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Co–Cu–La catalysts for selective CO_2 hydrogenation to higher hydrocarbons

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Physicochemical analysis

The X-ray diffraction analysis (XRD) of the powdered samples was carried out on a DRON-3 X-ray diffractometer (FeKα radiation).

The structure and elemental composition of the surface were studied by scanning electron microscopy (SEM) on a Zeiss Ultra plus instrument equipped with a JCXA-733 Superprobe X-ray spectral microanalyzer (JEOL, Japan).

The specific surface area of the samples was determined using the BET method by nitrogen on a Sorbi-M setup (Meta, Novosibirsk).

The catalysts were investigated by temperature-programmed reduction (TPR) using a chromatographic type instrument. A catalyst sample (50 mg) was placed in a quartz flow reactor, purged with dried He at 300 °C for 1 h and then cooled to 70 °C in the He flow. For recording the hydrogen absorption curves, the reactor was heated to 700 °C at a rate of 20 °C min^{-1} in a mixture flow of H_2 (10.0 vol%) and Ar (90.0 vol%).

Evaluation of catalyst activity

Catalytic tests were carried out in a flow-through reactor unit with a steel tube reactor heated by an electric furnace. A 1000 mg sample of the catalyst (100–300 μm fraction) was placed in isothermal zone of the reactor between two quartz sand layers. The catalyst was activated before testing by passing H_2 with a flow rate 2 nl h^{-1} at 400 °C for 4 h. After activation, the cooled reactor was fed with gas containing 22% CO_2, 70% H_2 and 8% Ar as an internal standard and pressure was maintained at 10 bar. The gas flow rate was maintained at 2 ± 0.05 nl h^{-1} and controlled by mass-flow regulator. The temperature was raised to 200 °C.

Composition of tail gas (Ar, CO_2, CO, CH_4, C_2, C_3 and C_4) was analyzed every 8 h on stream by using 'CRYSTALLUX 4000M' instruments equipped with two 1 m × 3 mm columns with molecular sieves 5A (for Ar, CH_4 and CO) and Porapak Q (C_2, C_3, C_4 and CO_2), He as carrier gas, TCD. The CO_2 conversion and selectivity for carbon-containing synthesis products were

calculated from chromatographic data. Specific activity of the samples was calculated by relating the CO_2 conversion rate to the mass of cobalt in the catalyst. The selectivity to C_{5+} was calculated from the total mass balance and the amount of C_1–C_4 and CO_2 gases.

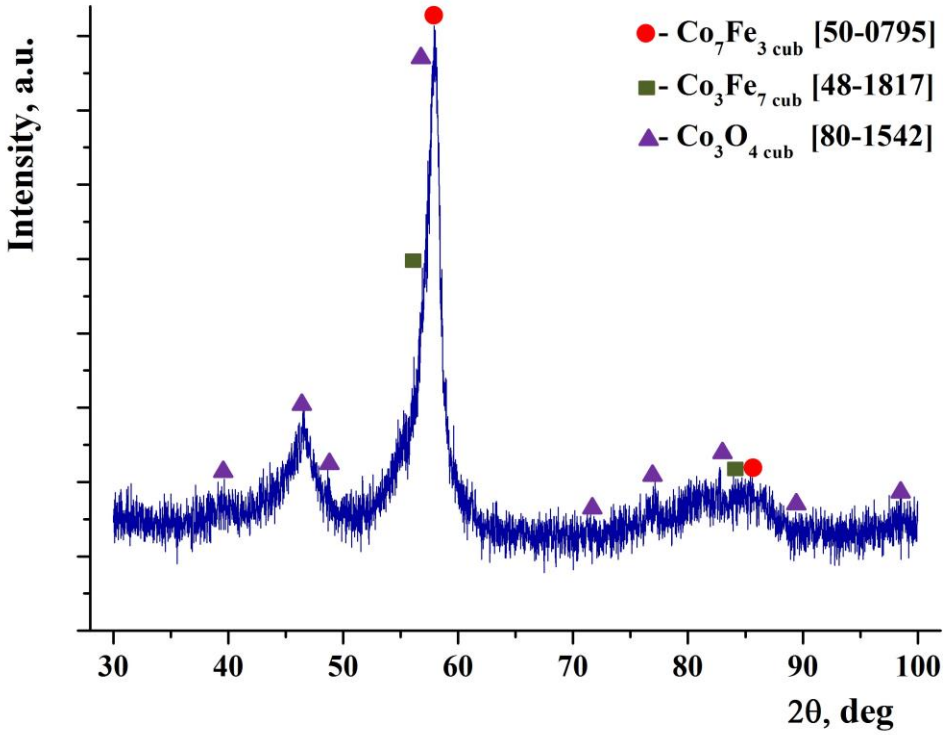

Figure S1 X-ray diffraction patterns of freshly prepared 65Co–30Fe–5La.

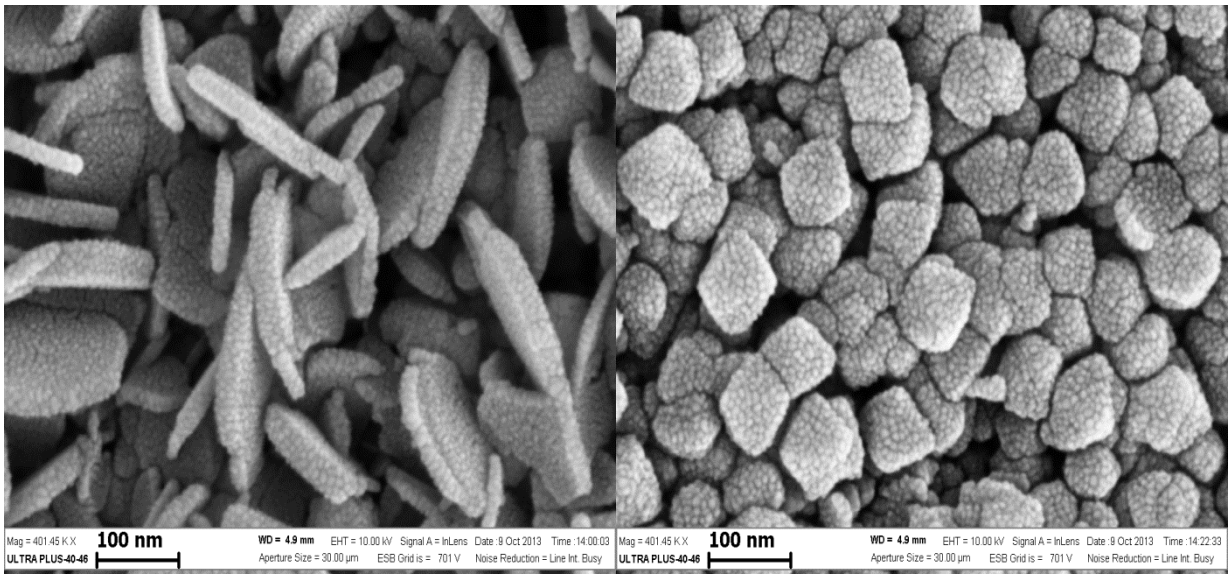

Figure S2 SEM images of 85Co–10Cu–5La.

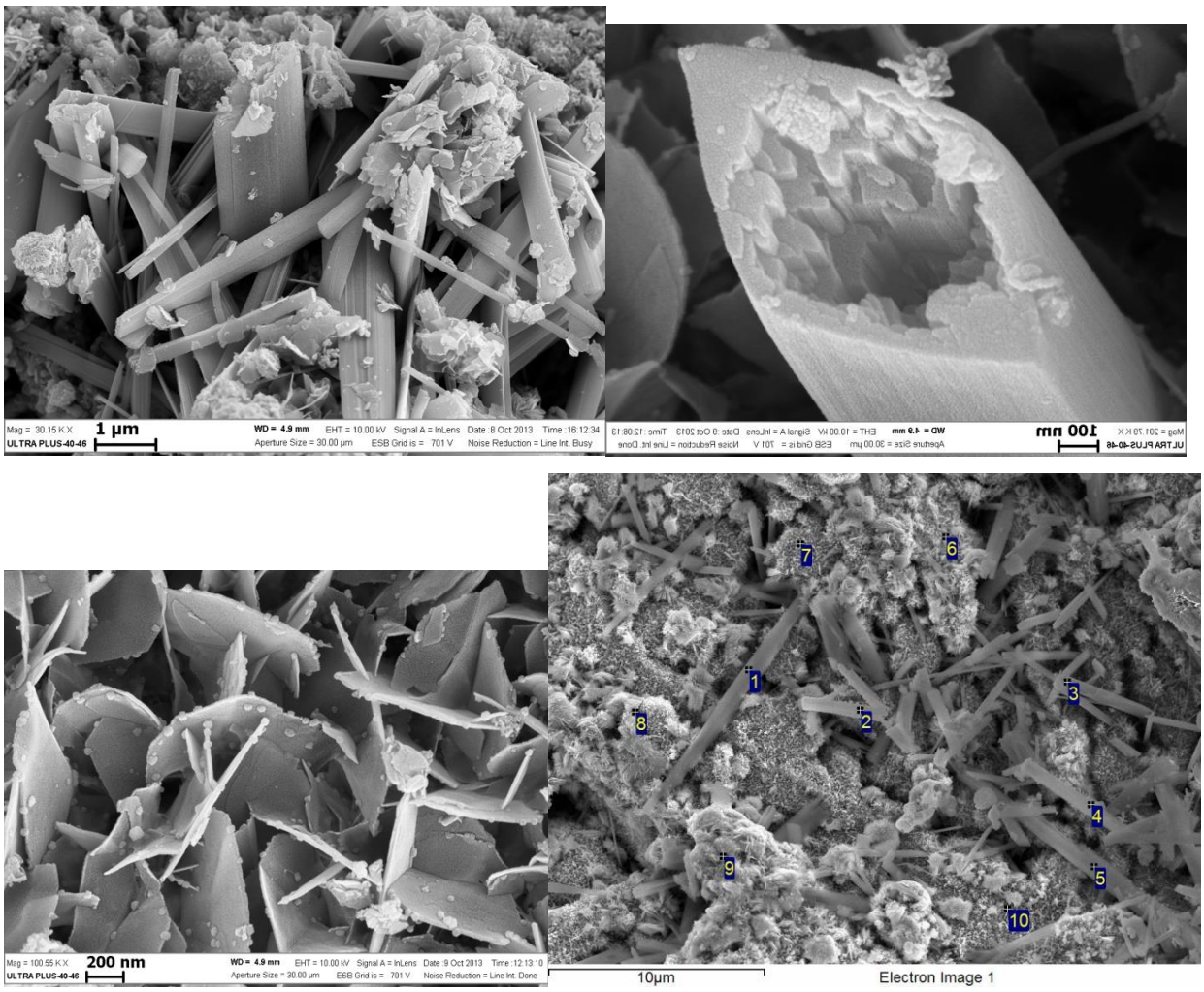

Figure S3 SEM images of 65Co–30Cu–5La with electron probing sites.

Table S1 Elemental composition (wt%) of 65Co–30Cu–5La in the sites shown in Figure S2.

Site no.	O	Al	Co	Cu	La
1	27.15	0.34	11.79	59.49	1.23
2	23.12	0.40	14.20	61.03	1.25
3	30.60	0.39	10.98	57.79	0.24
4	27.41	0.55	25.32	46.68	0.00
5	30.79	0.39	8.74	60.08	0.00
6	27.79	0.88	31.54	39.78	0.00
7	29.25	0.67	58.83	11.01	0.24
8	30.52	0.36	36.53	31.16	1.43
9	23.60	0.30	12.14	63.11	0.86
10	2.82	0.10	36.91	50.59	9.58

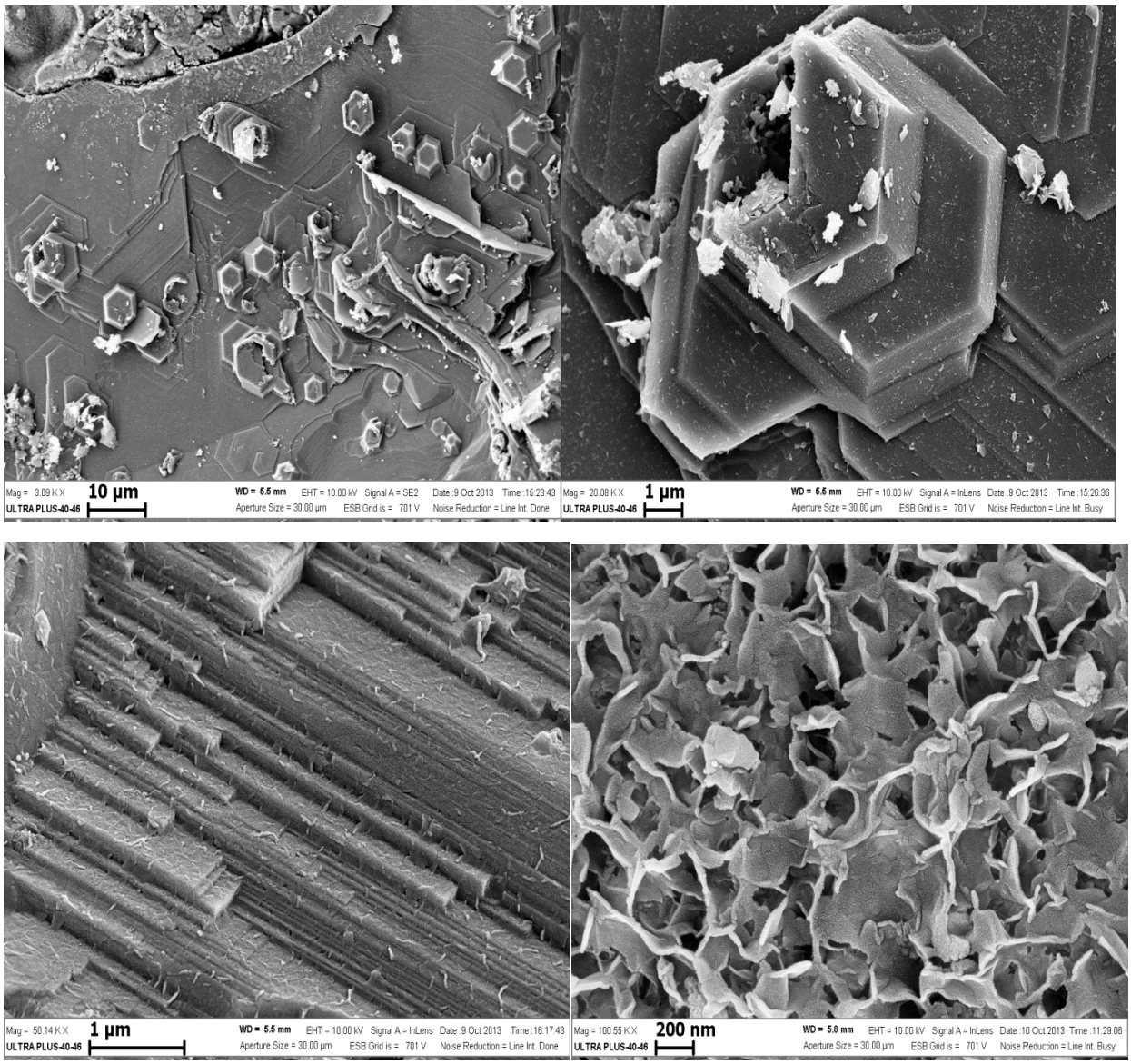

Figure S4 SEM images of 45Co–50Cu–5La.

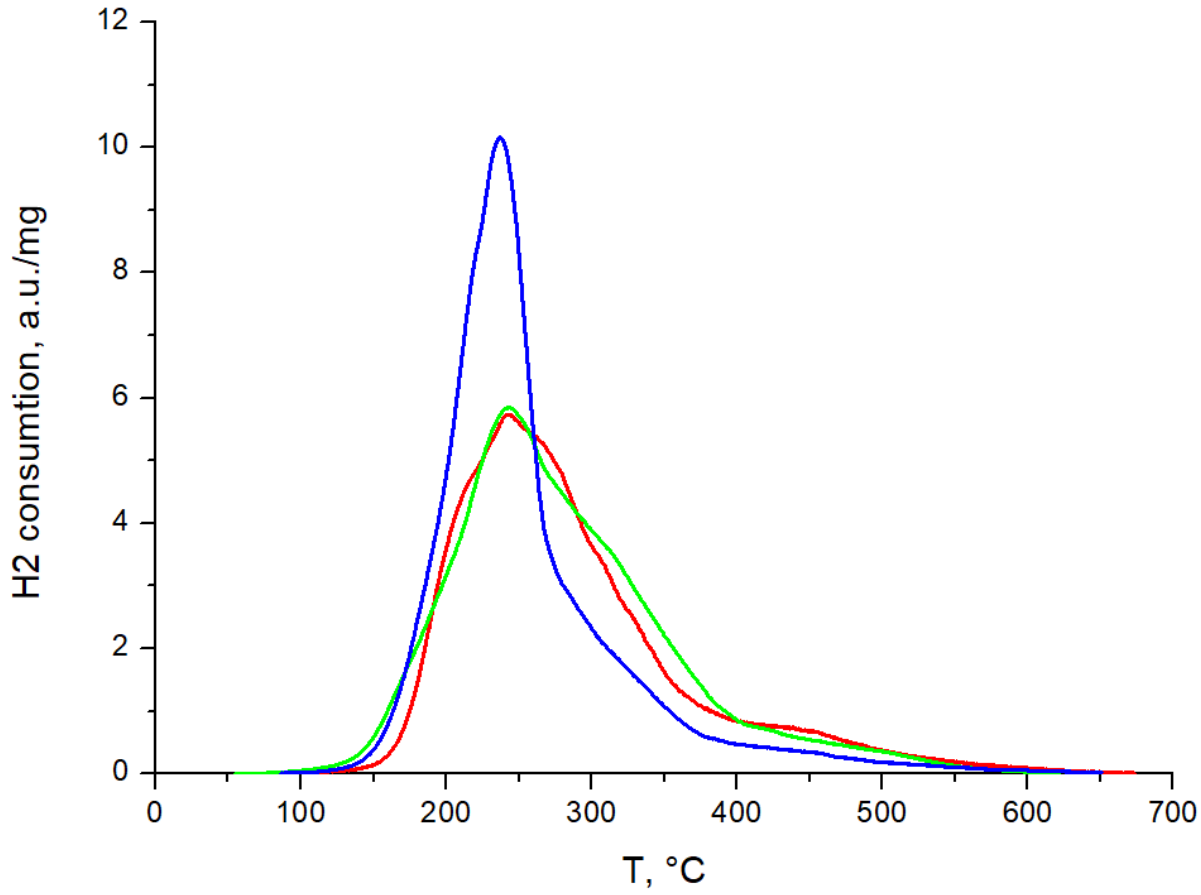

Figure S5 TPR profiles of the catalysts: **red** – 85Co–10Cu–5La, **green –** 65Co–30Cu–5La and **blue** – 45Co–50Cu–5La.

Table S2 Total H_2 uptake during TPR, mmol g^{-1}

Catalyst	H_2 uptake/mmol g^{-1}
85Co–10Cu–5La	6.40
65Co–30Cu–5La	6.46
45Co–50Cu–5La	6.77

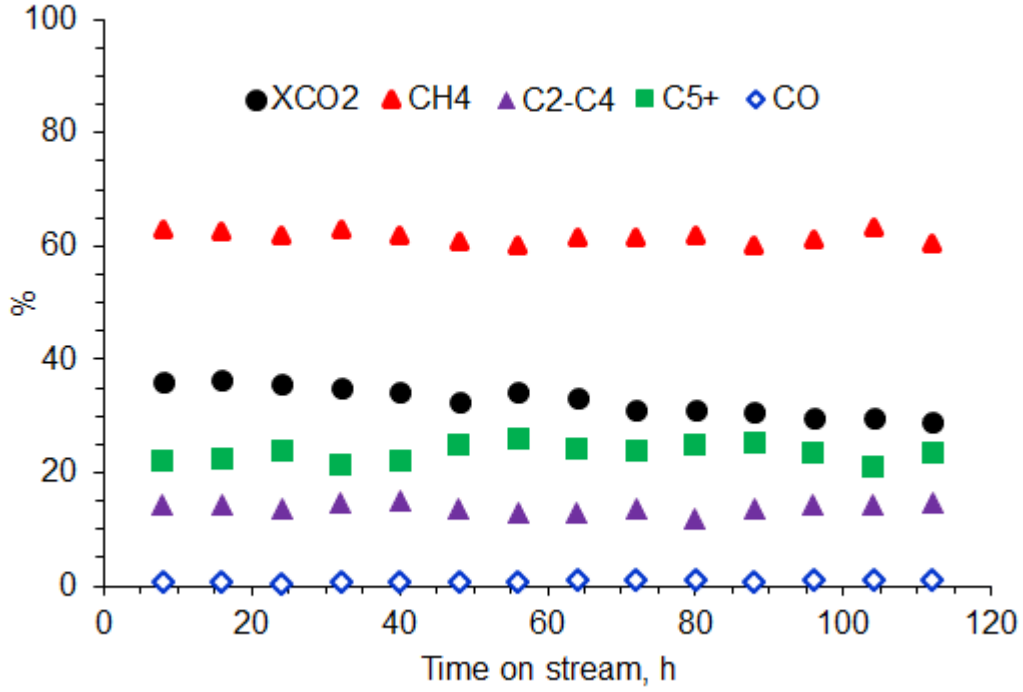

Figure S6 Catalytic performance of 65Co–30Cu–5La as a function of time on stream. Reaction conditions: P = 10 bar, T = 200 °C, gas flow rate 2 nl h^{-1} g^{-1},
H_2 : CO_2 : Ar = 22 : 70 : 8.