Supporting Information

Copper-Cobalt Alloy Nanonets as Superior Catalysts for Higher Alcohols Synthesis from Syngas

Chao Huang,[‡a] Peiyu Ma,[‡a] Ruyang Wang,[a] Wenjie Li,[a] Jingyan Wang,[a] Hongliang Li,[a] Yisheng Tan,[b] Lei Luo,*[a] Xu Li*[a] and Jun Bao[a]

[a]National Synchrotron Radiation Laboratory, Collaborative Innovation Center of Chemistry for Energy Materials, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230029, Anhui, China

[b]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

*Corresponding author. E-mail: luol@ustc.edu.cn (L.L.); uxil@ustc.edu.cn (X.L.);
‡These authors contributed equally.

Calculation of catalyst evaluation:

CO conversion, the selectivity of alcohols and STY were calculated according to the following equations:

$$X_{CO} = \frac{CO_{in} - CO_{out}}{CO_{in}}$$

$$S_i = \frac{n_i}{n_{CO_2} + n_{CH} + \sum\left(n_{c_j}\right)_{Alc}} \times 100\%$$

$$STY_{Alc} = \frac{m_{liquid} \times (1 - w_{H_2O})}{m_{cat} \times t} = {g}/{\left(kg_{cat} \cdot h\right)}$$

where CO_{in} and CO_{out} are the moles of CO in the feed-gases and off-gases, respectively; n, i represents the number of carbon atoms and moles of a carbon-containing product, respectively; where the m_{liquid} represents the mass of liquid product collected; mcat represents the quality of the catalyst; W_{H_2O} represents the mass fraction of water in the collected liquid product; j indices carbon number of j alcohol.

The alloying degree of CuCo in the catalysts is determined by the following equation:

$$a = \frac{\sqrt{2}\lambda}{\sin\theta_{max}}$$

$$X_{Cu} = \frac{a_{CuCo} - a_{Co}}{k}$$

$$Cu_{alloy} = \frac{X_{Cu}}{(1 - X_{Cu})(Cu/Co)_{actu}}$$

where θ_{max} is the strongest diffraction peak position. λ is the is the wavelength of the X-ray in the characterization of XRD. a_{CuCo} and a_{Co} represent the lattice parameter of catalysts and k is a constant = 0.352. $(Cu/Co)_{actu}$ is the actual Cu/Co atomic ratio.

Supplementary Figures:

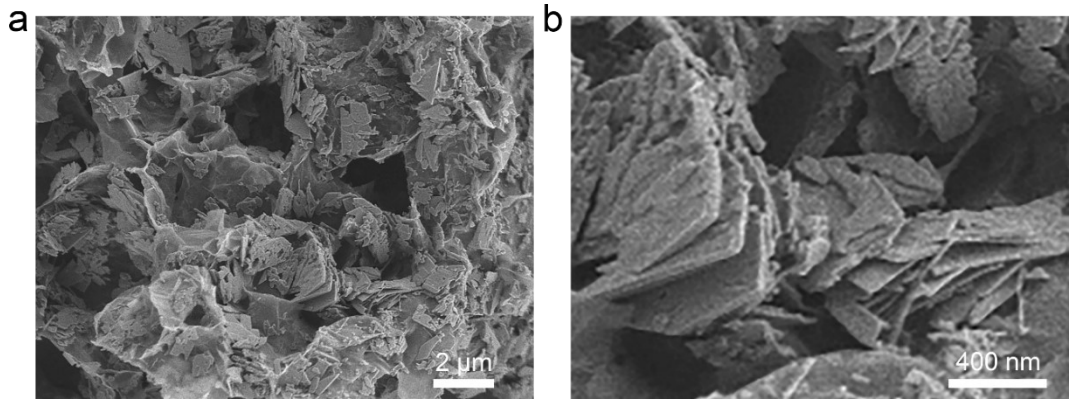

Fig. S1 SEM image of the CuCo carbonate nanoplatelets with GO.

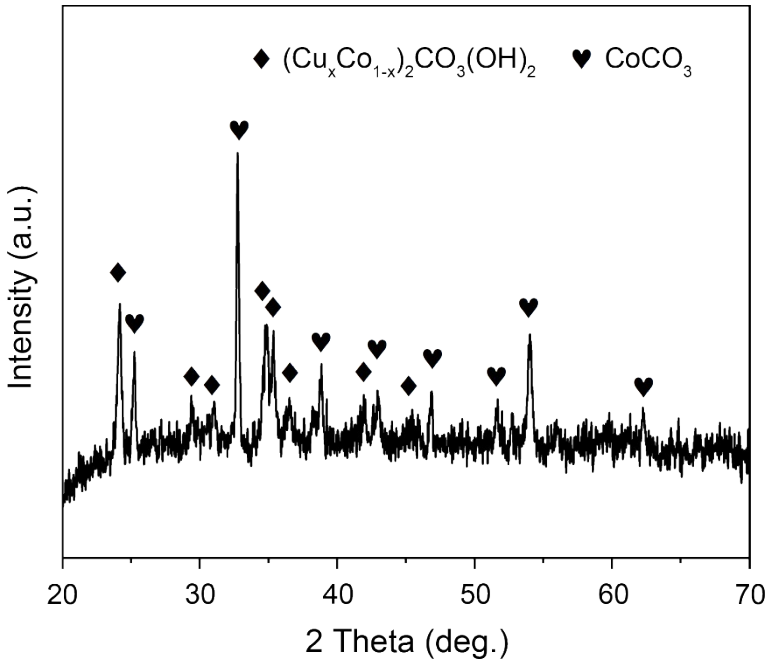

Fig. S2 XRD pattern of the CuCo carbonate nanoplatelets with GO.

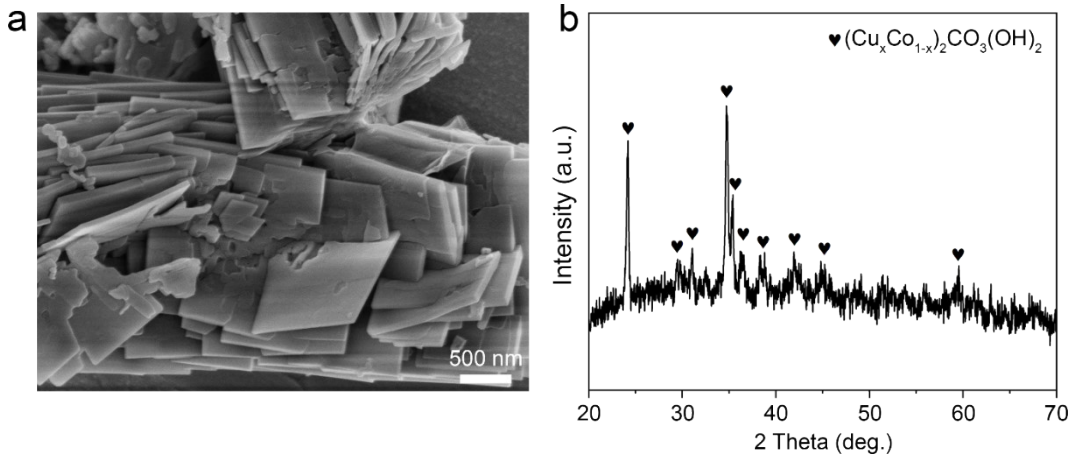

Fig. S3 SEM image (a) and XRD pattern (b) of the CuCo carbonate nanoplatelets without GO.

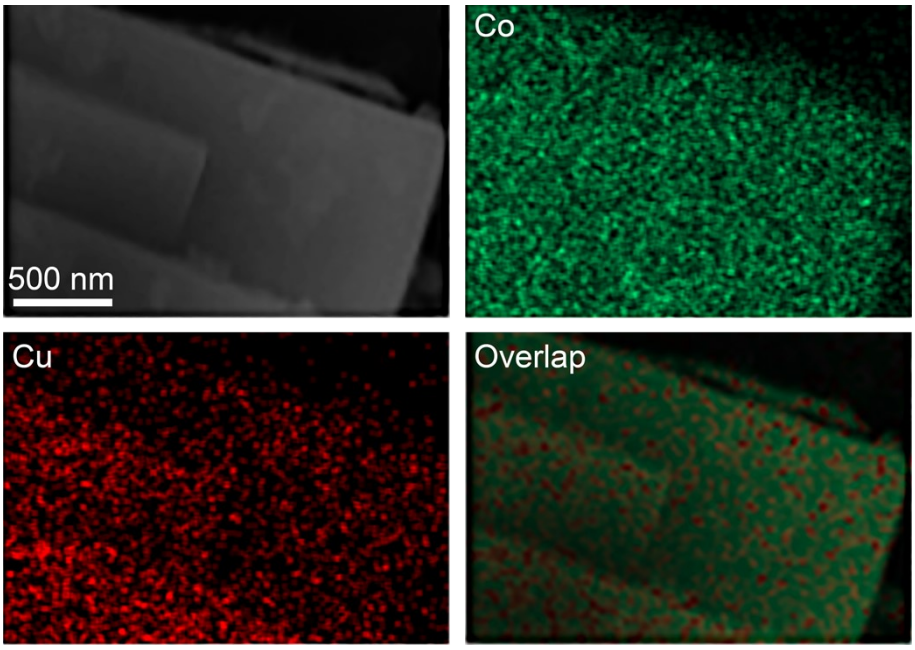

Fig. S4 EDX-mapping of sample prepared by Cu/Co nitrates precursor.

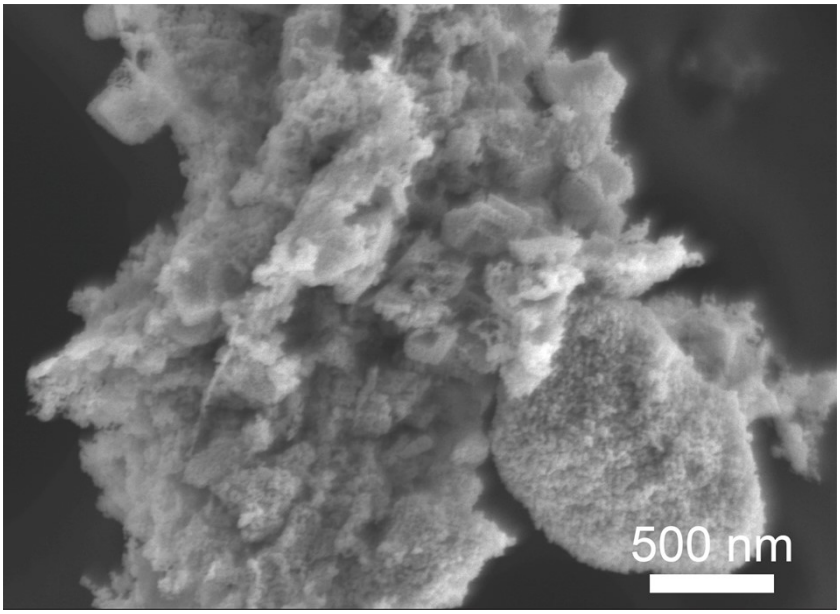

Fig. S5 SEM image of sample prepared by Cu/Co carbonates precursor.

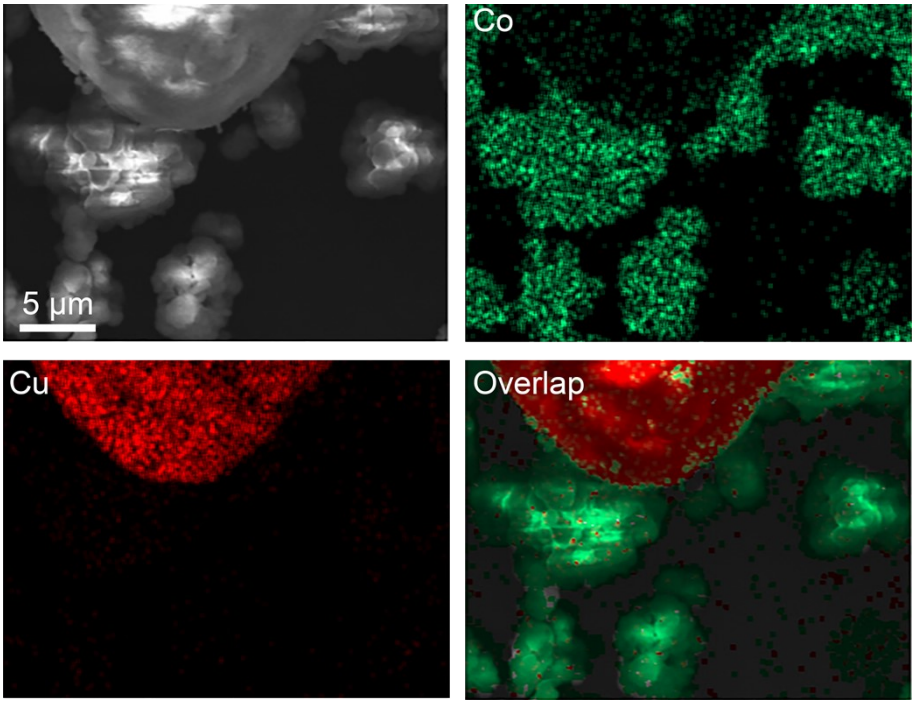

Fig. S6 EDX-mapping of sample prepared by Cu/Co carbonates precursor.

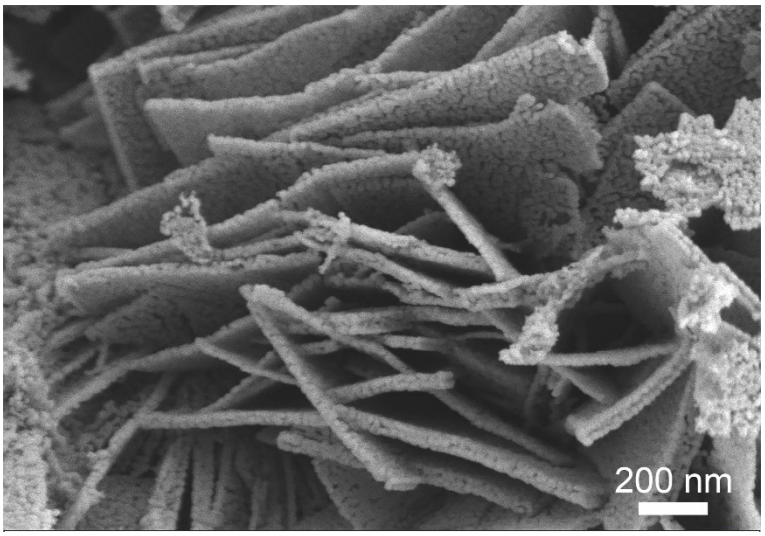

Fig. S7 SEM image of CuCo-400 oxide precursor.

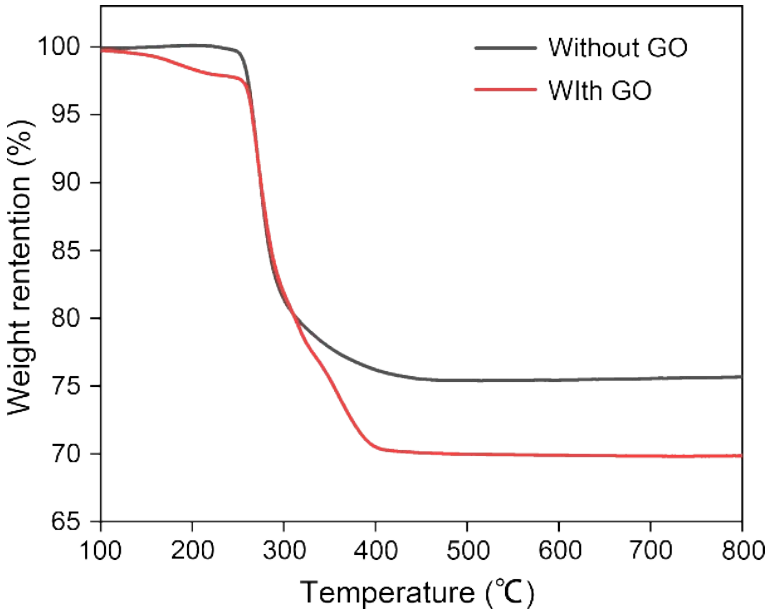

Fig. S8 TG curves of CuCo carbonate nanoplatelets.

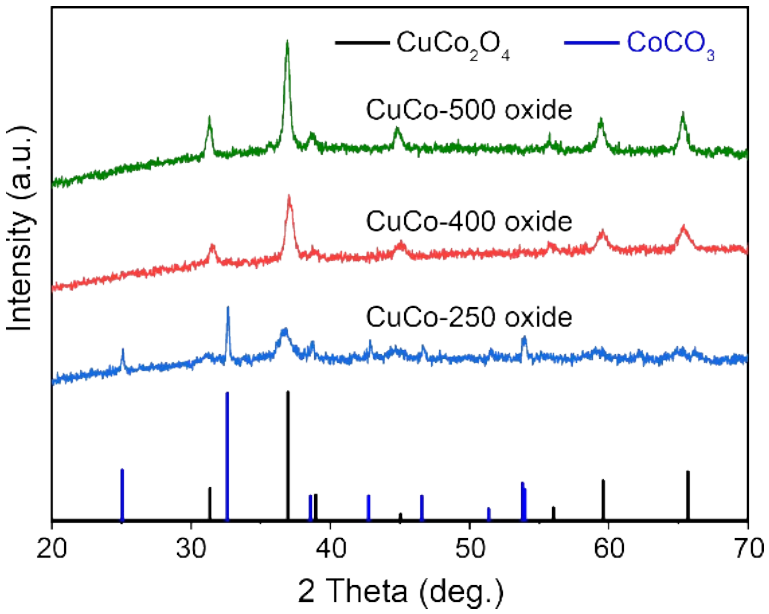

Fig. S9 XRD patterns of the CuCo-X oxide precursors.

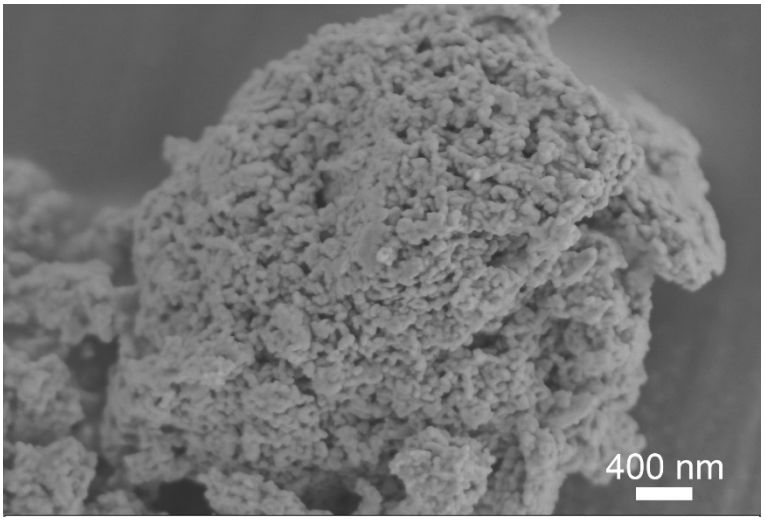

Fig. S10 SEM image of CuCo-500 oxide precursor.

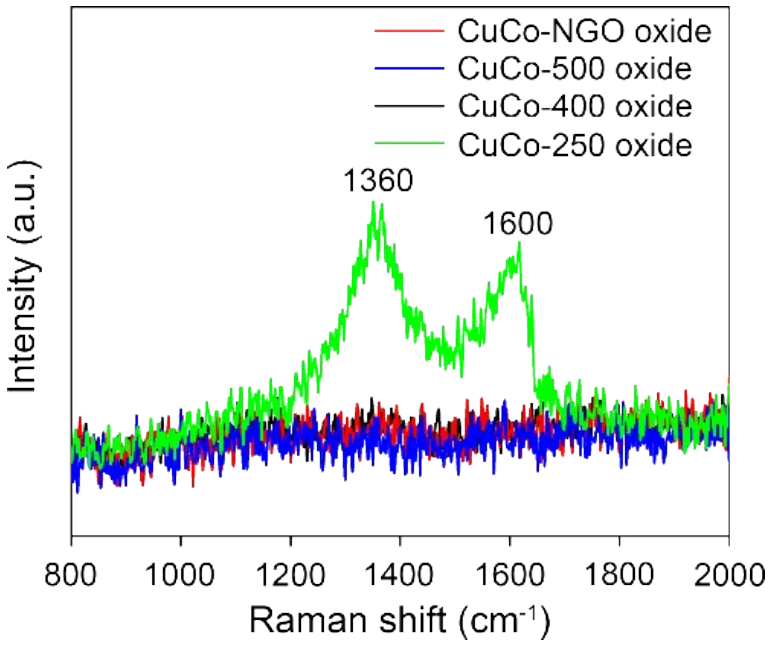

Fig. S11 Raman spectra of catalysts oxide precursors.

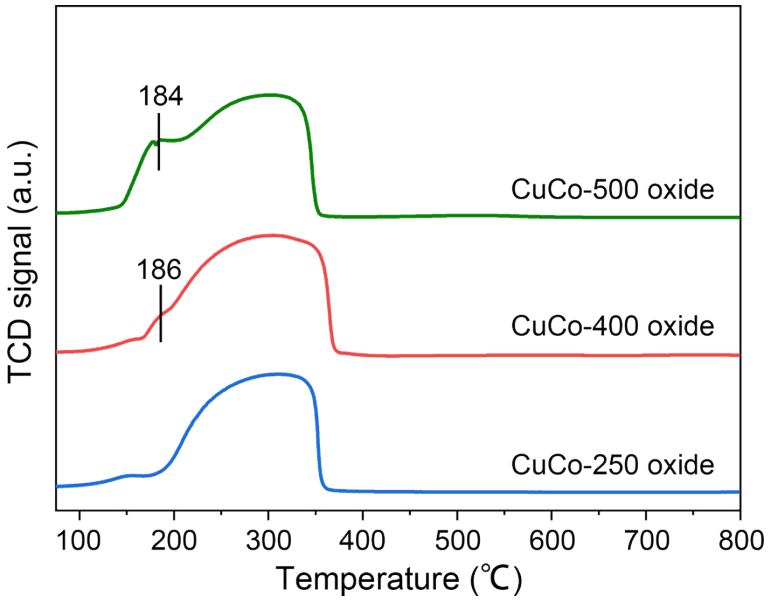

Fig. S12 H_2-TPR profiles of CuCo-X oxide precursors.

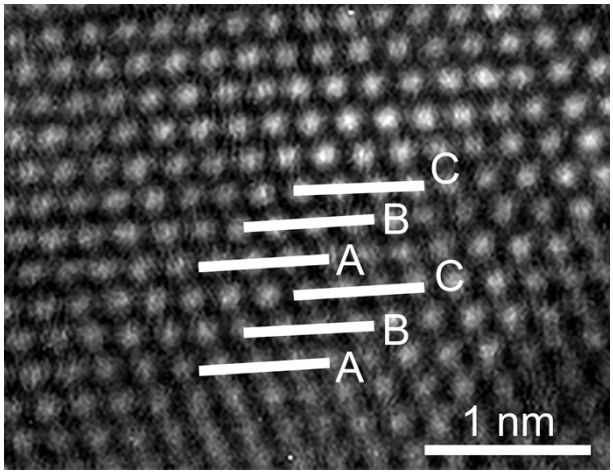

Fig. S13 HRTEM of CuCo-400.

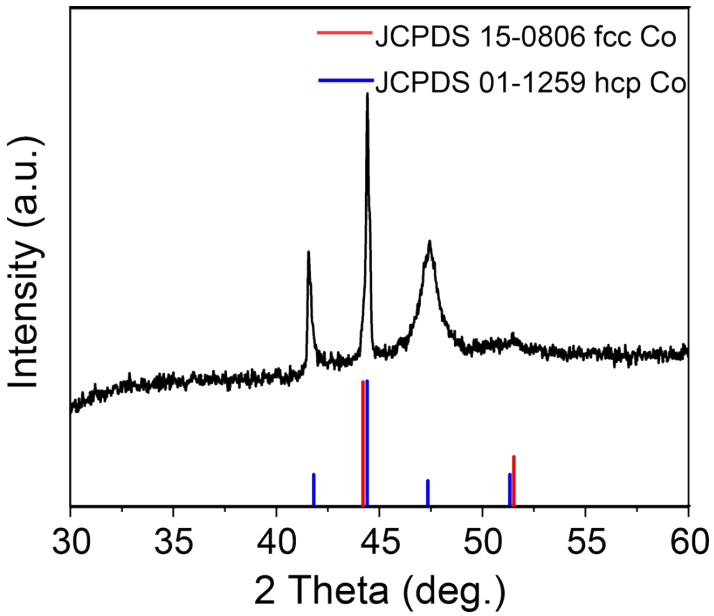

Fig. S14 XRD patterns of Co-400 catalyst.

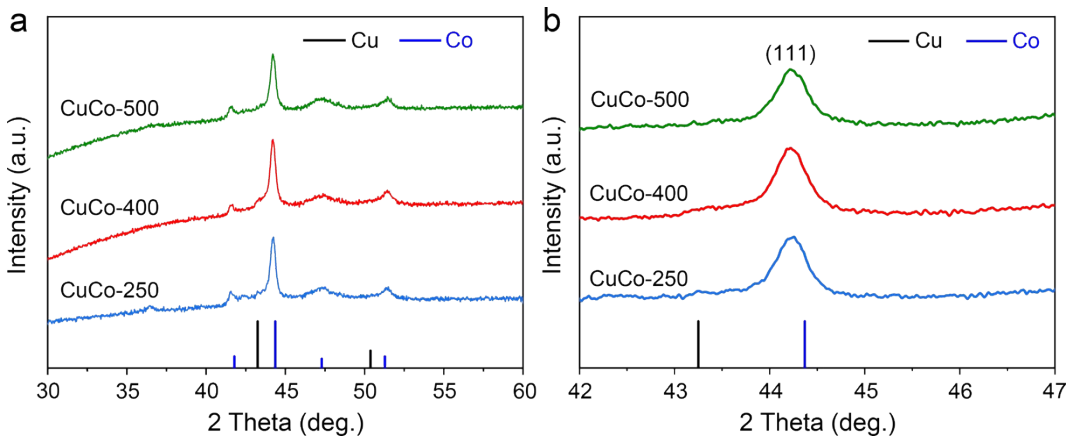

Fig. S15 (a) XRD patterns of reduced catalysts; (b) XRD patterns in the 42-47° region of (a).

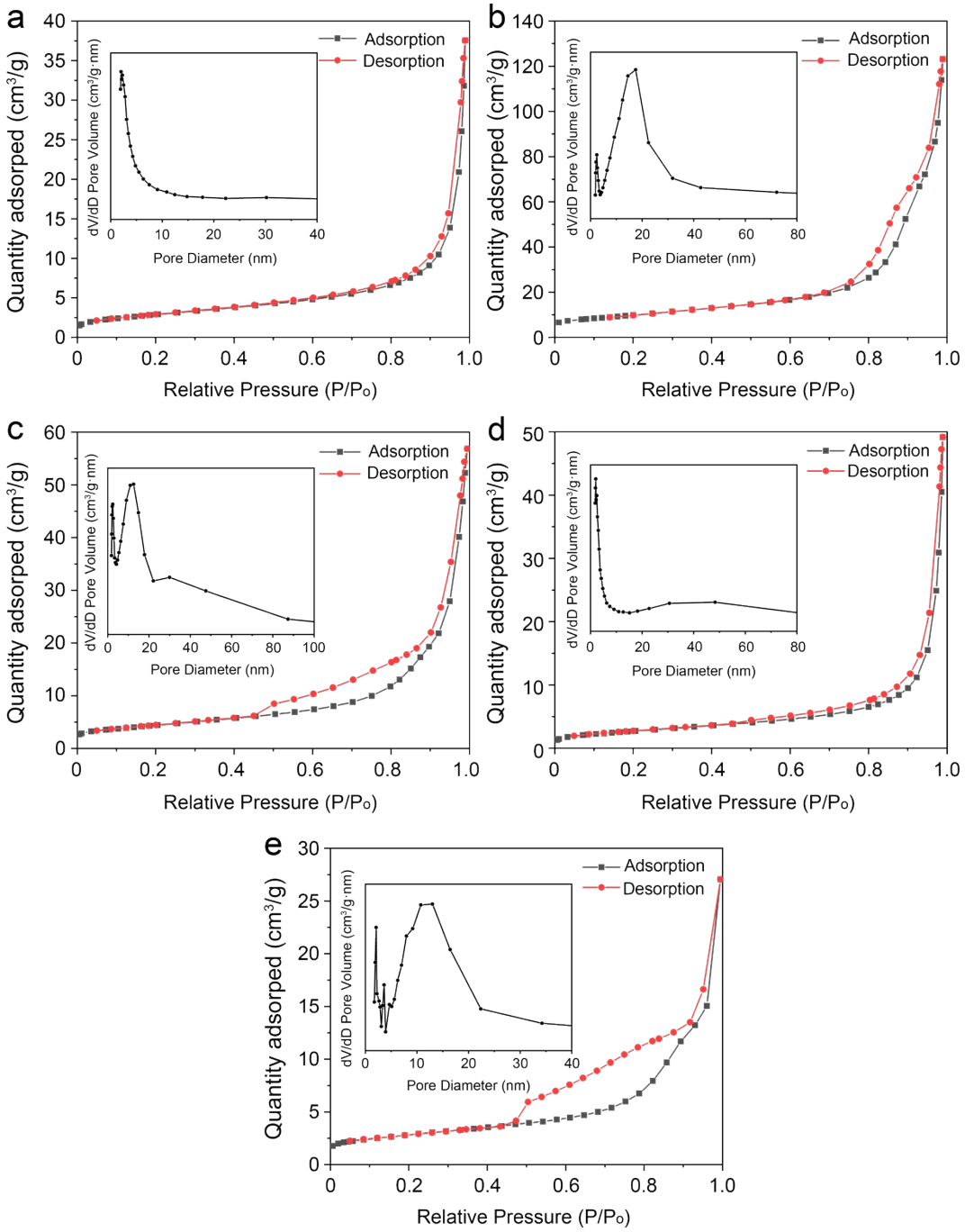

Fig. S16 N_2 adsorption-desorption isotherm of CuCo-250 (a), CuCo-400 (b), CuCo-500 (c), CuCo-NGO (d), CuCo-CP (e). The inset shows the BJH pore size distribution curve.

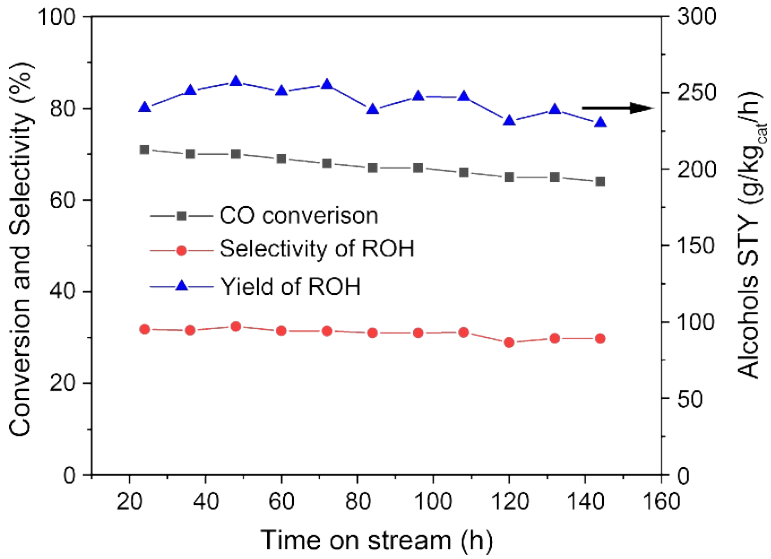

Fig. S17 Stability test over the CuCo-400 catalyst with the reaction time on stream under the following conditions: T = 260 ℃, P = 5 Mpa, WHSV = 2400 mL/(g_{cat}·min), and H_2/CO = 2.

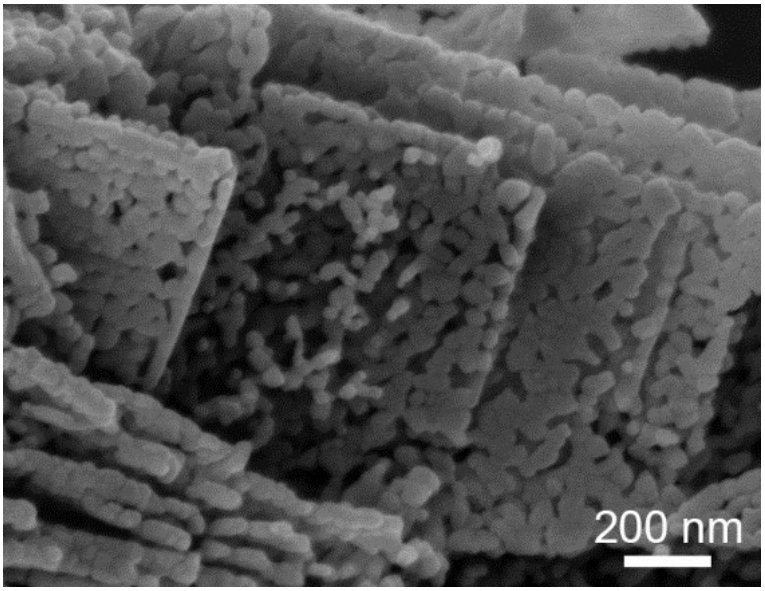

Fig. S18 SEM image of the CuCo-400 catalyst.

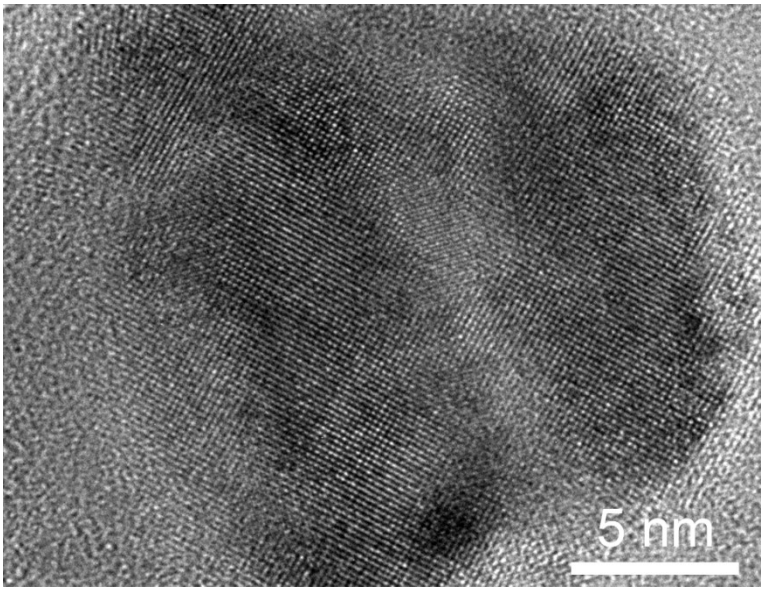

Fig. S19 HRTEM image of CuCo-CP catalyst.

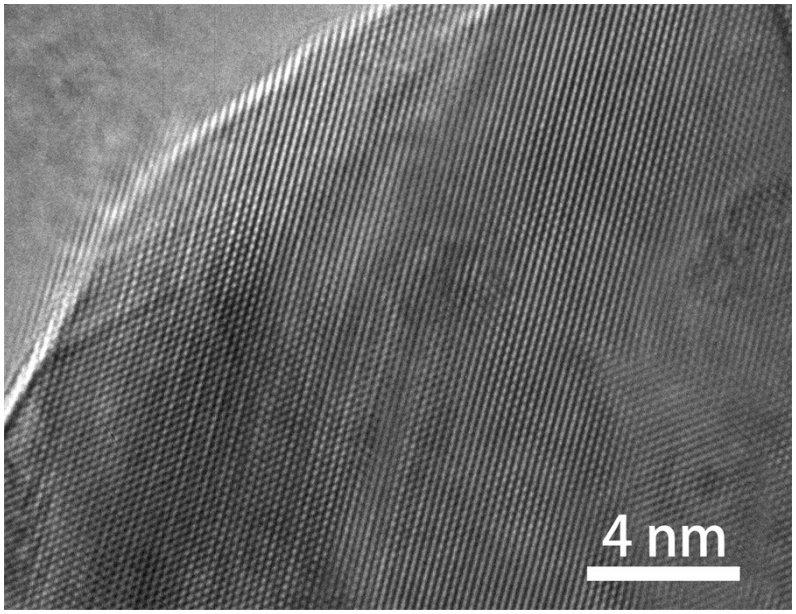

Fig. S20 HRTEM image of CuCo-CP catalyst.

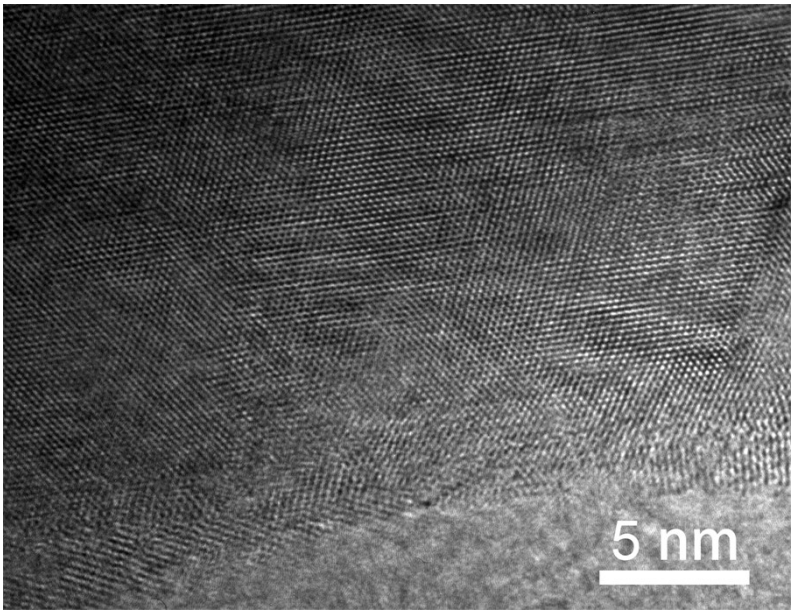

Fig. S21 HRTEM image of CuCo-500 catalyst.

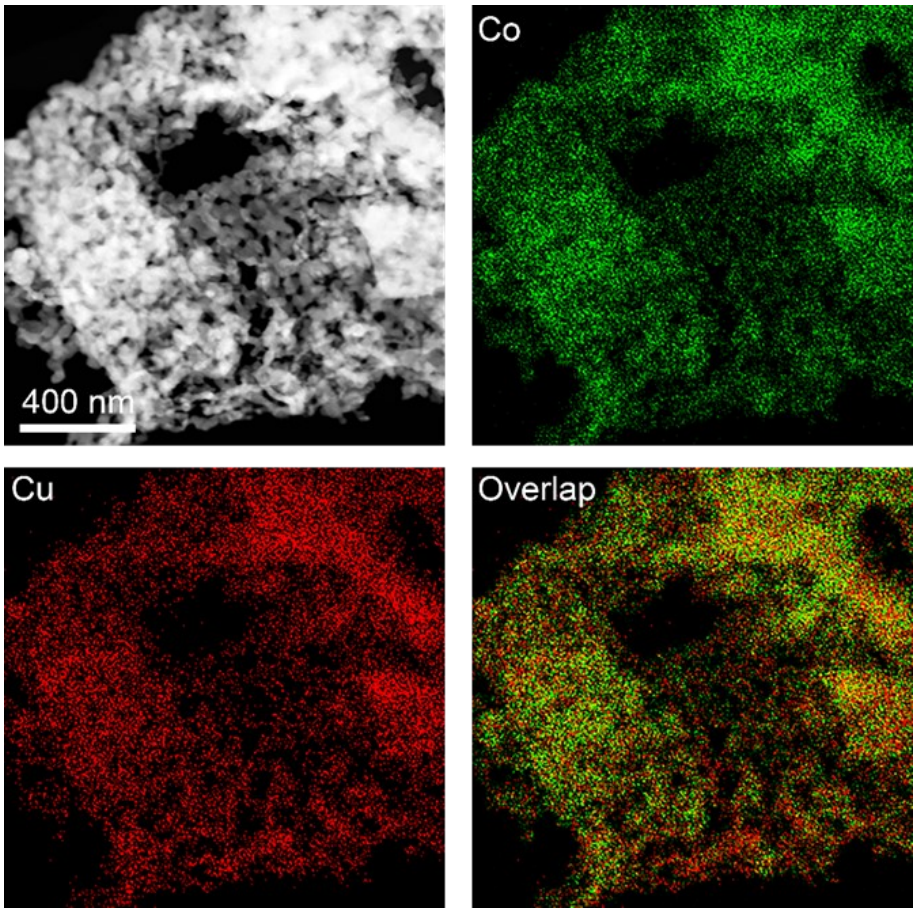

Fig. S22 EDX mappings of CuCo-400.

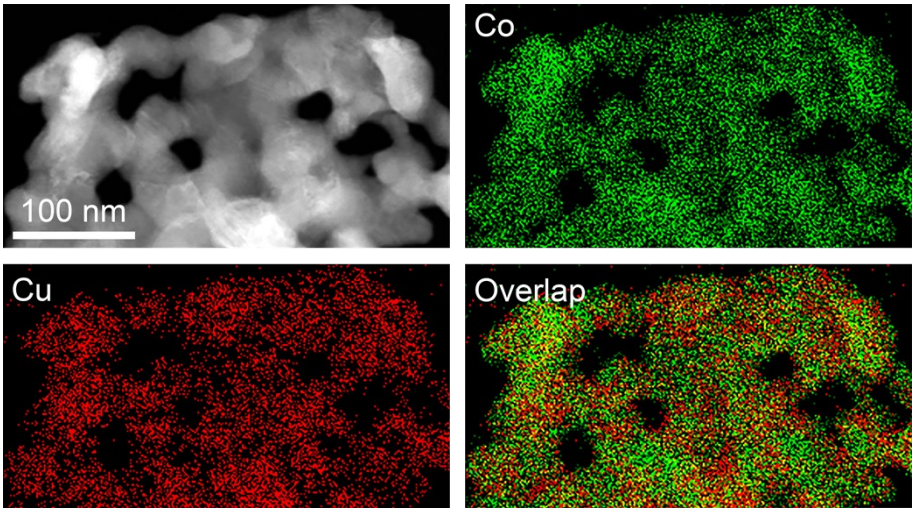

Fig. S23 EDX mappings of CuCo-400.

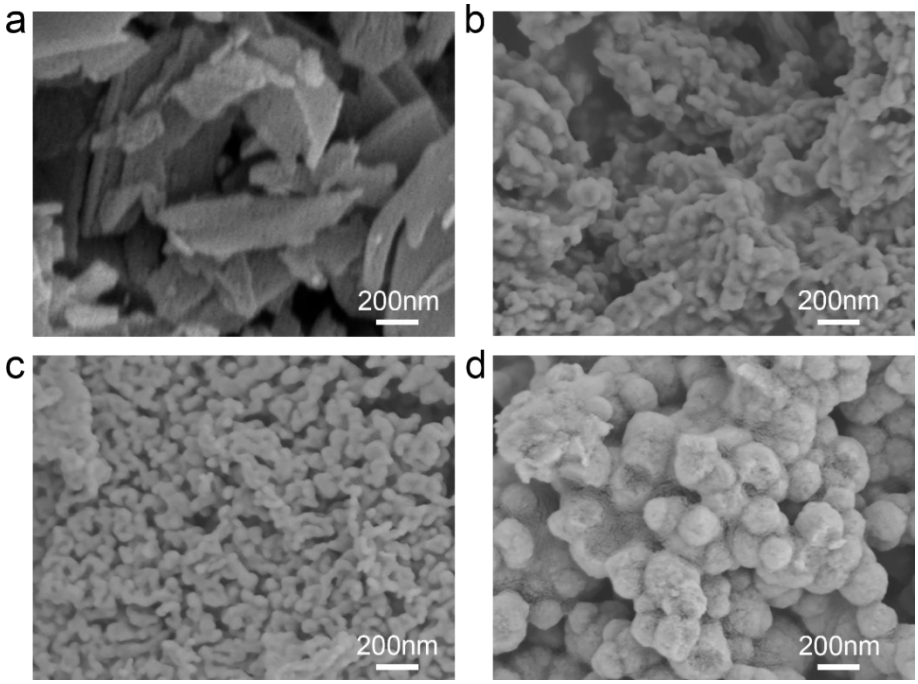

Fig. S24 SEM image of (a) CuCo-250, (b) CuCo-500, (c) CuCo-NGO and (d) CuCo-CP.

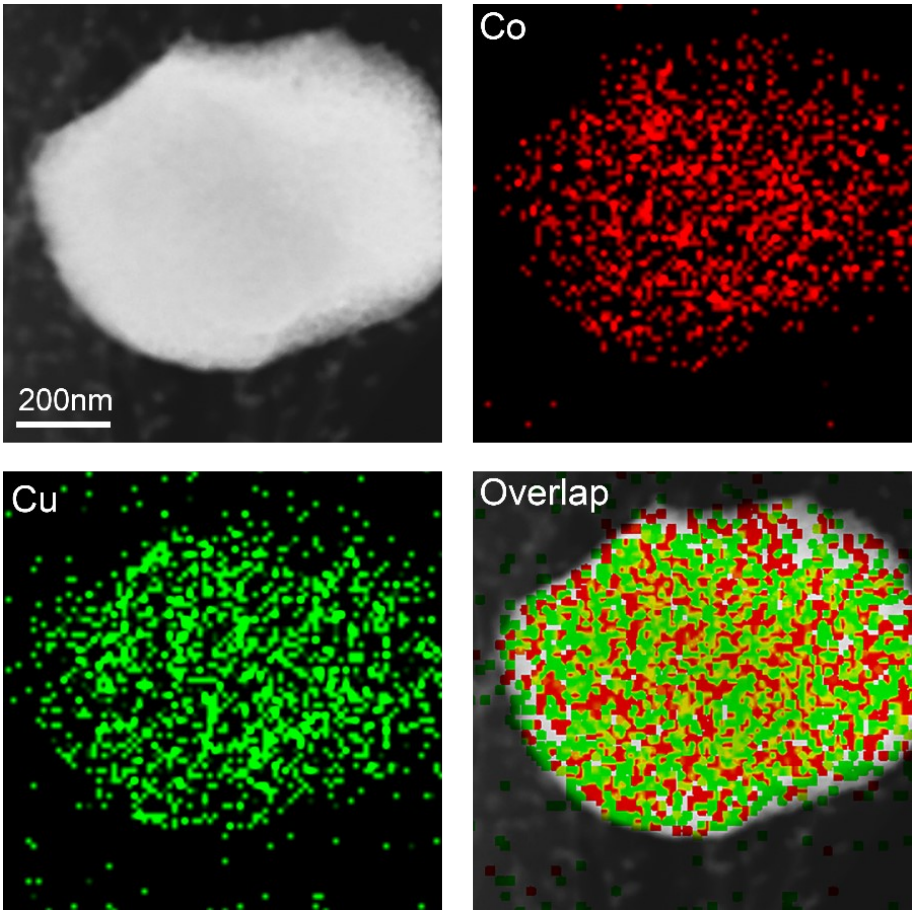

Fig. S25 EDX mappings of CuCo-CP.

Tab. S1 Textural properties of the catalysts.

Catalysts	BET surface area (m^2/g)	Pore volume (cm^3/g)
CuCo-250	10.5	0.03
CuCo-400	35.4	0.19
CuCo-500	15.7	0.06
CuCo-NGO	9.5	0.01
CuCo-CP	9.9	0.02

Tab. S2 The carbon balance of catalysts in HAS reaction.

Catalysts	carbon balance (%)
CuCo-250	95.6
CuCo-400	95.8
CuCo-500	98.9
CuCo-NGO	94.3

Tab. S3 Catalytic performance of different CuCo-based catalysts for HAS.

Catalysts	T (°C)	P (Mpa)	GHSV (h^{-1}) or WHSV (mL $g_{cat}^{-1}min^{-1}$)	CO. Conv. (%)	S_{ROH} (%)	$C_{2+}OH$/ ROH	STY of $C_{2+}OH$ ($g/kg_{cat}/h$)	Ref.
3Cu-5Co/(Mn−Al)	260	5.0	5000	33.4	39.7 (wt.%)	57.3 (wt.%)	63.0 ($mg/mL_{cat}/h$)	1
Cu_2Co_1Al	270	2.5	7500	29.2	44.0	59.3	—	2
Cu-Co/(5Mn/3Al)	260	5.0	5000	32.9	35.3	56.0	—	3
$5Co2.5Cu/SiO_2$	260	5.0	14900	2.0	11.9	34.9	—	4
CuCo	270	2.5	7500	36.2	40.7	54.9	—	5
$Cu_{0.25}Co_{0.75}$	250	3.0	3900	71.3	13.8	81.5	132.4	6
$15Cu5Co/Al_2O_3$	250	2.0	1800	23.2	23.3	79.3	198.0	7
$CuCoMg_{0.5}$	270	2.5	7500	30.7	46.9	60.3	—	8
CuCo-400	260	5.0	2400	66.5	31.5	92.3 (wt.%)	228.2	This work

Tab. S4 The Cu/Co ratios on catalysts surface calculated from the XPS results.

Catalysts	Co^0 (Atomic %)	Co^{2+} (Atomic %)	$Cu^{0/+}$ (Atomic %)
CuCo-250	42.5	31.2	26.3
CuCo-400	44.1	25.1	30.8
CuCo-500	28.0	22.3	49.7
CuCo-NGO	35.8	39.2	25.1
CuCo-CP	22.4	19.6	58.0

Tab. S5 The semi-quantification results of CoCu alloy in catalysts.

Catalysts	The degree of alloy
CuCo-250	0.237
CuCo-400	0.301
CuCo-500	0.301
CuCo-NGO	0.067

Reference

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