Supporting Information

For

Synthesis of bio-derived 1,4-butanediol from succinic acid esterification and hydrogenation over CuFeAl catalysts

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A. Supporting experimental sections

1. Chemicals

All chemicals and reagents were obtained from commercial suppliers and used without further purification: Methanol (CH_4O, Sinopharm Chemical Reagent Co., Ltd.), succinic acid ($C_4H_6O_4$, Shanghai Aladdin Biochemical Technology Co., Ltd.), dimethyl succinate ($C_6H_{10}O_4$, Shanghai Aladdin Biochemical Technology Co., Ltd.), 1,4-dioxane ($C_4H_8O_2$, Shanghai RichJoint Chemical Reagents Co., Ltd.), gamma butyrolactone ($C_4H_6O_2$, Shanghai Aladdin Biochemical Technology Co., Ltd.), 1,4-butanediol ($C_4H_{10}O_2$, Shanghai Aladdin Biochemical Technology Co., Ltd.), tetrahydrofuran (C_4H_8O, Shanghai Aladdin Biochemical Technology Co., Ltd.), copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$, Sinopharm Chemical Reagent Co., Ltd.), iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, Sinopharm Chemical Reagent Co., Ltd.), aluminum nitrate ($Al(NO_3)_2{\cdot}9H_2O$, Sinopharm Chemical Reagent Co., Ltd.), magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$, Sinopharm Chemical Reagent Co., Ltd.), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, Sinopharm Chemical Reagent Co., Ltd.), nickel nitrate ($Ni(NO3)_2{\cdot}6H_2O$, Sinopharm Chemical Reagent Co., Ltd.), strontium nitrate ($Sr(NO3)_2$, Sinopharm Chemical Reagent Co., Ltd.), barium nitrate ($Ba(NO_3)_2$, Sinopharm Chemical Reagent Co., Ltd.), sodium hydroxide ($Na(OH)_2$, Sinopharm Chemical Reagent Co., Ltd.), sodium carbonate (Na_2CO_3, Sinopharm Chemical Reagent Co., Ltd.), phosphotungstic acid ($H_3O_{40}PW_{12}{\cdot}xH_2O$, Beijing Innochem Technology Co., Ltd.), silicotungstic acid ($H_4[Si(W_3O_{10})_4]{\cdot}xH_2O$, Beijing Innochem Technology Co., Ltd.), ZSM-5 (East China Normal University), MCM-41 (East China Normal University), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd.), hydrogen (H_2, Shanghai Pujiang Specialty Gas Co., Ltd.).

2. Catalyst preparation

The ternary Cu_1-M_1-Al_1-LDHs (M= Fe, Mg, Co, Ni, Sr or Ba) precursors were prepared by a co-precipitation method. Take the preparation of $Cu_1Fe_1Al_1$ as an example, $Cu(NO_3)_2\cdot 3H_2O$ (10 mmol), $Fe(NO_3)_2\cdot 6H_2O$ (10 mmol) and $Al(NO_3)_3\cdot 9H_2O$ (10 mmol) were dissolved in 50 mL of deionized water to give a mixed salt solution. NaOH and Na_2CO_3 were dissolved in 50 mL of deionized water to form a mixed base solution, where $[OH^-] = 1.8([M^{2+}] + [M^{3+}])$ and $[CO_3^{2-}] = 2[M^{3+}]$. Then, the metallic salt solution and the base solution were simultaneously added dropwise into a round-bottom flask and stirred at 50 °C for 5 h. The resulting brownish green precipitate was washed with deionized water until pH=7.0 and finally dried at 80 °C for 12 h. Next, the LDHs precursor was calcined in static air at 450 °C for 4 h to obtain $Cu_1Fe_1Al_1$-mixed metal oxide (MMO). Finally, the resultant $Cu_1Fe_1Al_1$ catalyst was obtained after reduction in H_2 at 350 °C for 3 h. Other $Cu_1M_1Al_1$ and CuFeAl catalysts with different Cu/Fe/Al molar ratios (Cu/Fe/Al = 1/1/0.5 or 1/0.5/1) were also prepared using the similar procedures. For reference, Cu_1Fe_1, Cu_1Al_1 and Fe_1Al_1 samples were also prepared by the same co-precipitation method.

3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded to analyze the structure and crystallinity of samples on a Bruker D8 Advance powder diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å, 35 kV, 25 mA). The scanning range (2θ) was from 10° to 80° with a speed of 20° min^{-1}. ICP-OES was adopted to determine the actual content of Cu, Fe and Al with a Thermo Elemental IRIS Intrepid II XSP inductively coupled plasma optical emission spectrometer. Transmission electron microscopy (TEM) images were taken with an FEI Tecnai G2-TF30 microscope at an acceleration voltage of 300 kV. N_2 adsorption-desorption isotherms of the samples were measured on a Quantachrome Autosorb-3B system at 77 K after the samples were degassed under vacuum at 100 °C for 6 h. The specific surface area was calculated using the BET (Brunauer-Emmett-Teller) equation according to the adsorption branch. The thermogravimetric analysis (TGA) of the sample was conducted from RT to 800 °C in air with a Mettler Toledo TGA/ SDTA851e apparatus.

The reducibility of as-calcined catalyst precursors was investigated by hydrogen temperature-programmed reduction (H_2-TPR) on a Micromeritics AutoChem II chemisorption analyzer equipped with a thermal conductivity detector (TCD). Briefly, 100 mg of the sample was treated in He (99.999%, 30 $mL \cdot min^{-1}$) at 300 °C for 1 h. After the sample was cooled down to ambient temperature, the reduction program started in 10% H_2-Ar gas (30 $mL \cdot min^{-1}$) at a ramping rate of 10 $°C \cdot min^{-1}$ up to 800 °C. Temperature-programmed desorption of ammonia (NH_3-TPD) was measured using the Micromeritics AutoChem II chemisorption analyzer as well to study the surface acidity of the catalysts. In a typical procedure, 100 mg of the sample was pretreated in 10% H_2-Ar gas (30 $mL \cdot min^{-1}$) at 350 °C for 3 h and then cooled down to 60 °C under He (99.999%, 30 $mL \cdot min^{-1}$). Then, NH_3 was adsorbed till saturation at this temperature in 10% NH_3-He gas (30 $mL \cdot min^{-1}$) for 30 min. Next, the temperature was raised to 100 °C to remove the physically adsorbed NH_3. Finally, NH_3-TPD profiles were recorded in He (99.999%, 30 $mL \cdot min^{-1}$) from 100 °C to 800 °C at a ramping rate of 10 $°C \cdot min^{-1}$.

Cu dispersion was determined by N_2O-titration using TP5080 apparatus equipped with a TCD (Xianquan Instrument, Tianjin). Before the analysis, the samples (100 mg) were treated in He (30.0 $mL \cdot min^{-1}$) at 300 °C for 1 h, followed by reduction in 10% H_2/N_2 (30 $mL \cdot min^{-1}$) and the temperature was increased from RT to 500 °C at a ramping rate of 5 °C·min^{-1}. After cooling to 50 °C, the reactor was subsequently flushed with He for 30 min to remove H_2 completely. Measurement was initiated by switching from He to 10% N_2O/He. In the line between the reactor and the TCD, a cold trap selectively removed N_2O from the gas. Consequently, the nitrogen evolved by reaction (1) was detected without interference from other species as a peak on the baseline of the continuous TCD-signal. The amount of nitrogen evolved can be accurately computed from the peak area. Cu dispersion was calculated by dividing the amount of surface Cu atoms by the total number of supported Cu atoms per gram of catalyst. The metallic Cu surface area was calculated based on an atomic Cu surface density of 1.46×10^{19} Cu atoms per m^2.

$$\mathrm{N_2O + 2Cu \rightleftharpoons Cu_2O + N_2} \quad (1)$$

Moreover, the surface chemical state of Cu or Fe was also characterized using X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with Al Kα radiation (1486.6 eV) as the incident beam. Before measurement, the samples were pretreated *in situ* under flowing H_2 (99.999%, 30 mL·min^{-1}) in a reactor attachment of the XPS spectrometer at 350 °C for 3 h. All binding energies (BEs) were corrected with the C1s peak at 284.8 eV as a reference. Spectral fitting and peak integration were conducted using the Avantage software.

4. Catalytic evaluation

4.1. SA esterification to DMS

In a typical catalytic test, a mixture including methanol (30 mL), SA (1 g), and catalyst (0.1 g) was added to a 50 mL stainless-steel autoclave with an internal glass vessel. After being sealed, the autoclave was heated to 120 °C and maintained for 3 h with a stirring of 600 rpm. After the reaction, the liquid product was analyzed by a Shimadzu QP-2010 Ultra GC-MS equipped with a Rxi®-5SilMS column. For recycling experiments, 1g of fresh SA was added to the solution in order to investigate the reusability of phosphotungstic acid without any work-up.

4.2. One-pot DMS hydrogenation to BDO

The one-pot hydrogenation of DMS was performed in a 50 mL stainless-steel autoclave. In a typical run, 0.2 g of the as-calcined catalyst precursor was pre-reduced in a specially designed quartz tube at 350 °C for 3 h before use. After the catalyst was cooled to RT, the catalyst was transferred immediately to the stainless-steel autoclave with the protection of a mixture of 9 mL 1,4-dioxane without further exposure to air and then mixed with 8 mmol of DMS. After being sealed and flushed with H_2 for three times, the autoclave was charged with H_2 to a specific pressure. The autoclave was then heated to the set temperature (T_1) and maintained at this temperature for proper time (t_1) with a stirring of 800 rpm. After that, the temperature was cooled down naturally to a lower temperature (T_2) and the hydrogenation was continued for an additional proper time (t_2) with a stirring of 800 rpm. For convenience, the corresponding temperature and time of the two-stage reaction were denoted as $T_1(t_1)$-$T_2(t_2)$. Finally, the reaction mixture was cooled to RT and the products were analyzed using a Shimadzu QP-2010 Ultra GC-MS equipped with a Rxi®-5SilMS column. For recycling experiments, the used catalyst was washed with 1,4-dioxane and then centrifuged 3 times. After that, the recycled catalyst without any activation was directly mixed with fresh substrate and solvent for the next cycle.

To investigate the long-term stability of the catalyst, the catalyst was also applied to the second-stage GBL hydrogenation to BDO in a fixed-bed reactor (with 550 mm length and 12 mm inner diameter). Typically, 1 g of as-calcined catalyst precursor (20 to 40 meshes) was placed in the center of the reactor. Before the reaction, the catalyst precursor was reduced in hydrogen (99.99%, 50 mL/min) at 350 °C for 3 h, and then the reactor was cooled to 190 °C and the hydrogen pressure was adjusted to 4.5 MPa. After that, 10 v% GBL in 1,4-dioxane (WHSV of GBL = 0.1 h^{-1}) was pumped to the reactor with an H_2/GBL molar ratio of 50:1. The samples were collected every 4-5 h and analyzed by a Shimadzu QP-2010 Ultra GC-MS equipped with a Rxi®-5SilMS column.

B. Supporting Tables and Figures

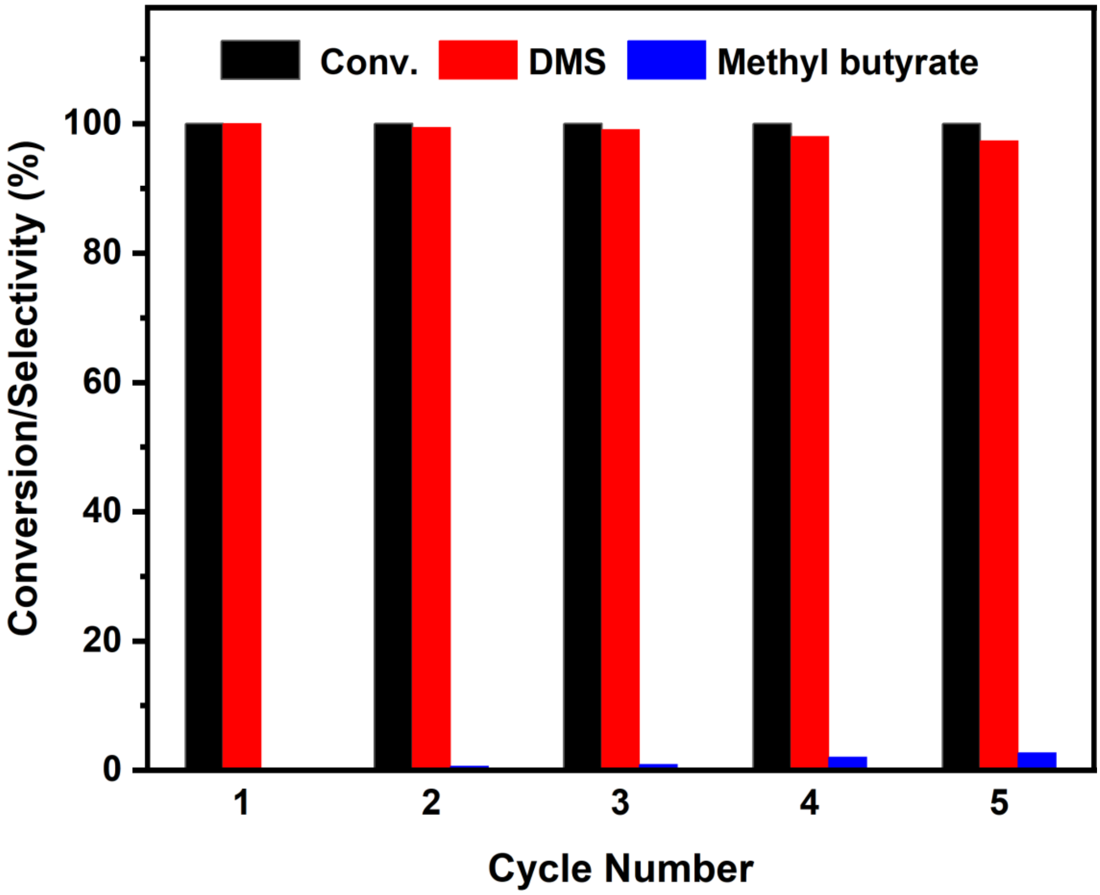
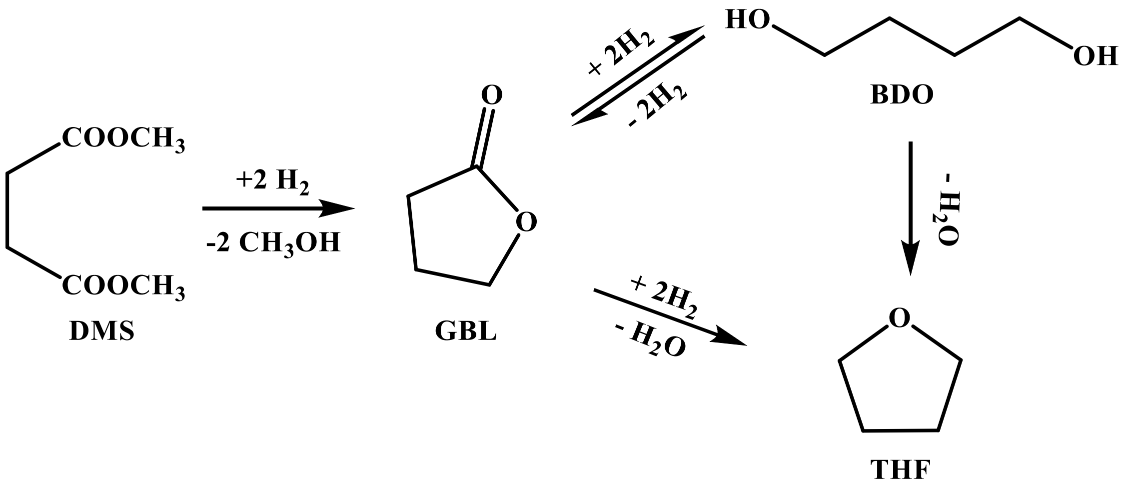


Fig. S1 Reusability of the phosphotungstic acid catalyst in a batch reactor.

Reaction conditions: 1 g of SA, 30 mL of methanol, 0.1 g of catalyst, 120 °C, 3 h, 600 rpm.



Scheme S1 Reaction pathway for the catalytic conversion of DMS to BDO.

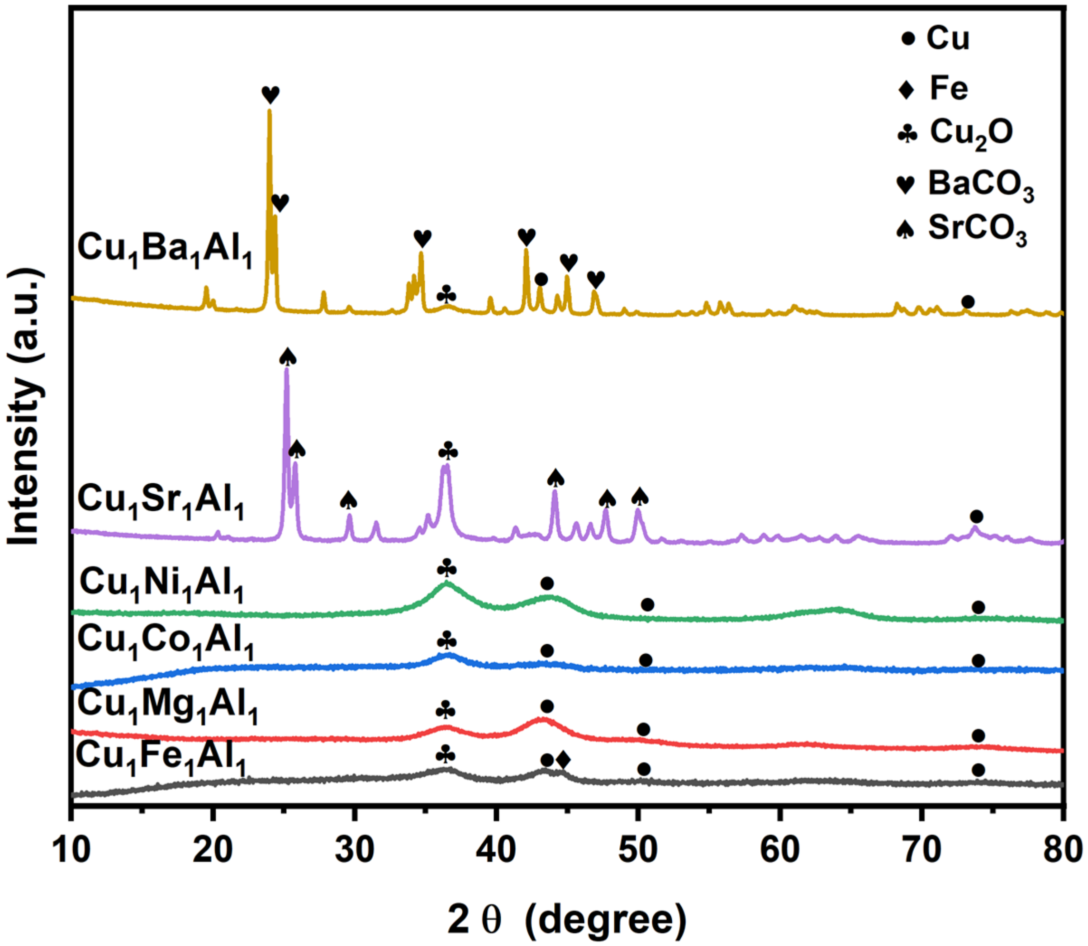


Fig. S2 XRD patterns of as-reduced Cu$_1$M$_1$Al$_1$ catalysts.

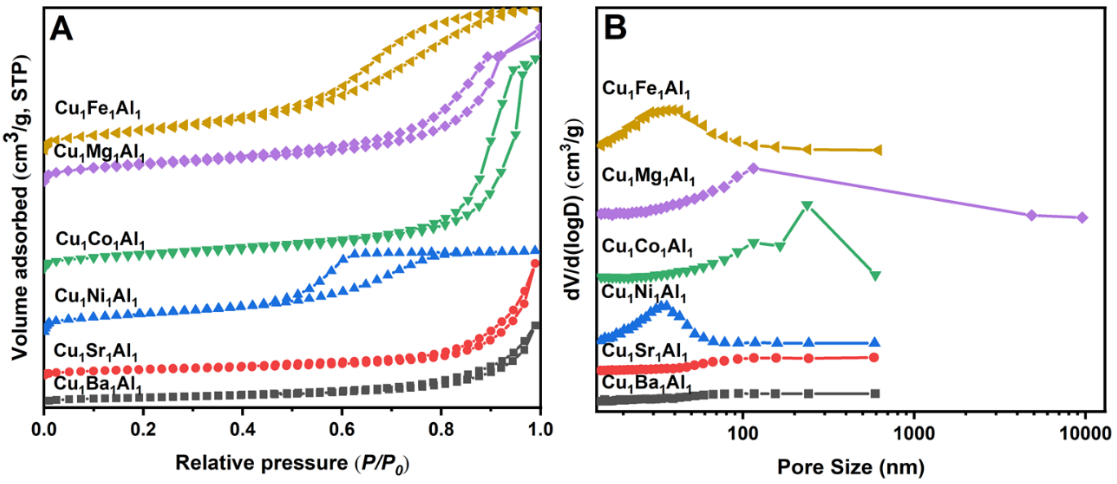


Fig. S3 (A) N_2 physisorption isotherms and (B) pore size distributions of as-calcined $Cu_1M_1Al_1$ catalysts.

Table S1 Physicochemical properties of $Cu_1M_1Al_1$ catalysts.

1	Catalyst	S_{BET} [a] ($m^2 \cdot g^{-1}$)	V_P [a] ($cm^3 \cdot g^{-1}$)	D_P [a] (nm)
2	$Cu_1Ba_1Al_1$	42	-	-
3	$Cu_1Sr_1Al_1$	39	-	-
4	$Cu_1Ni_1Al_1$	134	0.20	30
5	$Cu_1Co_1Al_1$	99	0.48	94
6	$Cu_1Mg_1Al_1$	118	0.34	59
1	$Cu_1Fe_1Al_1$	149	0.36	31

[a] Determined by nitrogen sorption.

Table S2 Thermodynamic parameters of GBL hydrogenation to BDO calculated by HSC Chemistry 6 software.

T/°C	ΔH/kJ·mol^{-1}	ΔS/J·K^{-1}·mol^{-1}	ΔG/kJ·mol^{-1}	K/(*10^{-4})	Log(K)
150	-82.84622	-234.57424	16.41388	94.1	-2.02634
160	-82.65967	-234.13853	18.75743	54.7	-2.26219
170	-82.47325	-233.71304	21.09668	32.6	-2.4869
180	-82.28701	-233.29744	23.43172	19.9	-2.7012
190	-82.10098	-232.89138	25.76266	12.4	-2.90579
200	-81.91522	-232.49455	28.08958	7.9	-3.10128
210	-81.72975	-232.10665	30.41258	5.1	-3.28826
220	-81.54461	-231.72738	32.73174	3.4	-3.46725
230	-81.35984	-231.35645	35.04716	2.3	-3.63873
240	-81.17547	-230.99361	37.3589	1.6	-3.80316
250	-80.99152	-230.63858	39.66705	1.1	-3.96094

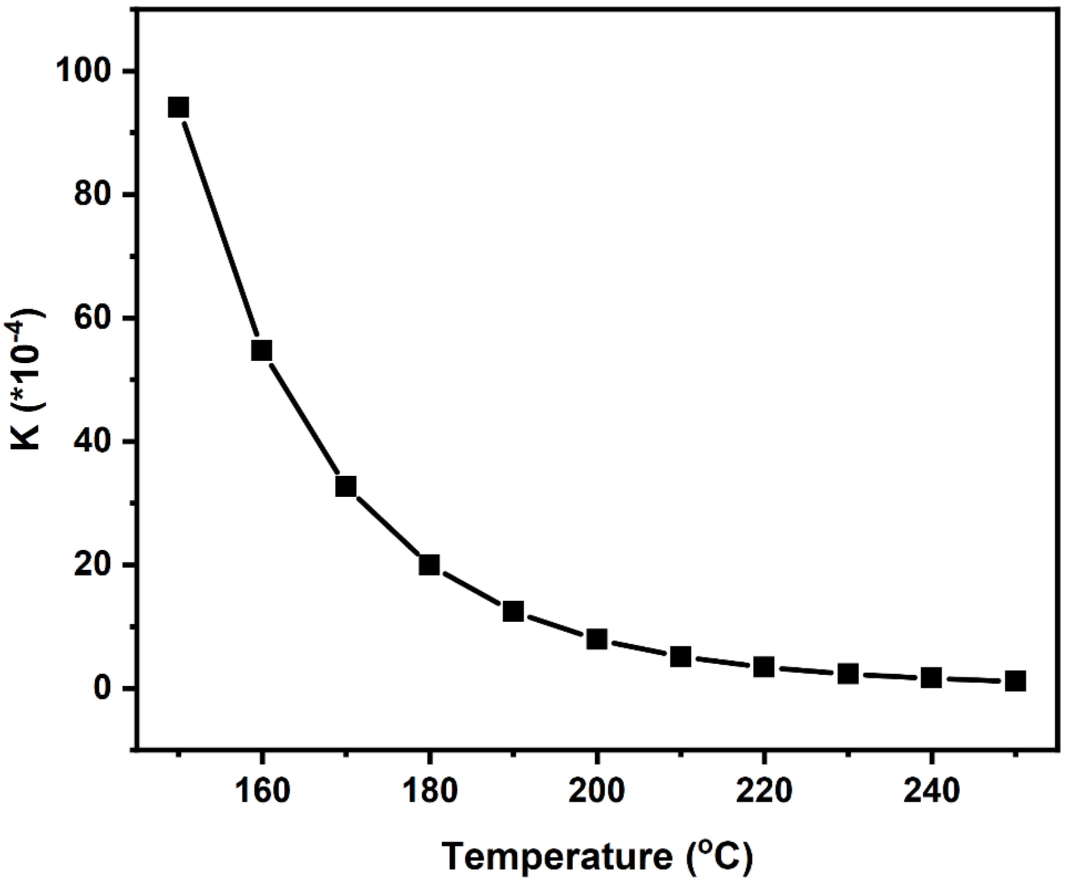


Fig. S4 GBL to BDO equilibrium constant K versus reaction temperatures.

Table S3 Hydrogenation of DMS to BDO in different solvents.

Entry	Solvents	Conv. (%)	Sel. (%)			
			GBL	BDO	THF	Others [c]
1 [a]	1,4-Dioxane	100	5.7	91.2	3.1	-
2 [a]	H_2O	53.3	13.6	-	1.9	84.5
3 [a]	Methanol	93.4	15.1	74.1	6.3	4.5
4 [a]	Ethanol	100	9.9	49.6	3.3	37.2
5 [b]	-	90.1	41.4	29.5	16.7	12.4

[a] Reaction conditions: 8 mmol of DMS, 9 mL of solvent, 0.2 g of $Cu_1Fe_1Al_{0.5}$, 240 °C (4 h)-190 °C (16 h), 5 MPa of H_2, 800 rpm;

[b] Reaction conditions: 40 mmol of DMS, 1 g of $Cu_1Fe_1Al_{0.5}$, 240 °C (4 h)-190 °C (16 h), 7 MPa of H_2, 800 rpm;

[c] Others mainly include 2-methoxyoxolane, 4-methoxy-1-butanol, methyl 4-methoxybutanoate, methyl 4-hydroxybutanoate, methyl butyrate, diethyl succinate and butanedioic acid, 1-ethyl 4-methyl ester, etc.

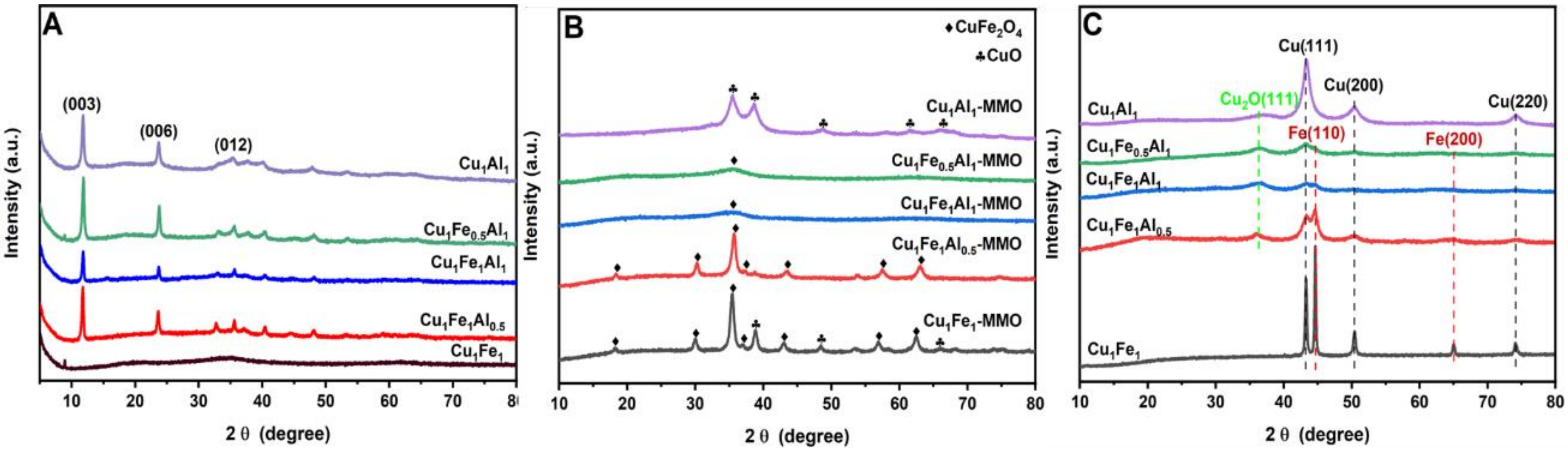


Fig. S5 XRD patterns of (A) various CuFeAl LDH precursors, (B) as-calcined CuFeAl catalysts, and (C) as-reduced CuFeAl catalysts.

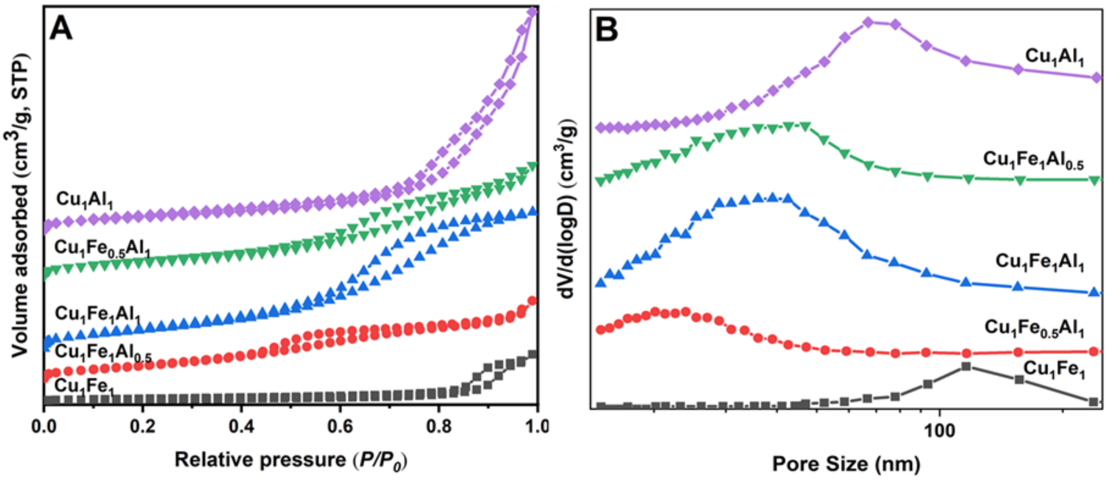


Fig. S6 (A) N_2 physisorption isotherms and (B) pore size distributions of as-calcined CuFeAl catalysts.

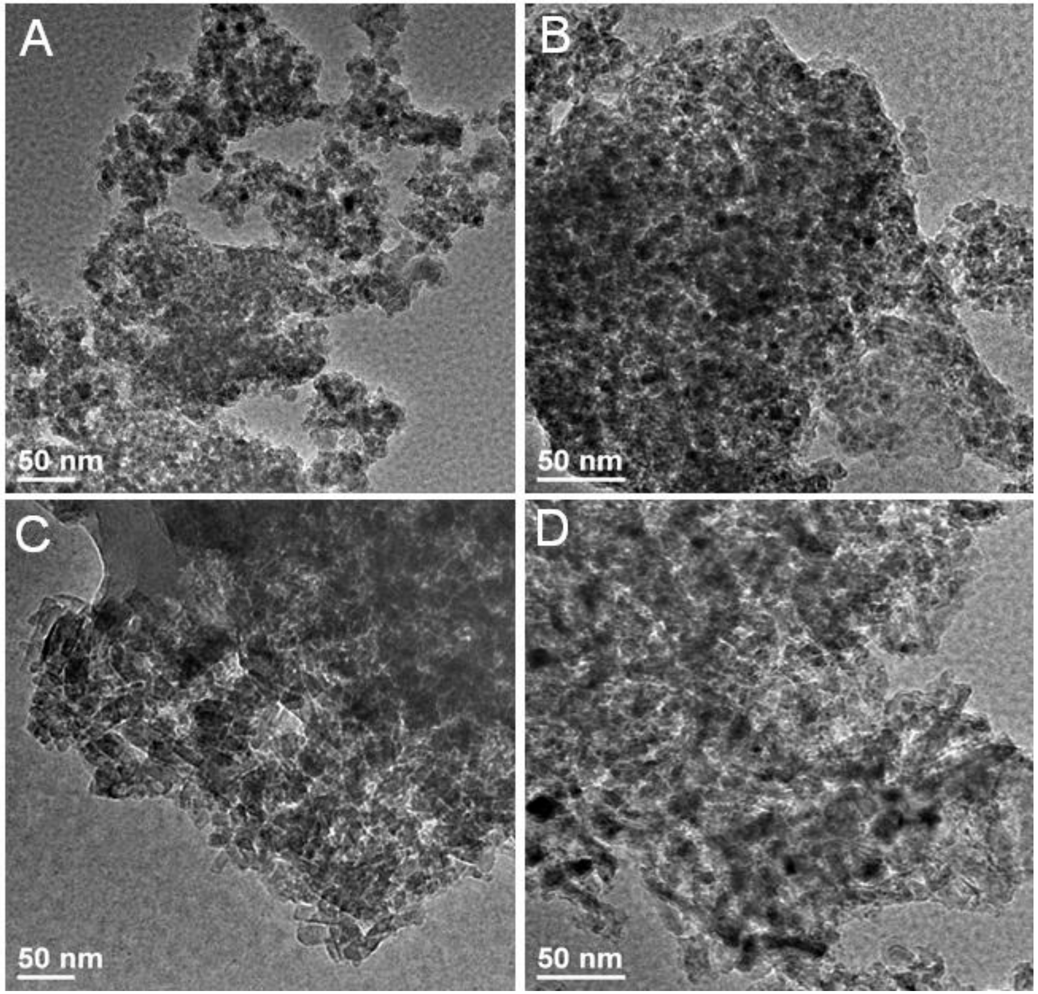


Fig. S7 TEM images of the as-reduced (A) $Cu_1Fe_1Al_1$, (B) $Cu_1Fe_{0.5}Al_1$, (C) Cu_1Fe_1, and (D) Cu_1Al_1.

Table S4 H_2-TPR results for various samples.

Catalyst	Cu content [a] (wt%)	Fe content [a] (wt%)	H_2 uptake [b] (mmol/$g_{cat.}$)
Fe_1Al_1	0	43	1.02
Cu_1Fe_1	45	38	2.92
$Cu_1Fe_1Al_{0.5}$	36	30	2.48
$Cu_1Fe_1Al_1$	27	23	2.80
$Cu_1Fe_{0.5}Al_1$	40	17	2.71
Cu_1Al_1	48	0	2.96

[a] Cu content was measured by ICP-OES;

[b] Amount of H_2 consumption was determined from H_2-TPR results.

Table S5 Surface state of Cu for various catalysts.

Catalyst	Kinetic energy (eV)		$Cu^0/(Cu^0+Cu^+)$
	Cu^0	Cu^+	
Cu_1Fe_1	918.2	915.4	0.50
$Cu_1Fe_1Al_{0.5}$	919.0	916.8	0.54
$Cu_1Fe_1Al_1$	919.3	916.9	0.55
$Cu_1Fe_{0.5}Al_1$	919.1	917.1	0.56
Cu_1Al_1	919.0	917.0	0.52

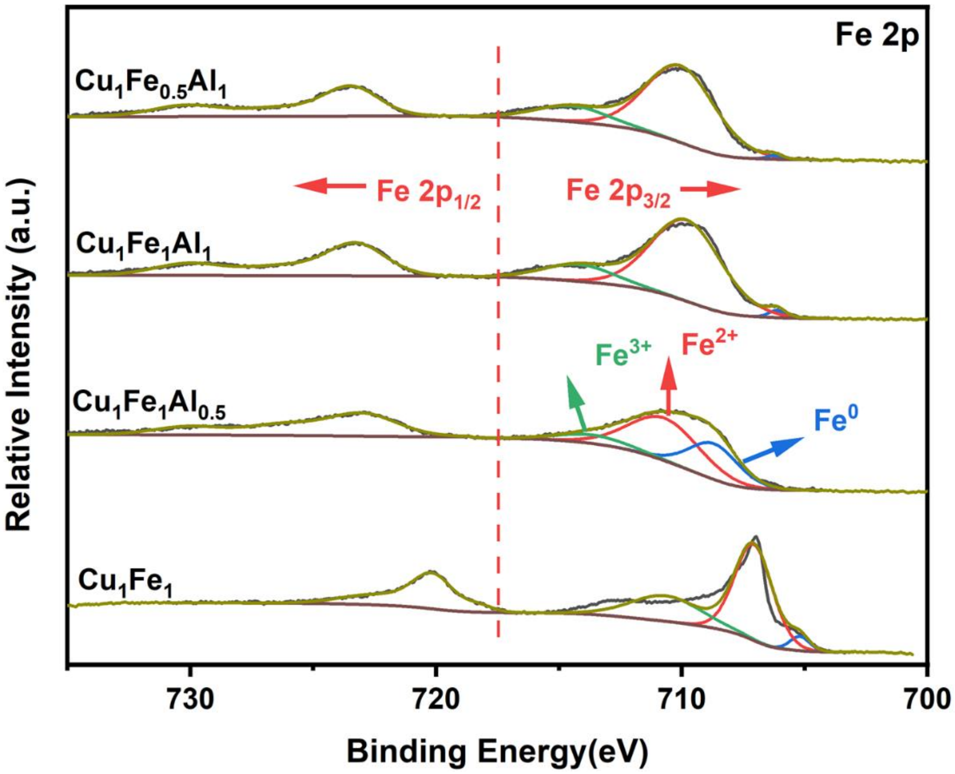


Fig. S8 Fe2p XPS spectra of as-reduced catalyst samples after *in situ* pretreatment in hydrogen at 350 ^oC for 3 h.

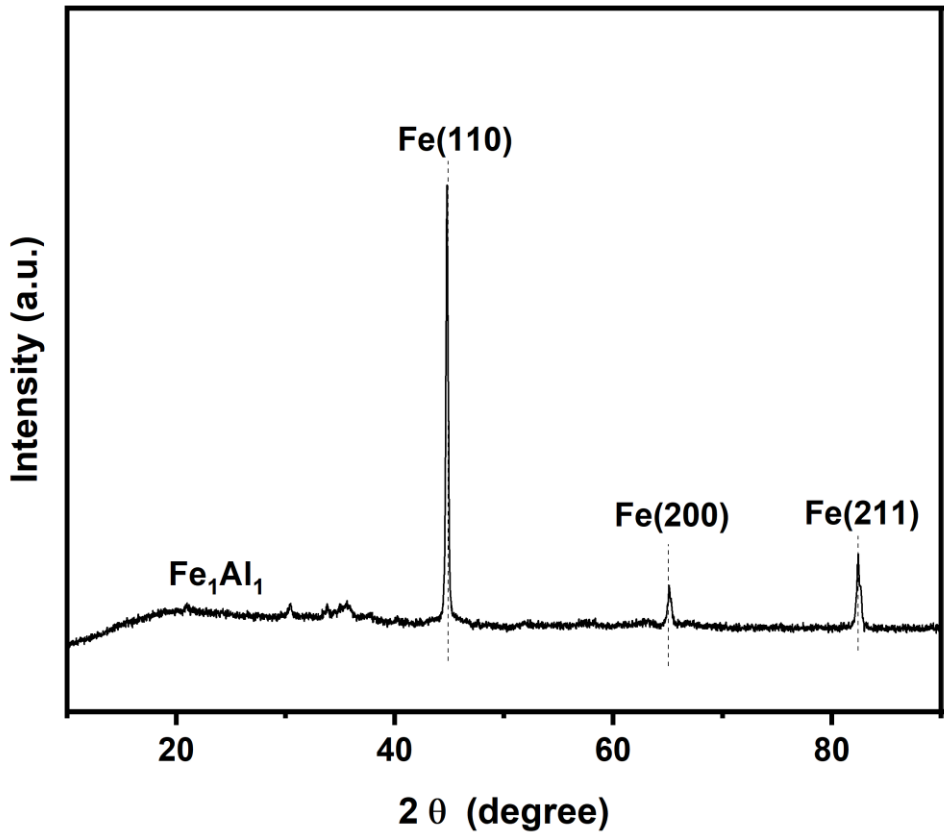


Fig. S9 XRD patterns of Fe_1Al_1 after reduced at 750 ℃ for 3 h in pure H_2.

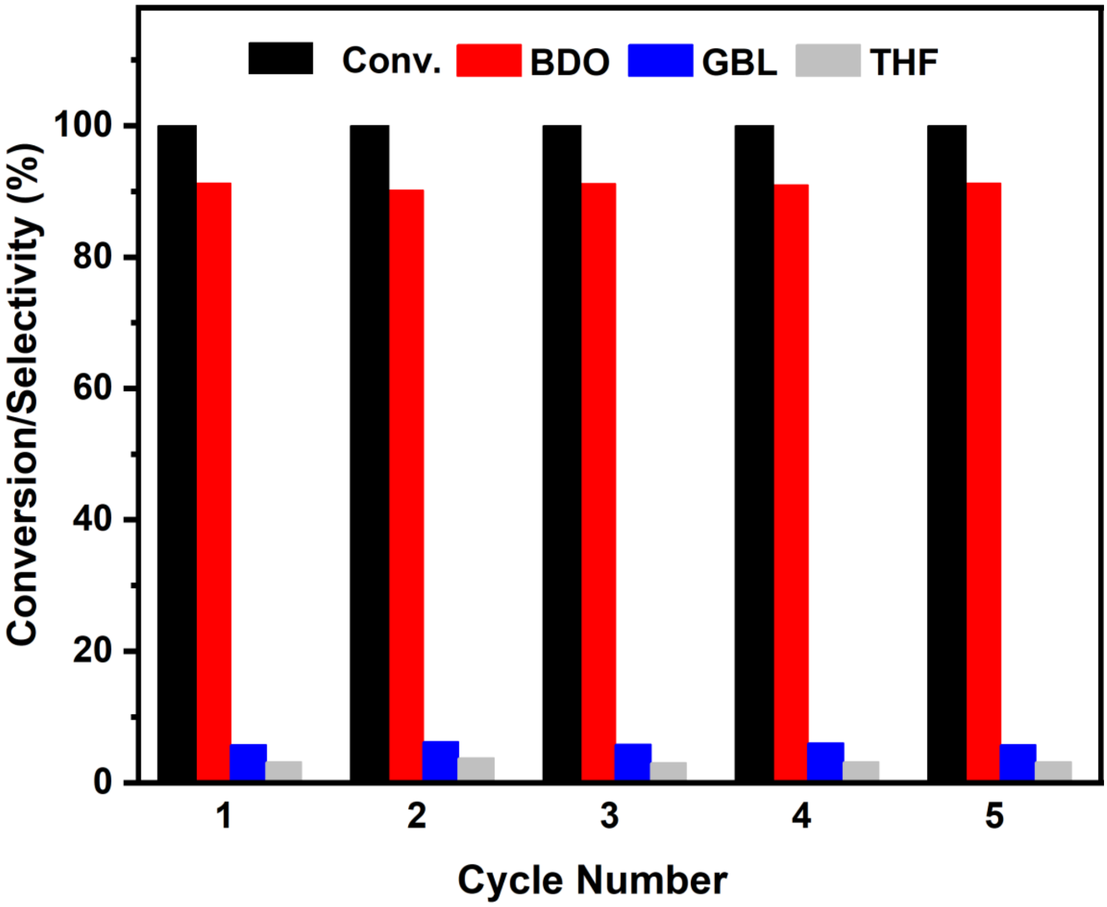


Fig. S10 Reusability of the $Cu_1Fe_1Al_{0.5}$ catalyst in a batch reactor.

Reaction conditions: 8 mmol of DMS, 9 mL of 1,4-dioxane, 5 MPa of H_2, 0.2 g of $Cu_1Fe_1Al_{0.5}$, 240 °C (4 h)-190 °C (16 h), 800 rpm.

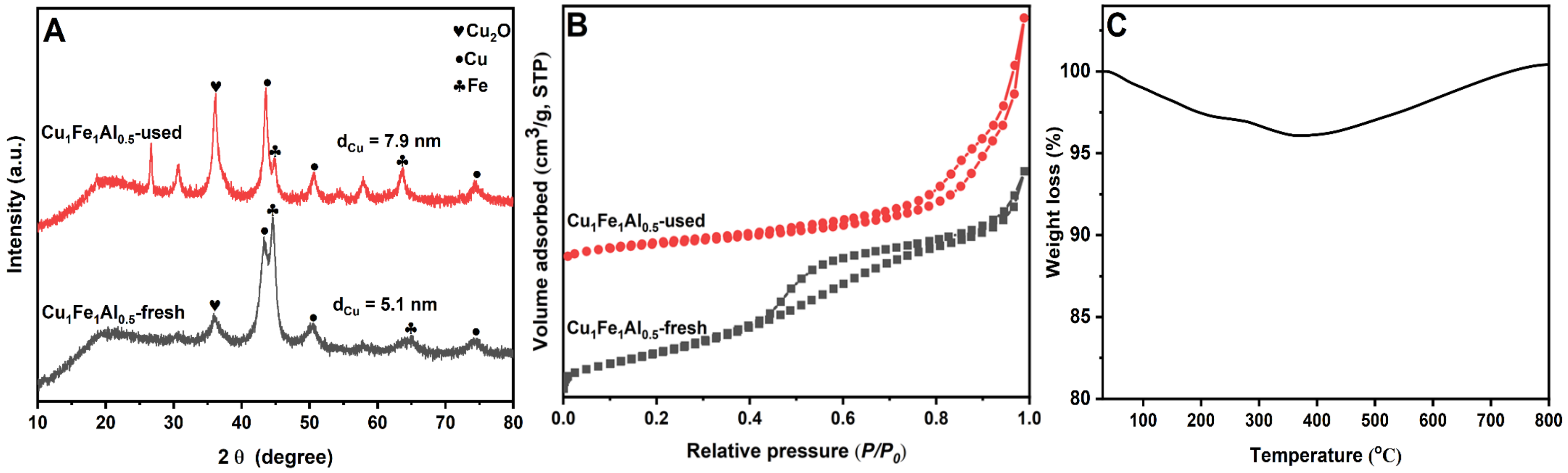


Fig. S11 (A) XRD patterns and (B) N_2 physisorption isotherms of the fresh and used $Cu_1Fe_1Al_{0.5}$ catalyst. (C) TG curve of the used $Cu_1Fe_1Al_{0.5}$ catalyst.

Table S6 Physicochemical parameters of the $Cu_1Fe_1Al_{0.5}$ catalyst before and after long-term stability test.

Entry	Catalyst	S_{BET} [a] ($m^2 \cdot g^{-1}$)	Composition [b] (wt%)		
			Cu	Fe	Al
1	Fresh	109.4	36	30	6
2	Used	104.3	35	28	6

[a] BET specific surface area;

[b] Determined by ICP-OES analysis.