

Supplementary Information

Cu/MOF-808 catalyst for transfer hydrogenation of 5-Hydroxymethylfurfural to 2, 5-Furandimethanol with formic acid mediation

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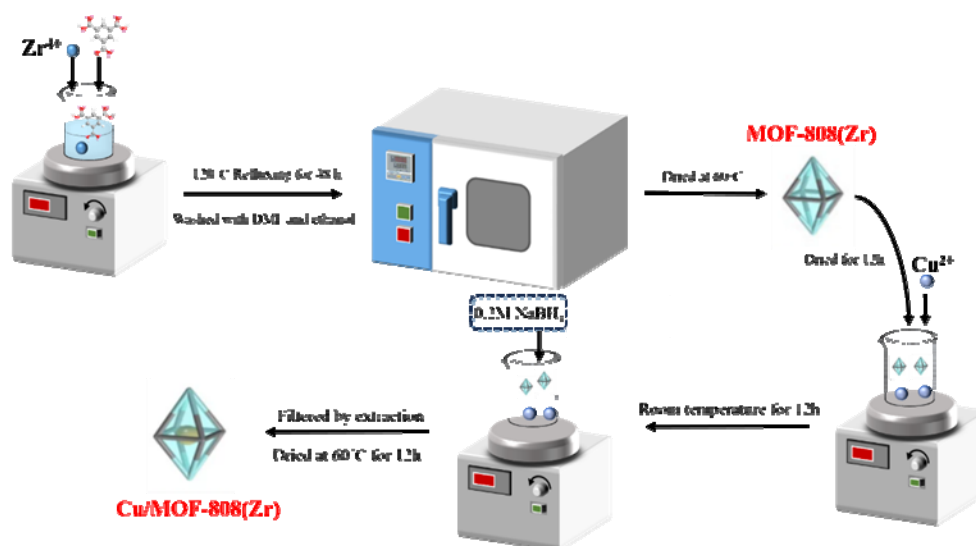


Figure S1 Schematic diagram of the synthesis of Cu/MOF-808 (Zr) catalysts

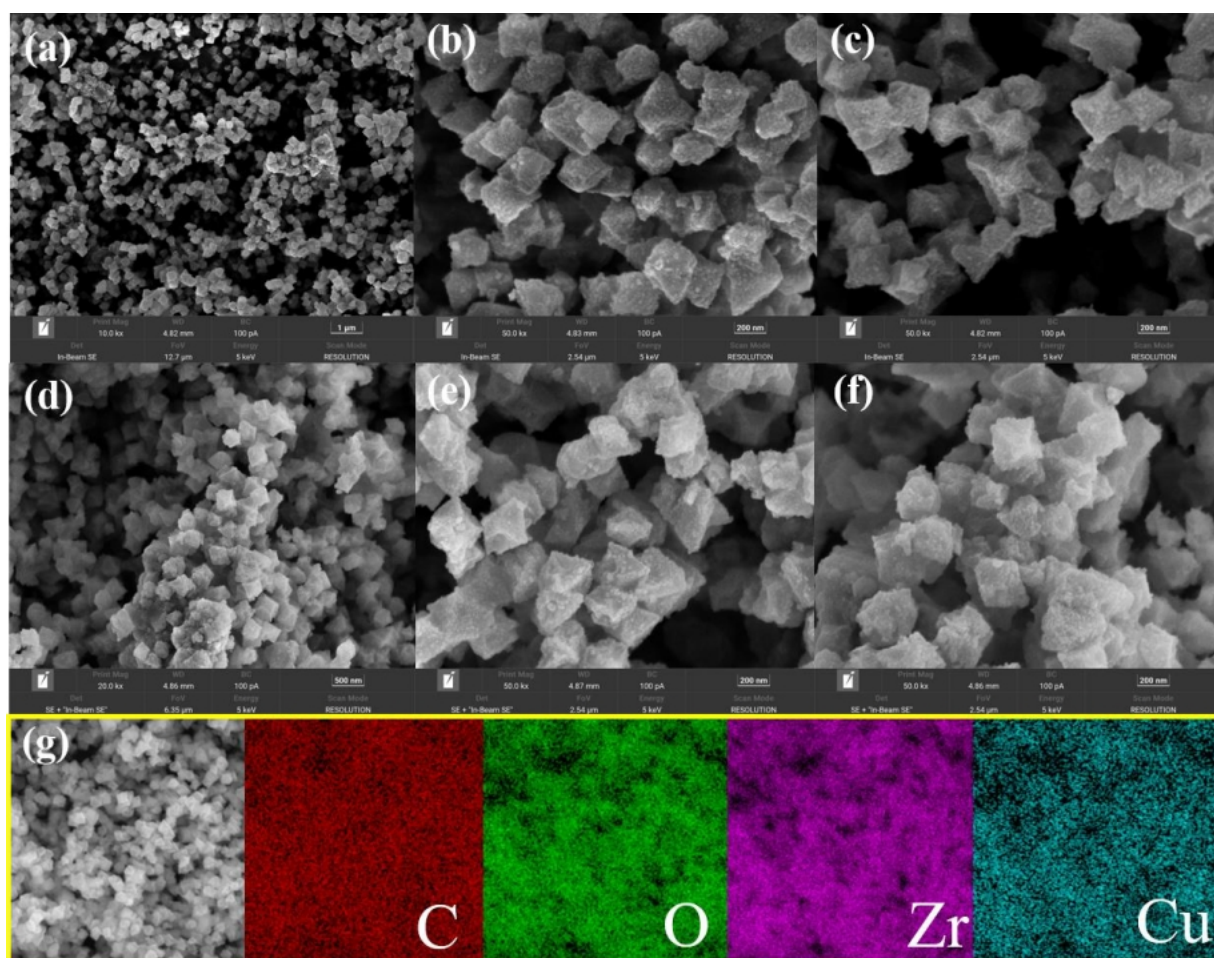


Figure S2 (a-c) SEM images of MOF-808, (d-f) SEM images of 3wt%-Cu/MOF-808(Zr), and (g) corresponding EDS mapping of 3wt%-Cu/MOF-808(Zr)

Instrumental techniques for the characterization of the catalysts:

- X-ray diffraction (XRD): X-ray diffraction (XRD) analysis of the sample to be tested using the D8-ADVANCE instrument to analyze the phase and composition of the synthesized material. Cu K α was used as the radioactive source for the analysis, and the scanning rate was 5 °/min, and the test results were compared with the standard card.
- Fourier transform infrared spectroscopy (FT-IR): Interactions between different functional groups of the prepared catalyst were analyzed using a Nicolet 6700 Fourier transform infrared spectrometer (FT-IR) with a scanning range of 400-4000 cm⁻¹. Using the tableting method, the sample to be tested and pure KBr are mixed and ground evenly into transparent sheets.
- Scanning electron microscope (SEM): The surface topography of the sample was observed and analyzed using the Zeiss Gemini SEM 500/300 field emission scanning electron microscope in Germany. The magnification is 12-2000000 and the operating voltage is 40 KV. After drying and grinding before the sample test, a small amount of the sample is coated on the substrate conductive adhesive, and then sent to the sample analysis room after purging.
- N₂ adsorption-desorption isotherm (BET): The pore size and specific surface area of the prepared catalyst were determined by using the BSD-PM2 instrument manufactured by Beijing Best Instrument Manufacturing Co., Ltd. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area of the sample, and the Horvath-Kawazoe (HK) model was used to calculate the pore size distribution of the sample.
- X-ray photoelectron spectroscopy (XPS): The chemical composition and elemental valence states of the catalyst sample surface were analyzed using the ESCALAB 250XI multifunctional X-ray photoelectron spectrometer (XPS).
- Thermogravimetric analysis (TG): Thermogravimetric analysis of the catalyst was performed using the NETZSCH TG209 thermogravimetric analyzer with a temperature rise rate of 10 K/min and a test temperature of 293 K-1173 K.
- Pyridine adsorption infrared spectroscopy (Py-IR): The type of catalyst acid

center was analyzed using the Tensor-27 pyridine adsorption infrared spectrometer (Py-IR) manufactured by Bruker in the United States. At 1450 cm⁻¹ and 1540 cm⁻¹ wavelengths in the infrared spectrum, the characteristic peaks of the Lewis and Brønsted acid sites are respectively.

Experimental process and component analysis of HMF catalytic transfer hydrogenation to BHMF:

HMF, formic acid, catalyst and solvent were added to the PTFE-lined reactor, the sealed reactor was purged with N₂ three times and then filled with N₂, and the heating rate was set to 10°C/min. After the reaction is complete and the reactor is cooled, the reaction products are filtered using a 0.22 μm organic phase needle filter. Quantitative analysis using gas chromatography (GC) and qualitative analysis using gas chromatography-mass spectrometry (GC-MS).

Product analysis methods:

A GC-MS (Agilent 7890-5975C) and a GC (Agilent 6890, HP-5 capillary column, 30.0 × 250 mm × 0.25 mm) were used for the qualitative and quantitative analysis of the reaction products. The analytical procedure was: the inlet temperature was 280°C and N₂ was used as the carrier gas. After a dwell time of 1 min at 50°C, the sample was ramped up to 100°C at 15°C/min and then held for 2 min at 10°C/min to 250°C for 2 min and then ramped up to 280°C at 5°C/min for 5 min. 1 μL of each sample was injected into the gas chromatograph and the concentrations of HMF and BHMF in the mixture were determined from the standard curve. The conversion of the reactants, the selectivity and the yield of the products were calculated by applying the following equations:

$$\text{Conversion, \%} = \left(1 - \frac{\text{mole of unreacted HMF in products}}{\text{initial mole of HMF}} \right) \times 100\% \quad (\text{S1})$$

$$\text{Yield, \%} = \frac{\text{mole of BHMF in products}}{\text{initial mole of HMF}} \times 100\% \quad (\text{S2})$$

$$\text{Selectivity, \%} = \frac{\text{BHMF yield}}{\text{HMF conversion}} \times 100\% \quad (\text{S3})$$

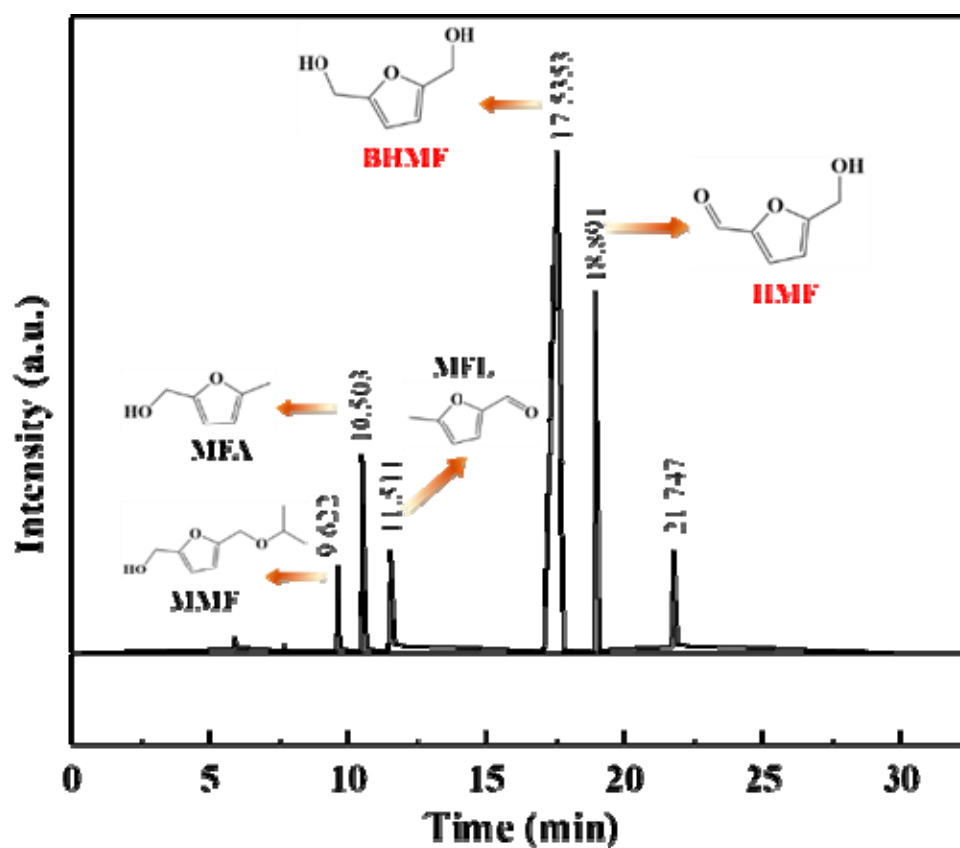


Figure S3 GC-MS chromatogram of BHMf prepared by catalytic conversion of HMF

Table S1 Acid amounts of MOF-808(Zr) and 3wt%-Cu/MOF-808(Zr) catalysts

	Total acids (mmol/g)	Medium and strong acid (mmol/g)	Medium and strong acid content (%)
MOF-808 (Zr)	22.71	1.01	4.45
1wt%-Cu/MOF-808(Zr)	11.34	0.72	6.38
3wt%-Cu/MOF-808(Zr)	10.23	0.75	7.35
5wt%-Cu/MOF-808(Zr)	9.39	0.51	5.42

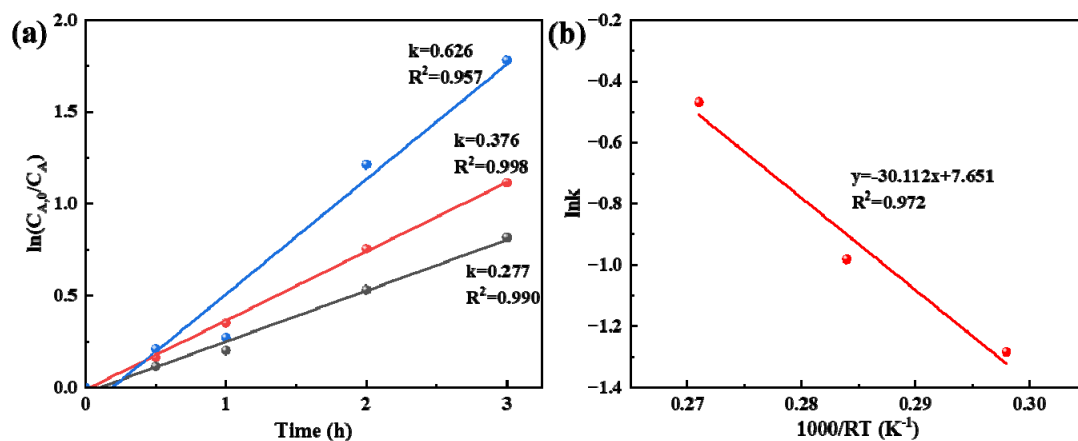


Figure S4 (a) $\ln(C_{A,0}/C_A)$ vs. reaction time plots of HMF hydrogenation over catalyst,
 (b) Relationship between $\ln k$ and $1/T$ in the conversion of HMF

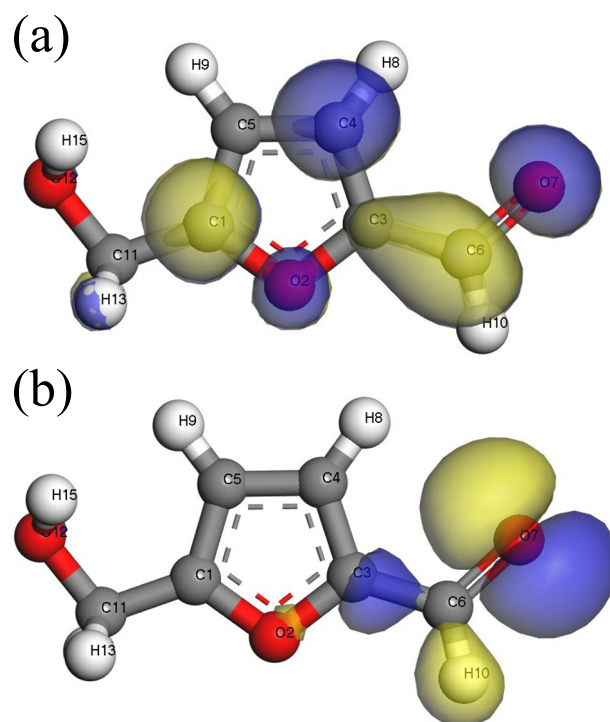


Figure S5 (a) HOMO and (b) LUMO plots of HMF

Table S2 calculated Fukui index of HMF

atom	f^-	f^+	f^0
C (1)	0.09	0.103	0.097
O (2)	0.047	0.064	0.056
C (3)	0.040	0.043	0.042
C (4)	0.072	0.105	0.088
C (5)	0.060	0.063	0.061
C (6)	0.102	0.144	0.123
O (7)	0.299	0.175	0.237
H (8)	0.036	0.047	0.042
H (9)	0.039	0.042	0.040
H (10)	0.077	0.064	0.070
C (11)	0.022	0.023	0.023
O (12)	0.034	0.035	0.035
H (13)	0.033	0.036	0.035
H (14)	0.032	0.035	0.034
H (15)	0.017	0.019	0.018