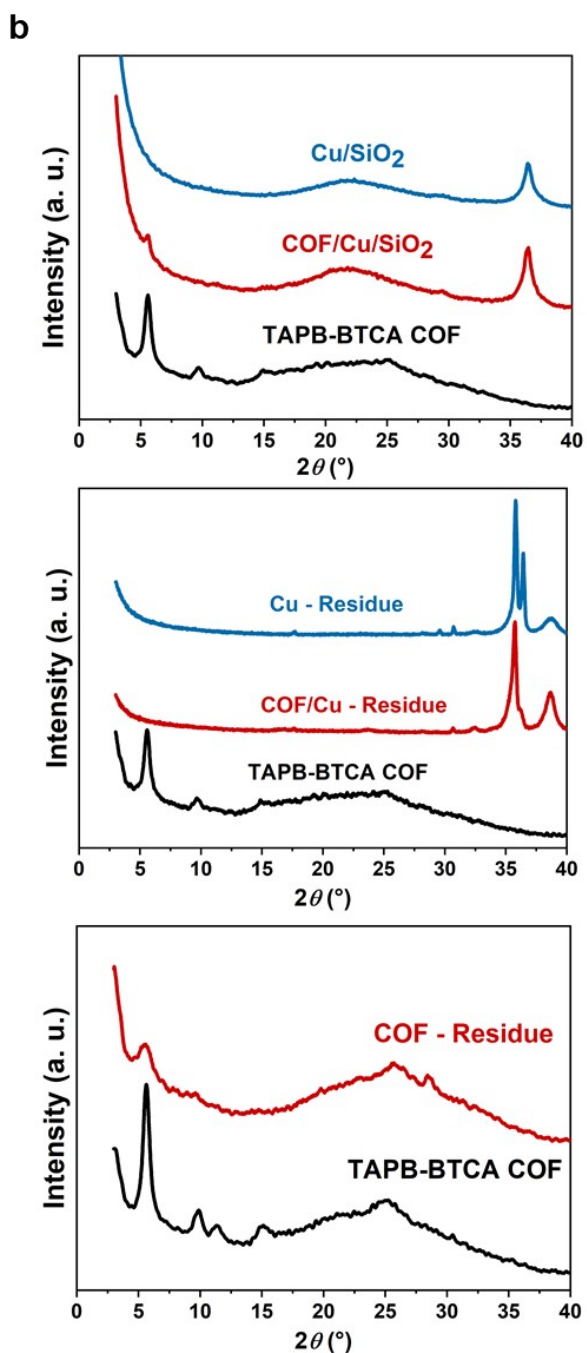
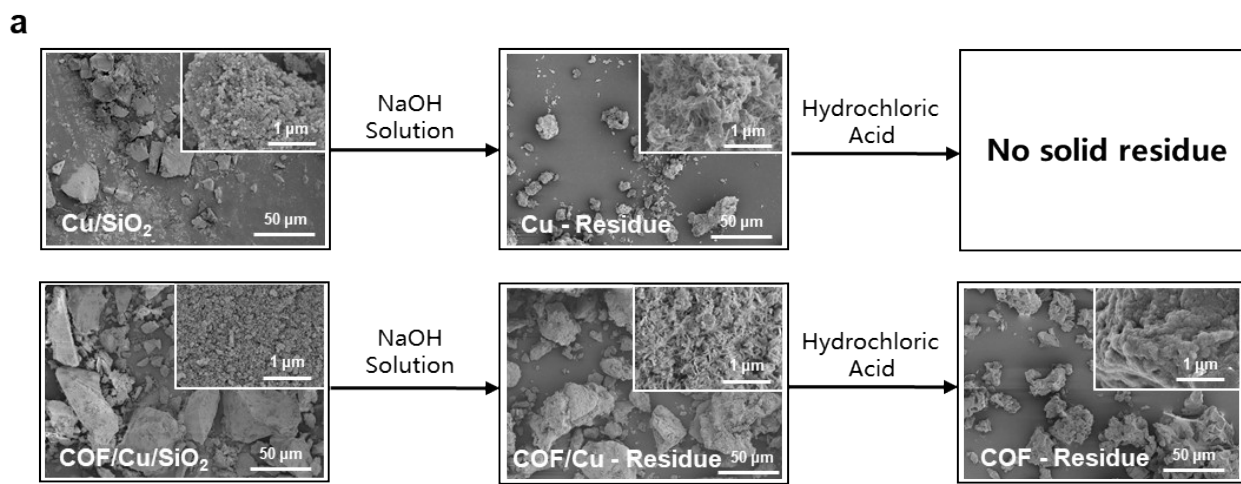


Fig. S9. a) Etching process and FESEM images of Cu/SiO<sub>2</sub> and COF/Cu/SiO<sub>2</sub>. b) PXRD patterns of Cu/SiO<sub>2</sub>, COF/Cu/SiO<sub>2</sub>, TAPB-BTCA COF and their solid residues. c) FT-IR spectra of Cu/SiO<sub>2</sub>, COF/Cu/SiO<sub>2</sub>, TAPB-BTCA COF and their solid residues.

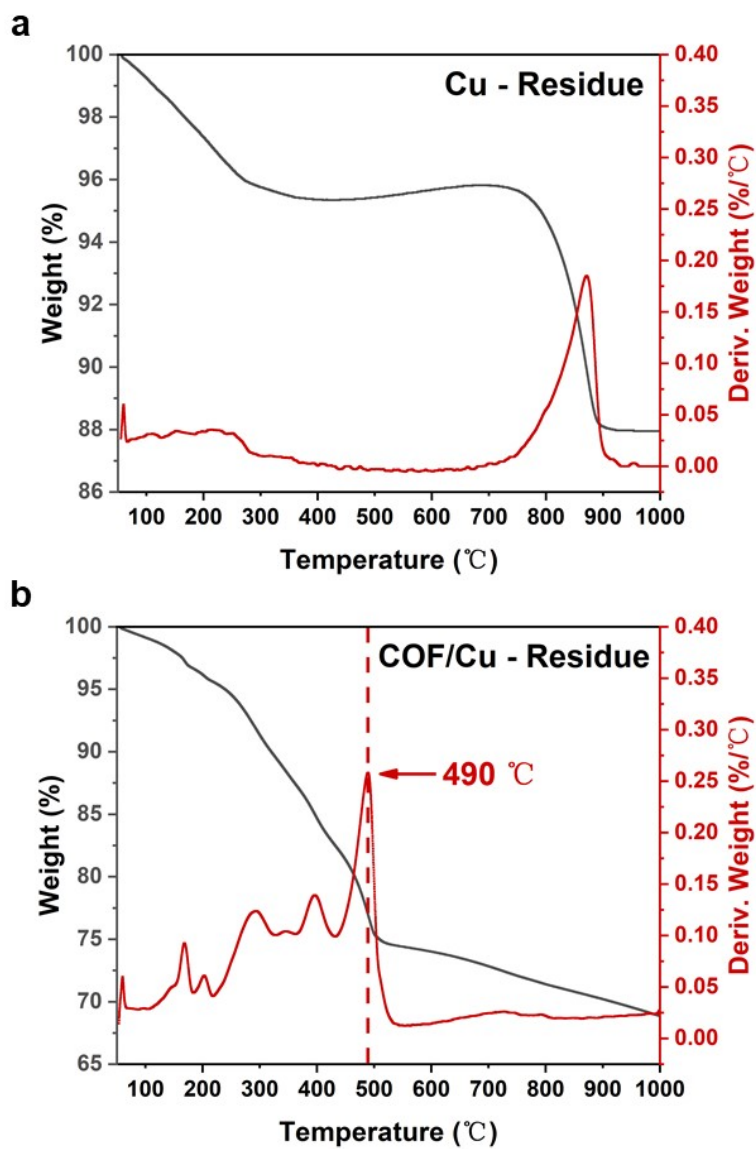


Fig. S10. TGA thermograms of Cu-Residue(a), COF/Cu-Residue (b).

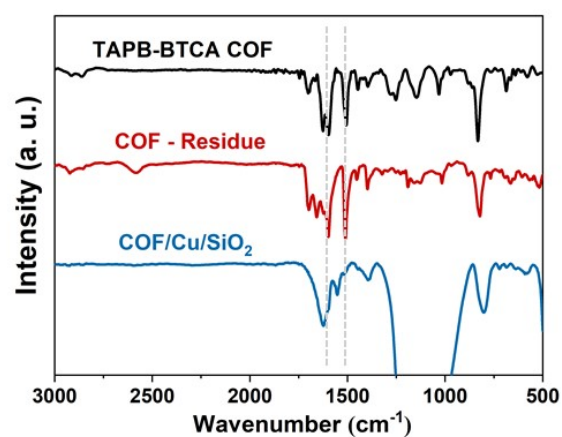


Fig. S11. FT-IR spectra of COF/Cu/SiO<sub>2</sub>, TAPB-BTCA COF and COF-Residue.

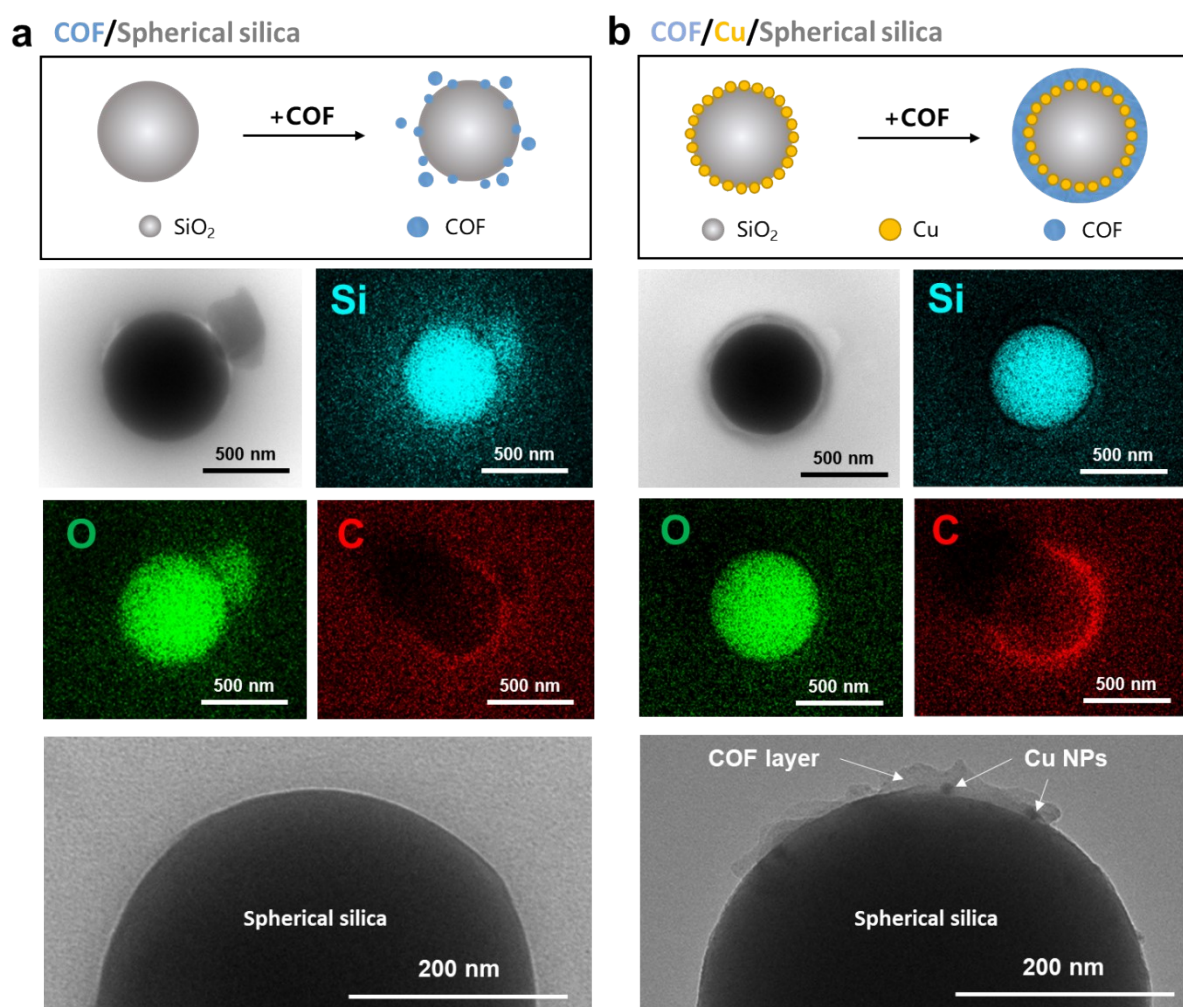


Fig. S12. TEM images, and Si, O and C elemental mapping of COF/spherical silica (a) and COF/Cu/Spherical silica (b).



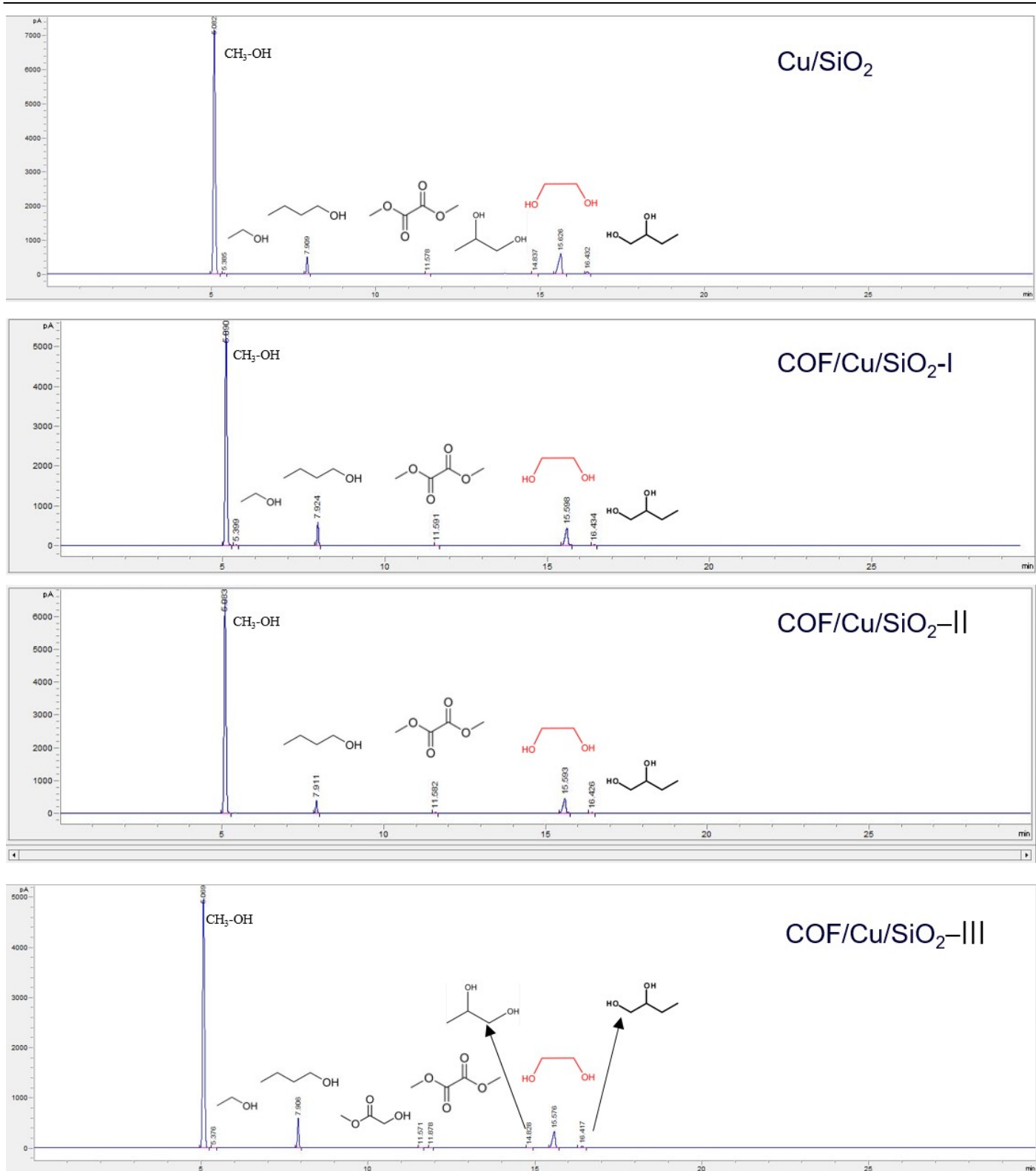


Fig.S13. GC signals of the liquid products of DMO hydrogenation over COF/Cu/SiO<sub>2</sub> catalyst in Fig. 2b.

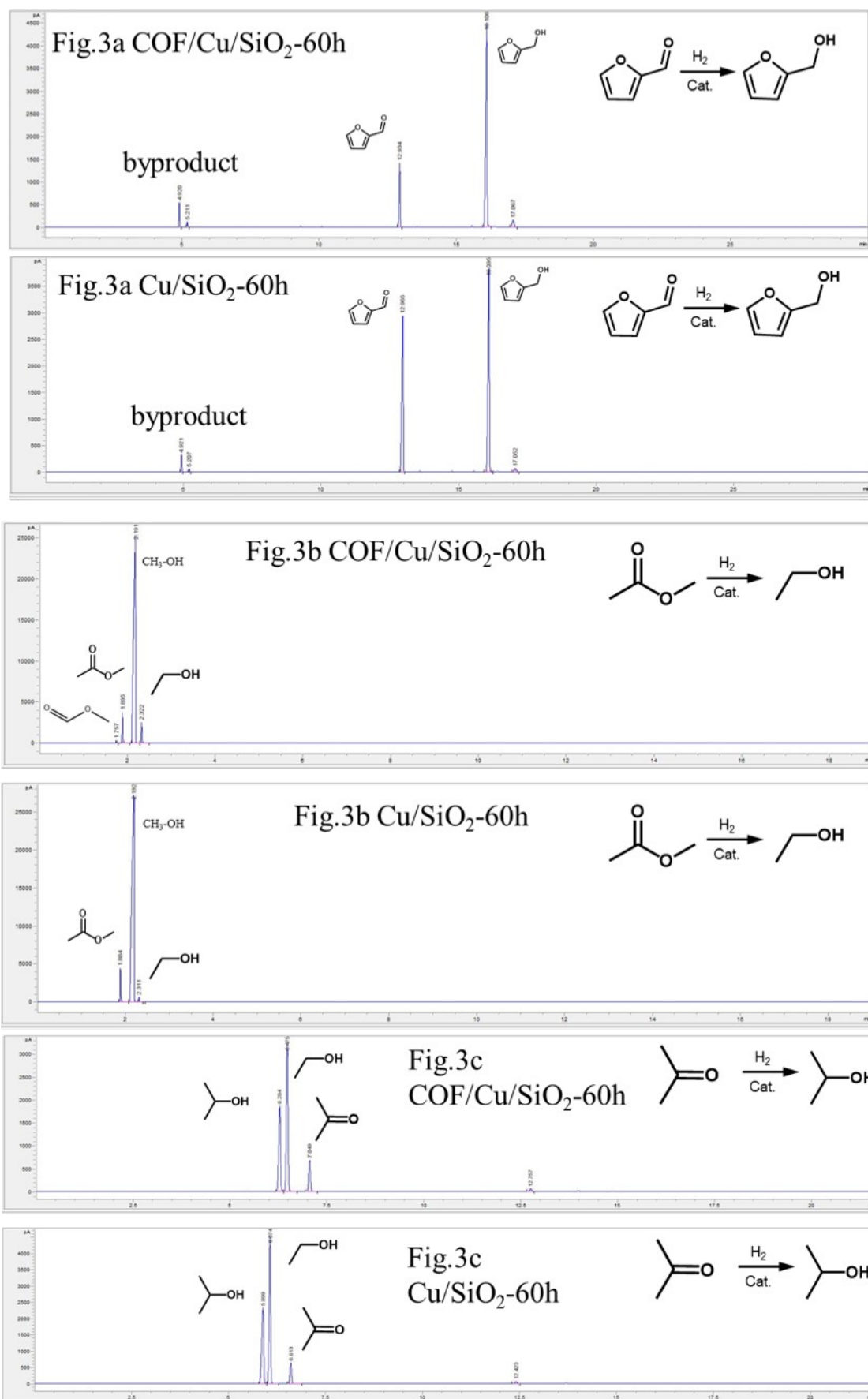


Fig. S14. GC signals of the liquid products in Fig. 3.

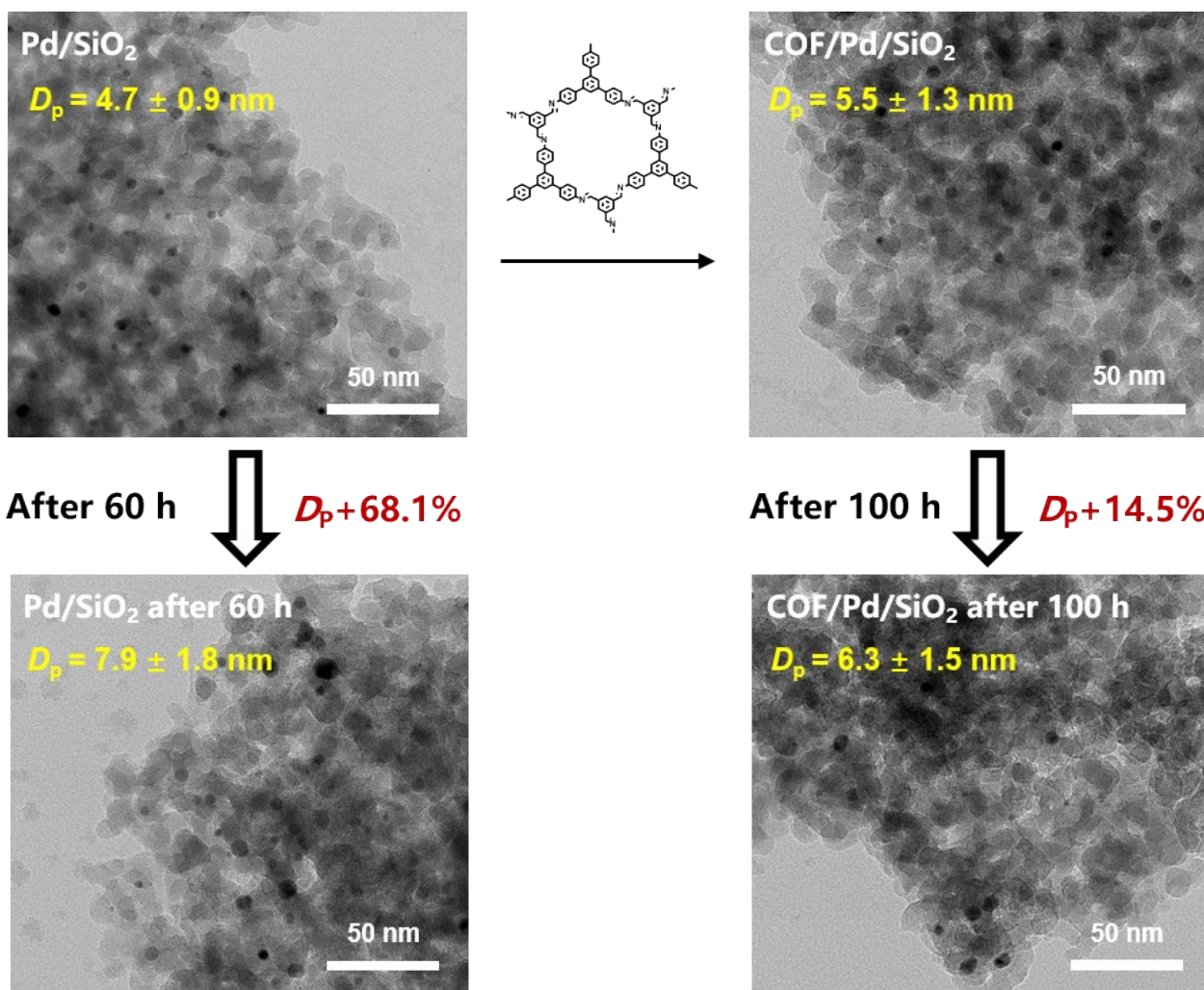


Fig. S15. TEM image of Pd/SiO<sub>2</sub>, COF/Pd/SiO<sub>2</sub>, Pd/SiO<sub>2</sub> after 60 h reaction and COF/Pd/SiO<sub>2</sub> after 100 h reaction.

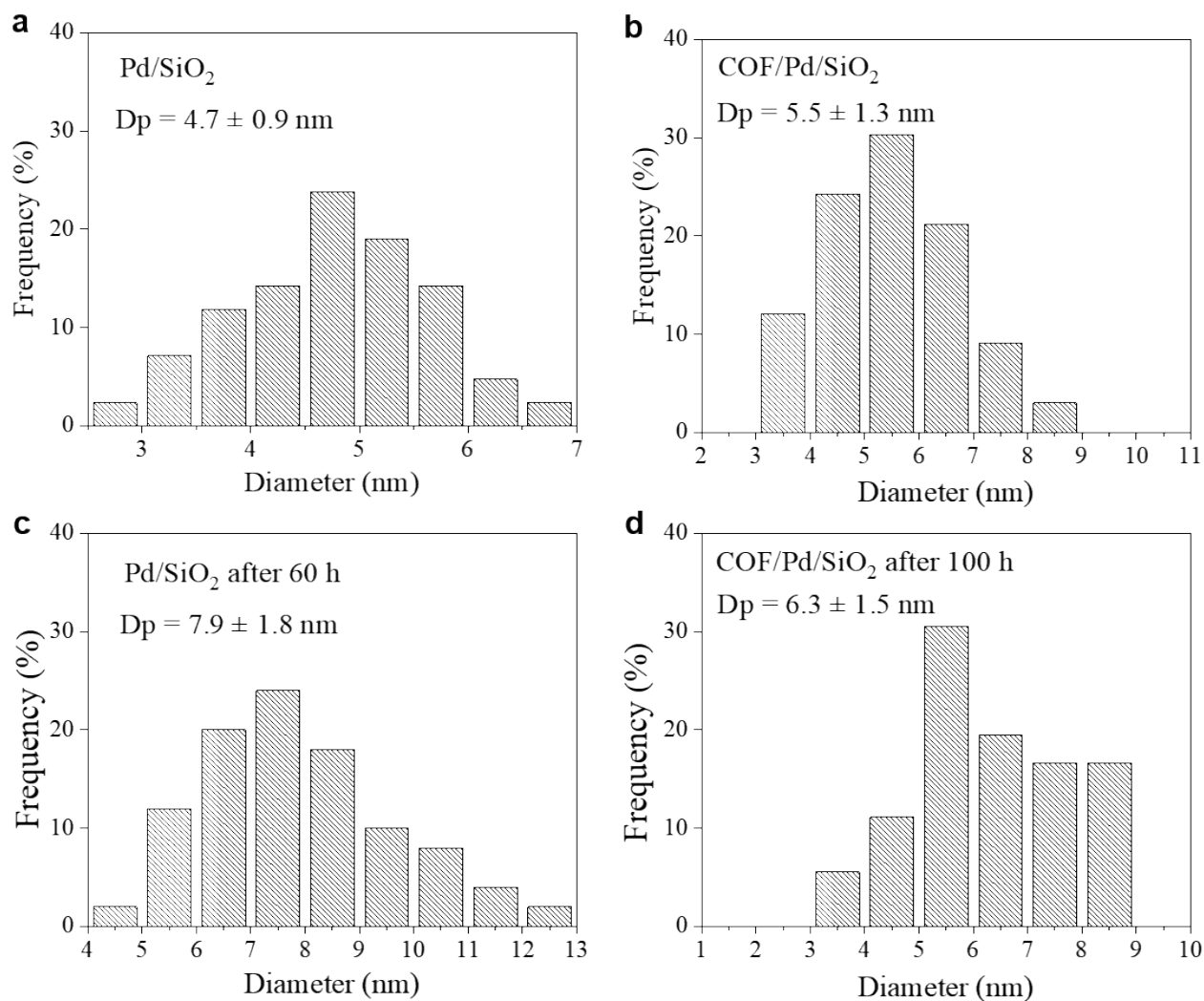


Fig. S16. Nanoparticle distributions of Pd/SiO<sub>2</sub>, COF/Pd/SiO<sub>2</sub>, Pd/SiO<sub>2</sub> after 60 h reaction and COF/Pd/SiO<sub>2</sub> after 100 h reaction.