Electronic Supplementary Material (ESI) for Faraday Discussions
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Electronic Supplementary Information (ESI)

In-situ characterization of Co-Cu oxides for catalytic application

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Section 1: Surface components

Table ESI 1 The curve fitting results of Co $2p_{3/2}$ and its satellite of Co-Cu oxide films

Item	Name	Co_3O_4			$CuCo_2O_4$		
		Position	FWHM	% Area	Position	FWHM	% Area
Co $2p_{3/2}$	I	779.8	1.49	44.66	779.5	1.58	44.66
	II	781.1	1.74	31.25	780.9	1.70	31.25
	III	782.4	2.30	15.18	782.2	2.15	15.18
Satellites	IV	785.1	4.40	3.57	785.2	4.60	3.57
	V	789.9	3.01	5.35	789.7	3.41	5.35

Table ESI 2 The curve fitting results of Cu $2p_{3/2}$ and its satellite of Co-Cu oxide films

Item	Name	$CuCo_2O_4$			CuO		
		Position	FWHM	% Area	Position	FWHM	% Area
Cu $2p_{3/2}$	i	933.7	2.20	29.83	933.7	2.20	29.54
	ii	935.0	3.00	31.75	935.1	3.00	31.43
Satellites	iii	941.1	1.30	2.88	941.1	1.36	2.85
	iv	942.2	3.861.997	26.90	942.3	3.92	26.63
	v	944.3	1.40	5.76	944.3	1.36	5.70
Cu^{1+}		932.4	1.09	2.88	932.4	0.95	3.84

Table ESI 3 The curve fitting results of O 1s of Co-Cu oxide films

Item	Co_3O_4			$CuCo_2O_4$			CuO		
	Position	FWHM	% Area	Position	FWHM	% Area	Position	FWHM	% Area
O_{Lat}	530.12	1.177	56.35	529.77	1.200	30.24	529.81	1.095	22.77
O_{Ad}	531.54	1.741	40.10	531.96	1.932	69.76	532.07	2.476	77.23
O_{Sub}	533.24	1.705	3.55	-	-	-	-	-	-

Note: O_{Lat}, O_{Ad} and O_{Sub} refer to lattice, adsorbed and sublattice oxygen, respectively.

Tables ESI 1-3 show the curve fitting results of Co $2p_{3/2}$, Cu $2p_{3/2}$ and O 1s as well as their corresponding satellits of the prepared Co-Cu oxides. As shown in Fig. 4 in the main text, $CuCo_2O_4$ exhibits quite similar Co 2p and Cu 2p shapes to those measured for Co_3O_4 and CuO, respectively. For O 1s, a significant difference is observed in terms of components. From Co_3O_4 to CuO, the amount of lattice oxygen decreases and adsorbed oxygen increases. Moreover, a small quantity of sublattice oxygen was observed in the prepared Co_3O_4 films, while such component was not measured in $CuCo_2O_4$ and CuO samples. All fits were done according to high quality reference data published by Biesinger et al.[1, 2]

Section 2: Comparison of the catalytic performance

Table ESI 4 Overview of the catalytic performance of CO and propene oxidation with Co-Cu oxides and some catalysts in the literature

Material	Weight (mg)	Gas composition	WHSV [a] ($ml\ g^{-1}\ h^{-1}$)	T_{50} [b] (°C)	Ref.
$CuCo_2O_4$	12	1% CO/10% O_2 in Ar	75000	190	This work
Co_3O_4 thin film	12	1% CO/ 10% O_2 /89% Ar	75000	335	[3]
Pt/Al_2O_3	2/200	1% CO/1.38% O_2 in N_2	90000	333	[4]
α-Fe_2O_3 thin film	20	1% CO/10% O_2/ 89% Ar	45000	320	[5]
Bare mesh	-	1% CO/10% O_2 in Ar	-	684	This work
$CuCo_2O_4$	12	1% C_3H_6/10% O_2 in Ar	75000	330	This work
CuO	12	1% C_3H_6/10% O_2 in Ar	75000	272	[6]

Co_3O_4	12	1% C_3H_6/10% O_2 in Ar	75000	347	[3]
Co_3O_4	12	2% C_3H_6/ 20%O_2 in Ar	75000	354	[7]
$Cu_{0.72}Co_{2.28}O_4$	40	13% C_3H_6/ 52%O_2 in N_2	15000	275	[8]
$Co_{2.66}Mn_{0.34}O_4$	12	2% C_3H_6/ 20%O_2 in Ar	75000	321	[7]
α-Fe_2O_3 at 400 °C	20	1% C_3H_6/10% O_2 in Ar	45000	355	[9]
Au/Al_2O_3	200	1.5% C_3H_6/ 4% O_2 in He	22500	349	[10]
$Au/Li_2O/Al_2O_3$	200	1% C_3H_6/ 9% O_2 in He	225000	327	[11]
$Au/MgO/Al_2O_3$	200	1% C_3H_6/ 9% O_2 in He	214286	359	[11]
$La_{1.7}Sr_{0.3}CuO_4S_{0.2}$	200	0.1% C_3H_6/ 5% O_2 in N_2	30000	419	[12]
Bare mesh	-	1% C_3H_6/10% O_2 in Ar	-	529	This work

Note: [a] WHSV is weight hourly space velocity; [b] T_{50} refers to the temperatures at which 50% propene is converted.

Table ESI 4 compares the catalytic performance of the deposited Co-Cu oxides with that of the selected catalysts in the literature. Special attention is paid to the comparison of the catalytic performance with noble metals and transition metal oxides. As can be seen from the table, both noble metals and transition metal oxides present attractive results in terms of CO and propene oxidation. For CO oxidation, Co-Cu oxides exhibit lower T_{50} than Pt/Al_2O_3 and other Co-based oxides. Although Co-Cu oxides are slightly less active than CuO, their performances are comparable with the active $Au/Li_2O/Al_2O_3$ and Co_3O_4. Moreover, Co-Cu oxides own better thermal stability than CuO and Co_3O_4, demonstrating that Co-Cu binary oxides have more potential to be applied in the real catalytic oxidation processes.

Section 3: Experimental conditions

Table ESI 5 Experimental conditions for the preparation of Co-Cu oxides

Precursors	$Co(acac)_3$, $Cu(acac)_2$
Solvent	Ethanol
Concentration of precursor	5 mM
Frequency	4 Hz
Opening time	2.5 ms
Evaporation temperature	220 °C

Transportation temperature	220 °C
Substrate temperature	400 °C
Deposition pressure (mbar)	30
N_2 (SLM)	0.5
O_2 (SLM)	1.0
Substrates	Silicon, planar and bare mesh of stainless steel

Section 4: High resolution helium ion micrographs (HIM)

Additional micrographs of the $CuCo_2O_4$ films:

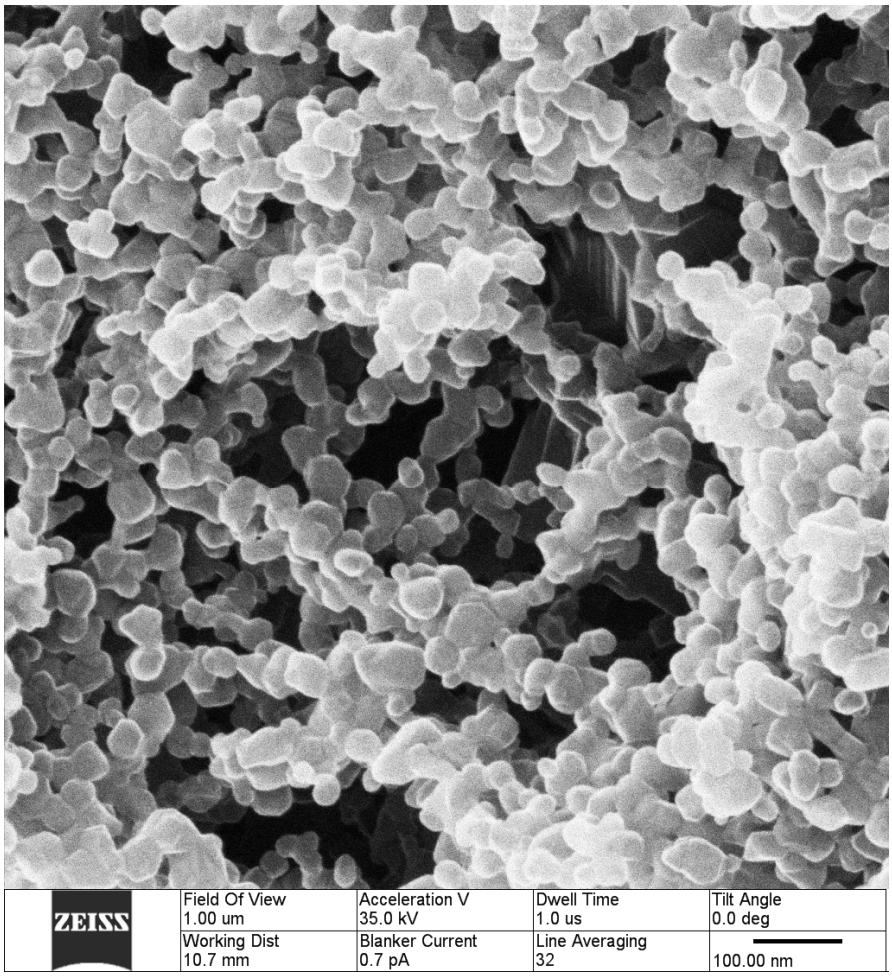

Fig. ESI 1 HIM images of $CuCo_2O_4$ films on stainless steel mesh used for catalytic test.

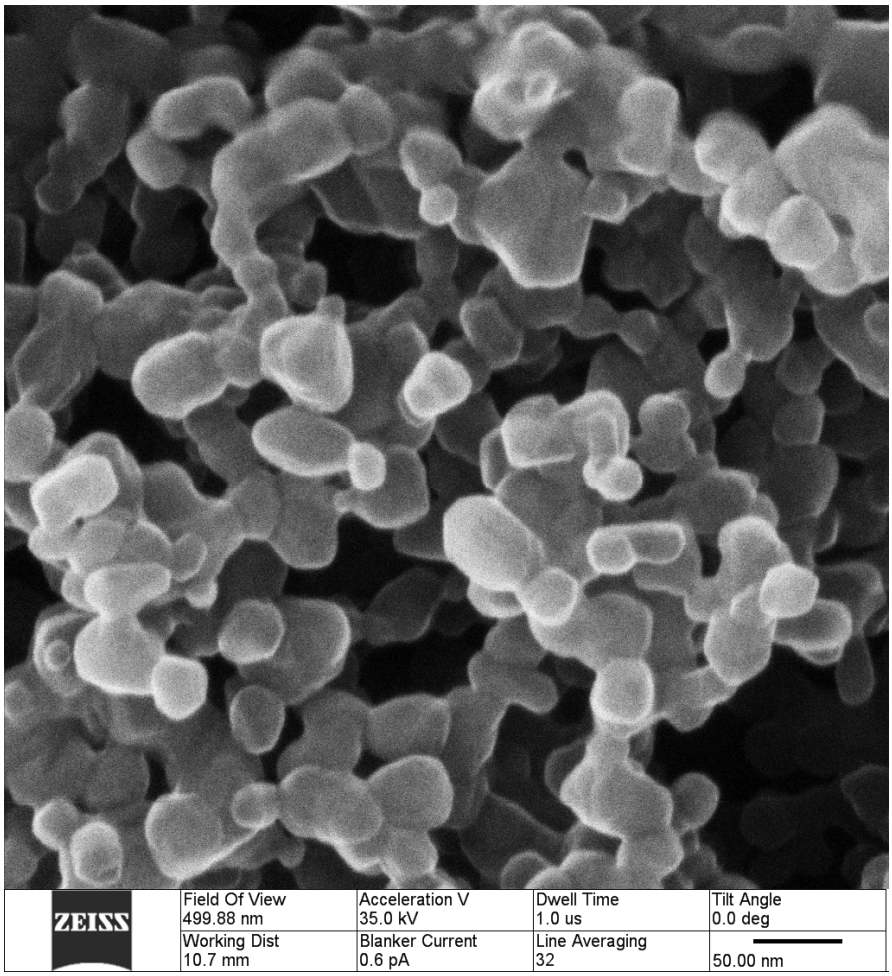

Fig. ESI 2 HIM images of $CuCo_2O_4$ films on stainless steel mesh used for catalytic test.

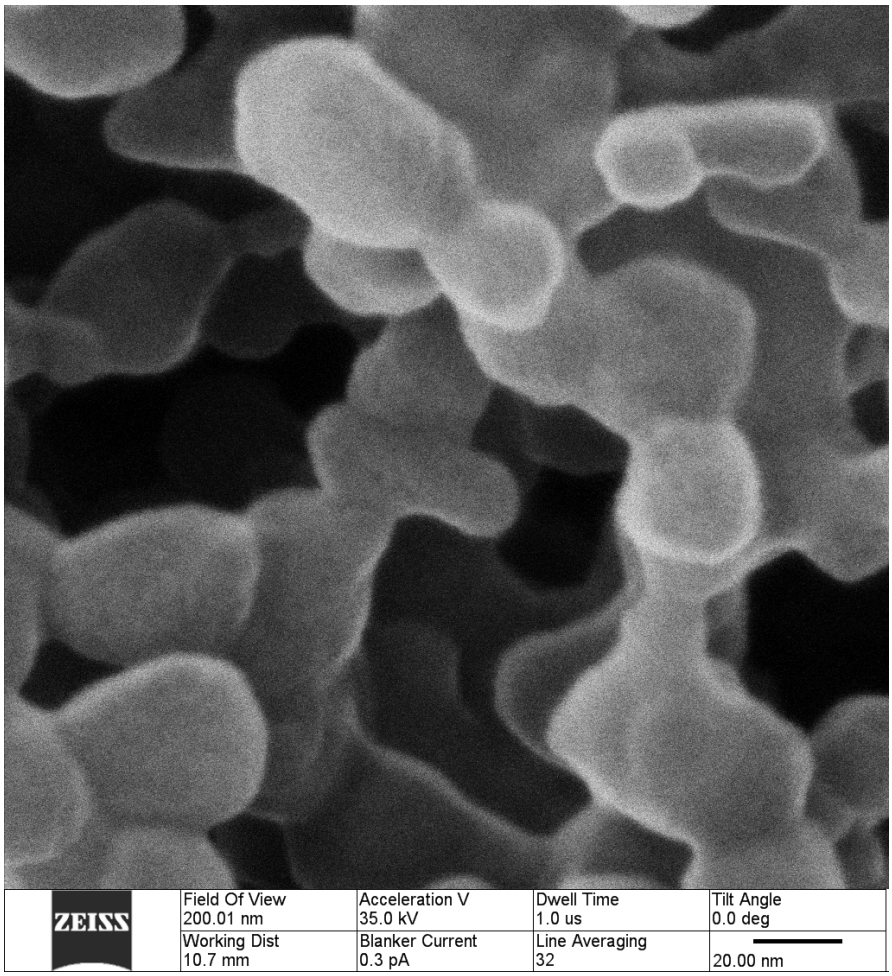

Fig. ESI 3 HIM images of $CuCo_2O_4$ films on stainless steel mesh used for catalytic test.

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