

## Supplementary Information.

### 1/ Detailed calculations of CO conversion ( $X_{CO}$ ) and products selectivities ( $S_j$ )

$$X_{CO}(\%) = 100 \times \frac{(n_{CO})_{in} - (n_{CO})_{out}}{(n_{CO})_{in}}$$

Where  $(n_{CO})_{in}$  and  $(n_{CO})_{out}$  are the molar flow rates of CO in and out of the reactor.

### Selectivity in a $j$ product containing $i$ carbon atoms:

$$S_j(\%) = 100 \times \frac{i \times n_j}{(n_{CO})_{in} - (n_{CO})_{out}}$$

Where  $n_j$  is the molar flow rate of the product  $j$  out of the reactor.

Example for  $CH_4$  selectivity:

$$S_{CH_4}(\%) = 100 \times \frac{n_{CH_4}}{(n_{CO})_{in} - (n_{CO})_{out}}$$

The selectivity of  $C_5+$  products (products with at least 5 carbon atoms) was calculated as:

$$S_{5+}(\%) = 100 - (S_{C1} + S_{C2} + S_{C3} + S_{C4})$$

Where  $S_{C1}$ ,  $S_{C2}$ ,  $S_{C3}$  and  $S_{C4}$  are the selectivities in products with 1, 2, 3 and 4 carbon atoms respectively.

### Yield $\eta_j$ in a $j$ product:

$$\eta_j(\%) = \frac{X_{CO} \times S_j}{100}$$

### 2/ TOF calculation

$$TOF (molCO.molCosurf^{-1}.s^{-1}) = \frac{100 \times X_{CO} \times (n_{CO})_{in} \times M(Co)}{m_{catalyst} \times \%Co \times D}$$

Where  $(n_{CO})_{in}$  is expressed in  $mol.s^{-1}$ , cobalt molar mass  $M(Co)$  in  $g.mol^{-1}$ , catalyst weight  $m_{catalyst}$  in g, cobalt loading  $\%Co$  in wt% and dispersion  $D$  in %.

A corrected TOF was also calculated taking into account the cobalt reduction degree ( $\Delta$  expressed in %):

$$TOF_{corr} (molCO.molCosurf^{-1}.s^{-1}) = \frac{100 \times X_{CO} \times (n_{CO})_{in} \times M(Co)}{m_{catalyst} \times \%Co \times D} \times \frac{100}{\Delta}$$

### 3/ Quantification of CoO on X-ray diagrams and estimation of reduction degree

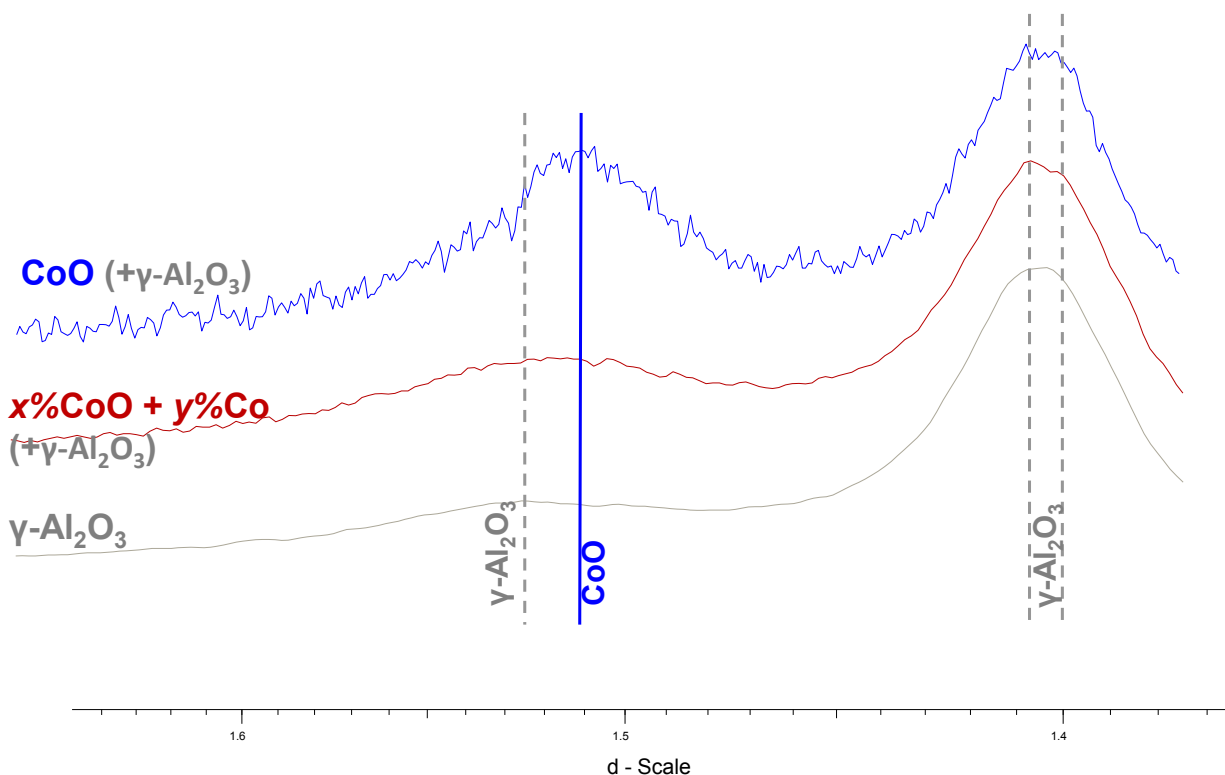
During *in situ* reduction of the catalyst, crystalline changes were followed by XRD. Around 250°C under hydrogen, only CoO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were detected and the corresponding diffraction pattern was used as intern reference “100%CoO” (**Figure S1**).

The signals assigned to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> being constant during activation and reaction, it was possible to subtract their contribution from the *operando* diagrams, using as extern reference the diffraction pattern of the pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used for the catalyst preparation. The diagrams were normalized with respect to the area at 1.41 Å exclusively assigned to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The area  $A_{1.51}$  of the diffraction peak at 1.51 Å was used to quantify CoO, as:

$$\%CoO = 100 \times \frac{A_{1.51} - A_{alumina\ REF}}{A_{CoO\ REF} - A_{alumina\ REF}}$$

Where  $A_{alumina\ REF}$  and  $A_{CoO\ REF}$  are respectively the areas at 1.51 Å on the diffraction patterns of the references  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 100%CoO.

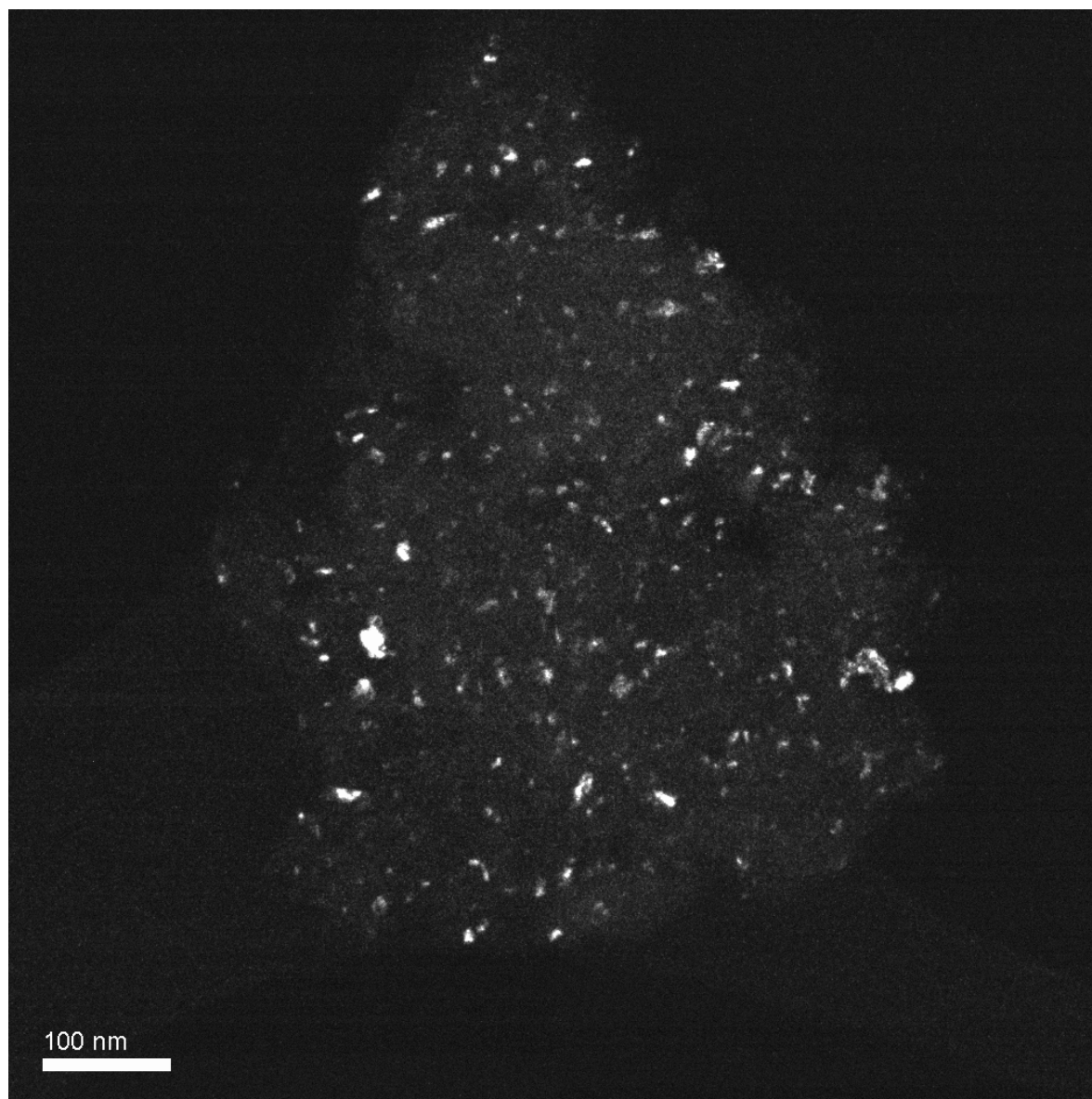


**Figure S1.** Diffraction patterns of CoO/alumina, alumina and a Co/alumina catalyst containing fcc Co and CoO crystalline phases.

If CoO and Co are the only cobalt-containing phases, then:

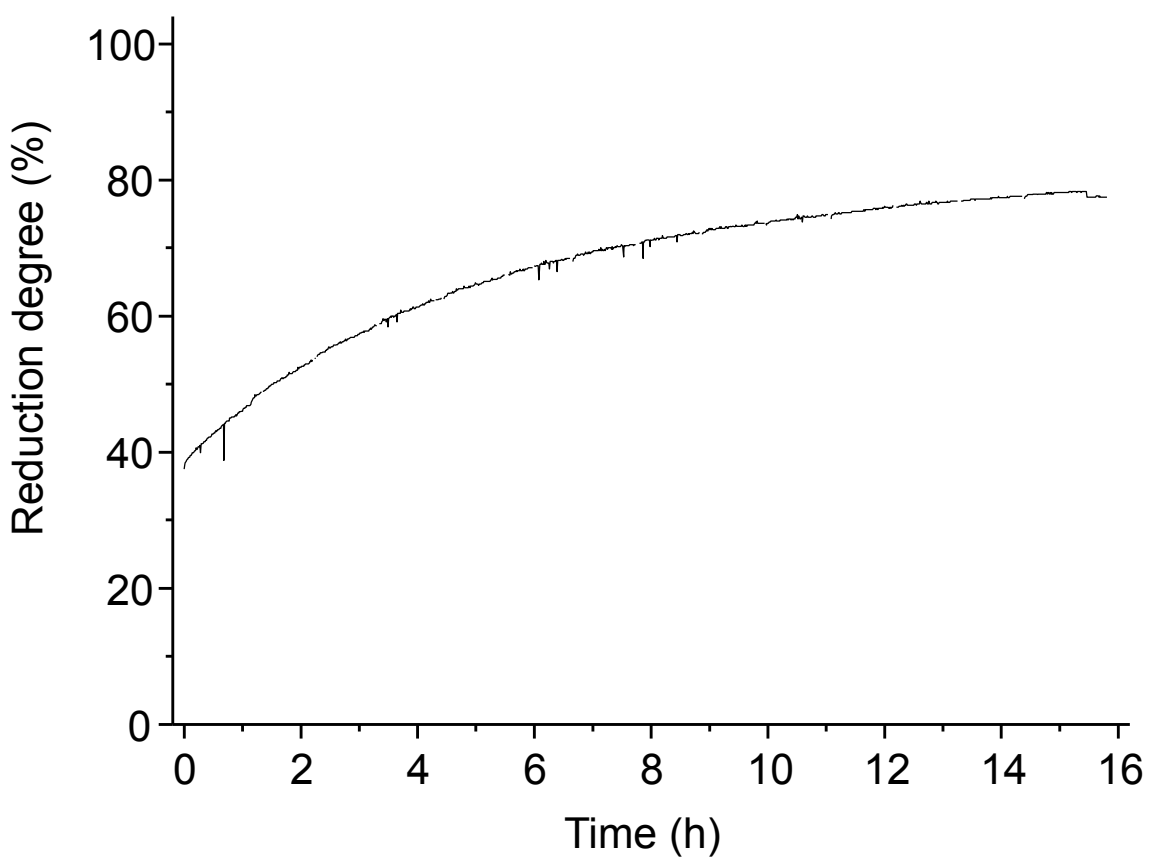
$$d = \text{Reduction Degree (\%)} = \%Co = 100 - \%CoO$$

### 4/ TEM measurements



**Figure S2.** TEM picture of the Co/alumina catalyst.

## 5/ Magnetism measurements



**Figure S3.** Reduction degree of the Co/alumina catalyst as a function of time under H<sub>2</sub> flow at 500 °C