

Supporting Information

MFI zeolite with confined adjustable synergistic Cu sites for the hydrogenation of levulinic acid

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I. General

1. Materials

Tetrapropylammonium hydroxide (TPAOH, 40 wt% aqueous solution) was purchased from Shanghai Bide Medical Technology Co., Ltd. Tetraethoxysilane (TEOS, AR), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (AR), SiO_2 , NaF (AR), acetone, n-hexanol, levulinic acid (LA, AR), γ -valerolactone (GVL, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 81/1$) was purchased from the Catalyst Plant of Nankai University. Deionized water was purchased from Hangzhou Wahaha Group Co. Ltd. All the reagents were used without any pretreatment.

2. Characterization

The element contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an Optima 7000DV (PerkinElmer) spectrometer. In a typical test, 50 mg of zeolite sample was dissolved in the mixture of 2 mL of HF, 2 mL of H_2SO_4 and 4 mL of HNO_3 , and then diluted to 250 mL with deionized water.

JEOL Model JEM-2010 LaB6 TEM system were used to collect transmission electron microscopy (TEM) images. The samples for TEM analysis were prepared by dipping the carbon-coated copper grids into an ethanol solution of the sample and allowed to dry under ambient conditions.

Powder X-ray diffraction (XRD) analysis for catalysts was carried out on TTR-III X-ray diffractometer (Japan). The monochromatized radiation ($\lambda = 1.54056 \text{ \AA}$) used Cu-K α . The 2θ ranges were 5° - 65° .

Tandem temperature-programmed desorption-oxidation-reduction (H_2 -TPD- N_2O -titration- H_2 -TPR) was performed on an automatic chemical adsorption instrument (VDSorb 91i, Quzhou Vodo Instrument Co., Ltd). The catalyst was first reduced by 30 sccm 5% H_2 /Ar for 2 h at 400°C . After cooling down to 40°C and purged with Ar for 1 h, the TPD was processed under 30 sccm Ar flow with ramping rate of $10^\circ\text{C}/\text{min}$. Then cooling down to 100°C , N_2O titration was used to oxidize the exposed Cu in catalyst surface. Then the catalyst was again temperature-programmed reduced by 30 sccm 5% H_2 /Ar.

In-situ X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ScientificTM ESCALAB 250Xi spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) operating at 150 W. Samples were first reduced in H_2 atmosphere at 400°C for 2 h and cooled down to be analyzed under vacuum ($P < 10^{-8}$ mbar) with a pass energy of 100 eV (survey scans) or 50eV (high-resolution scans). The XPS test was proceeded by Qian Wang from SCI-GO (www.sci-go.com). All peaks were calibrated with C1s peak binding energy at 284.8 eV for adventitious carbon.

In-situ X-ray absorption spectroscopy (XAS) measurements were carried out at the XAS Beamline at the Australian Synchrotron, using a set of liquid nitrogen cooled Si(111) monochromator crystals. The electron beam energy is 3.0 GeV. With the

associated beamline optics (Si-coated collimating mirror and Rh-coated focusing mirror), the harmonic content of the incident X-ray beam was negligible. The catalysts were pretreated inside the beamline under H₂ at 400 °C for 2 h and then cooled down to room temperature. The beam size was about 1x1mm. Note that a single XAS scan took ~1 h. XANES was analyzed by Athena software. The Cu distribution in Figure 3E was calculated by linear combination fitting of XANES using normalized $\mu(E)$ spectra (shown in Figure 3B) with Athena software. The detailed principle and method could be checked on the official website of Athena software (<http://bruceravel.github.io/demeter/documents/Athena/analysis/lcf.html>).

The N₂ adsorption-desorption isotherms of samples were measured at 77 K (Tristar II 3020M, Micromeritics, America). Sample pre-activation procedure: degas at 120 °C for 2 h and then activate at 300 °C for 2 h. The sample weight after activation was 0.1 g. According to the N₂ adsorption/desorption isotherm, the surface area and pore size distribution of the catalyst were calculated by BET and BJH methods, respectively. The BET surface area were calculated using desorption data with P/P₀ ranges from 0.05 to 0.25. As zeolite micropore was too narrow for multilayer adsorption of N₂, the BET equation was modified by Gerald Pickett's method (J. Am. Chem. Soc., 1945, 67, 1958-1962). The adsorption parameter was set as 1.5. All the C values were positive. The t-plot analysis was calculated using adsorption data with P/P₀ ranges from 0.05-0.15, 0.15-0.65, and 0.65-0.70.

FT-IR spectra were measured with a Nicolet 8700 FT-IR spectrometer at room

temperature in the 4000-550 cm^{-1} region. Before the adsorbed-FT-IR test, the catalyst was immersed in 12.5 wt% LA or GVL solution and stirred at room temperature for 12 h at a stirring speed of 300 r/min. Then, the catalyst was washed by centrifugation to remove LA or GVL physically adsorbed by the catalyst. Finally, the catalyst was dried at room temperature followed by FT-IR detection.

II. Experimental

1. Catalyst Preparation

1.1 Synthesis of ZKD-5 catalysts

The ZKD-5 was synthesized by hydrothermal method with a rapidly-mixing-at-high-temperature procedure.

In a typical procedure, TEOS (6 g) and TPAOH (3.59 g) were mixed with deionized water (5.00 g) in a 50 mL centrifuge tube while being slowly magnetically stirred (350 rpm) at 60 °C in an oil bath for 12 h. Then $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution (Si/Cu molar ratio were 11, 23, 47, 95 and 191) and NaF solution (Cu/Na=2) were added into the hot aged silica gel rapidly and then well mixed by drastic mechanical vibration for seconds. The mixture was heated in a 50 mL Teflon-lined autoclave (HTG-50-SS2, Anhui CHEM^N Instruments Co. Ltd.) and at 170 °C for 24 h. The zeolite was collected after filtration, washing with water, and drying at 105 °C. The zeolite thus obtained was calcined at 550 °C in air for 2 h with a heating ramp of 3 °C/min. All catalysts mentioned above

were reduced at 400 °C for 2 h with a heating ramp of 3 °C/min under an H₂ flow of 100 mL/min before use.

To make H-type zeolite for comparison (Table S5), the above reduced zeolite was ion-exchanged by following method: 1 g of ZKD-5 was mixed with 20 mL of 1 M NH₄NO₃ solution at 70 °C for 1 h. Then the mixture was centrifuged to remove the liquid supernatant and washed by pure water for three times. The above-described ion-exchange was repeated for three times to ensure most of Na⁺ were changed to NH₄⁺. Then the ammonium type zeolite was calcined again to make an H-type zeolite.

1.2 Synthesis of Cu-based supported-catalysts

The supported-catalysts were prepared by wet impregnation method. The supports (2 g) and corresponding amount of Cu(NO₃)₂•3H₂O (Si/Cu = 47/1) were mixed with acetone (200 g) while being magnetically stirred at 45 °C for 24 h. After elimination of the water by rotary evaporation and drying at 80 °C, the solid sample was calcined at 550 °C in air for 2 h with a heating ramp of 3 °C/min. According to the different supports selected, the samples were named Cu/S-1, Cu/SiO₂ and Cu/HZSM-5 respectively.

All catalysts mentioned above were reduced at 400 °C for 2 h with a heating ramp of 3 °C/min under an H₂ flow of 100 mL/min before use.

2. Catalytic tests and product analysis

The hydrogenation of LA was performed in a 25 mL NSC-type reactor purchased from Anhui CHEM^N Instruments Co. Ltd. Specific steps: 1 mmol LA and 100 mg catalyst were dispersed in 8 g distilled H₂O solution. Before the reaction, the reactor was purged three times with hydrogen and then charged with hydrogen to corresponding pressure. The reaction was heated by a thermocouple and stirred by magnetic force at a speed of 800 r/min. After the reaction was completed, the reactor was put into cold water and cooled to room temperature followed by releasing the gas. In the manuscript, the influence of different reaction conditions (reaction temperature, hydrogen pressure and time) on the catalytic activity was investigated.

The product was analyzed by the Shimadzu Nexis 2030 gas chromatography (GC) instrument equipped with an RTX-65 column (30 m×0.32 mm×0.25 μm) and a flame ionization detector. The gas flow rate of GC was set as follows: 40 mL/min N₂, 32 mL/min H₂ and 200 mL/min air. The temperature of injection port and flame ionization detector was 250 °C and 270 °C, respectively. The initial temperature of the chromatographic column was 50 °C and rose to 190 °C at a rate of 10 °C/min. Next, it went up to 250 °C and keep for 3 min with a rate of 20 °C/min. The amount of reactants and products is determined by the internal standard method, where the internal standard was n-hexanol. Levulinic acid conversion and product yields were calculated using the following equations.

$$\text{Conversion (\%)} = \frac{\text{Moles of feedstock consumed}}{\text{Moles of feedstock input}} \times 100\%$$

$$\text{Product yield (\%)} = \frac{\text{Moles of product}}{\text{Moles of feedstock input}} \times 100\%$$

III. Results and discussion

Table S1. Performance of various Cu-based catalysts for the hydrogenation of levulinic acid in previous literatures.

Entry	Catalyst	Cu Content	T (°C)	P ^c (MPa)	Solv.	Conv. (%)	Sele. (%)	Ref.
1	CuPS	26 ^a	130	1.2	THF	95.7	89	[1]
2	Cu powder	100 ^a	250	-	H ₂ O	93.9	98	[2]
3	Ni-Cu/Al ₂ O ₃	12 ^a	250	4 (N ₂)	2-PrOH	100	82.3	[3]
				4	1-BuOH	100	68.3	
4	Cu-ZrO ₂	50 ^b	200	3.4	H ₂ O	100	100	[4]
	Cu-Al ₂ O ₃	50 ^b				100	100	
5	Cu-WO ₃ /ZrO ₂ -CP	30 ^a	200	5	ethanol	100	94	[5]
					H ₂ O	100	99	
6	Cu-ZrO ₂	51.8 ^b	200	3.5	H ₂ O	~100	~100	[6]
7	CuAl	75 ^b	110	3	ethanol	100	95.3	[7]
	CuMgAl	15 ^b				100	86.5	
8	Cu-Fe	50 ^b	200	7	H ₂ O	98.7	91.6	[8]
9	CuCr	66.7 ^b	250	4	-	85.6 ^d	98.6	[9]
10	Ni _{4.59} Cu ₁ Mg _{1.58}	10.2 ^b	142	2	methanol	100	98.1	[10]
	Al _{1.96} Fe _{0.70}							
11	Cu/Ni/Mg/Al	23.1 ^b	140	3	dioxane	100	100	[11]
12	Cu _{0.8} Ag _{0.8} /Al ₂ O ₃	7 ^b	180	1.4	THF	100	>99	[12]

a. The mass fraction of Cu in catalyst; b. The molar fraction of Cu in catalyst; c. All the pressures were initial hydrogen pressure unless otherwise noted; d. The feedstock was ethyl levulinate.

Table S2. Physical and chemical properties of the samples.

Samples	S_{BET} (m^2/g) ^a	S_{ext} (m^2/g) ^b	S_{micro} (m^2/g) ^b	V_{total} (cm^3/g) ^c	Pore Size (nm) ^d
ZKD-5 (11)	313	215	98	0.08	4.37
ZKD-5 (23)	327	146	181	0.18	4.65
ZKD-5 (47)	331	100	232	0.32	8.82
ZKD-5 (95)	372	108	264	0.33	8.65
ZKD-5 (191)	376	101	275	0.30	7.54
Cu/S-1	322	88	233	0.37	9.99

a. S_{BET} were calculated using the Pickett's modified BET equation with adsorption layer of 1.5; b. S_{ext} , S_{micro} , and V_{micro} were calculated using the t-plot method; c. V_{total} was calculated under pressure $P/P_0 = 0.95$. d. Pore Size were calculated by BJH method.

Table S3. Performance of various Cu-based catalysts for the hydrogenation of LA

Entry	Catalyst	T (°C)	P (MPa)	Time (h)	Conv. (%)	Yield (%)
1	ZKD-5 (11)	130	4	5	99	99
2	ZKD-5 (11)	140	4	5	100	100
3	ZKD-5 (23)	130	4	5	82	82
4	ZKD-5 (23)	130	4	7	100	100
5	ZKD-5 (23)	140	4	5	100	100
6	ZKD-5 (47)	130	4	5	59	59
7	ZKD-5 (47)	130	4	12	100	100
8	ZKD-5 (47)	140	4	5	81	81
9	ZKD-5 (47)	150	4	5	100	100
10	ZKD-5 (47)	130	3	5	29	29
11	ZKD-5 (47)	130	5	5	61	61
12	ZKD-5 (95)	130	4	5	41	41
13	ZKD-5 (95)	130	4	18	100	100
14	ZKD-5 (95)	140	4	5	62	62
15	ZKD-5 (95)	150	4	5	80	80
16	ZKD-5 (95)	160	4	5	95	95
17	ZKD-5 (95)	170	4	5	100	100

Table.S4 The content of elements in catalyst and reaction solution.

Samples	Cu (wt %) ^a	Na (wt %) ^a	F (wt %) ^b
ZKD-5(47)-fresh	2.17	1.07	-
ZKD-5(47)-used	2.15	1.04	-
reaction solution	0.005	0.05	n.d.

a. The contents of Cu and Na were calculated based on ICP-OES analysis. The metal

total content in solution

content in reaction solution was calculated by: $\frac{\text{total content in solution}}{\text{total content in fresh catalyst}}$.

b. The content of F was tested by ion chromatography. Because the catalyst was dissolved in mixed acid containing HF, the F content of catalyst could not be detected. The F content in reaction solution was detected by ion chromatography and was not detected, indicating no F leaching during the reaction.

Table S5. Performance of ZDK-5(47) catalysts for the hydrogenation of LA

Entry	Catalyst ^a	Substrate concentration (mmol)	T (°C)	P (MPa)	Time (h)	Conv. (%)	Yield (%)
1	ZKD-5 (47)	1	150	4	5	100	100
2	ZKD-5 (47)	2	150	4	5	100	100
3	ZKD-5 (47)	5	150	4	5	100	100
4	ZKD-5 (47) ^b	Solvent free	150	4	12	100	95
5	ZKD-5 (47) ^c	1	150	4	5	100	100
6	H-ZKD-5 (47) ^d	1	150	4	5	100	100

a. All the reactions kept same reactant/copper ratio. b. 50 g pure LA and 5 g ZKD-5 (47) was used without any solvent. c. the catalyst was synthesized using NaOH instead of NaF. d. the catalyst was ion-exchanged by NH₄⁺ and then calcined to make a H-form zeolite.

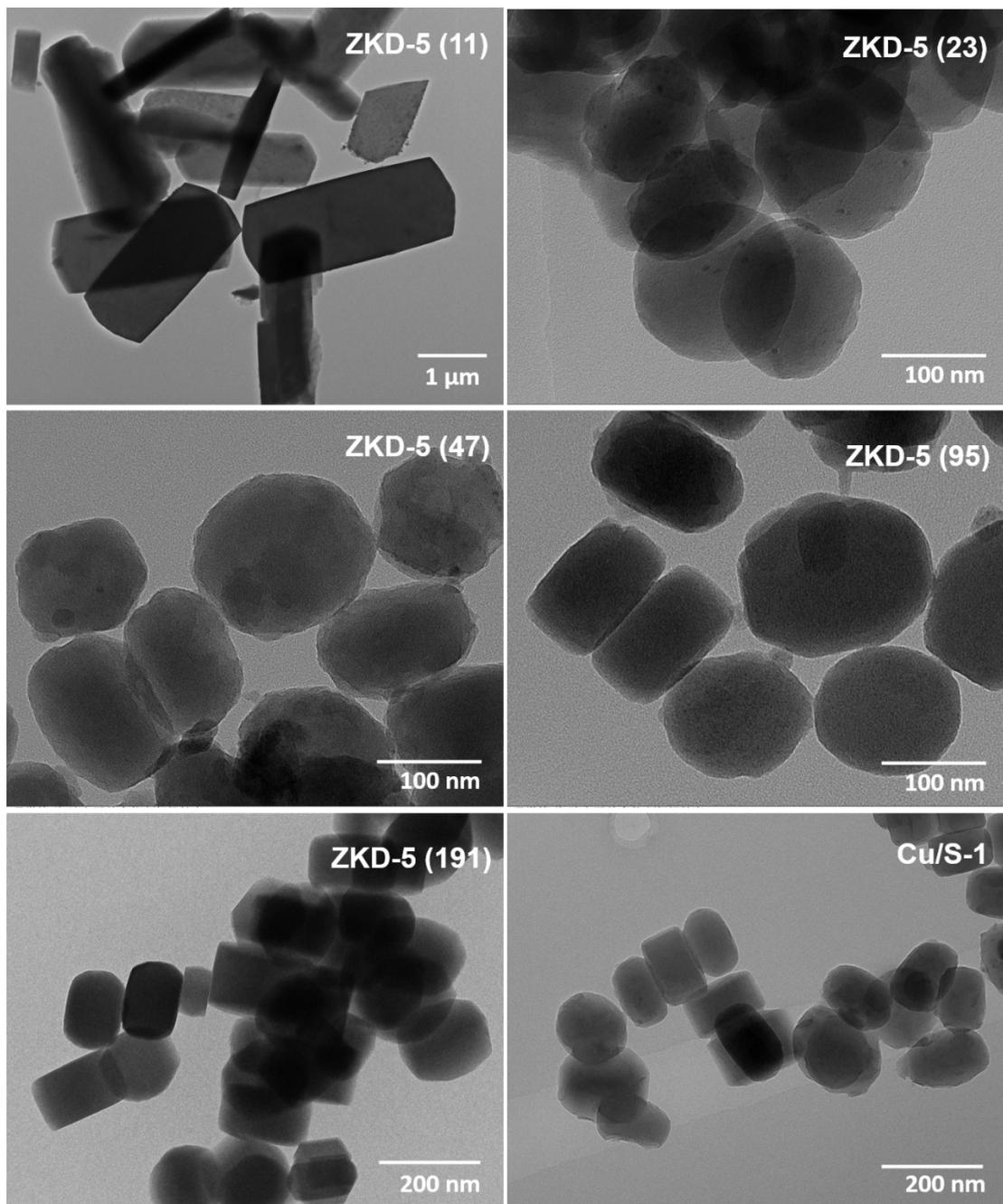


Figure S1. TEM images of ZKD-5 (11, 23, 47, 95, 191) and Cu/S-1.

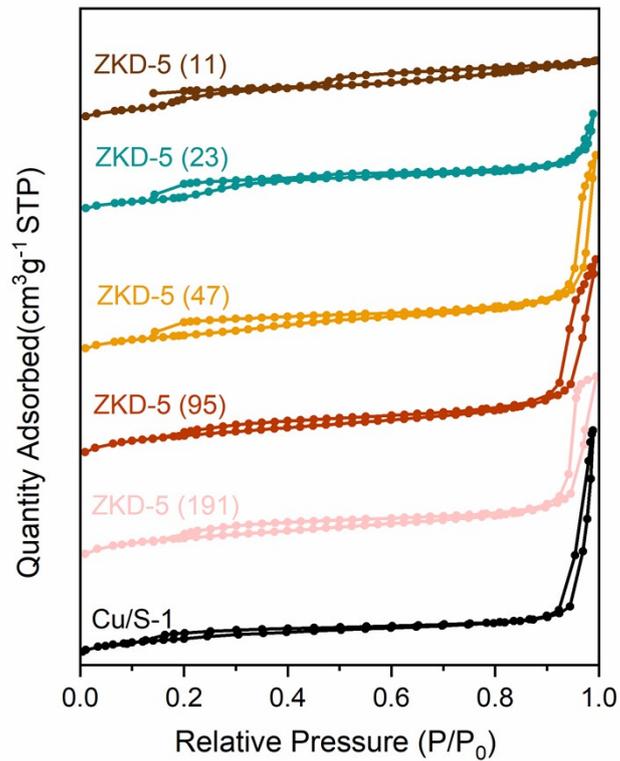


Figure S2. N₂ adsorption/desorption isotherms of as-prepared samples.

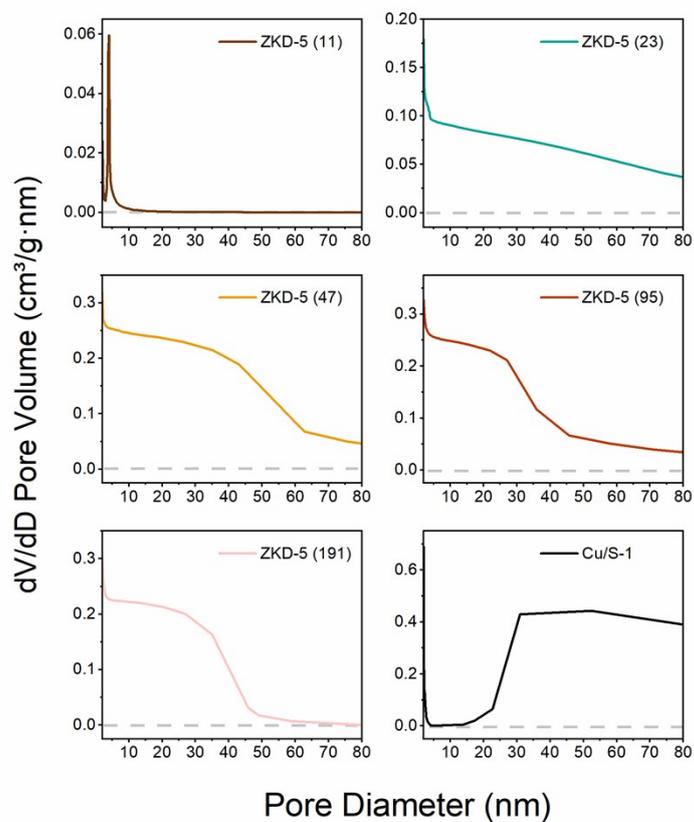


Figure S3. BJH pore size distribution of as-prepared samples.

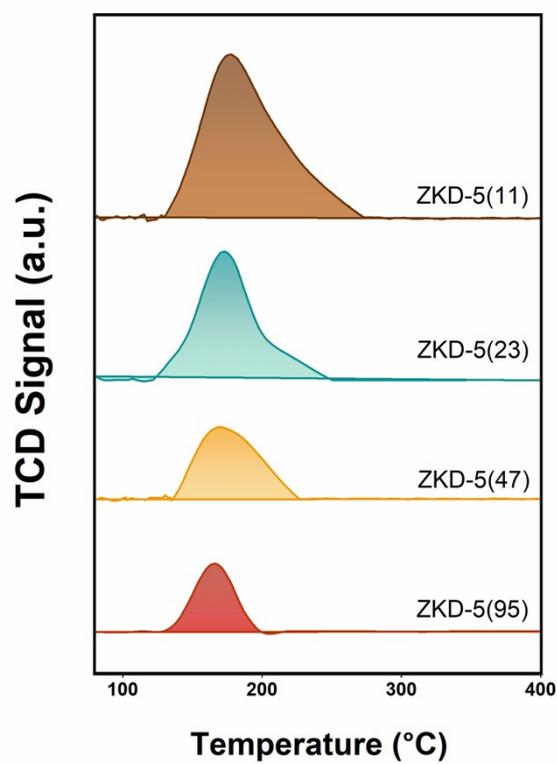


Figure S4. H₂-TPR profiles in H₂-TPD-N₂O-titration-H₂-TPR test.

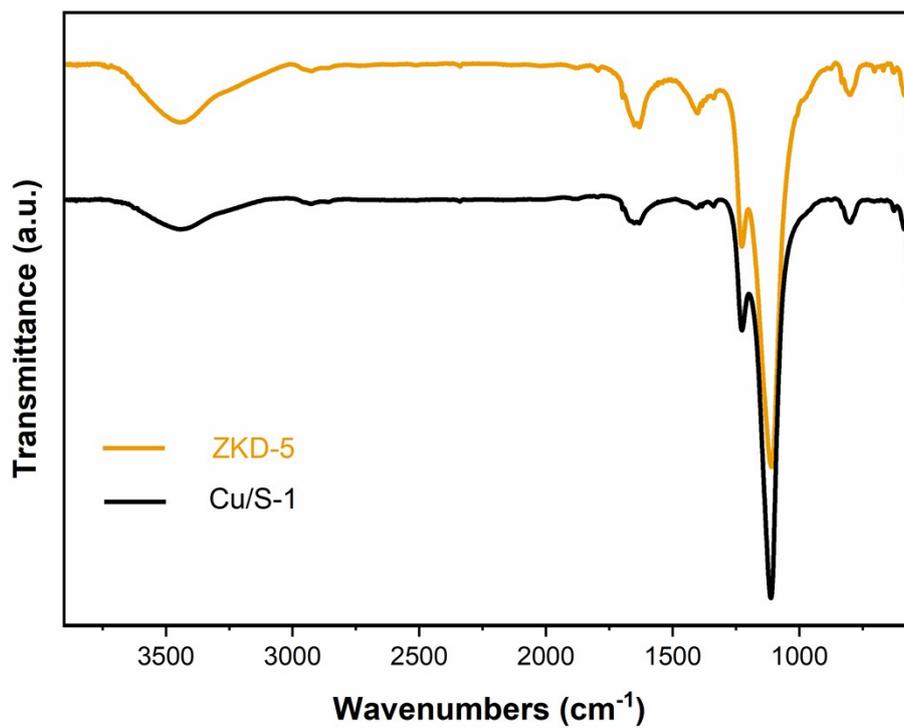


Figure S5. FT-IR spectra of ZKD-5 and Cu/S-1.

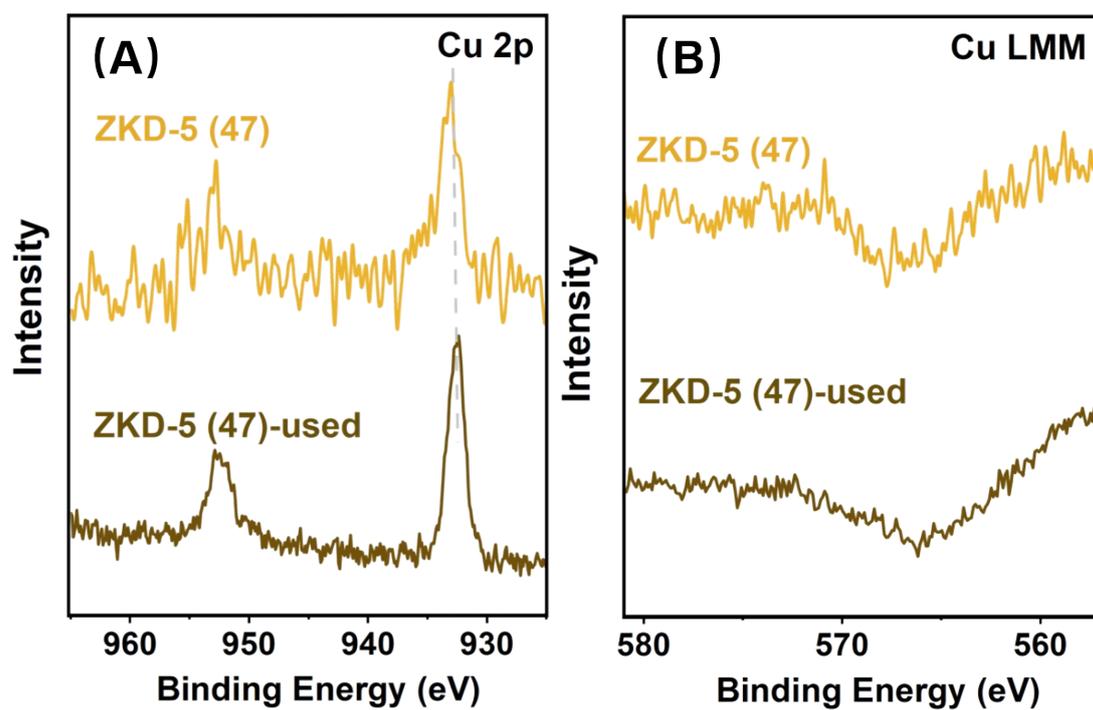


Figure S6. XPS spectra of fresh and used ZKD-5(47) catalyst. (A) *in-situ* XPS spectra of Cu 2p; (B) LMM Auger spectra of Cu.

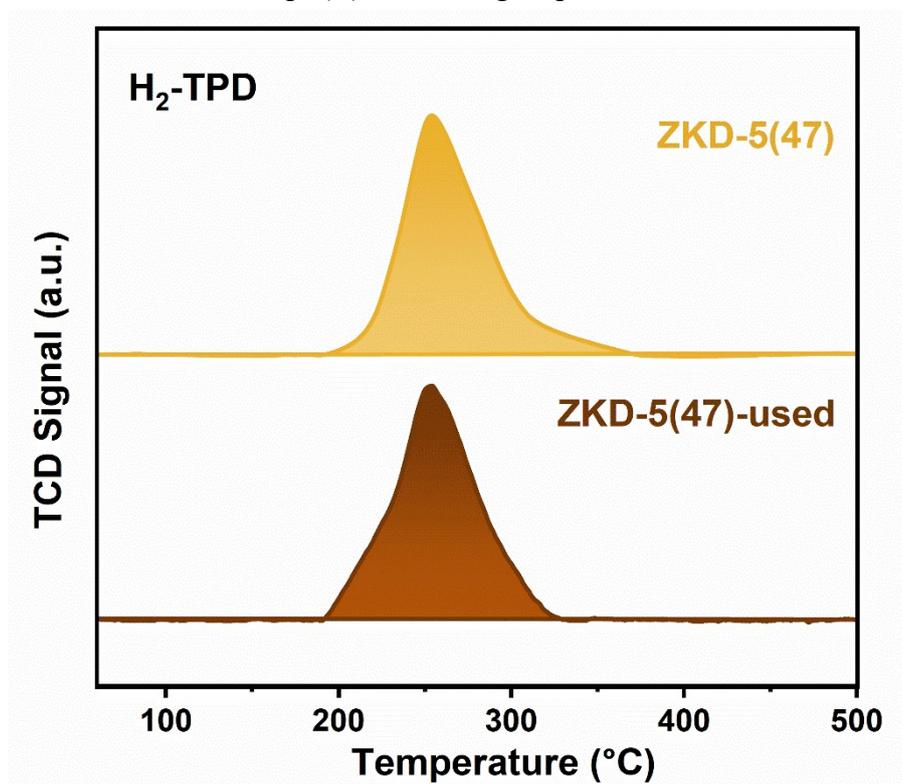


Figure S7. H₂-TPD profiles of fresh and used ZKD-5(47) catalyst.

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