

Supporting Information

Experimental Section

Synthesis of Ca-Al mixed metal oxides (CaAlO)

CaAl-LDH precursors with the Ca/Al molar ratios of 3.0, 4.0 and 5.0 were prepared by ultrasonic assisted precipitation method. Typically, firstly, adding calcium oxide to 100 ml deionized water under ultrasound in 30 min to form calcium hydroxide suspension, followed by a dropwise addition of aqueous $\text{Al}(\text{NO}_3)_3$ solution (100 ml) under ultrasound for another 60 min. The resulting suspension was recovered by dispersion and centrifugation in deionized water and dried at 70 °C overnight. The obtained CaAl-LDH samples were calcined in air at 500 °C for 6 h, and denoted as CaAlO.

Synthesis of CaAlO-supported copper-based catalysts

CaAlO-supported copper-based catalysts were synthesized by impregnation method. In a typical procedure, firstly, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3.42 g) was dissolved in 100 ml deionized water to form solution, and then CaAlO support (3.0 g) was added into the above solution. The mixed solution was aged at 60 °C for 30 min and the resulting gel was washed with deionized water and dried at 70 °C for overnight. The obtained samples were calcined in air at 500 °C for 6 h, pelletized, crushed, and sieved to 40-60 meshes. Subsequently, the obtained samples were reduced in a 10 % H_2/Ar atmosphere at 350 °C for 2 h at a ramping rate of 2 °C/min, and denoted

as Cu- x , where x means the Ca/Al molar ratio. For comparison, different supports (CaO, MgO, Al₂O₃, SiO₂) also were used to synthesize supported Cu-based catalysts with the Cu loading of about 25.0 wt % by impregnation method.

Characterization

X-ray diffraction (XRD) data were collected on Shimadzu XRD-6000 diffractometer with graphite-filtered Cu K α source ($\lambda = 0.15418$ nm).

Elemental analysis was performed using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscopy (ICP-AES) after the samples were dissolved in dilute hydrochloric acid (6.0 M).

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a JEOL 2100 operated at an accelerating voltage of 200 kV. High-angle annular dark-field scanning TEM-energy-dispersive X-ray spectroscopy (HAADF-STEM) images were recorded on a JEOL2010F instrument.

Positron annihilation spectroscopy (PAS) was carried out by using a fast/slow coincidence ORTEC system with a time resolution of 210 ps full width at halfmaximum in the transmission mode.

X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer at a base pressure of 2×10^{-9} Pa using Al K α X-ray radiation (1486.6 eV photons). X-ray induced Auger spectra (XAES) were carried out on a PHI Quantera SXM using Al K α X-ray as the excitation source.

The reduction behavior of calcined samples was studied by hydrogen temperature-programmed reduction (H₂-TPR) using Micromeritics ChemiSorb 2920 instrument. The sample (0.1g), which was put in a quartz U-tube reactor, was degassed at 200 °C for 2 h under argon flow (40 mL/min). TPR was performed in a stream of 10% v/v H₂/Ar (40 mL/min) at a heating rate of 5 °C /min from 50 °C. The effluent gas was detected by a thermal conductivity detector (TCD).

The surface areas of Cu⁰ particles for samples were determined by H₂-N₂O titration using a Micromeritics ChemiSorb 2920 instrument. Firstly, a H₂-TPR process for the sample was performed in 10% H₂/Ar mixture up to 350 °C. After cooling down to 60 °C, the gas was switched to 10% N₂O/N₂ (40 ml/min) and the sample was oxidized for 1 h. Finally, another H₂-TPR was carried out up to 350 °C. Copper surface area was calculated by assuming spherical shape of the Cu metal particles and a surface concentration of 1.47×10^{19} Cu atoms/m².

Temperature-programmed desorption of CO₂ (CO₂-TPD) and NH₃ (NH₃-TPD) were conducted on a ChemiSorb 2920 instrument. The calcined catalyst precursor (100 mg) was reduced with 10% H₂/Ar mixture at 350 °C for 2 h and then held under He flow (40ml/min) for 1 h. As for CO₂-TPD measurements, after cooling to 30 °C, the sample was exposed to pure CO₂ (40 ml/min) for 1 h. Subsequently, the sample was purged with He (40 ml/min) for 1 h and then heated to 800 °C at a rate of 5 °C /min. Desorption of CO₂ was monitored by the TCD. As for NH₃-TPD measurements, after cooling to 30 °C, the sample was treated with a flowing NH₃ gas mixture (5% in He) for 1.5 h. Subsequently, the sample was purged with He (40 ml/min) for 1 h and then heated to 800 °C at a rate of 5 °C /min. Desorption of NH₃ was monitored by the TCD.

In situ Fourier transform infrared (FT-IR) spectra of CO₂, butanol or pyridine absorption were recorded on a Thermo Nicolet 380 FT-IR spectrometer. The calcined catalyst precursor powder (50 mg) pressed into a self-supporting wafer was placed into an evacuable IR cell with CaF₂ windows. The sample was reduced with 10% H₂/Ar mixture at 350 °C for 2 h and evacuated for 1 h. As for FT-IR of CO₂ adsorption measurements, after cooling to 30 °C, the sample was exposed to CO₂ for 1 h. Then physisorbed CO₂ was removed by evacuation and the samples were heated stepwise under vacuum. FT-IR data were recorded at 400 °C. As for FT-IR of butanol adsorption measurements, after cooling to 30 °C, butanol was introduced and balanced for 1 h. Then, physisorbed butanol was removed by evacuation. FT-IR data were recorded under vacuum at 30 °C. As for FT-IR of pyridine adsorption measurements, after cooling to 30 °C, pyridine was introduced and balanced for 1 h. Then, physisorbed pyridine was removed by evacuation. FT-IR data were recorded under vacuum at 30 °C.

Catalytic performance test

The transfer hydrogenation of FOL was conducted on a stainless-steel fixed-bed tubular reactor with an inner diameter of 10 mm. The samples (1.5 g), which were loaded into reactor with quartz powders packed in both sides of the catalyst bed with a height of approximately 27 mm, reduced in a 10% H₂/N₂ atmosphere at 350 °C for 2 h. Afterward, mixture of FL and 1,4-BDO (molar ratio 1) were fed into the reactor at a N₂/mixture molar ratio of 13 at 210 °C, and the room-temperature liquid hourly space velocity (LHSV) was 1.8 h⁻¹. Finally, water produced in liquid products was quantitatively analyzed by an Agilent GC7890B gas chromatograph equipped with GDX-103 column (2m×3mm) and thermal conductivity detector (TCD) based on

external standard method. And, liquid organic products containing FL, 1,4-BDO, FOL, GBL and/or by products (2-MF and THF) were analyzed by an Agilent GC7890B gas chromatograph equipped with DB-WAX capillary column (30.0 m×250 μm×0.25 μm) and flame ionization detector (FID). Correspondingly, the weight percentages of liquid organic components were calculated based on a modified area normalization method, where FL was used as standard substance to obtain relative mass calibration factors of other components ($f'_{FL}=1.0$). For example, the weight percentage of 1,4-BDO ($W_{1,4-BDO}$ %) could be calculated according to following equation:

$$W_{1,4-BDO} (\%) = \frac{A_{1,4-BDO} \times f'_{1,4-BDO} \times (100 - W_w)}{A_{FL} \times f'_{FL} + A_{1,4-BDO} \times f'_{1,4-BDO} + A_{FOL} \times f'_{FOL} + A_{GBL} \times f'_{GBL} + A_{2-MF} \times f'_{2-MF} + A_{THF} \times f'_{THF}}$$

where W_w is the weight percentage of water produced (%), A is the peak area of certain organic component in GC spectrum, and f' is the relative mass calibration factor of certain organic component.

The conversions and selectivities with the experimental errors less than 3 % were obtained through at least 3 parallel experiments. The conversions of FL and 1,4-BDO, selectivities and yields are calculated according to the following equations:

$$\text{Conversion (\%)} = \frac{\text{amount of FL (or 1,4-BDO) converted (mol)}}{\text{total amount of FL (or 1,4-BDO) in the feed (mol)}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{amount of FL (or 1,4-BDO) converted to a product (mol)}}{\text{total amount of FL (or 1,4-BDO) converted (mol)}} \times 100$$

$$\text{Yield (\%)} = \text{Conversion} \times \text{Selectivity} \times 100$$

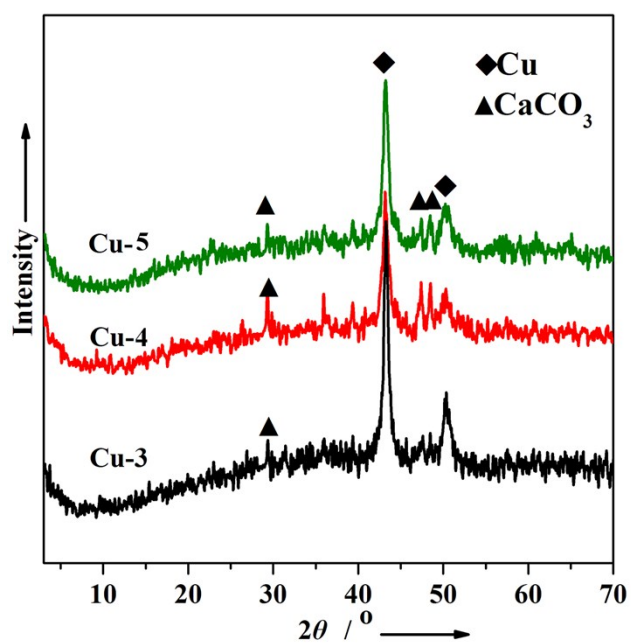


Fig. S1 XRD patterns of Cu-x catalysts

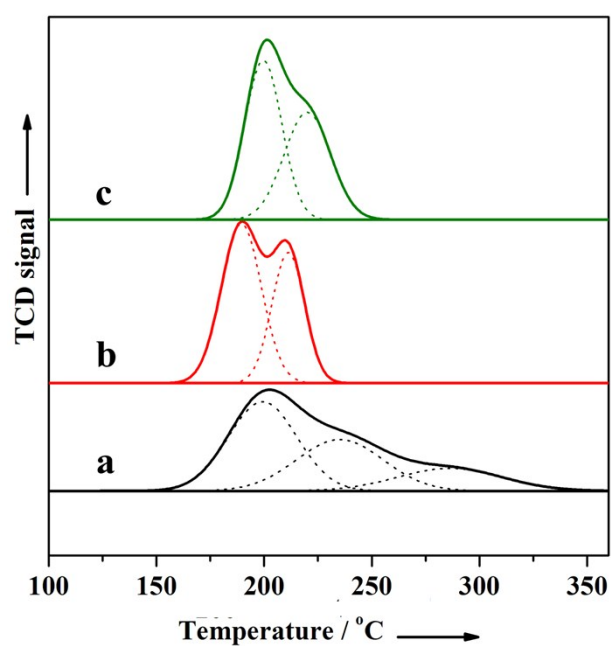


Fig. S2 H_2 -TPR profiles of calcined catalyst precursor with different Ca/Al atom ratio: (a) 3.0; (b) 4.0 and (c) 5.0.

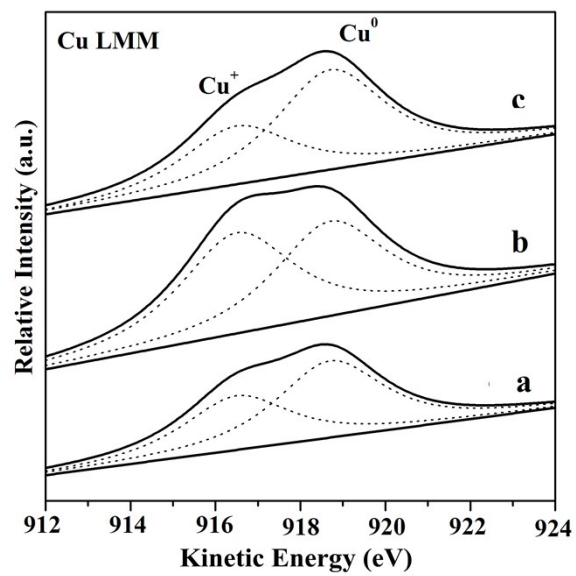


Fig. S3 Cu LMM XAES of Cu-3 (a), Cu-4 (b) and Cu-5 (c) samples.

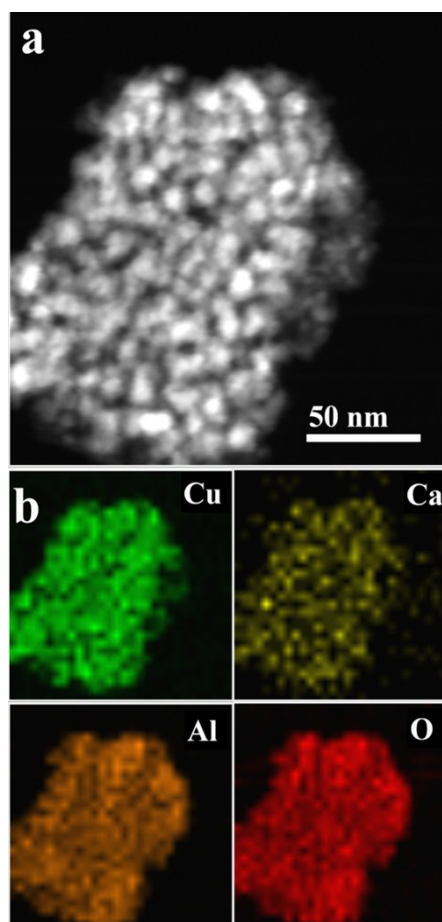


Fig. S4 HAADF-STEM image (a) of Cu-4 catalyst with the EDS mapping (b).

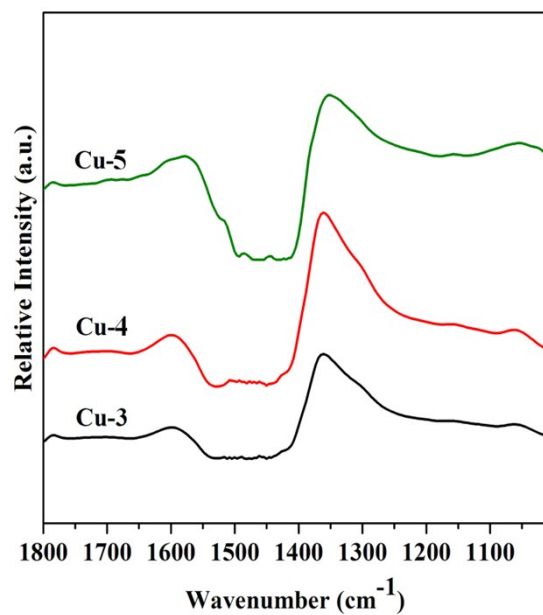


Fig. S5 FT-IR profiles of CO₂ adsorption over Cu-x catalysts recorded at 400 °C.

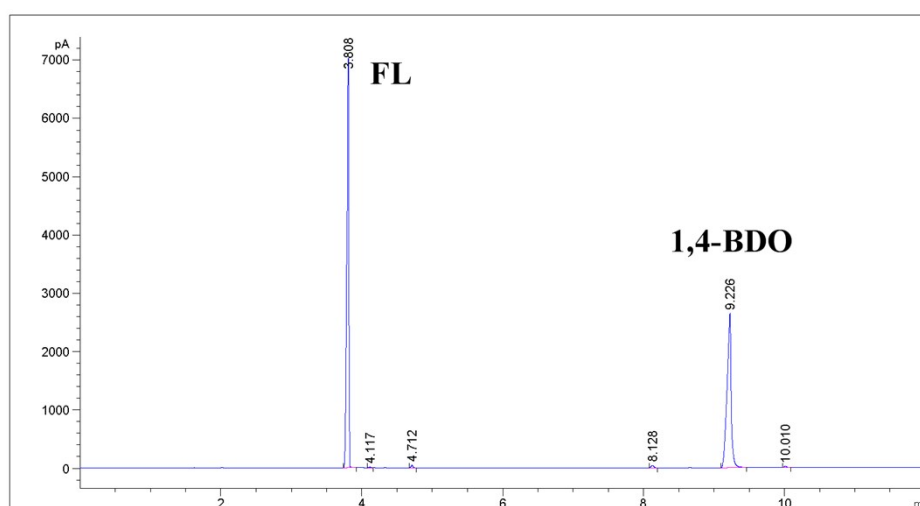


Fig. S6 Gas chromatogram spectrum of reactants before hydrogenation of FL and dehydrogenation of 1,4-BDO.

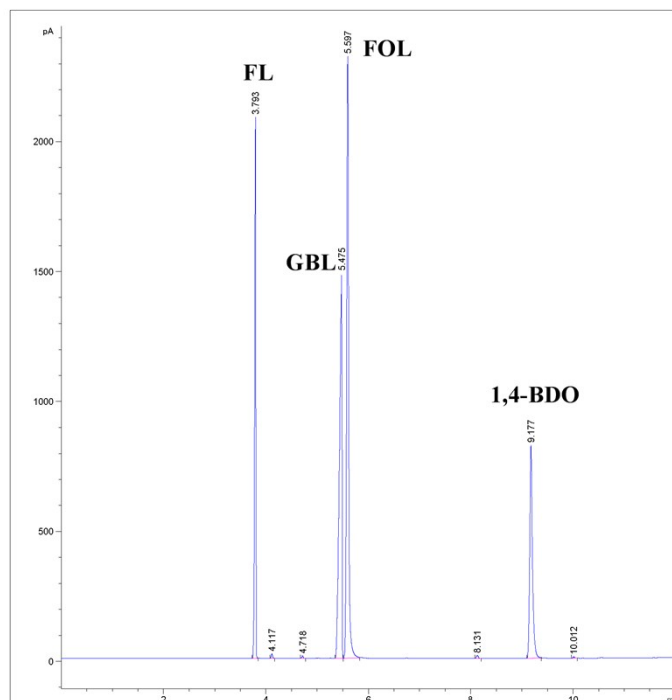


Fig. S7 Gas chromatogram spectrum of products after hydrogenation of FL and dehydrogenation of 1,4-BDO over the Cu-3 catalyst.

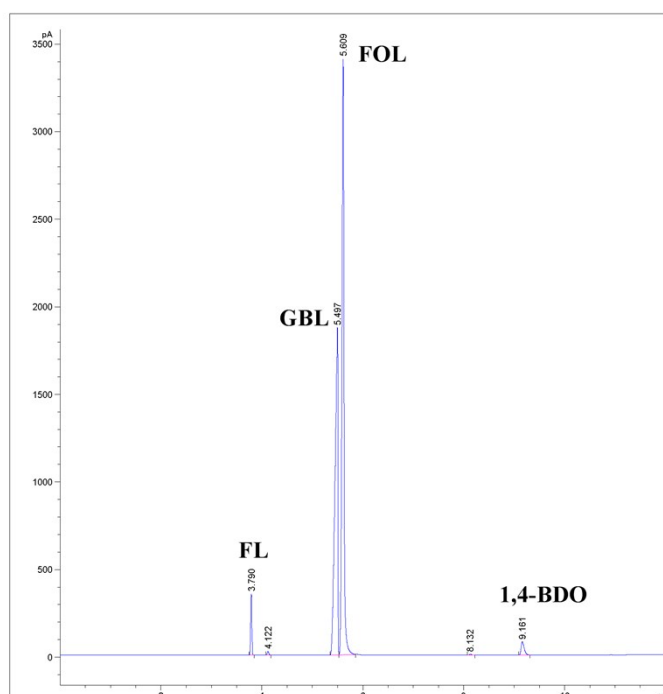


Fig. S8 Gas chromatogram spectrum of products after hydrogenation of FL and dehydrogenation of 1,4-BDO over the Cu-4 catalyst.

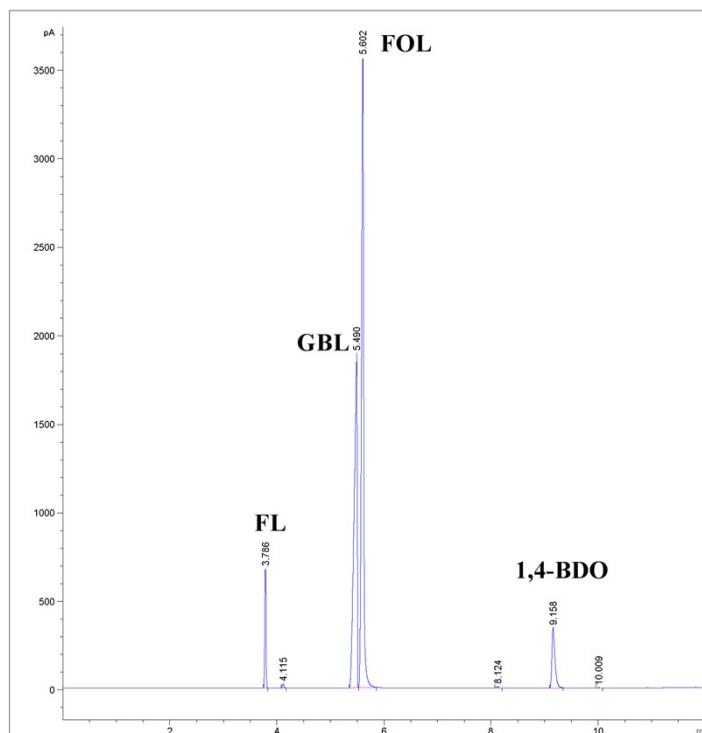


Fig. S9 Gas chromatogram spectrum of products after hydrogenation of FL and dehydrogenation of 1,4-BDO over the Cu-5 catalyst.

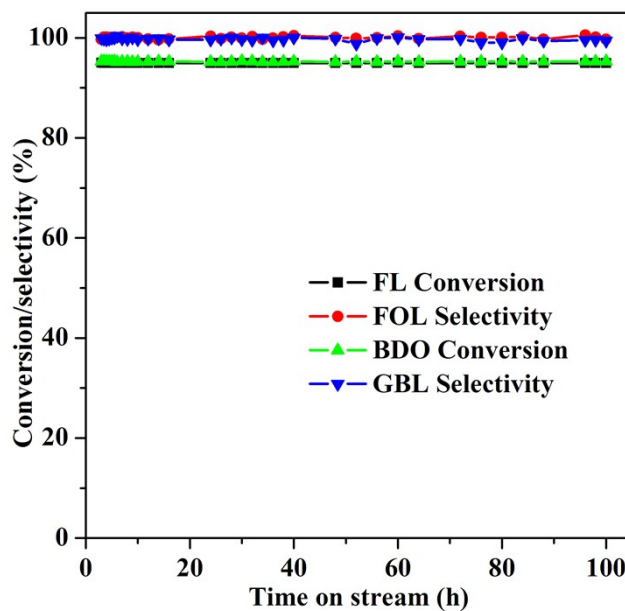


Fig. S10 Catalytic performance as a function of reaction time over the Cu-4 catalyst.

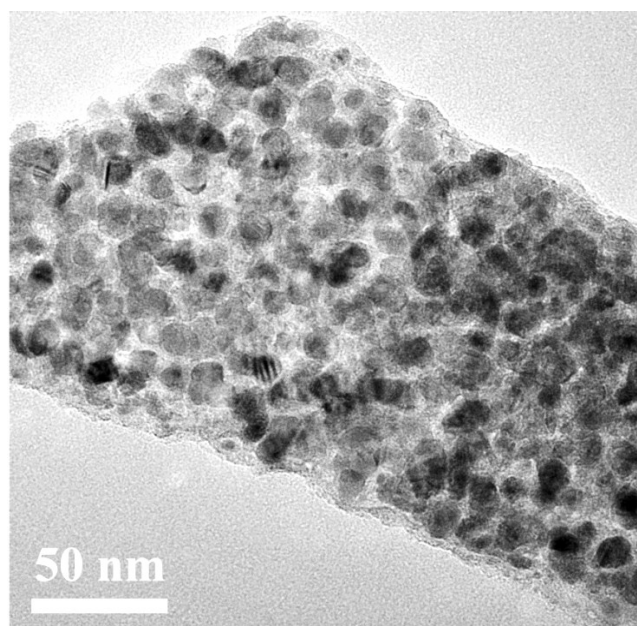


Fig.S11 TEM image of Cu-4 catalyst after a 100 h reaction.

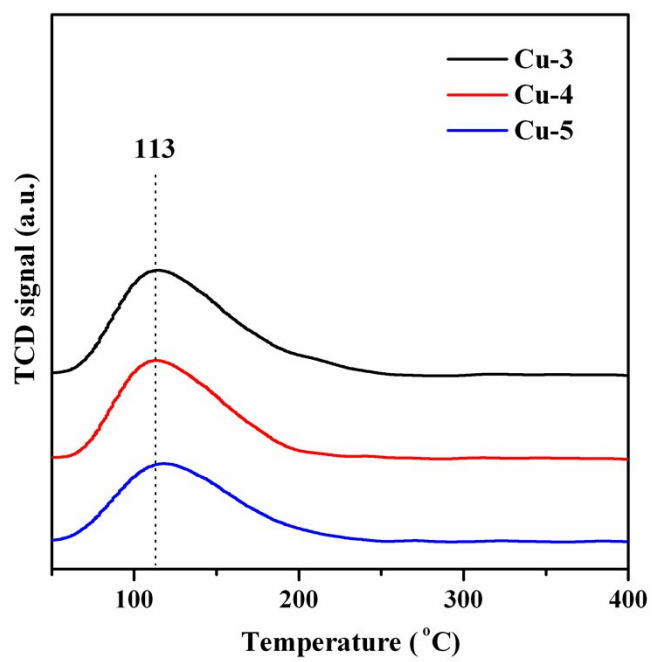


Fig. S12 NH₃-TPD profiles of Cu-*x* catalysts

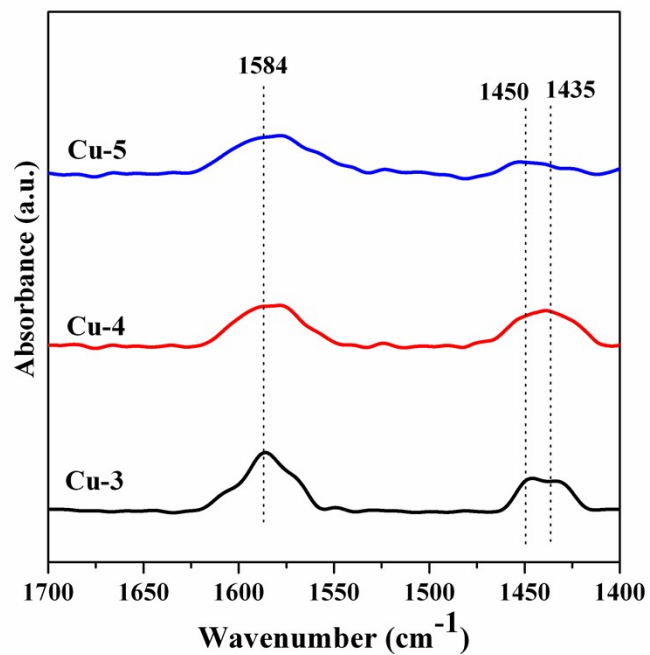


Fig. S13 FT-IR spectra of pyridine adsorption over Cu-*x* catalysts recorded at 30 °C.

Table S1 Positron lifetimes and relative intensities of samples

Sample	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	I_2/I_1
CaAlO ^a	0.1878	68.6	0.4247	29.1	2.50	2.3	0.42
Cu-4	0.1812	65.9	0.4110	31.5	1.69	2.6	0.48

^a : The Ca/Al atom ratio is 4.0

Table S2 Catalytic performance of different catalysts ^a

Catalysts	Conversion (%)		Selectivity (%)	
	1,4-BDO		GBL	
Cu-3	50.4		100	
Cu-4	89.2		100	
Cu-5	82.7		100	
Cu/CaO	12.8		100	
CaAlO	1.1		100	

^a Reaction conditions: LHSV(1,4-BDO) = 0.9 h⁻¹, n (N₂):n (1,4-BDO) = 13, reaction temperature = 210 °C and reaction pressure = 1 atm.

Table S3 Catalytic performance of different catalysts ^a

Catalysts	Conversion (%)			Selectivity (%)		
	FL	1,4-BDO	FOL	2-MF	GBL	
Cu-3	78.3	46.3	87.2	12.8	100	
Cu-4	99.0	83.6	70.3	29.7	100	
Cu-5	95.4	78.4	75.2	24.8	100	
Cu/CaO	41.5	20.0	90	10	100	
CaAlO	1.6	1.3	100	0	100	

^a Reaction conditions: LHSV(FL+1,4-BDO)=0.9 h⁻¹, n (50% H₂/N₂ mixture):n (FL+1,4-BDO) = 13, reaction temperature = 210 °C and reaction pressure = 1 atm.