

Supplementary Information

1. Experimental

1.1 Chemicals

All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. Furfural (Sinopharm Chemical Reagent Co., Ltd, 99.9%), furfuryl alcohol (Aladdin Reagent, 98%), 1, 2-pentanediol (Aladdin Reagent, 98%), 1, 5-pentanediol (Aladdin Reagent, 98%), methyl furan (Aladdin Reagent, 98%), 2-propanol (Kermel, 99%), tetrahydrofurfuryl alcohol (Aladdin Reagent, >98%), 1-pentanol (Aladdin Reagent, 98%), Cu powder (Macklin, 99.9%, 60-100 nm), CuAl alloy (Jiangsu Raney Metal Technology Co., LTD), Ammonium metatungstate (Aladdin Reagent, 99.5%), Tin (II) acetate (Energy chemical, 97%), AlOOH (Sinopharm Chemical Reagent Co., Ltd, 99.9%), Octane (Macklin, >99.9 (GC)).

1.2 Catalyst preparation

Metal oxides (MnO_2 , WO_3 , MoO_3 , SnO_2 , Al_2O_3) modified Cu powder catalysts were prepared through a simple impregnation method. Specifically, a certain amount of metal precursor was dissolved in 50 g deionized water upon adding Cu powder. The mixture was stirred for about 3 h under N_2 atmosphere at 298 K. Excess water was removed with a rotary evaporator under reduced pressure at 333 K. The obtained solid was dried at 393 K overnight under reduced pressure, calcined at 723 K for 4 h under N_2 . The loading of metal oxide was about 1.0 wt%.

MnO_2 modified Cu catalyst (MnO_2/Cu) was prepared by two steps: (1) loading MnO_2 on CuAl alloy through simple impregnation and calcination processes; (2) leaching Al in MnO_2/CuAl (about 60 μm , Cu:Al = 1:2) with 30 wt% NaOH solution at 50 °C. About 30 ml NaOH solution was used for leaching Al from 4 g MnO_2/CuAl in 70 min. The leaching rate of Al was carefully controlled through controlling the dropping rate of NaOH solution. Specifically, 0.3 ml/min NaOH solution was dropped into the solution containing MnO_2/CuAl in the initial 30 min. After the leaching process, the catalyst was washed several times with deionized water to remove residual soluble Al compounds in the liquid until the pH value reaches 7.0. Finally, the prepared sample MnO_2/Cu was stored in isopropanol (IPA).

1.3 Catalytic reaction and catalyst recycling

The hydrogenation of furfural and other reactants was carried out in a 10 mL Teflon-lined stainless-steel autoclave. Reactants, furfural and furfuryl alcohol were first purified through distillation under reduced pressure at about 100 °C. The purified reactants are used for the subsequent quantification and transformation. Specifically, 85 mg catalyst, 2 ml isopropanol (IPA) and 0.5 g reactant were added to the autoclave. Then the autoclave was sealed and filled with 4.5 MPa H₂ upon purging with H₂ eight times. During the reaction, the temperature was maintained at 170 °C and the stirring rate was 500 rpm. After the reaction, a specific amount of diluent IPA (about 20 ml) and internal standard octane (about 100 mg) was added for quantification. Reusability test of catalyst was conducted under the same procedures above. After each reaction run, the catalyst was recovered, washed with isopropanol and centrifuged for five times before the next reaction. The liquid product was analyzed by off-line gas chromatography (Agilent, 7890A) using a FID detector and a HP-5 capillary column (0.32 mm×30 m×0.25 μm). The conversion of reactants and selectivity of the liquid product were calculated by the following equations (1) and (2).

$$(1) \text{ Conversion \%} = \frac{\text{moles of reactant converted} * 100\%}{\text{initial moles of reactant}}$$

$$(2) \text{ Yield \%} = \frac{\text{carbon moles of one specific product} * 100\%}{\text{initial moles of reactant}}$$

1.4 Characterization Details

The surface composition and the binding energy (B.E.) of the catalysts were determined by X-ray photoelectron spectra (XPS) on an ESCALAB250 X-ray photoelectron spectrometer with carbon as the internal standard (C 1s = 284.6 eV). The surface atomic ratio of Cu⁺ to Cu on the catalyst MnO₂/Cu was calculated by using the equation (3).

$$(3) \frac{n_i}{n_j} = \frac{I_i}{I_j} \times \frac{\sigma_j}{\sigma_i} \times \frac{E_{k_j}^{0.6}}{E_{k_i}^{0.6}} ; n: \text{Number of atoms}; I: \text{Intensity}; E_k: \text{Kinetic energy}; \sigma: \text{cross section.}$$

Powder XRD patterns of the samples were acquired on a X'Pert PRO (PANalytical) diffractometer equipped with a Cu K α radiation source ($\lambda = 0.15432$ nm) operated at 40 kV and 40 mA, in the 2θ range from 5° to 80°.

High-resolution transmission electron micrographs (HRTEM) of samples were obtained on a JEM-2100 microscope operated at 200 kV. The scanning electron micrograph (SEM) was obtained on a field emission scanning electron microscope (FESEM, JEOL, JSM-7800F, 15 kV). Sub-ångström resolution HAADF-STEM images and energy-dispersive X-ray spectroscopy (EDX) elemental mapping were obtained on a JEOLJEM-ARM200F STEM/TEM, also equipped with a CEOS probe corrector, at a resolution of 0.08 nm. Before microscopy examination, the samples were suspended in ethanol and dispersed onto a copper grid or carbon film.

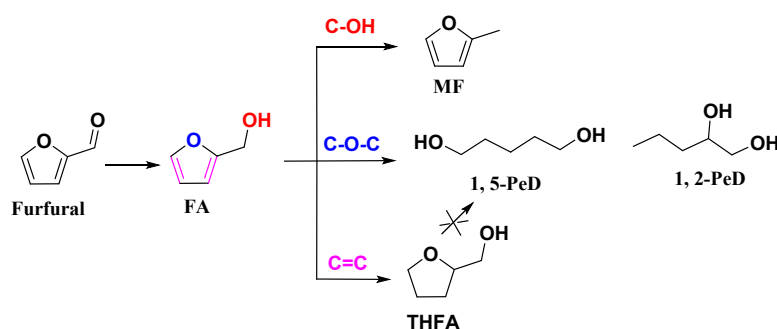
An infrared diffuse reflectance accessory was used for the infrared (IR) measurements. The accessory was purchased from Pike Technologies. The middle-IR instrument model is Thermo Scientific Nicolet iS50 with mercury cadmium telluride (MCT) detector. The resolution is 4 cm⁻¹ for the IR experiment, which was measured using 32 scans. The samples were pretreated at 40 °C for 2 h under Ar atmosphere (30 cm³ min⁻¹). About 30 mg of furfuryl alcohol solution (10 wt%) in CH₃CN was dropped on the sample. The infrared spectra of furfuryl alcohol adsorbed on catalysts were collected at 40 °C upon removing CH₃CN and weakly adsorbed furfuryl alcohol at 40 °C for about 30 min under Ar atmosphere (30 cm³ min⁻¹).

2. Supporting results

Table S1. Catalytic performance of furfural and FA hydrodeoxygenation over non-noble metal catalysts in literature and this work

Catalyst	Conditions	Conv. %	Yield %					
			1, 5-PeD	1, 2-PeD	MF	THFA	Others	
10Cu-LaCoO ₃ ¹	1.1 g cat. 1.5 g FA	140 °C, 6MPa, 2 h	94.6	36.9	13.9	-	33.7	15.5
10Cu/Al ₂ O ₃ ²	2g cat. 0.4 g FA	140 °C, 6 MPa, 8 h	60.4	13.7	29.4	6.0	2.2	8.9
Cu _{1.8} Mg _{1.2} Al ³	40 mg cat. 0.2 g Furfural	140 °C, 4 MPa, 3h	100	5.3	24.4	0	1.6	50.8
CoAl-spinel nanoparticles ⁴	40 mg cat. 0.4g Furfural	150°C, 3 MPa H ₂ 8h	100	29.8	0	0	0	69.3
		170°C, 2 MPa H ₂ 8h	100	14.4	8.7	0	0	33.5
Raney Cu ⁵	85 mg cat. 0.5 g Furfural	170 °C, 4.5 MPa, 6h	100	0	34.1	34.6	8.6	22.6
MnO ₂ /Cu [#]	85 mg cat. 0.5 g FA	170 °C, 4.5 MPa, 6h	81.1	10.6	39.7	11.6	7.7	11.5
		170 °C, 6 MPa, 6h	100	11.1	42.9	7.9	6.7	6.8

[#] MnO₂/Cu catalyst prepared in this work



Scheme 1 Reaction pathways of furfural hydrogenation over MnO₂/Cu catalyst

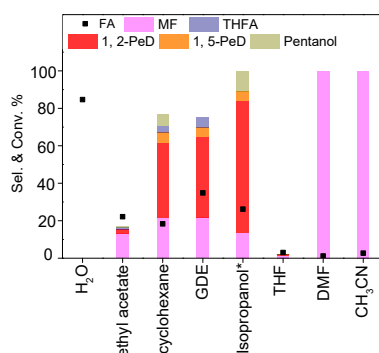


Figure S1 Catalytic performance of the hydrogenation of furfural alcohol in several solvents. GDE is the abbreviation of glycol dimethyl ether. DMF is the abbreviation of N, N-dimethyl formamide. THF is the abbreviation of tetrahydrofuran. Reaction conditions: Catalyst 160 mg, FA 0.5 g, solvent 2 ml, 160 °C, 5.5 h, 4 MPa H₂, *170 °C, Catalyst 85 mg, 3 h, 4.5 MPa H₂.

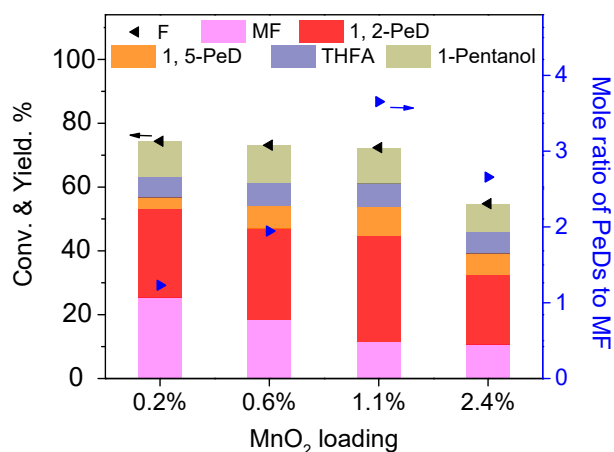


Figure S2 Catalytic performance of FA hydrogenation over Cu based catalysts with different MnO₂ loading. Catalyst 85 mg, FA 0.5 g, IPA 2 ml, 4.5 MPa H₂, 170 °C, 3 h.

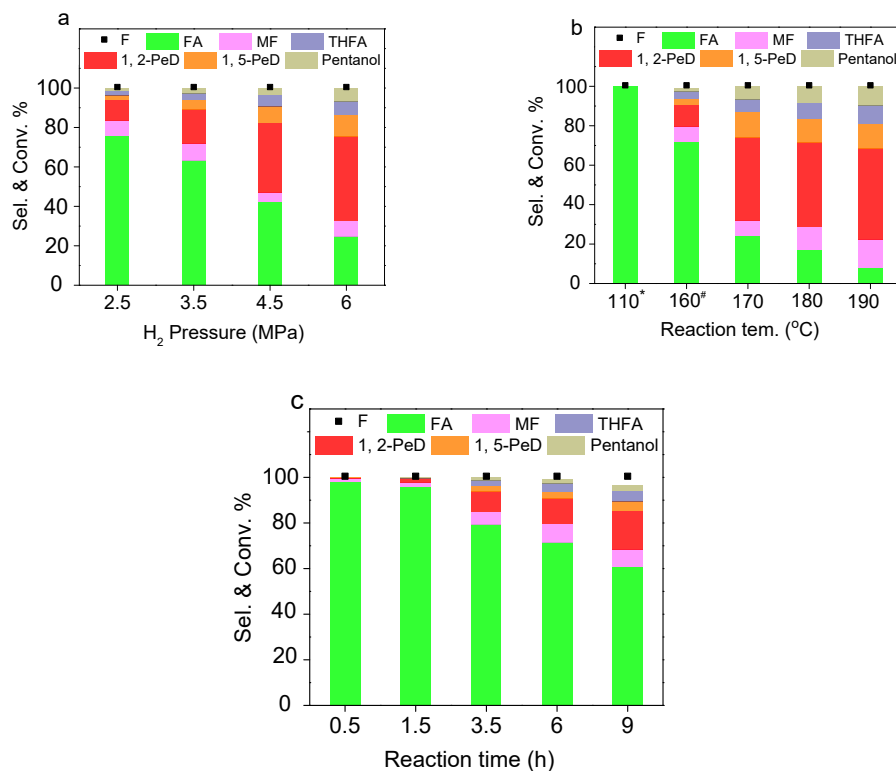


Figure S3 Catalytic performance of furfural (F) hydrogenation over MnO₂/Cu catalyst (a) under different H₂ pressure (reaction condition: Catalyst 85 mg, F 0.5 g, IPA 2 ml, 170 °C, 6 h); (b) at different reaction temperature (reaction condition: Catalyst 85 mg, F 0.5 g, IPA 2 ml, 6 MPa, 6 h. *4.5 MPa, 2 h, #4 MPa); and (c) at different reaction time (reaction condition: Catalyst 73 mg, F 0.5 g, IPA 2 ml, 4 MPa, 160 °C.)

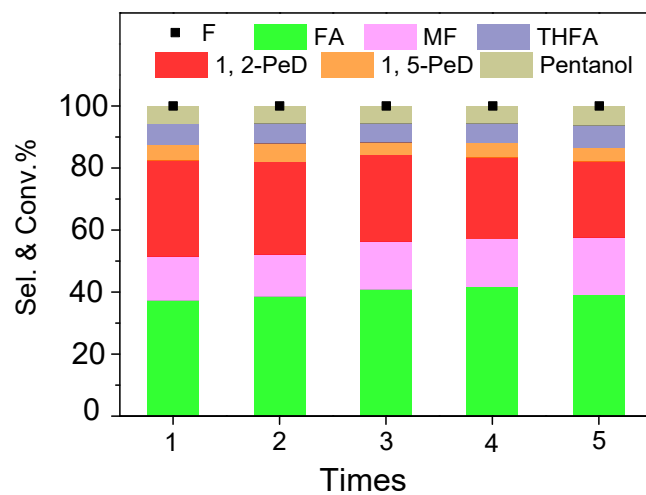


Figure S4 The conversion and product distribution in furfural hydrogenation over the MnO_2/Cu catalyst in five successive runs. Reaction conditions: MnO_2/Cu catalyst 85 mg, 0.5 g furfural (F), isopropanol 1.6 g, 170 °C, 4.5 MPa H_2 , 6 h

Table S2 Hydrogenation of furan derived compounds over Cu based catalysts

Entry	Catal.	Feed	Conv. %	Sel. %					Mole Ratio (PeDs : MF)
				FA	MF	1, 2-PeD	1, 5-PeD	Others	
1	MnO ₂ /Cu powder	FA	25.7	--	13.5	70.4	4.9	11.1	5.60
2	WO ₃ /Cu powder	FA	100	--	62.4	0	0	--	0
3	MoO ₃ /Cu powder	FA	36.1	--	22.8	10.4	0	0	0.46
4	SnO ₂ /Cu	Furfural	99.3	78.1	16	4.3	0	0	0.27
5	Al ₂ O ₃ /Cu powder	FA	14.3	--	10.1	4.2	0	0	0.41

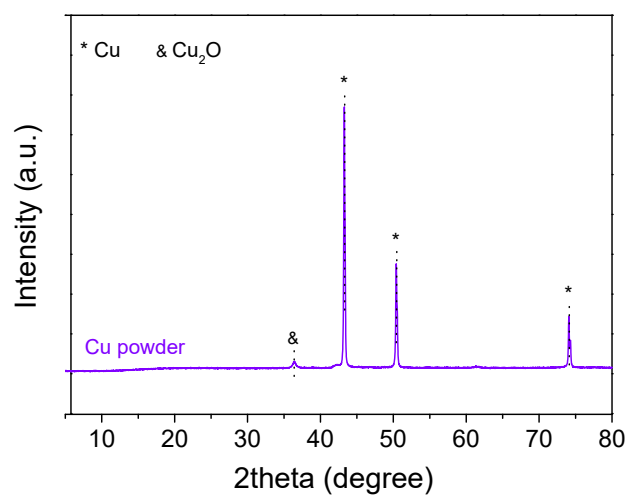


Figure S5 XRD patterns of Cu powder

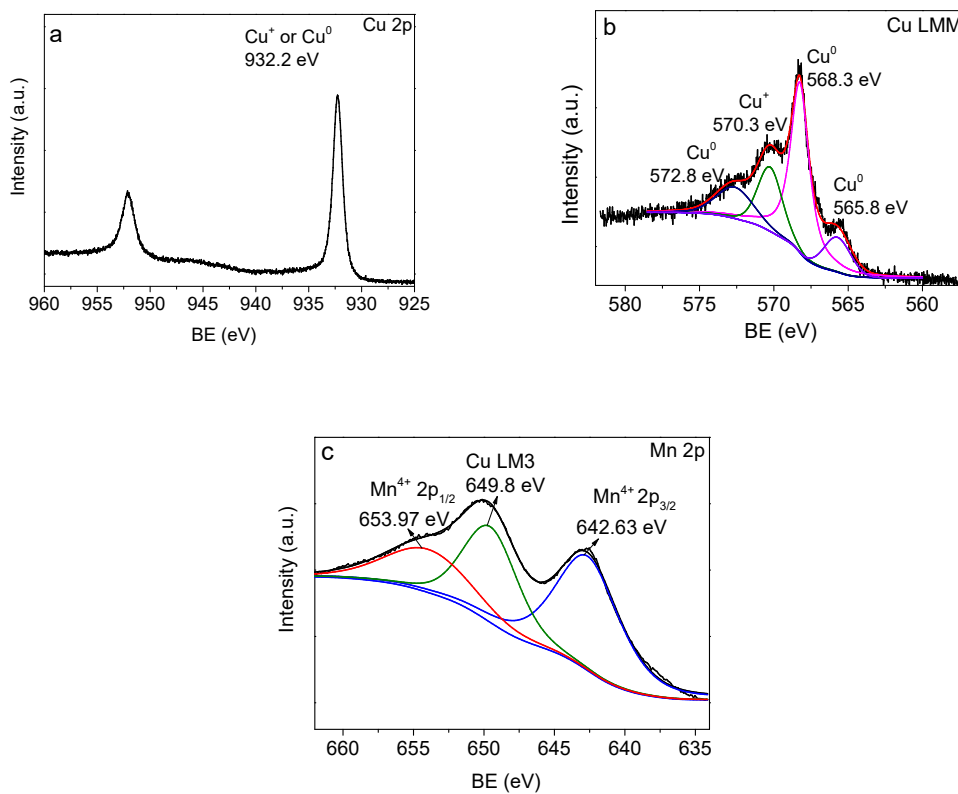


Figure S6. X-ray photoelectron spectra of MnO₂/Cu catalyst surface. (a) Cu2p spectrum; (b) Peak fitting of the Cu LMM spectrum; (c) Mn2p spectrum. BE is the abbreviation for binding energy.

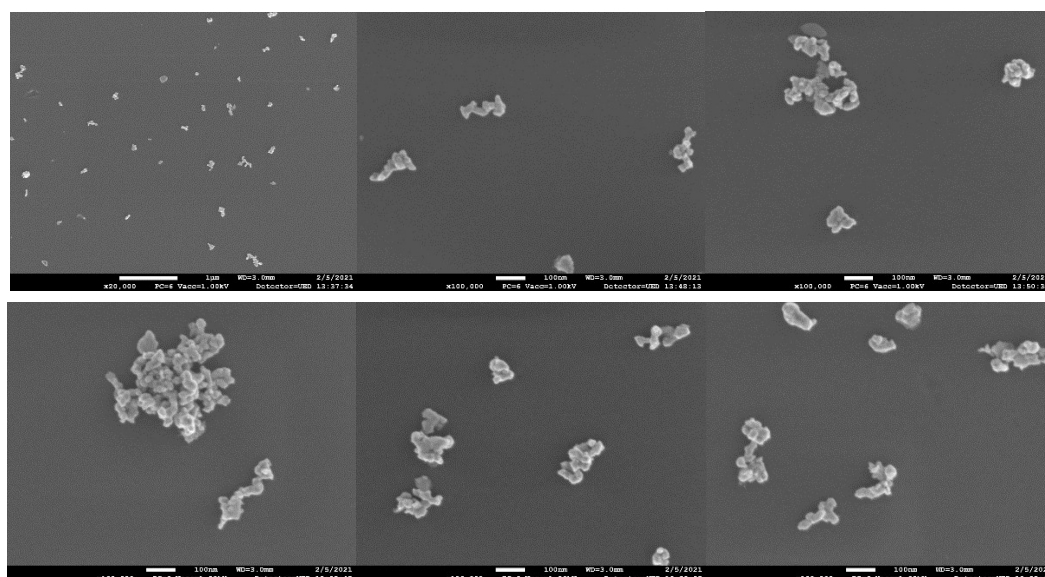


Figure S7 SEM images of MnO₂/Cu catalyst

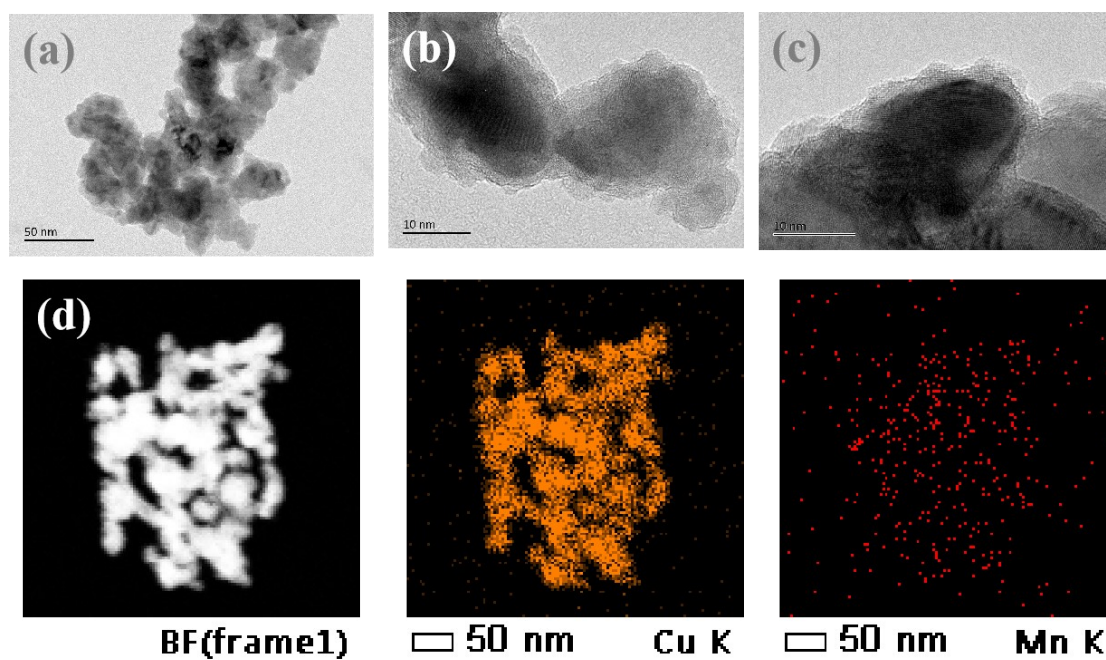


Figure S8 HAADF-STEM images and EDX mapping images of MnO₂/Cu catalyst

Reference

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