

Supporting Information of

Cu/SiO₂ synthesized with HKUST-1 as precursor: high ratio of Cu⁺/(Cu⁺+Cu⁰) and rich oxygen defects for efficient catalytic hydrogenation of furfural to 2-methyl furan

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Experimental section

1. Catalyst synthesis

Chemical Materials. Analytically pure 1,3,5-Benzenetricarboxylic acid (H₃BTC), Cu(NO₃)₂·3H₂O, *N,N*-dimethylformamide (DMF), ethanol, acetone, aqueous ammonia, silica and tetraethoxysilane (TEOS) were purchased from Aladdin Chemical Reagent Co., Ltd. Deionized water (18 MΩ·cm) were used throughout the experiments.

Synthesis of Cu/SiO₂-MOF catalyst. ① HKUST-1 preparation: Firstly, 1.69 g of Cu(NO₃)₂·3H₂O was dispersed in 60 mL of DMF containing 1.00 g of H₃BTC, and the mixture was stirred for 1 h under room temperature. Secondly, the slurry was transferred into a 20 mL Teflon container and allowed to react for 24 h at 70 °C, and then cooled naturally. Thirdly, the precipitate was centrifuged washed with ethanol, water and acetone for at least 3 times. Finally, the prepared samples were dried at 120 °C under vacuum for 12 h denoted as HKUST-1. ② Cu/SiO₂-MOF preparation: Firstly, 5.0 g of HKUST-1 powder was dispersed in 22.0 g of distilled water, and then 37.0 g of ethanol and 28.5 g of TEOS were added. Secondly, the suspension was stirred and heated in water bath at 65 °C for 2 h, and then aged at room temperature for 24 h. Finally, the prepared samples were dried and calcined in static air for 5 h denoted as Cu/SiO₂-MOF catalyst.

Synthesis of Cu/SiO₂-AE catalyst. Firstly, 1.14 g Cu(NO₃)₂·3H₂O was dissolved in 30 mL of deionized water, and 25% of aqueous ammonia was added drop by drop until the pH value reaching about 12. Secondly, 3.0 g of silica gel was added and stirred at room temperature for 5 h. Thirdly, the suspension was heated at 90 °C until the pH

value decreasing to 6~7. After centrifugation and wash, the solid sample was then dried at 120°C overnight and finally calcined at 450 °C in atmosphere for 5 h.

Synthesis of Cu/SiO₂-TI catalyst. Firstly, 1.14 g Cu(NO₃)₂·3H₂O was dispersed in 30 mL of distilled water. Secondly, 3.0 g of silica gel was added and stirred at room temperature for 5 h. Thirdly, the suspension was heated at 90 °C to evaporate the solvent. Finally, the dried solid powder was calcined at 450 °C in atmosphere for 5 h.

2. Catalyst characterizations

Cu/SiO₂-MOF, Cu/SiO₂-AE and Cu/SiO₂-TI catalysts were characterized by N₂ adsorption-desorption isotherms, inductively coupled plasma (ICP) spectroscopy, Fourier translation infrared (FT-IR) spectroscopy, powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and *in situ* electron spin resonance (ESR) and so on.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES): The content of each element in the catalyst sample was determined by a PerkinElmer Optima 8300 inductively coupled plasma atomic emission spectrometer. The test process was as follows, Firstly, the catalyst sample was dissolved in hydrofluoric acid to ensure that it was completely dissolved and in a clear state. Finally, the solution was diluted to a suitable test range. The five standard solutions were prepared to construct the external standard curve. The content of elements in the samples was determined by external standard curve.

Powder X-ray diffraction (PXRD): The crystal structure of the sample was characterized using a Japanese Rigaku Ultima IV X-ray diffractometer. The scanning

parameters were: Cu K α X-ray source, $\lambda = 1.5406 \text{ \AA}$, tube voltage of 35 kV, tube current of 25 mA, scanning range of 5–80°, scanning speed of $5^\circ \cdot \text{min}^{-1}$, and scanning step of 0.02°.

X-ray photoelectron spectroscopy (XPS): The valence state of the metal Cu on the surface of the catalyst was measured with a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. Al K α was selected as the X-ray emission source ($h\nu = 1486.6 \text{ eV}$). The binding energy (BE) was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.58 eV. Wagner – database of experimental sensitivity factors be used, based on $F_{1s} = 1$.

Transmission electron microscopy (TEM): Concerning on the TEM conditions, the samples prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The samples morphology and particle sizes were measured by a TEM at 200 kV using a FEI Tecnai G2 F30 microscope.

Fourier-Transform infrared spectroscopy (FT-IR): catalyst samples were measured using a Nicolet Nexus 670 Fourier-transform infrared spectrometer. The test resolution was 4 cm^{-1} , the test wavenumber range $400\text{--}4000 \text{ cm}^{-1}$, and the number of scans was 64. Before the measurement started, background collection (empty sample cell) was required.

Brunauere-Emmette-Teller (BET) surface areas were calculated from Wafers of compressed catalysts samples were mounted in the FTIR cell and degassed in vacuum of 107 Pa at 573 K for 2 h.

In situ electron spin resonance (*in situ* ESR) signals were recorded with a Bruker A300 spectrometer. 30 mg powder sample was pressed into a self-supporting *in situ* ESR quartz tube. Prior to the ESR measurement, the tube was treated under dynamic vacuum (3.6×10^{-4} kPa) to remove surface contaminants.

H₂-TPR and N₂O chemisorption: In order to obtain the dispersion of Cu nanoparticles in Cu/SiO₂ catalysts, H₂-TPR and N₂O chemisorption were carried out on the Altamira Instruments 300 (AMI-300) with a thermal conductivity detector (TCD) at atmospheric pressure. The catalyst sample was placed in a U-tube reactor and outgassed at 120 °C under Ar for 30 minutes. After cooling to room temperature under Ar, the gas was switched to a 10% H₂/Ar mixture stream flowing at 30 mL·min⁻¹. Then, the sample was heated to 500 °C at a ramping rate of 10 °C·min⁻¹. The amount of H₂ consumed was monitored by TCD and denoted as X. The reduced sample was cooled to 65 °C and isothermally purged with Ar for 30 minutes, then exposed to 5% N₂O/Ar mixture gas with 30 mL·min⁻¹) for 30 minutes to ensure complete oxidation of naked metallic copper. All naked metallic copper would be oxidized in a 5% N₂O/Ar stream according to the reaction: $2\text{Cu(s)} + \text{N}_2\text{O} \rightarrow \text{Cu}_2\text{O(s)} + \text{N}_2$, where Cu(s) represents surface Cu atom. The samples were then flushed with Ar to remove the 5% N₂O/Ar mixture gas and cooled to room temperature. Finally, the gas was switched to a 10% H₂/Ar mixture stream flowing at 30 mL·min⁻¹ and the sample was heated to 300 °C at a ramping rate of 10 °C·min⁻¹. The amount of H₂ consumed was monitored by TCD and denoted as Y. The dispersion of Cu nanoparticles in samples were calculated by $D_{\text{Cu}}=2Y/X*100\%$.

3. Catalyst evaluation

The catalytic evaluations for FF hydrogenation reaction were tested on a homemade setup. As shown in **Fig. S1**, the fixed bed reactor includes two gas pipelines (H₂ for reactants and N₂ for sweeping), one liquid pipeline (FF solution), preheating vaporizer, fixed-bed tubular reactor, condenser and sample collector. The vaporizer, reactor, condenser, collector and all pipelines are made of 316 L stainless steel. The internal diameter of tubular reactor is 10 mm. The temperature was controlled with an electrical-heating with accuracy of ± 1 °C. For each test, 1.0 g of catalyst with two layers of quartz wool was placed in the tubular reactor before and after the catalyst layer. The catalyst was first reduced at 400 °C for 1 h in H₂ flow and then cooled down to reaction temperature. 0.2 mol·L⁻¹ of FF dissolved in MeOH or THF medium was fed using a syringe pump with velocity of 0.5 mol·L⁻¹, which was vaporized completely in the evaporation chamber before entering the reactor. A pressure sensor was connected into the fixed-bed reactor, displaying that the actual reaction pressure value was 0.11 MPa. The products were collected by cold trap and further analyzed by a gas chromatograph (GC, Agilent 6890) equipped with a flame ionization detector and an HP-INNOWAX capillary column (HewlettePackard Company, 30 m×0.32 mm×0.50 mm) using DMF as internal standard.

The FF conversion and product yield were defined as follows respectively:

$$FF \text{ conversion (\%)} = \frac{(\text{moles of } FF)_{in} - (\text{moles of } FF)_{out}}{(\text{moles of } FF)_{in}} \times 100\%$$

$$Product_i \text{ yield (\%)} = \frac{\text{moles of product}_i}{(\text{moles of } FF)_{in}} \times 100\%$$

It should be noted that the measured pressure at the front end of the fixed-bed reactor was atmospheric pressure. Due to the catalyst bed layer in reactor, however, the actual pressure inside the reactor was slightly higher than atmospheric pressure to overcome the pressure drop caused by the catalyst bed layer. In order to measure the actual reaction pressure, a pressure sensor was connected into the fixed-bed reactor, displaying that the actual reaction pressure value was 0.11 MPa, which was approximately equal to the atmospheric pressure because the thin catalyst bed layer.

4. Hydrogen spillover phenomenon

In our experiment, 10 mg of catalyst sample and 1 g of WO_3 powder were mixed and ground, and then put into a transparent quartz tube. The mixture sample and pure WO_3 powder were treated with H_2 flow at room temperature for 1 h.

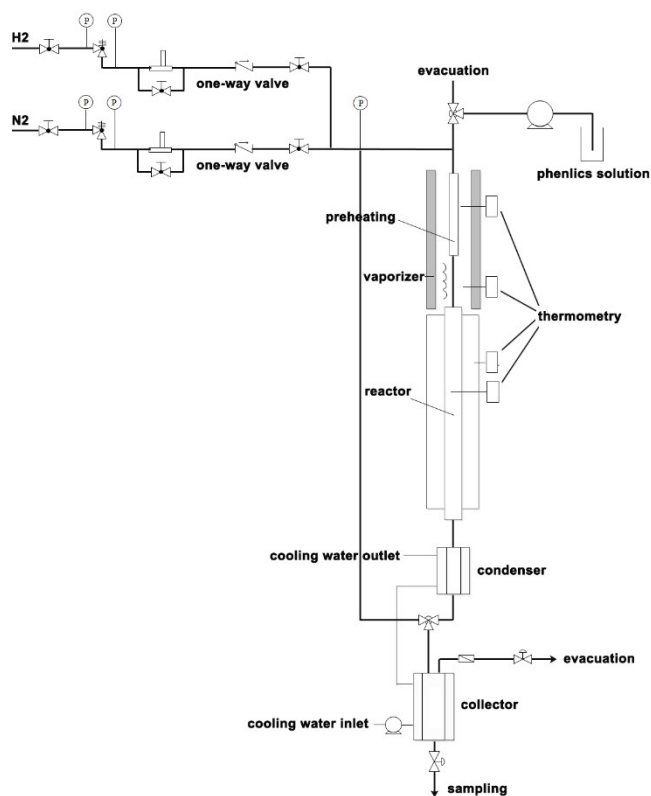


Fig. S1 Schematic of catalyst evaluation device for FF hydrogenation reaction.

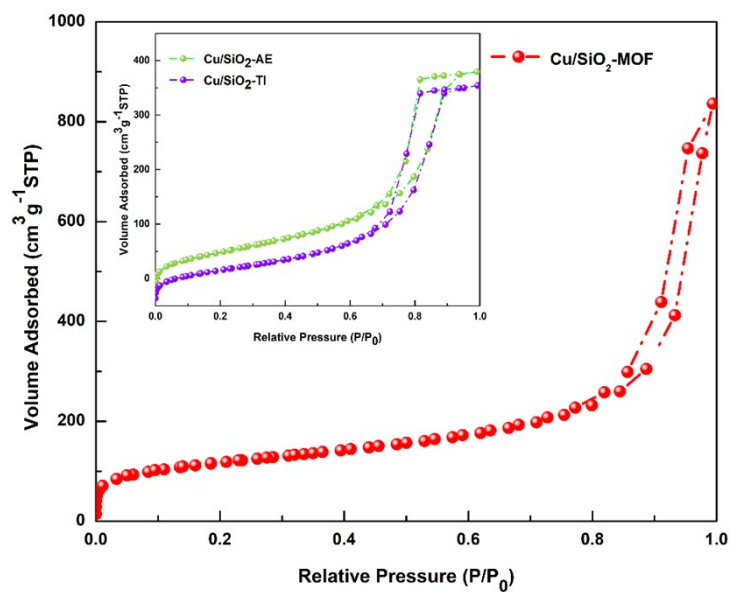


Fig. S2 The N₂ adsorption-desorption isotherms of different Cu/SiO₂ catalysts.

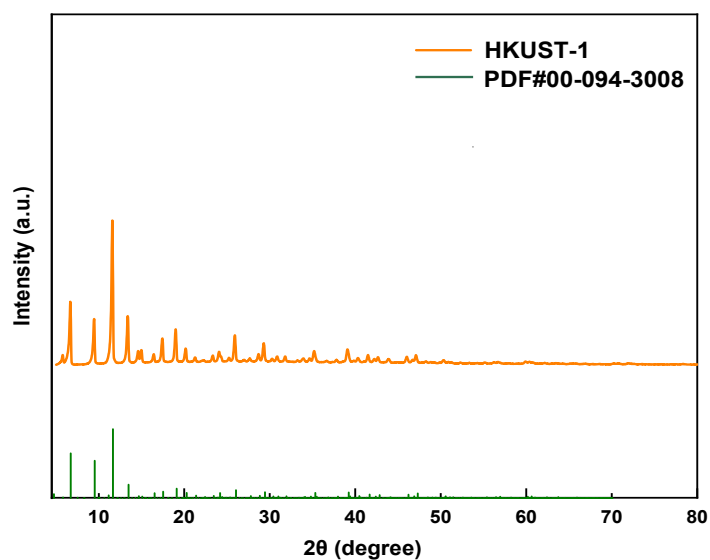


Figure S3. PXRD patterns of the as-synthesized HKUST-1 precursor.

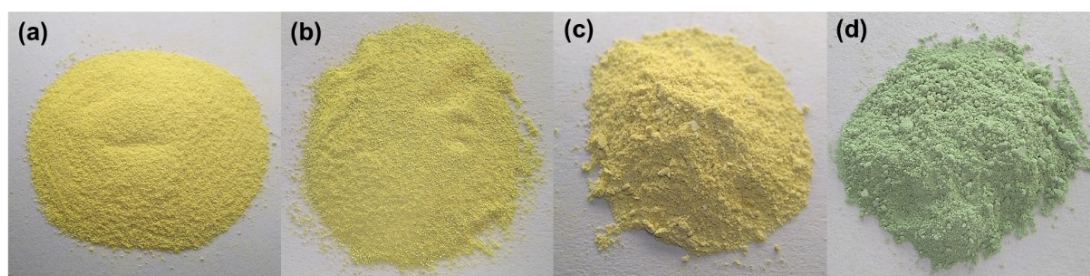


Fig. S4 The images of pure WO₃ (a) before and (b) after H₂ treatment, and mixture of WO₃ and Cu/SiO₂-MOF catalyst (c) before and (d) after H₂ treatment.

Table S1 Kinetic parameters for FF hydrogenation over Cu/SiO₂-TI catalyst.

T (°C)	T (K)	FF conversion (%)	<i>k</i>
80	353.15	0.04048	0.00138
100	373.15	0.07854	0.00273
120	393.15	0.17155	0.00627
140	413.15	0.37445	0.01564
160	433.15	0.66124	0.03608

Table S2 Kinetic parameters for FF hydrogenation over Cu/SiO₂-AE catalyst.

T (°C)	T (K)	FF conversion (%)	<i>k</i>
80	353.15	0.15348	0.00555
100	373.15	0.38498	0.01620
120	393.15	0.63679	0.03376
140	413.15	0.79929	0.05353
160	433.15	0.91516	0.08223

Table S3 Kinetic parameters for FF hydrogenation over Cu/SiO₂-MOF catalyst.

T (°C)	T (K)	FF conversion (%)	<i>k</i>
60	333.15	0.55124	0.02671
80	353.15	0.83501	0.06006
100	373.15	0.87576	0.06951
120	393.15	0.97023	0.11715