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Supporting Information

hcp-Co Nanowires Grown on Metallic Foams as Catalysts for Fischer–Tropsch Synthesis

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Supporting information

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Materials and methods

The copper foam was purchased from Neyco (Cu 99.9%) and used directly without further treatment. The nickel foam was purchased from GoodFellow (Ni 95%). Silica-alumina was obtained from Sasol. The metal precursor [Co{N(SiMe$_3$)$_2$}$_2$(THF)] was furnished by NanoMeps (Toulouse, France). Hexadecylamine (HDA) (Aldrich, purity 98%),) and lauric acid (LA) (Acros, purity 99%) were kept in the glove box and used as received. Anhydrous anisole was purchased from Aldrich (99.7%) and kept in the glove-box under activated molecular sieves in order to remove traces of water. Toluene was purchased from Fischer Chemical (purity 99%), degassed by argon bubbling, introduced in a glove box and kept under molecular sieves to remove traces of water.

Catalyst preparation

The cobalt nanowires were grown on the foam by following a modified version of an already published procedure (N. Liakakos, et al, *ACS Nano*, 2015, **9**, 9665-9677).

Co on Cu foam

- In a glovebox, a solution of [Co{N(SiMe$_3$)$_2$}$_2$(THF)] (135.3 mg, 0.3 mmol) in 10mL of anisole is added to a mixture of LA (120,9 mg, 0,6 mmol) and HDA (147.3 mg, 0.6 mmol) in 10 mL of anisole in a Fischer-Porter bottle (Co/LA/HDA ratio: 1/2/2, [Co] = 15.7 mM). After 10 minutes, the metallic foam (1700 mg) is added to the solution and the Fischer-Porter is evacuated and charged with 3 bar of H_2. The solution is then heated for 24h at 150°C. At the end of the reaction the solution is cooled down and the Fischer-Porter transferred to the glovebox. The foam is removed from the solution and washed 3 times with toluene, then washed 3 times with a solution of HDA in THF (tetrahydofuran) (10 mg/mL), placed in an ultrasonic bath during 2 minutes to remove any free nano-objects, and finally washed with toluene and dried in the glovebox. The Co content was determined by ICP to be 0.25% w/w.

Co on Ni foam

In a glovebox, a solution of [Co{N(SiMe$_3$)$_2$}$_2$(THF)] (67, 7 mg, 0,15 mmol) in 5 mL of anisole is added to a mixture of LA (60,7 mg, 0,3 mmol) and HDA (73,7 mg, 0,3 mmol) in 5 mL of anisole in a Fischer-Porter bottle (Co/LA/HDA ratio: 1/2/2, [Co] = 15,7mM). After 10 minutes, the metallic foam (531mg) and the rest of the procedure was kept identical as above. The Co content was determined by ICP to be 1,42 % w/w.

Reference Catalyst Co-Silica-Alumina

The conventional cobalt catalyst was prepared by incipient wetness impregnation of a $Co(NO_3)_2$. $6H_2O$ aqueous solution on a powder of silica-alumina Al_2O_3-SiO_2 (Al_2O_3: 95%, SiO_2: 5% - BET area = 171 $m^2.g^{-1}$ – pore volume = 0.52 $cm^3.g^{-1}$ – mean pore diameter = 9.2 nm, average particle size = 50µm). After the impregnation step, the solid was dried under air flow at 85°C during 5h and then calcined at 400°C during 4h. The impregnation drying and calcination steps where carried out twice in order to reach a Co content of 15%wt. The 15%Co-Silica-Alumina (typically 120 mg) was finally diluted with the support silica-alumina

(typically 2 gr) in order to reach a cobalt loading of Co comparable to the one of the Co catalyst on Cu foam.

Characterization

The FEG-SEM (Field Emission Gun-Scanning Electron Microscopy) observations were carried out on a JEOL 7800F.

The elemental analyses of cobalt were carried out by ICP-OES at the analytical service of the LCC (Laboratoire de Chimie de Coordination) after digestion with nitric acid, or at Mikroanalytisches Labor Pascher (Remagen, Germany).

The XRD analyses were performed on a Panalytical Empyrean (Co *Kα* = 1.789010 Å). To avoid any exposure to air of the Co containing samples, XRD samples were prepared in a glovebox. The samples were placed between two foils of kapton in a sample holder prior to the measurement. Highscore software and ICDD database were used for interpretation Cu: 00-004-0836, Co: 00-005-0727, Ni: 00-004-0850.

The XPS analyses were performed on a ThermoScientific Kalpha device. The photoelectron emission spectra were recorded using Al–Kα radiation from a monochromatized source. Whereas the samples were kept in a glovebox, they were exposed to air in order to introduce them in the device.

The magnetic measurements of the sample were performed on a Vibrating Sample Magnetometer (VSM) Quantum Design 6000, without any exposure to air. In a glovebox, standard VSM capsules were filled with a known amount of sample and sealed. ZFC was performed by cooling the sample down to 4 K without application of magnetic field and field-dependent magnetization was recorded at 5 K. The temperature was then increased to 300K, and a 5T magnetic field was applied. FC measurement was performed between -5T and 5T after cooling down to 5K while a 5T magnetic field was applied.

Fischer-Tropsch catalytic experiments

The Fischer-Tropsch catalysis was carried out in a fixed bed reactor (stainless steel, d_{int}= 8 mm) operating at a total pressure of 10 bar, H_2/CO = 2 molar ratio and the gas hourly space velocity (GHSV) was fixed at = 890 h^{-1}.

$$GHSV = V_{syngas}/V_{cb}$$

With V_{syngas} = syngas flow in cm^3h^{-1}, V_{cb}, = catalytic bed volume in cm^3

The homogeneous temperature zone of the catalytic bed was determined to be 4 cm in length and the catalyst bed location was limited to this area. Gaseous products (CO, C1-C5) were analyzed on-line by gas chromatography (Perkin Elmer Clarus 580 with both TCD and FID detector). Catalytic activity and selectivity were calculated after 75 h time on stream (TOS). The reaction rate is expressed in terms of mol of CO converted per total mol of cobalt in the catalyst per second. CO conversion was calculated by X_{CO} = ($mol_{CO,in}$ − $mol_{CO,out}$)/ $mol_{CO,in}$. The selectivity toward the products is expressed in %wt. The selectivity to C1 to C4

hydrocarbon was calculated as $S_{i,}$ = mol $_{i,C}$ / X_{CO}, and the selectivity to C5+ was defined as S_{C5+} = 1 − Σ$S_{i,C1\text{-}C4}$. The olefins/paraffins ratio was calculated for C3 products.

The CTY ($mol_{CO}.mol_{Co}^{-1}.s^{-1}$) was calculated with the formula :

$$\text{CTY } (\text{mol}_{CO}.\text{mol}_{Co}{}^{-1}.\text{s}^{-1}) = \frac{X_{CO}.mol_{CO,in}(mol.s^{-1}).M_{Co}(g.mol^{-1})}{m_{catalyst}(g).(\%Co/100)}$$

With M_{Co} the molar weight of cobalt (58.9 $g.mol^{-1}$), $m_{catalyst}$ the mass of catalyst and %Co the loading of cobalt w/w.

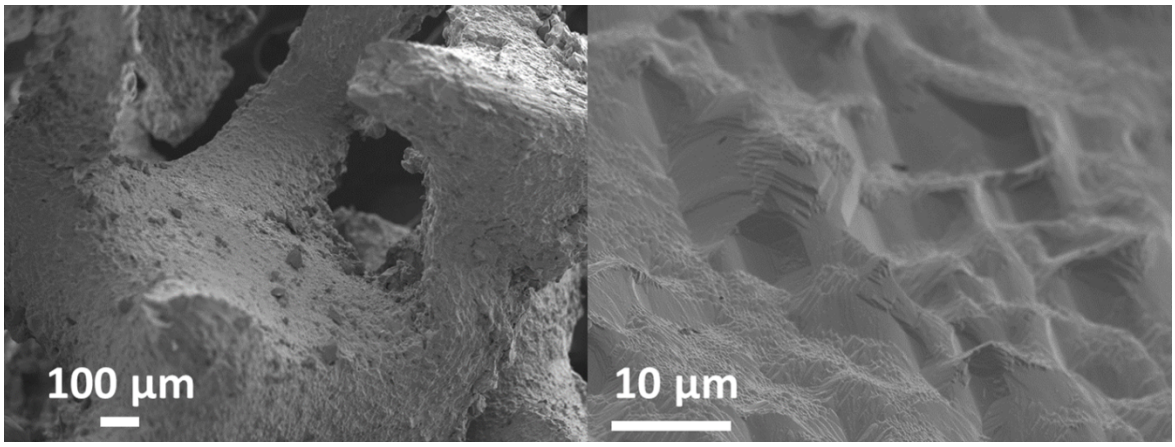
Diluted Co-silica-alumina reference catalyst:

Prior to the test the diluted reference catalyst (2 g, 0,85 % Co) was reduced in-situ in the reactor at 450°C during 16h under H_2 flow. Then, the temperature was reduced to 220°C and the gas flow was switched to syngas

Co/ Cu foam:

Prior to the test, the Co-Cu_{foam} catalyst (3.3g, 0.25 % Co) was loaded in a glovebox in the reactor tube and then connected to the reactor under argon flow to avoid any oxidation of the catalyst. The test was then conducted without any reduction step. The pressure was increased to 10 bar under argon flow and the reactor was heated to 220°C. As soon as the temperature reached 220°C the gas flow was switched to syngas.

Cu foam characteristics.



	Copper foam
Metal purity (%)	99.9
Gross density (g.cm^{-3})	0.8
Porosity (%)	91
Pores/cm	16
Thermal conductivity of bulk metal (W.m^{-1}.K^{-1})	399

Figure S1. SEM micrographs and characteristics of the Cu foam before Co growth.

Cu-foam aspect before and after Co growth and SEM of the Co wires on Cu foam.

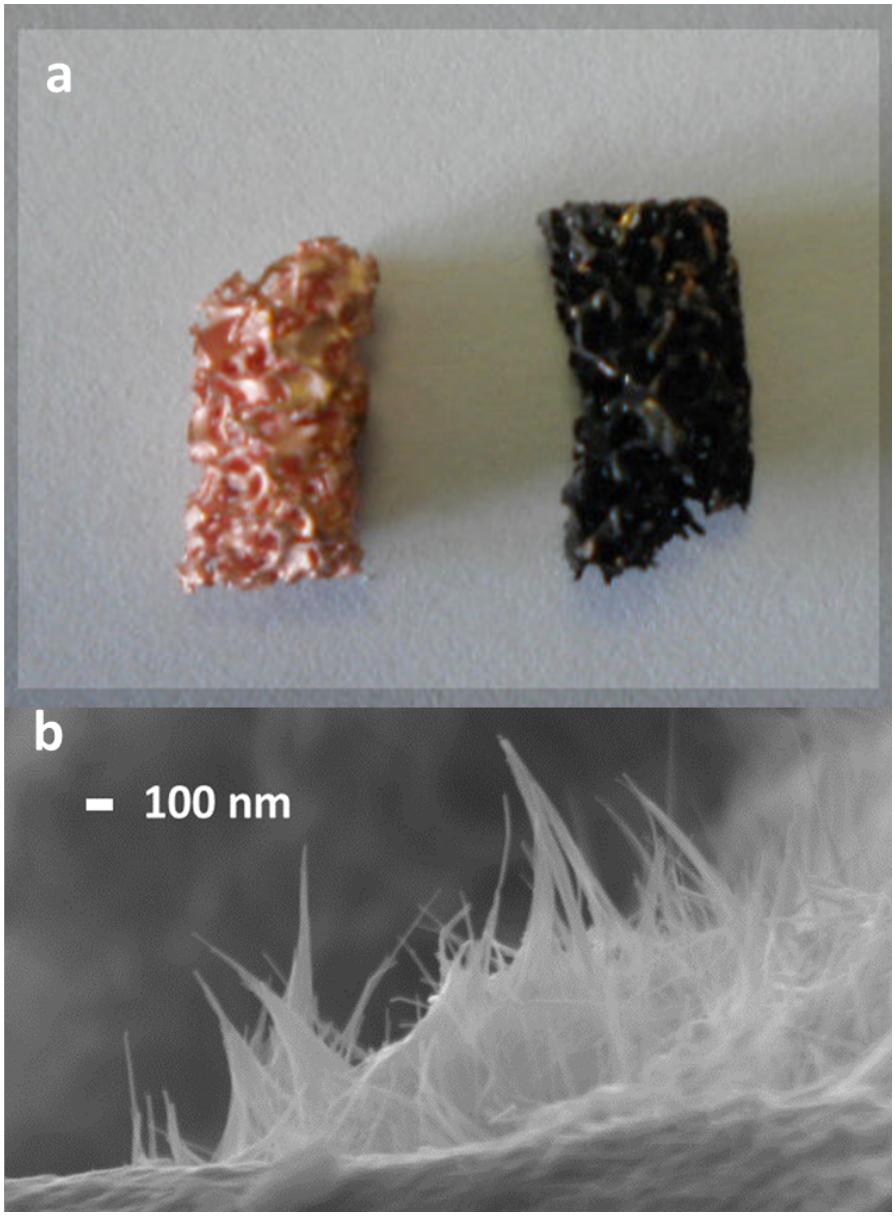


Figure S2: a) Photograph of as received Cu foam and a piece of Cu foam after Co growth, b) SEM image of a section of the Co/Cu_{foam} from which we can roughly evaluate nanowire length to be about 1 μm.

Magnetic measurement of the Co/Cu_{foam}.

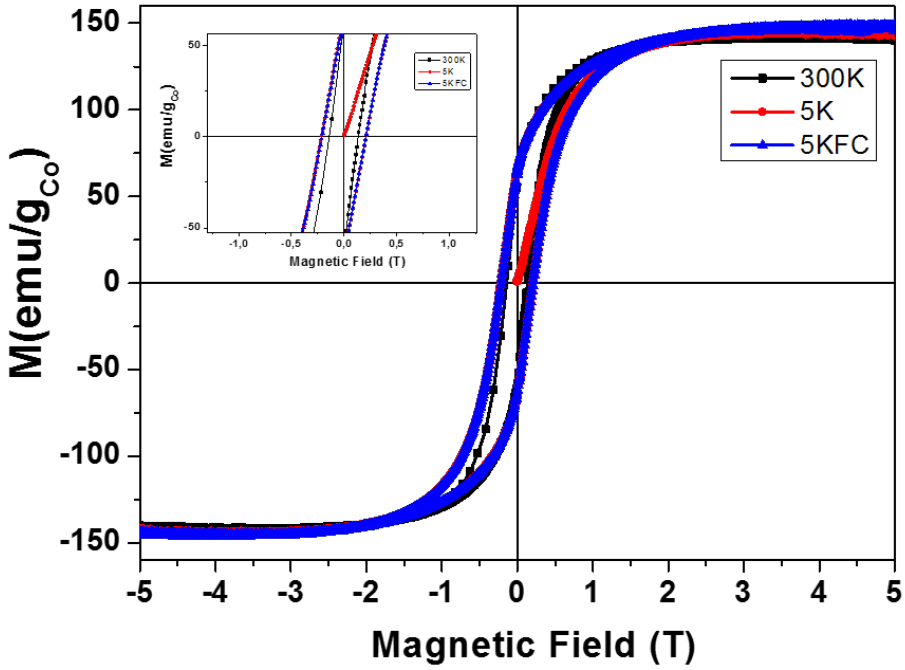


Figure S3: Hysteresis loops of 0.25% Co/Cu_{foam} (red curve: 5K Zero Field Cooling (ZFC); black curve 300K, blue curve: 5K Field Cooling (FC). The absence of exchange bias in the FC is in agreement with the absence of oxidized Co on the surface of the foam and therefore the presence of metallic Co.

XPS of Cu foam and of the Co/Cu_{foam}.

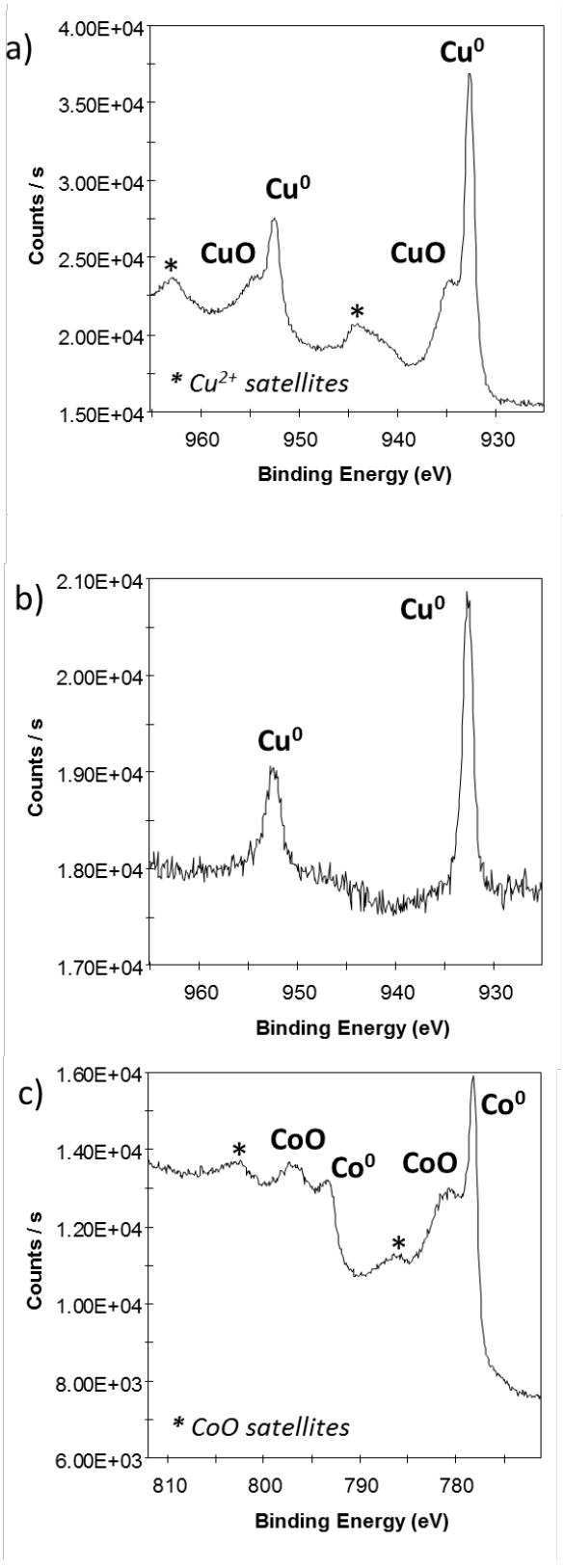


Figure S4: XPS spectra of: a) Cu 2p core level of the Cu foam; b) Cu 2p core level of the Co/Cu_{foam} monolith; and c) Co 2p of the Co/Cu_{foam} monolith.

SEM image of the Co/Cu$_{foam}$ after heat treatment under Ar/H$_2$.

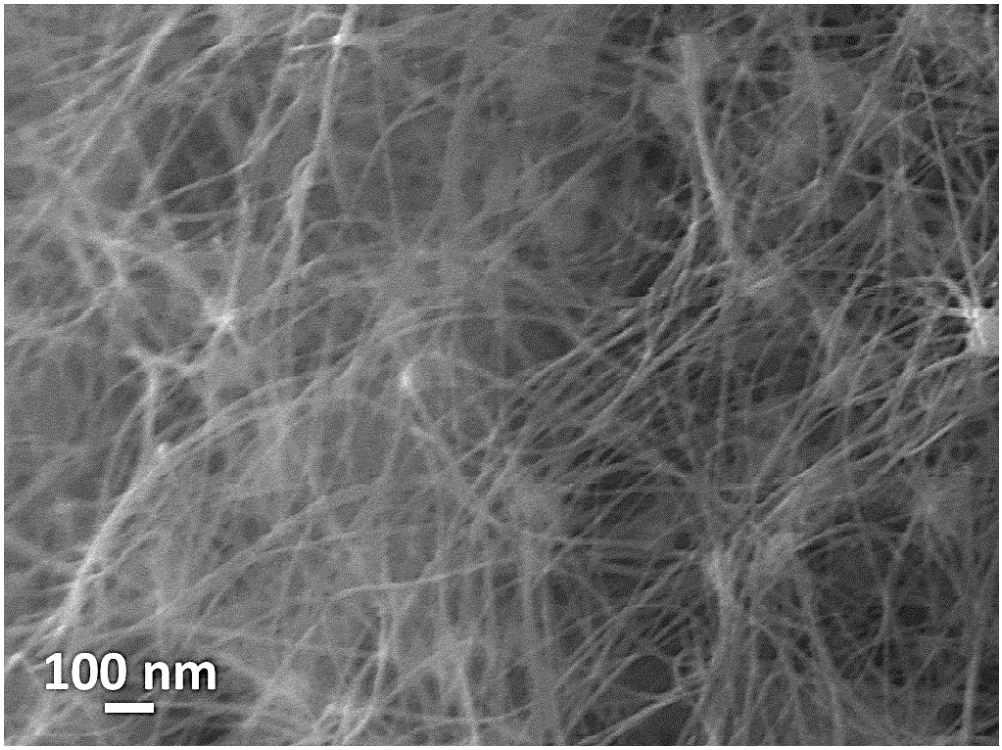


Figure S5. SEM image of the Co/Cu$_{foam}$ sample after 3h heat treatment at 350 °C under Ar/H$_2$ flow.

XRD and SEM of the 15%Co/Al_2O_3-SiO_2 catalyst.

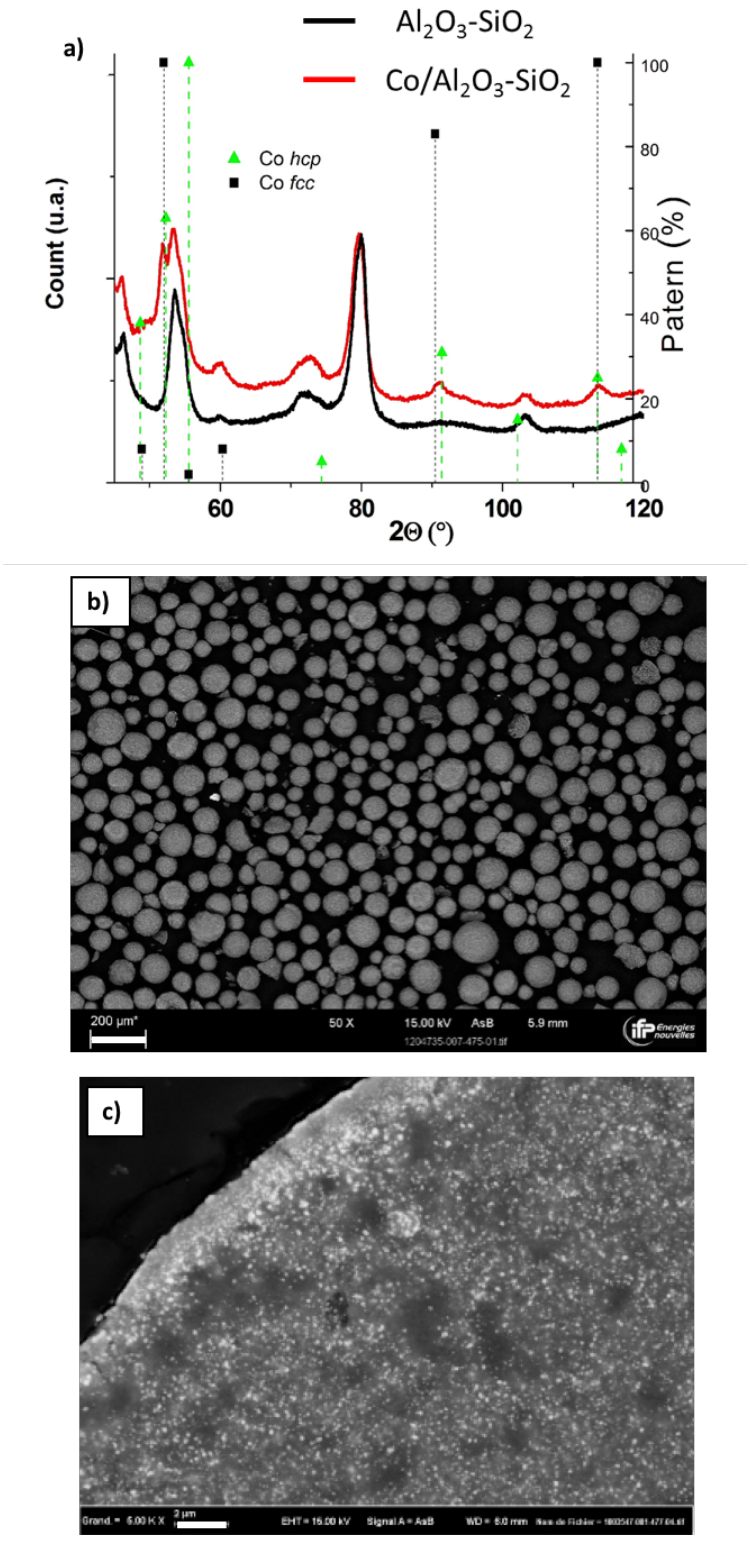


Figure S6: a) XRD of the reduced reference catalyst; b) SEM image of the 15%Co/Al_2O_3-SiO_2 reference catalyst (scale bar: 200µm); and c) SEM image of a grain slice of the 15%Co/Al_2O_3-SiO_2 reference catalyst, the bright spots corresponding to the Co particles (scale bar: 2µm).

Comparison of the cobalt time yields between different catalysts from the literature and the investigated catalysts

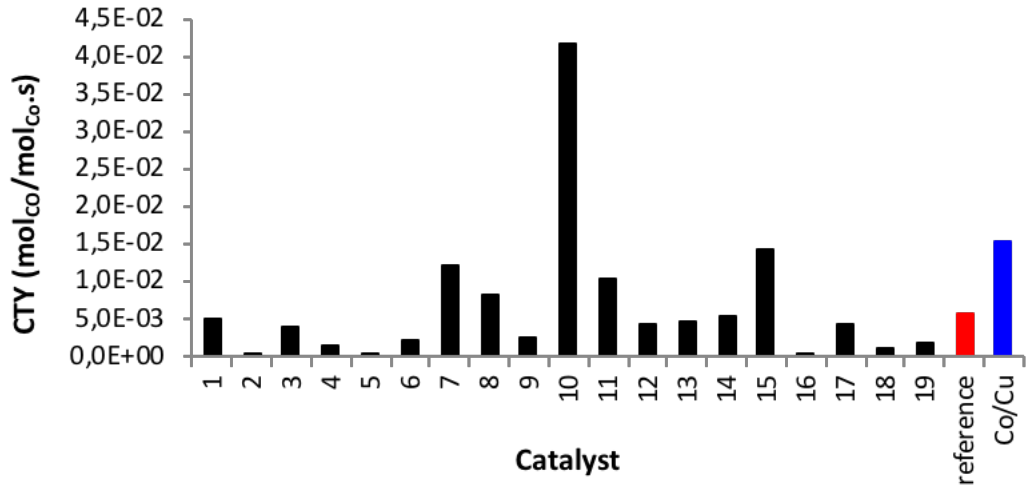


Figure S7. Comparison of our catalysts (reference and Co/Cu$_{foam}$) with catalysts found in the literature in studies performed under comparable conditions. These values were extracted whenever possible from the data given in the aticles. The CTY data analysis has taken into account the total Co amount. This amount coincides with the metallic cobalt amount in the case of the Co/Cu$_{foam}$ catalyst.

Catalyst	CTY ($mol_{CO}/mol_{Co}.sec^{-1}$)	Reference
1	5.0E-03	*Catal. Today*, **2009**, *142*, 70
2	3.5E-04	*Catal. Today*, **2013**, *215*, 121
3	4.0E-03	*J. Catal.*, **2018**, *359*, 92
4	1.6E-03	*App. Catal., A.*, **2017**, *539*, 48
5	1.7E-04	*App. Catal., A.*, **2007**, *326*, 164
6	2.2E-03	*Nanoscale*, **2017**, *9*, 570
7	1.2E-02	*J. Catal.*, **2013**, *299*, 67
8	8.2E-03	*RSC Adv.*, **2017**, *7*, 8852
9	2.7E-03	*Appl. Catal.* A, **2017,** *548*, 143
10	4.2E-02	*RSC Adv.*, **2016**, *6*, 104280
11	1.1E-02	*J. Catal.*, **2015**, *328*, 130
12	4.5E-03	*New J. Chem.*, **2016**, *40*, 9586

13	4.6E-03	*J. Catal.*, **2018**, *359*, 92
14	5.5E-03	*App. Catal. A.*, **2018**, *556*, 92
15	1.5E-02	*App. Catal. A.*, **2018**, *556*, 92
16	1.1E-04	*J. Mol. Catal.*, **2014**, *394*, 22
17	4.3E-03	*Ind. Eng. Chem. Res.*, **2014**, *53*, 1787
18	1.1E-03	*Ind. Eng. Chem. Res.*, **2018**, *57*, 3833
19	1.8E-03	*App. Catal. A.*, **2015,** *494*, 1
reference	5.8E-03	This work
Co/Cufoam	1.5E-02	This work

Activity of the catalysts during 75h TOS

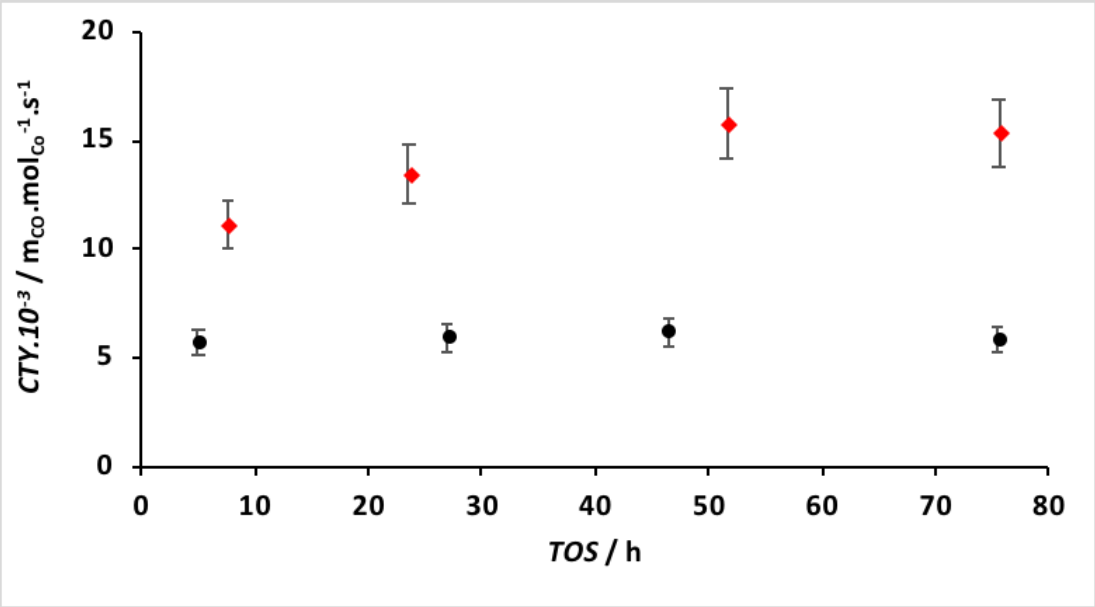


Figure S8: Comparison of the activity of the Co/Cu_{foam} catalyst (red diamonds) and the diluted 15%Co/Al_2O_3-SiO_2 reference catalyst (black circles) over 75 h TOS.

XRD of the Co foam and the Co/Cu$_{foam}$ **before and after catalysis.**

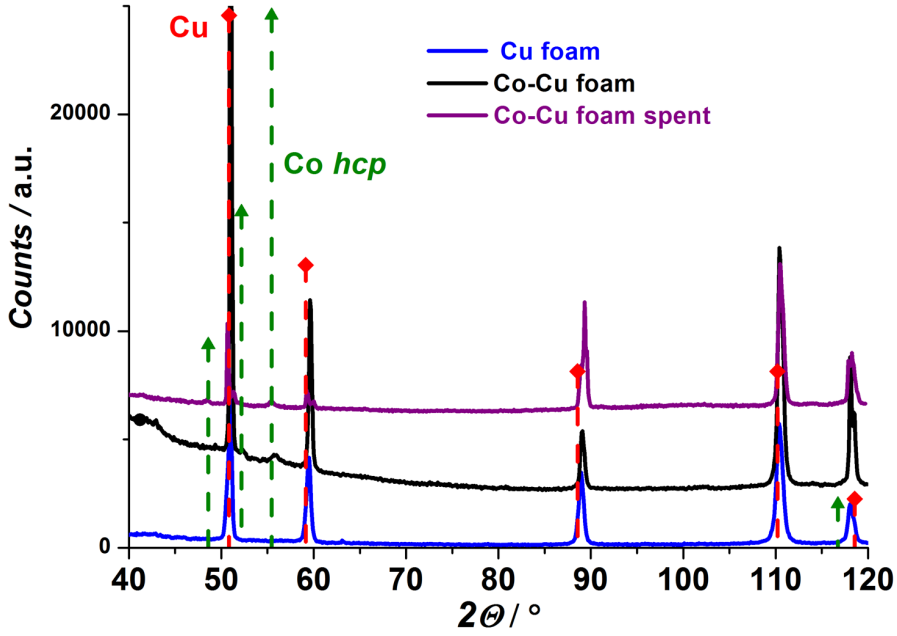
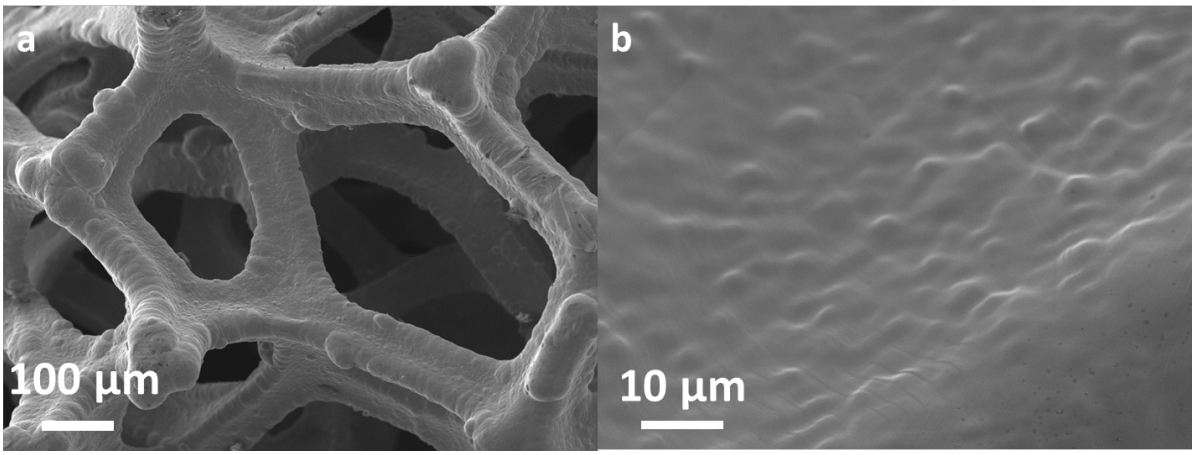


Figure S9. XRD diagrams of the Cu foam (blue line), the fresh Co/Cu$_{foam}$ catalyst (black line), and the spent Co/Cu$_{foam}$ catalyst (TOS=75h) (magenta line).

Ni foam characteristics.



	Nickel foam
Metal purity (%)	95
Gross density ($g.cm^{-3}$)	0.45
Porosity (%)	95
Pores/cm	20
Thermal conductivity of bulk metal ($W.m^{-1}.K^{-1}$)	91

Figure S10. SEM images of Ni foam before Co NWs growth and foam characteristics

XRD of the Ni foam and the Co/Ni$_{foam}$.

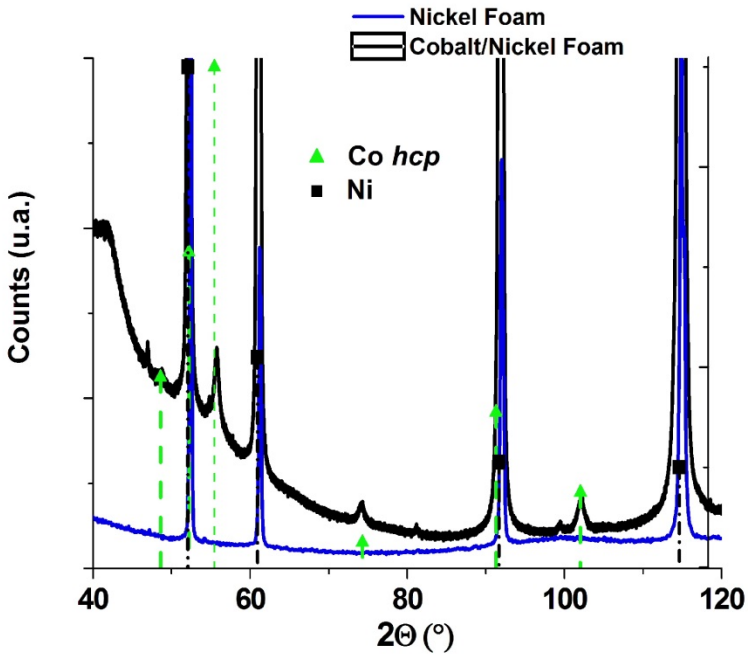


Figure S11. XRD diagrams of the Ni foam before (blue line) and after Co growth, 1.45% Co/Ni$_{foam}$ (black line).

XPS of the Ni foam and the Co/Ni$_{foam}$.

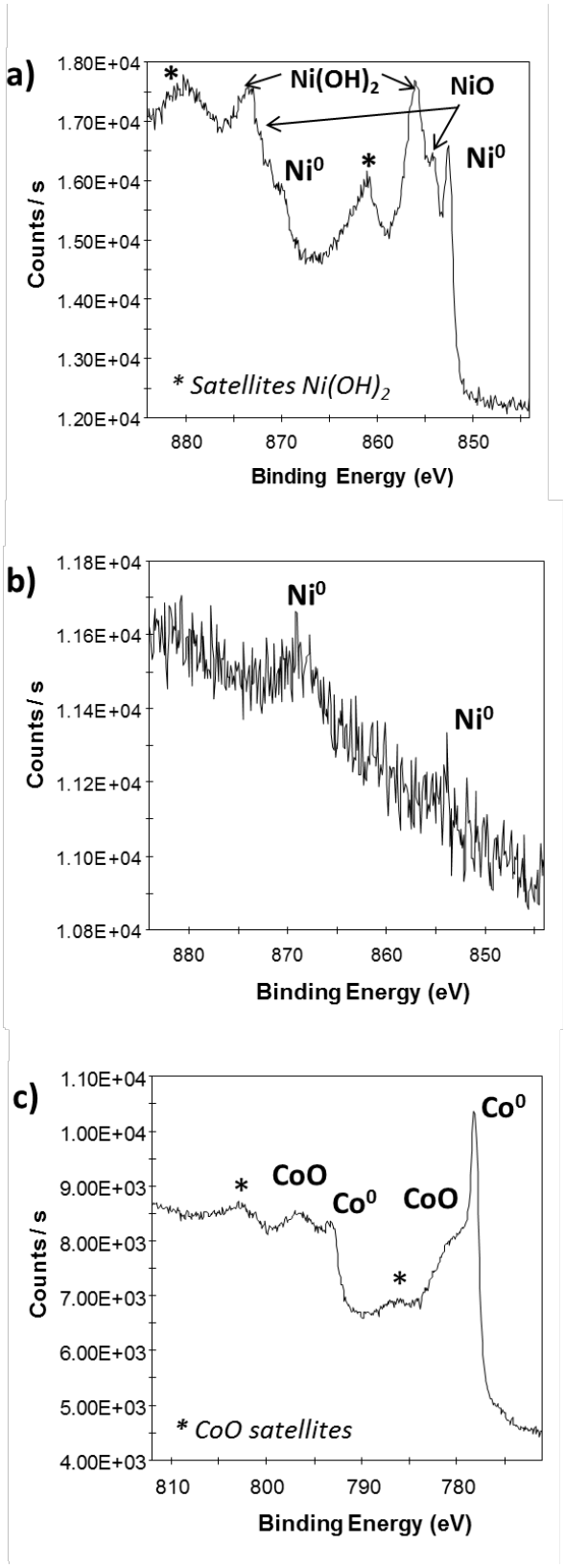


Figure S12. XPS spectra of: a) Ni 2p core level of the Ni foam; b) Ni 2p core level of the Co/Ni$_{foam}$ monolith and c) Co 2p core level of the Co/Ni$_{foam}$ monolith.