Supporting information

In-situ construction of an integrated SyA-Cu MOF/C,N-co doped CuO heterostructure for highly effective and rapid catalytic hydrogenation of 4-nitrophenol

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1. Experimental section

Reagents and materials: All chemical reagents were purchased from commercial suppliers and used as received without further purification. Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%) and Syringic acid ($C_9H_{10}O_5$, 98%) were purchased from Shanghai Titan Scientific Co., Ltd. Commercial Ni foam was purchased from Suzhou Cheng Er Nuo Technology Co., Ltd. 4-nitrophenol (4-NP) and 4-aminophenol (4-AP) were obtained from Shanghai Macklin Biochemical Co., Ltd. Tertiary butyl alcohol ($C_4H_{10}O$, 99%)and sodium borohydride ($NaBH_4$, 98%) were purchased from Aladdin Industrial Cooperation. Deionized (DI) water was homemade in the lab.

Physical characterizations:

XRD data were acquired by Brukef D8 instrument with Cu-Kα radiation. SEM measurements were carried out on a Hitachi S-4800 Scanning Electron microscope. TEM images were collected on a JEOL JEM 2100F electron microscopy. XPS spectra were recorded on a Kratos AXIS Ultra ^{DLD} X-ray photoelectron spectrometer. ^{1}H NMR spectra were acquired on a Bruker Avance NEO 600 MHz. Electron paramagnetic resonance (EPR) spectra were acquired on a Bruker EMXplus-6/1 spectrometer at room temperature.

1.1. Synthesis of gerhardtite $Cu_2(OH)_3(NO_3)$ on Nickel foam (CuHN/NF)

The gerhardtite $Cu_2(OH)_3(NO_3)$ was made via a molten method with a minor modification according to our previously published procedure.[21] First, 30 g of

$Cu(NO_3)_2 \cdot 3H_2O$ were placed in a 50 mL autoclave and heated to 140 °C until completely melted. Subsequently, the cleaned 6 cm × 6 cm Ni foam (NF) was dipped into the molten salt and allowed to react for 35 minutes at 140 °C. To get rid of extra molten salt, deionized water was used to wash the resulting NF pieces. Then, the prepared CuHN/NF was cut into pieces of 1.0 cm × 1.5 cm and the mass loading of $Cu_2(OH)_3(NO_3)$ on NF is 6.3 mg cm^{-2}.

1.2 Synthesis of MOF (SyA-Cu) and CuHN heterostructure on NF (SyA-Cu/CuHN/NF)

0.25 mmol syringic acid was added into 30 mL of N,N-dimethylformamide (DMF) and stirred for 15 min to completely dissolve it. Then it was transferred to 50 mL of PTFE liner and CuHN/NF (2.5 cm × 3.5 cm) was added. And the mixture was heated to 130 ℃ under solvothermal condition for 10 h, and then cooled to room temperature for 5 h. The as-prepared materials were washed with DMF and deionized water, and dried in vacuum at 60 ℃ for 8 hours to obtain SyA-Cu/CuHN/NF with a loading of 4.9 mg cm^{-2}.

1.3 Synthesis of MOF (SyA-Cu) and N doped CuO heterostructure on NF (SyA-Cu/C,N-CuO)

SyA-Cu/CuHN/NF(2.5 cm × 3.5 cm) was put into a tube furnace. Then it was heated to 250 ℃ in argon atmosphere for 100 min, continually calcined for 2 h, and finally cooled to room temperature for 2.5 h to obtain SyA-Cu/N-CuO/NF, which was cut to a size of 1 cm × 1.5 cm with a loading of 4.7 mg.cm^{-2}.

1.4 Catalytic hydrogenation reaction for 4-NP and product analysis

In a typical experiment of 4-NP reduction, 5 mmol $NaBH_4$ was added into 50 mL

of 4-NP (10 mM), leading to the change of color from pale yellow to bright yellow. Then, a piece of SyA-Cu/C,N-CuO foam (4.7 mg.cm^{-2}, 1.0 cm × 1.5 cm) was added and the reaction was initiated immediately. Every experiment was conducted at 25 ± 0.2 °C with constant stirring. 4-NP and its products were detected by high performance liquid chromatography (HPLC). The instrument was equipped with ultraviolet detector and C18 column (4.6 mm×250 mm). Specifically, 50 μL of reaction solution was absorbed during the reaction, diluted 25 times with ultrapure water, and analyzed by HPLC. The detection wavelength was 270 nm, the mobile phase was made up of a mixed solution of acetonitrile and 0.02 M formic acid (volume ratio: 73:27), with a flow rate of 1 mL/min. To evaluate the reusability, the catalyst was taken out from solution and reused in the next cycle without any treatment.

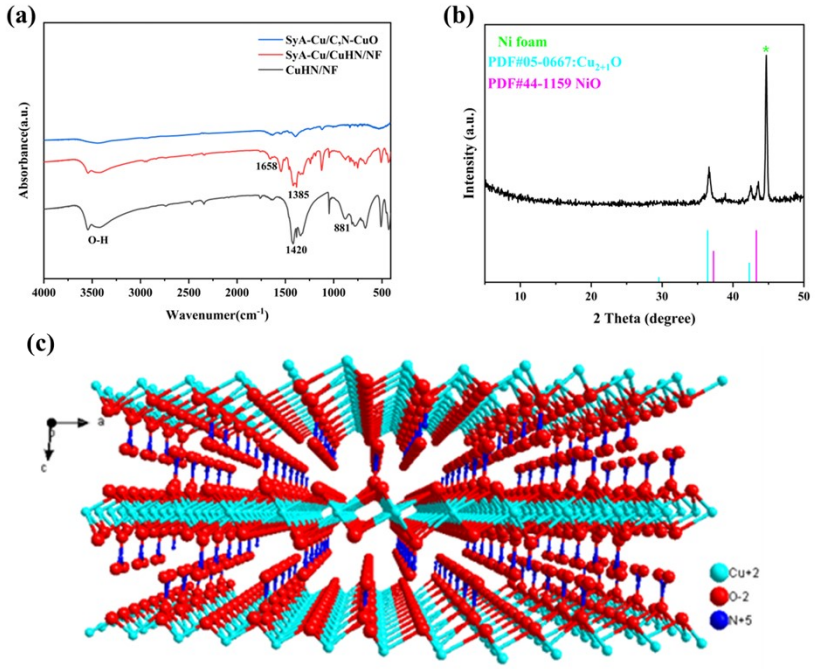

Fig. S1. (a) FTIR spectra of CuHN/NF, SyA-Cu/CuHN/NF, and SyA-Cu/C,N-CuO .(b) XRD patterns of SyA-Cu/CuHN/NF after calcination at 350°C.(c)2D structure of $Cu_2(OH)_3(NO_3)$.

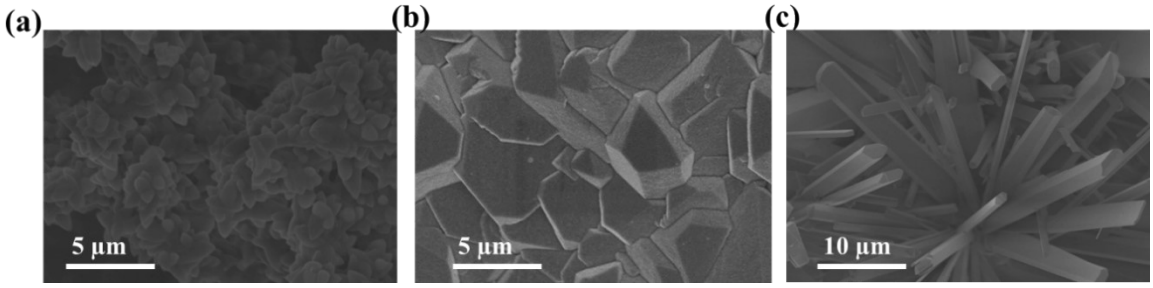

Fig. S2 SyA-Cu/C,N-CuO SEM images prepared by different Cu sources. (a) Cu $(NO_3)_2 \cdot 3H_2O$, (b) $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ (c) CuHN/CF.

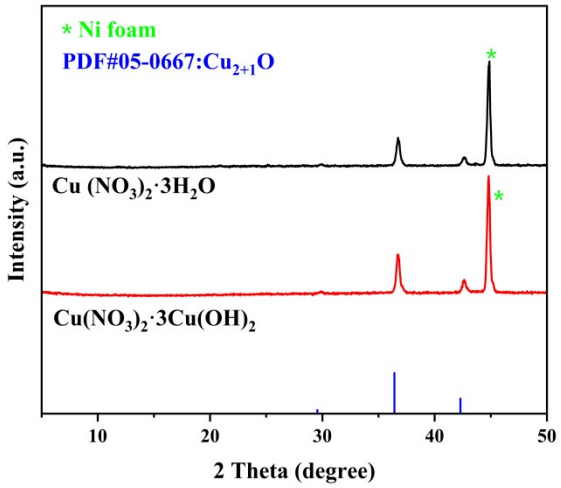

Fig. S3 SyA-Cu/C,N-CuO XRD patterns prepared by different Cu sources.

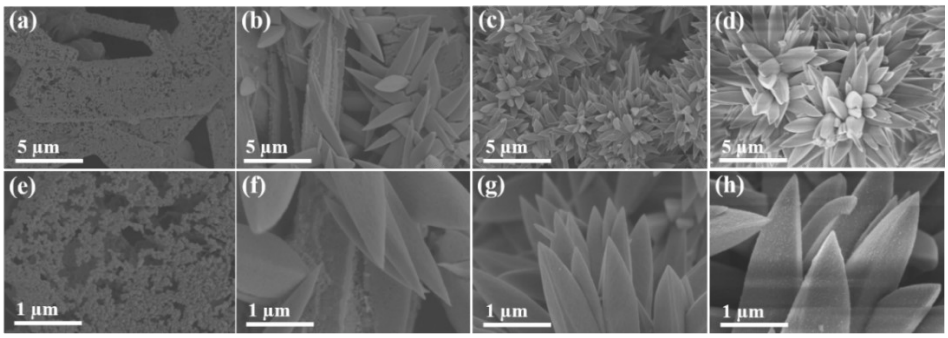

Fig. S4. Effect of syringic acid dosage on morphology of SyA-Cu/C,N-CuO catalyst, (a)(e) 0 mmol; (b)(f) 0.25 mmol; (c)(g) 1.25 mmol; (d)(h) 5 mmol.

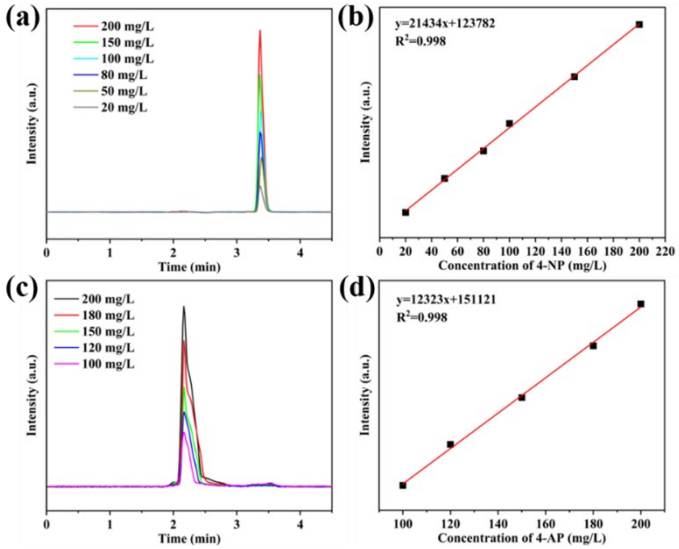

Fig. S5. HPLC chromatogram of standard samples at different concentrations; (a) 4-NP, (c) 4-AP; the fitted standard curve for (b) 4-NP, (d) 4-AP.

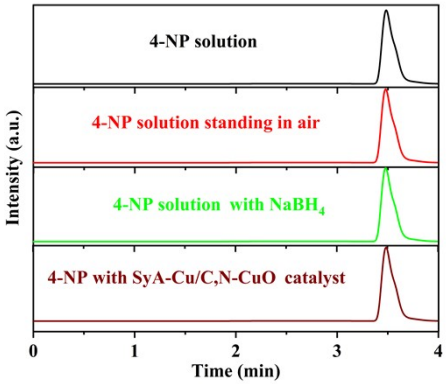

Fig. S6. (a) Liquid chromatogram of 4-NP solution; (b) liquid chromatogram of 4-NP solution after standing in air for 100 minutes; (c) liquid chromatogram of 4-NP solution after adding $NaBH_4$ for 100 minutes; (d) liquid chromatogram of 4-NP solution after the adding SyA-Cu/C,N-CuO catalyst for 100 minutes.

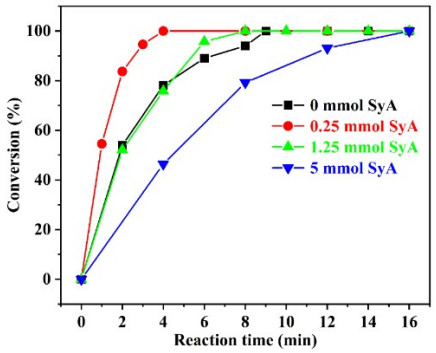

Fig. S7. Catalytic conversion efficiency of the SyA-Cu/C,N-CuO catalysts synthesized at different dosage of syringic acid.

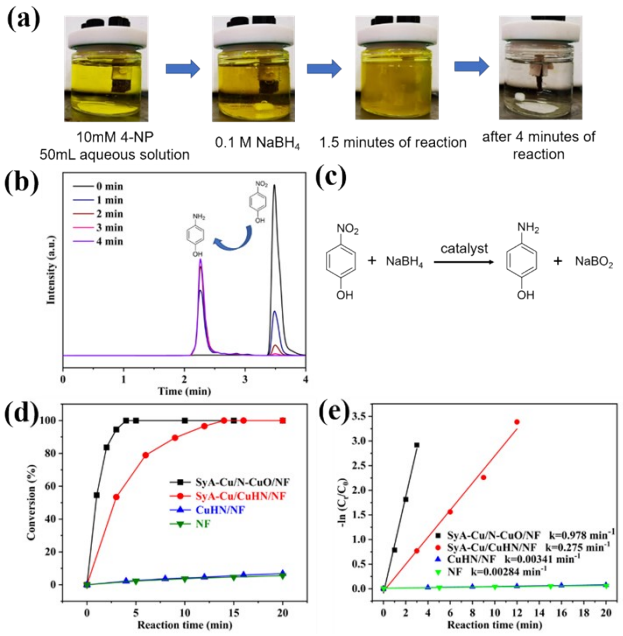

Fig. S8 (a) Photographs of 4-NP reduction catalyzed by SyA-Cu/C,N- CuO; (b) liquid chromatogram of 4-NP reduction catalyzed by SyA-Cu/C,N- CuO; (c) reduction reaction equation of 4-NP; (d) Catalytic conversion efficiency of SyA-Cu/C,N-CuO, SyA-Cu/CuHN/NF, CuHN/NF and NF; (e) plots of $\ln(C_t/C_0)$ vs. the reaction time.

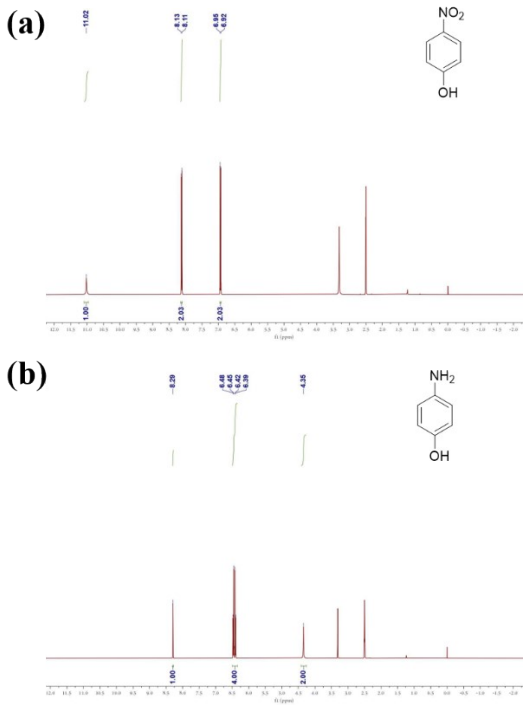

Fig. S9. (a) ^{1}H NMR spectrum of 4-nitrophenol, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.02 (s, 1H), 8.12 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H). (b) ^{1}H NMR spectrum of product, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (s, 1H), 6.49 – 6.35 (m, 4H), 4.35 (s, 2H).

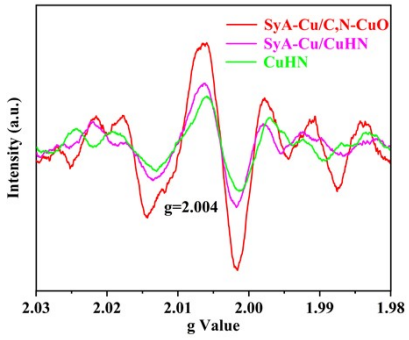

Fig. S10. EPR spectrum of CuHN, SyA-Cu/CuHN and SyA-Cu/N-CuO.

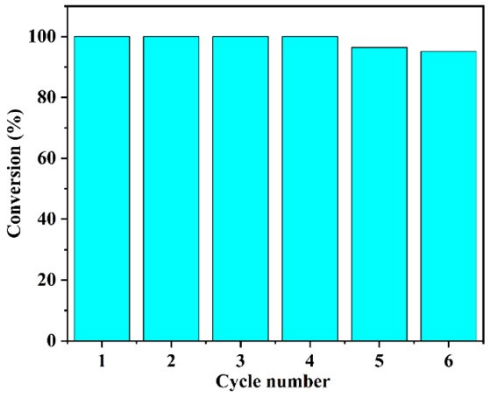

Fig. S11. Recycle testing of SyA-Cu/C,N-CuO catalyst.

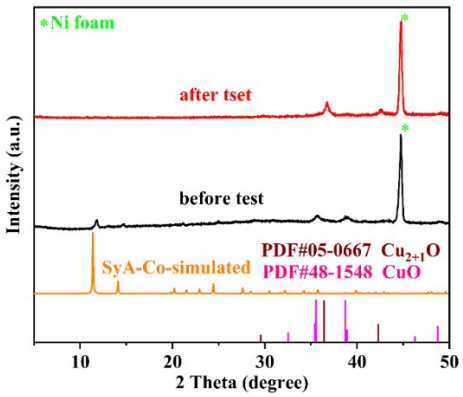

Fig. S12. XRD patterns of SyA-Cu/C,N-CuO before and after six-cycle test.

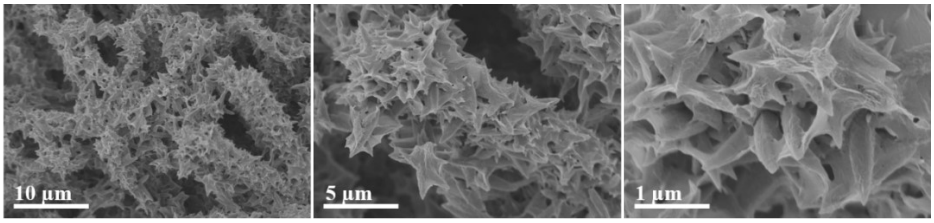

Fig. S13. SEM patterns of SyA-Cu/C,N-CuO after six-cycle test.

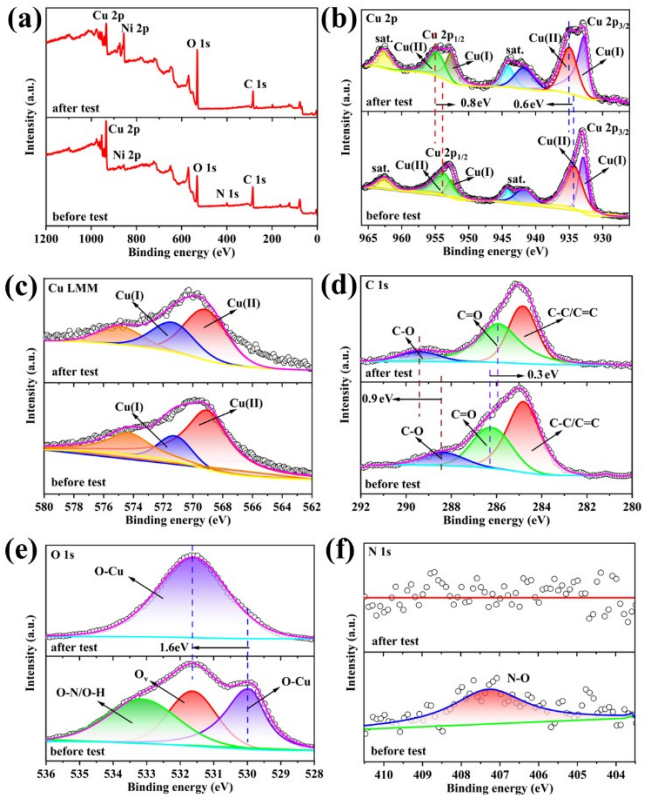

Fig. S14. (a) The XPS spectra of SyA-Cu/C,N-CuO before and after six-cycle test; high resolution XPS spectra of (b) Cu 2p, (c) Cu LMM, (d) C 1s, (e) O 1s and (f) N 1s.

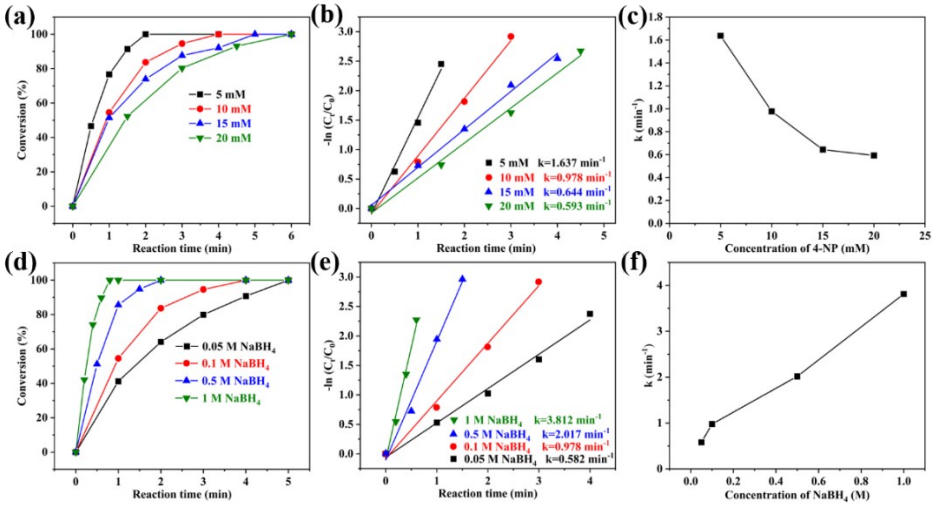

Fig. S15. The effect of concentration of 4-NP on (a) reduction efficiency and (b) plots of ln(C_t/C_0) vs. the reaction time over SyA-Cu/C,N-CuO; the effect of concentration of $NaBH_4$ on (d) reduction efficiency and (e) plots of ln(C_t/C_0) vs. the reaction time over SyA-Cu/C,N-CuO; the relationship of k with the concentration of (c) 4-NP and (f) $NaBH_4$.

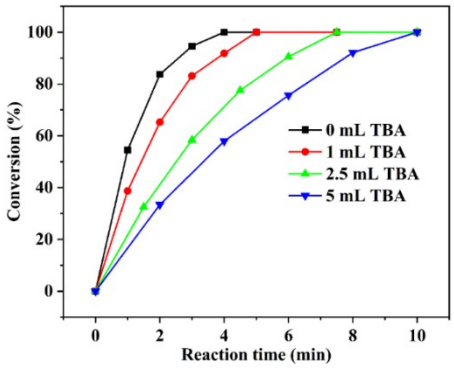

Fig. S16. Effect of TBA on catalytic reduction efficiency of SyA-Cu/C,N-CuO.

Table S1. Element content of SyA-Cu/C,N-CuO according to EDS results.

Element	Atomic Fraction (%)	Mass Fraction (%)
N	11.56	7.48
O	61.93	45.75
Cu	13.47	39.54
C	13.04	7.23

Table S2. Comparison of catalytic performance of SyA-Cu/C,N-CuO and other typical catalysts for 4-NP reduction.

Catalyst	n($NaBH_4$): n(4-NP)	k (min^{-1})	TOF (mmol/(mg·min))	E_a (kJ/mol)	Ref.
Cu-MOF-1	700:1	1.70	\	\	[1]
Cu/CuO-TiO_2	100:1	0.82	\	\	[2]
Cu/kaolin NC	700:1	1.23	\	\	[3]
PtCu NWN	100:1	0.80	\	\	[4]
$Cu_3(SDBA)_2(HSDBA)$	30:1	\	\	9.7	[5]
Cu_2O/MoS_x	100:1	\	8.5×10^{-2}	\	[6]
Cu foam	93:1	\	\	43.3	[7]
HKUST-1					
SyA-Cu/C,N-CuO	10:1	0.978	2.66×10^{-2}	46.75	**This work**

Reference

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