Supporting Information

Phase transition induced hydrogen activation for enhanced furfural reductive amination over CoCu bimetallic catalyst†

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1. Experimental sections

1.1 Experimental materials

FAL (99%), FFA (98%), benzaldehyde (98%), 3-phenylpropionaldehyde (95%) and cyclohexanone (99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Hydrazine hydrate (80%) was purchased from Tianjin Kemio Chemical Reagent Co., Ltd. Toluene (99.5%) was purchased from Xilong Scientific Co., Ltd. $Co(NO_3)_2·6H_2O$ (99%), Cu $(NO_3)_2·6H_2O$ and 2-octanone (98%) were purchased from Shanghai Aladdin Reagent Co., Ltd. Methanol (99%) and $(NH_4)_2CO_3$ were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. All chemicals were used as received without any further purification.

1.2 Catalyst preparation

$CoCu@CoCuO_x$ was synthesized by a co-precipitation method. Firstly, x mmol $Co(NO_3)_2·6H_2O$ and y mmol $Cu(NO_3)_2·6H_2O$ were dissolved in 200 mL deionized water to form solution A (x+y=20 mmol). Then, 23 mmol $(NH_4)_2CO_3$ was dissolved in 200 mL deionized water to form solution B. Subsequently, solution B was dropwise added to solution A until the pH reached 9. The suspension was aged at 65 °C for 1 h, followed by standing at room temperature for 12 h. Afterwards, the suspension was filtered, and the solid sample was dried at 100 °C for 12 h, and finally calcined at 450 °C for 4 h (heating rate = 5 °C/min). A suitable amount of sample was reduced at 250 °C under H_2 atmosphere for 2 h (heating rate =5 °C/min). After cooling to room temperature, the sample was treated in 1.5% O_2/N_2 atmosphere for 1 h, and the obtained sample was named $CoCu@CoCuO_x$ (x:y). Control catalysts $Co@CoO_x$ and $Cu@CuO_x$ were synthesized without the addition of $Cu(NO_3)_2·6H_2O$ or $Co(NO_3)_2·6H_2O$, respectively.

1.3 Catalyst characterization

Powder X-ray diffraction (XRD) was performed using a Panalytic Empyrea diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos XSAM800 spectrometer, with all binding energies calibrated against the C1s peak at 284.8 eV. N_2 adsorption-desorption isotherms were measured at -196 ^{o}C using an ASAP 2460 automatic surface area and pore size analyzer. Raman spectra were collected using a Lab RAM HR Evo confocal, which was equipped with a 532 nm Ar ion laser, with a range of 100 - 4000 cm^{-1}. N_2 adsorption-desorption isotherms were measured at -196 ^oC using an ASAP 2460 automatic surface area and pore size analyzer. Before physical adsorption measurements, all samples were degassed overnight at 250 ^oC. Scanning transmission electron microscope (STEM) images were recorded using a FEI Titan G260-300 instrument with an accelerating voltage of 200 kV. The electron paramagnetic resonance (EPR) spectra were collected on a Bruker EMXnano spectrometer at 77 K. The contents of Co were determined by Thermo Scientific iCAP PRO X inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Chemisorption measurements were carried out using an Auto Chem II 2920 (Micromeritics, USA) equipped with a thermal conductivity detector (TCD). For H_2-TPR, 100 mg catalyst was pretreated at 150 ^oC under He atmosphere for 0.5 h, then cooled to room temperature. After switching to H_2 atmosphere, the sample was heated to 600 ^oC at a rate of 10 ^oC/min, and the desorbed H_2 signal was collected. For H_2-TPD, 100 mg catalyst was pretreated at 250 ^oC under H_2 atmosphere for 0.5 h, then cooled to room temperature. After switching to He atmosphere and purging for 0.5 h, the sample was heated to 600 ^oC at a rate of 10 ^oC /min, and the desorbed H_2 signal was collected. For NH_3-TPD, 100 mg catalyst was pretreated at 250 ^oC under H_2 atmosphere for 0.5 h, then cooled to room temperature and treated in NH_3 atmosphere for 0.5 h. After switching to He atmosphere and purging for 0.5 h, the sample was heated to 600 ^oC at a rate of 10 ^oC /min, and the desorbed NH_3 signal was collected.

Hydrogen spillover experiment was studied as follows: WO_3 (1 g), catalyst (30 mg), and methanol (4 mL) were added to a reactor. The reactor was pressurized with 3 MPa H_2 and heated at 30 ^oC for 6 h. After cooling to room temperature, the reaction solution was removed and the color change of the solid powder was recorded.

PerkinElmer infrared spectrometer was used to measure Py-FTIR of samples. Initially, 20 mg catalyst was mixed with 100 mg SiO_2, pressed, and fixed in sample pool. The samples were then pretreated under vacuum at 300 °C for 1 h, followed by cooling to room temperature. Gaseous pyridine was introduced and adsorbed for 1 h. Subsequently, the gaseous pyridine was removed, and the Py-FTIR spectrum was collected at room temperature and 50 °C.

The in-situ FTIR spectra were recorded using the Thermo Scientific Nicolet iS50 FTIR spectroscopy. Initially, the catalyst was reduced in an H_2 atmosphere at 250 °C for 2 h, then cooled to room temperature and purged with an inert gas to remove background interference. An inert gas carrying FAL vapor was introduced for 15 min, followed by an inert gas purge for 15 min to remove gaseous and physically adsorbed FAL. Next, an NH_3/H_2 mixture was passed through the sample, followed by an inert gas purge to remove gaseous and physically adsorbed gas. The temperature was subsequently increased to 50 °C, and corresponding data were collected at 5 min, 10 min, 1 h, 2 h, 3 h, and 4 h, respectively.

1.4 Reductive amination of FAL

FAL reductive amination reaction was carried out in a 50 mL stainless steel autoclave with a glass liner. Initially, 0.24 mmol FAL, 2 mmol hydrazine hydrate, 0.5 mmol methylbenzene (internal standard), 30 mg catalyst and 4 mL methanol were added to the autoclave. After sealing and evacuating, the desired H_2 pressure was applied, and the autoclave was heated to a certain temperature. After the reaction, the autoclave was immediately cooled in cold water. The solid catalyst and reaction solution were separated by centrifugation, and the liquid was used for product analysis. Product analysis was performed using a gas chromatograph (GC 9790) equipped with an HP-5 column. The reaction products were identified by GC-MS (Agilent 7890A-5975C). FAL conversion, product yield, and selectivity were calculated using the following equations:

$$(1)\ FAL\ conversion\ (\%) = \left(1 - \frac{Moles\ of\ unreacted\ FAL}{Initial\ moles\ of\ FAL}\right) \times\ 100\%$$

$$(2)\ Product\ yield\ (\%) = \frac{Moles\ of\ obtained\ products}{Theoretical\ moles\ of\ products\ from\ \ conversion\ of\ FAL} \times\ 100\%$$

$$(3)\ Product\ selectivity\ (\%)\ = \frac{Product\ yield}{FAL\ conversion} \times\ 100\%$$

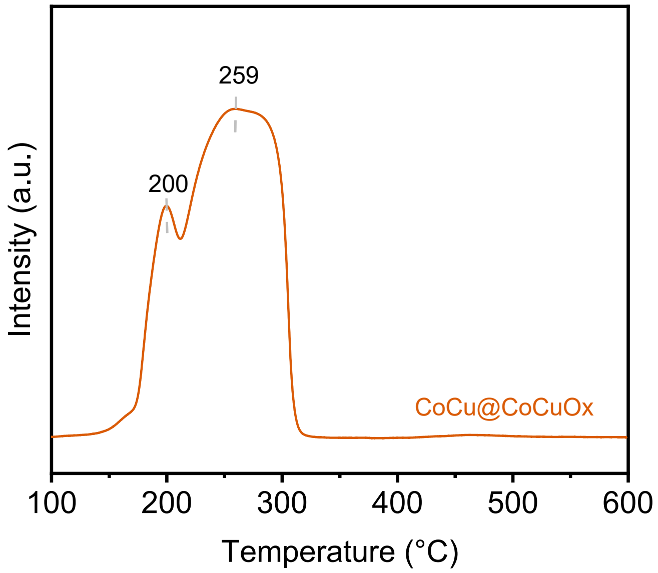

Fig. S1 H_2-TPR of CoCu@CoCuO$_x$ catalyst.

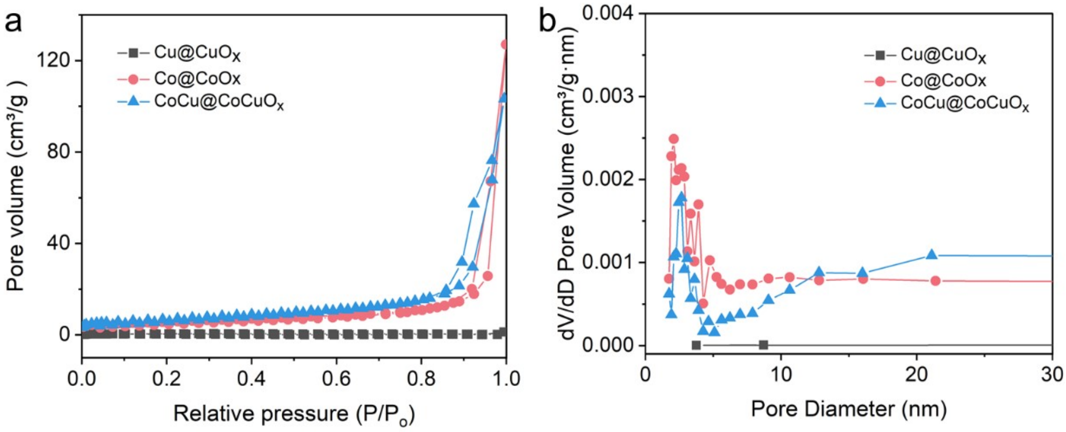

Fig. S2 (a) Isothermal adsorption-desorption and (b) pore size distributions of various catalysts.

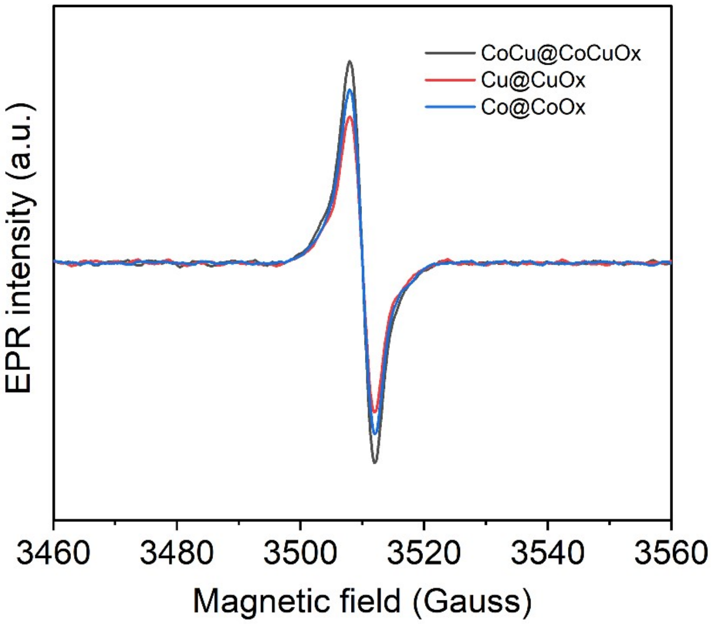

Fig. S3 EPR spectra of $Co@CoO_x$, $CoCu@CoCuO_x$ and $Cu@CuO_x$.

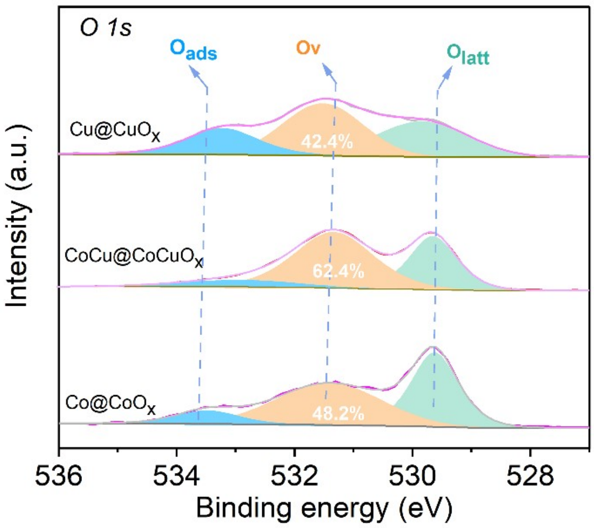

Fig. S4 O 1s XPS spectra of Co@CoO$_x$, CoCu@CoCuO$_x$ and Cu@CuO$_x$.

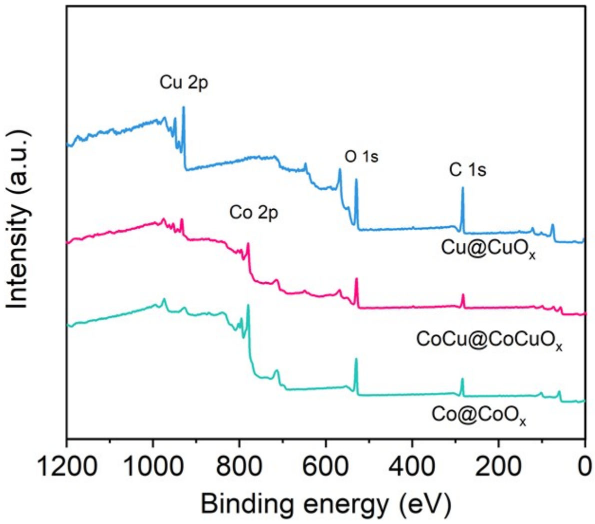

Fig. S5 XPS wide survey spectra of various catalysts.

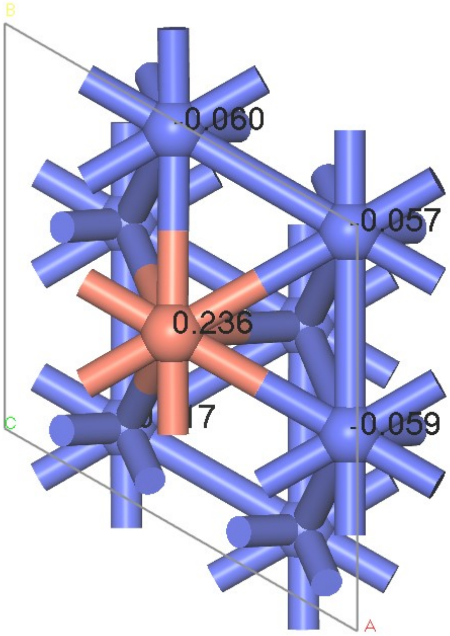

Fig. S6 Charge distribution on Cu and Co atoms of Co (fcc-111) model.

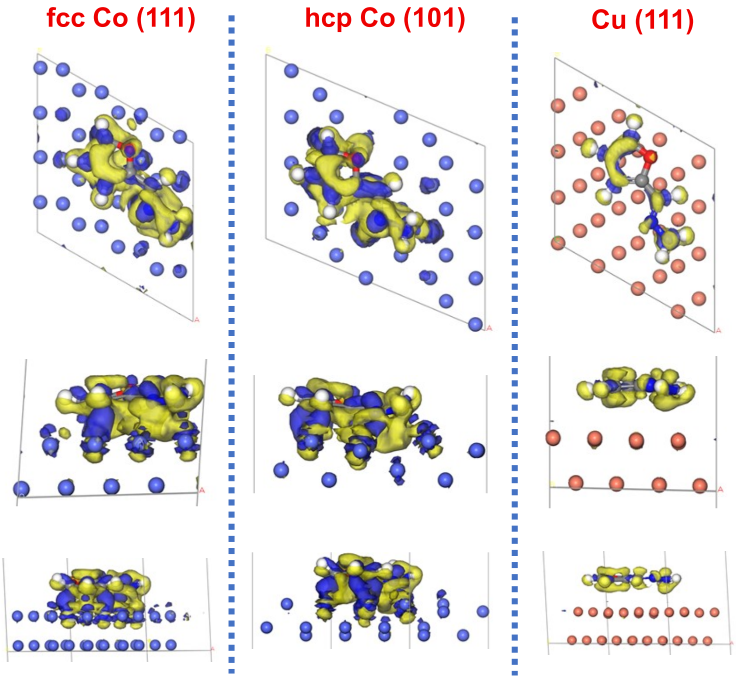

Fig. S7 The charge density difference map for adsorbed int. 3 on Co (fcc-111), Co (hcp-101), and Cu (fcc-111).

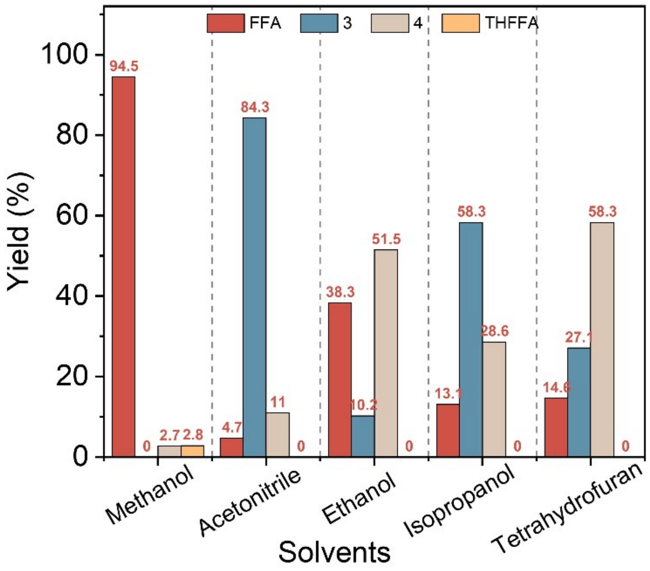

Fig. S8 Effects of solvent on the FAL reductive amination. Reaction conditions: FAL 0.24 mmol, methanol 4 mL, CoCu@CoCuO$_x$ 30 mg, 30 ^{o}C, 12 h. $N_2H_4{\cdot}H_2O$ 2 mmol. Note: FAL was fully converted.

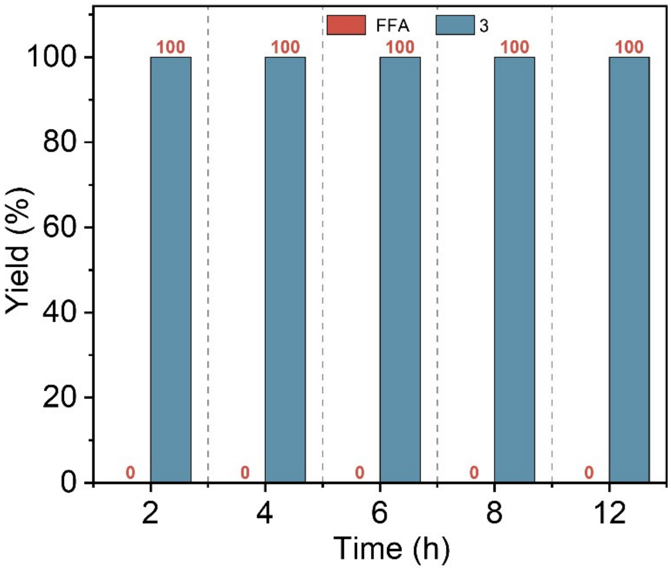

Fig. S9 Time curves of FAL reductive amination over Cu@CuO$_x$. Reaction conditions: FAL 0.24 mmol, $N_2H_4 \cdot H_2O$ 2 mmol, catalyst 30 mg, methanol 4.0 mL, H_2 3 MPa, 30 ^{o}C, 12 h. Note: FAL was fully converted.

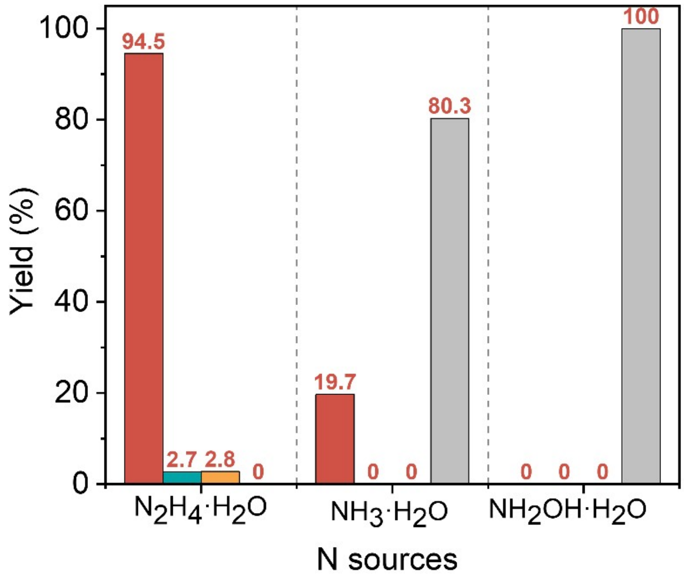

Fig. S10 Effects of nitrogen source on the FAL reductive amination. Reaction conditions: FAL 0.24 mmol, methanol 4 mL, CoCu@CoCuO$_x$ 30 mg, 30 ^{o}C, 12 h. nitrogen source 2 mmol, H_2 3 MPa. Note: FAL was fully converted.

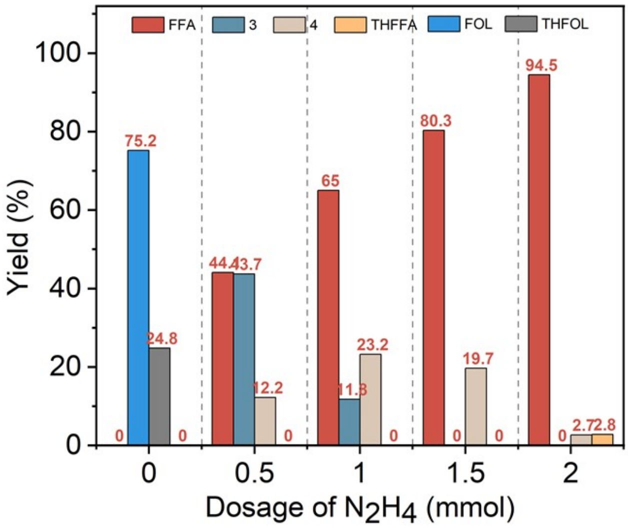

Fig. S11 Effects of hydrazine hydrate amount on FAL reductive amination. Reaction conditions: FAL 0.24 mmol, CoCu@CoCuO$_x$ 30 mg, nitrogen source 2 mmol, methanol 4 mL, H_2 3 MPa, 30 ^{o}C, 12 h.

Fig. S12 Effects of catalyst amount on FAL reductive amination. Reaction conditions: FAL 0.24 mmol, catalyst: CoCu@CoCuO$_x$, $N_2H_4{\cdot}H_2O$ 2 mmol, methanol 4 mL, H_2 3 MPa, 30 °C, 12 h.

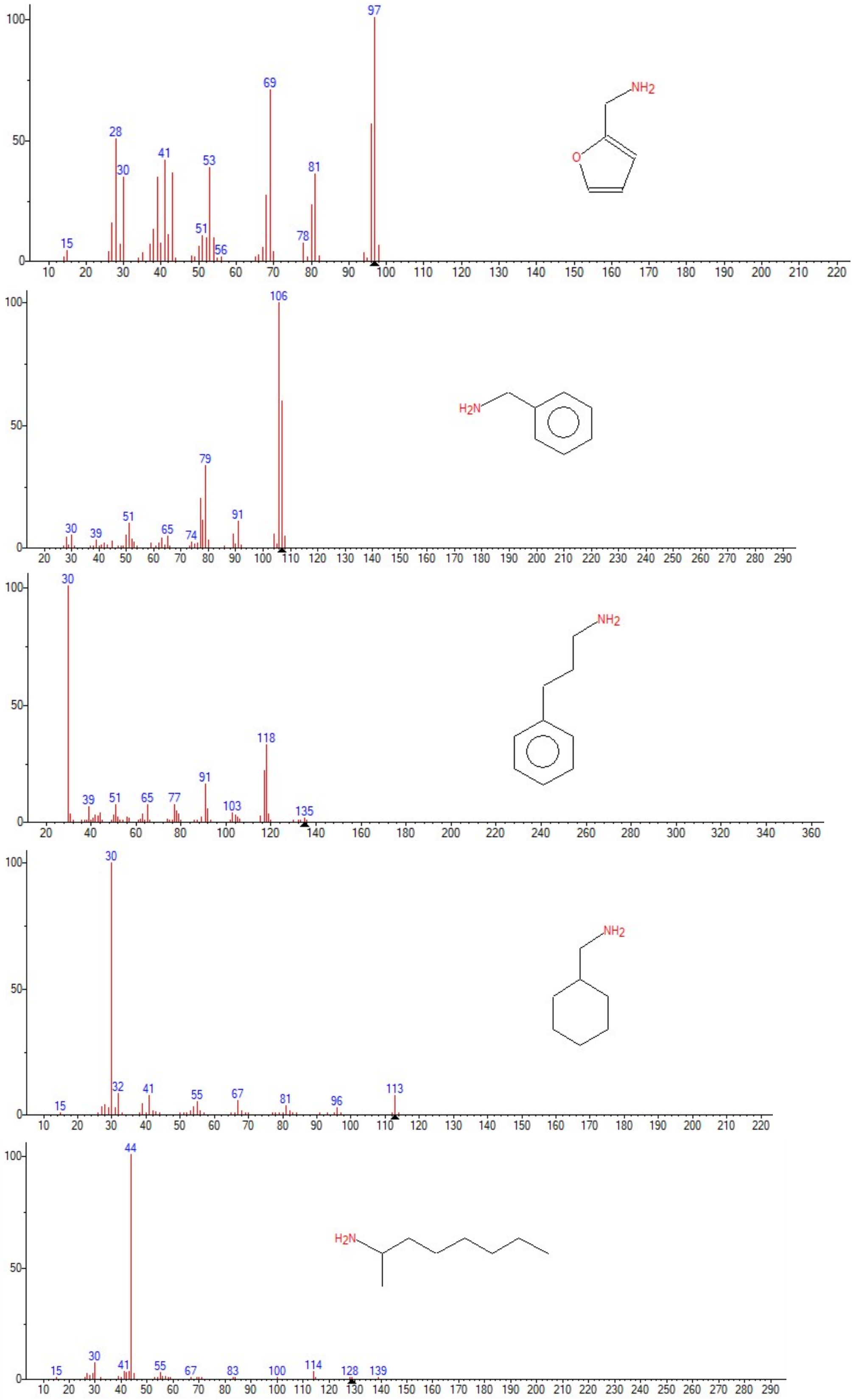

Fig. S13 MS of various amines.

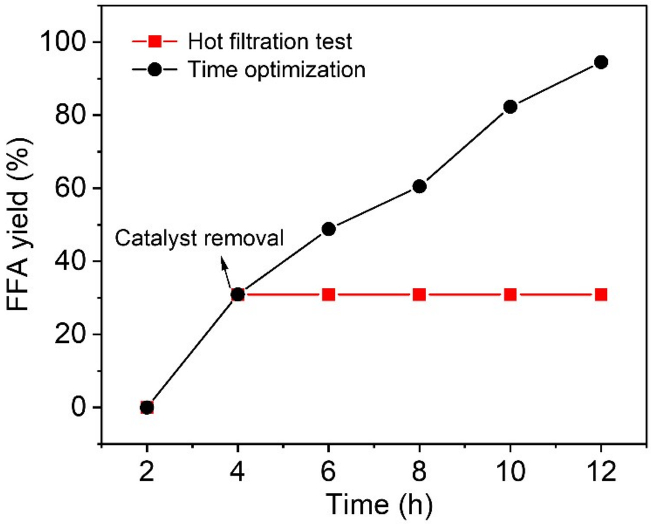

Fig. S14 Heat filtration experiment for CoCu@CoCuO$_x$. Reaction conditions: FAL 0.24 mmol, CoCu@CoCuO$_x$ 30mg, $N_2H_4 \cdot H_2O$ 2 mmol, methanol 4 mL, 3 MPa H_2, 30 ^oC.

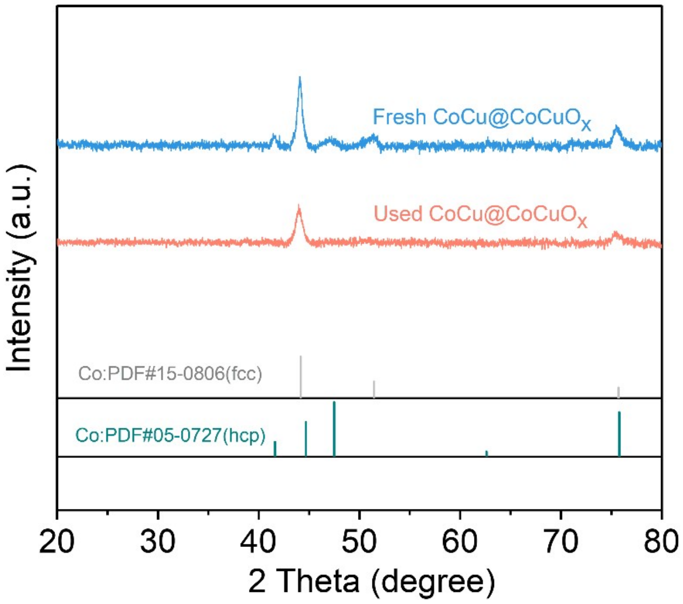

Fig. S15 XRD pattern of the spent catalyst.

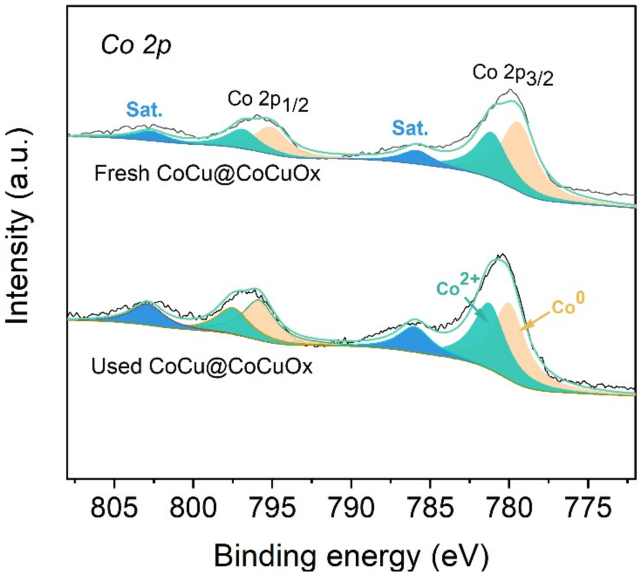

Fig. S16 Co 2p XPS spectra of the spent catalyst.

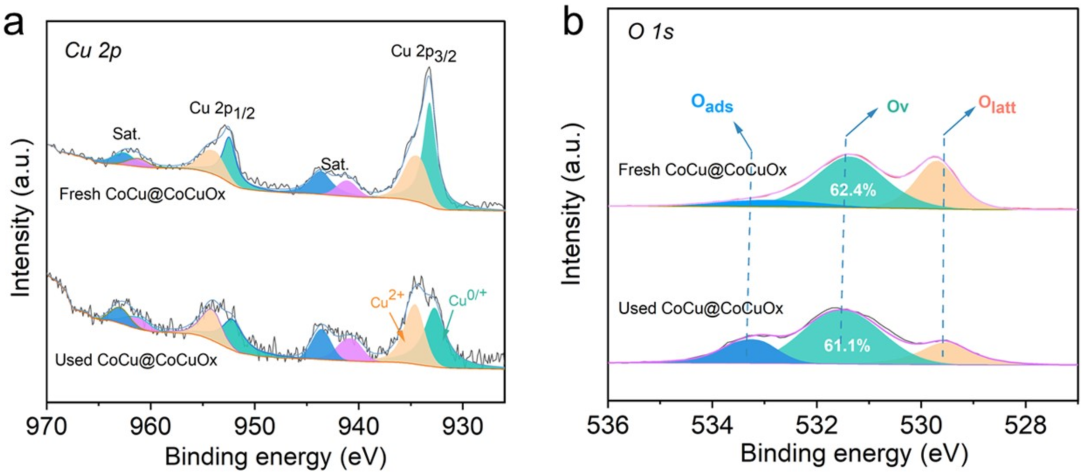

Fig. S17 (a) Cu 2p and (b) O 1S XPS spectra of the spent catalyst.

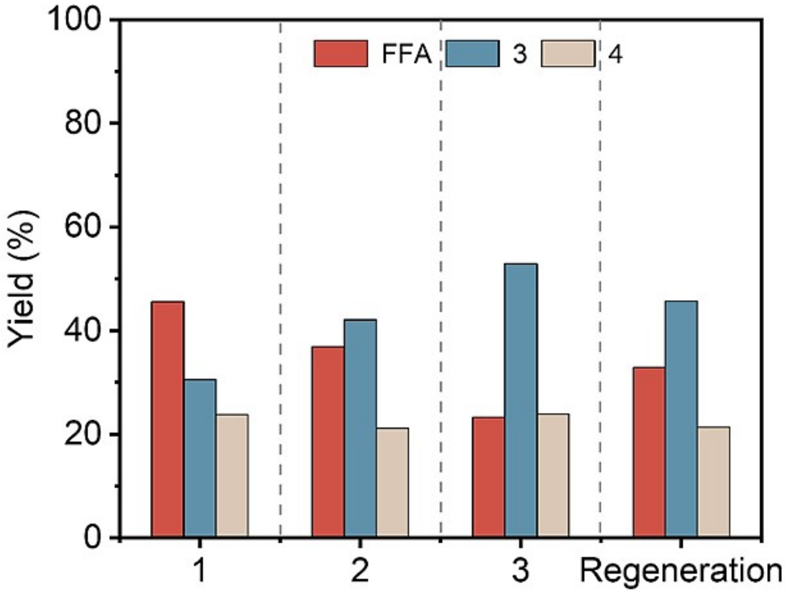

Fig. S18 Catalyst recycling at low FFA yield and subsequent regeneration via in-situ reduction.

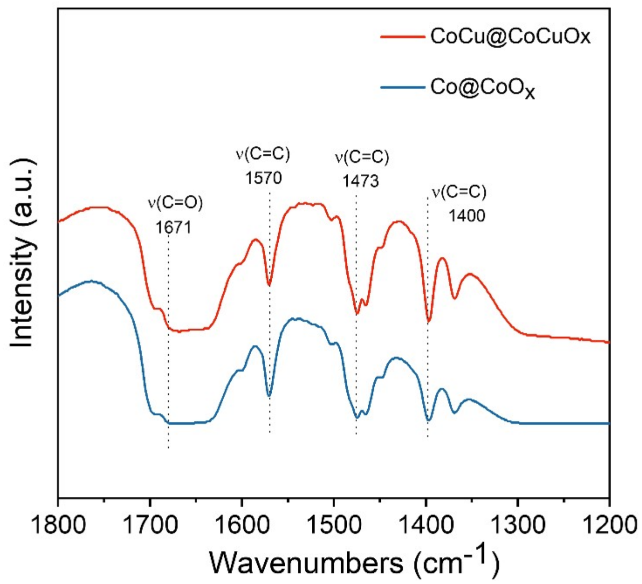

Fig. S19 In-situ FAL-absorbed FTIR spectra in absence of NH_3/H_2 on CoCu@CoCuO$_x$ and Co@CoO$_x$ catalysts.

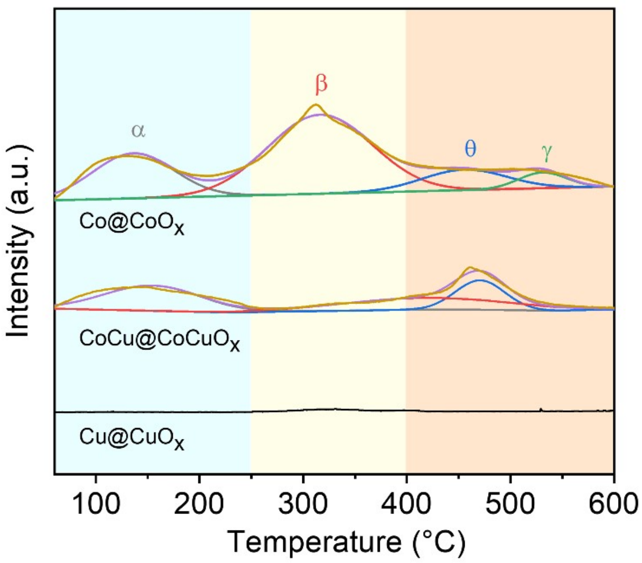

Fig. S20 NH_3-TPD profiles of Co@CoO$_x$, CoCu@CoCuO$_x$ and Cu@CuO$_x$.

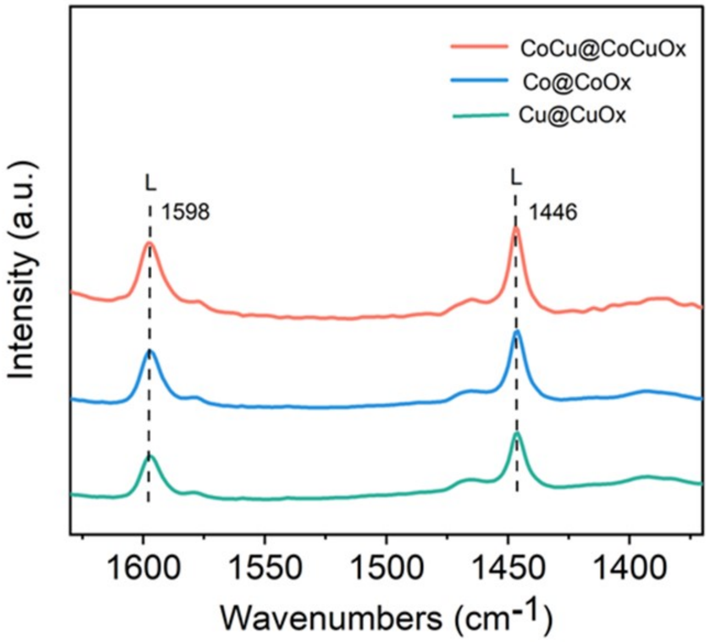

Fig. S21 Py-FTIR spectra of various catalysts.

Table S1 Physical properties of various catalysts.

Catalysts	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Co (wt. %) [a]	Cu (wt. %)
Co@CoO$_x$	24.1	0.160	24.9	72.4	-
CoCu@CoCuO$_x$	19.7	0.073	23.8	62.9	16.1
Cu@CuO$_x$	0.967	-	21.8	-	76.8

Table S2 Physical properties of various catalysts.

Catalysts	O 1s (%)	Co 2p (%)	Cu 2p (%)	Co^0:Co^{2+} ratio	$Cu^{0/+}$:Cu^{2+} ratio	O_v percentage （%）
Co@CoO_x	62.1	38.5	-	0.47:1	-	48.2
CoCu@$CoCuO_x$	62.0	30.0	8	1.49:1	1.58:1	62.4
Cu@CuO_x	61.4	-	38.6	-	1.86:1	42.4

Table S3 Charge distribution for adsorbed int. 3 on different crystal facets.

	Co (fcc-111)	Co (hcp-101)	Cu (fcc-111)
Charge on adsorbed complexes 3 (e)	0.1714	0.0917	0.0154
Charge on catalyst (e)	-0.1746	-0.0899	-0.0182

Table S4 Performance comparison with literature reports for FAL reductive amination.

Catalyst	Metals	N source	P_{H2} (MPa)	T (°C)	t (h)	Yield (%)	FFA productivity [a] （mmol·g^{-1}·h^{-1}）	Ref.
Ru/BNC	Noble metals	N_2H_4	2	80	16	99	0.75	[1]
0.3wt%Pt/TiO_2-A		N_2H_4	/	130	7	88	0.19	[2]
Co@CoO	Non-noble metals	N_2H_4	3	60	4	96.4	1.92	[3]
Ni/meso-Al_2O_3-600		N_2H_4	/	100	12	92	3.59	[4]
CoCu@CoCuO_x		**N_2H_4**	**3**	**30**	**12**	**94.5**	**0.63**	**This work**
CoCu@CoCuO_x[b]		**N_2H_4**	**3**	**100**	**1**	**88**	**52.8**	**This work**

[a] FFA productivity rate = molar amount of FFA/mass of catalyst/reaction time.

[b] Reaction conditions: FAL (1.2 mmol), catalyst (20 mg), $N_2H_4 \cdot H_2O$ (10 mmol), MeOH (8.0 mL), H_2 (3 MPa), 100 °C, 1 h.

References

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