

Supporting information

1/ TEM experiments

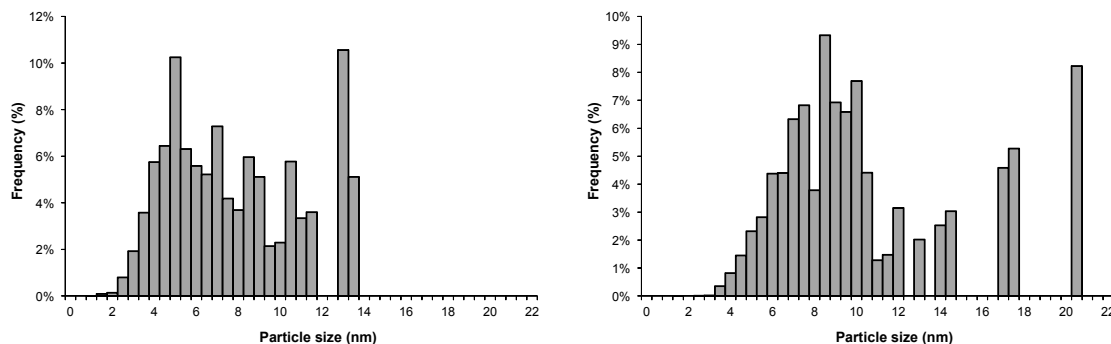


Figure S1. Particle size distribution (volume averaged) determined from TEM measurements: 7nm-Co/silica (left) and 12nm-Co/silica (right) catalysts before treatment.

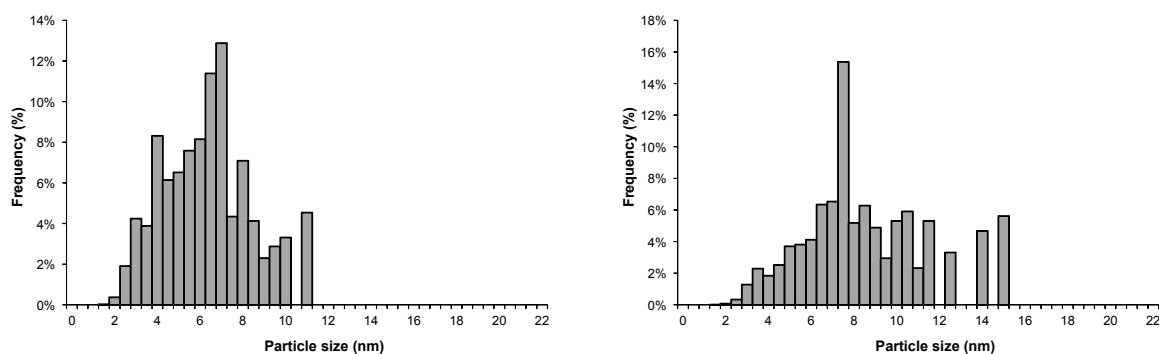


Figure S2. Particle size distribution (volume averaged) determined from TEM measurements: 7nm-Co/silica (left) and 12nm-Co/silica (right) catalysts after treatment.

2/ Quantification of crystalline phases

Before reduction, the catalyst was fully oxidized in the Co_3O_4 form.

During *in situ* reduction of the catalyst, crystalline changes were followed by XRD.

At 100 °C under hydrogen, Co_3O_4 was still the unique detected phase and the corresponding diffraction pattern was used as intern reference “ $\text{Co}_3\text{O}_{4\text{initial}}$ ”. The area $A_{65.2}$ of the diffraction peak at $65.2^\circ 2\theta$, typically assigned to Co_3O_4 , was used to quantify Co_3O_4 when it was not the only crystalline phase anymore (Eq. 1).

$$\% \text{Co}_3\text{O}_4 = 100 \times \frac{A_{65.2}}{A_{\text{Co}_3\text{O}_4 \text{ REF}}} \quad (\text{Eq. 1})$$

Where $A_{65.2}$ and $A_{\text{Co}_3\text{O}_4 \text{ REF}}$ are respectively the areas at $65.2^\circ 2\theta$ on the diffraction patterns of a mixture containing Co_3O_4 phase and of the Co_3O_4 reference.

Around 250°C under hydrogen, CoO was the unique detected phase and the corresponding diffraction pattern was used as intern reference “CoO_{REF}”. The area $A_{61.6}$ of the diffraction peak at 61.6°2θ was then used to quantify CoO (Eq. 2).

$$\%CoO = 100 \times \frac{A_{61.6}}{A_{CoO REF}} \quad (Eq. 2)$$

Where $A_{61.6}$ and $A_{CoO REF}$ are respectively the areas at 61.6°2θ on the diffraction patterns of a mixture containing CoO phase and of the CoO reference.

After reduction at 700 °C and cooling at 230 °C, when Co was the only detected phase (case for 12nm-Co/silica catalyst), the diffraction pattern was used as intern reference “Co REF”. The area $A_{44.2}$ of the diffraction peak at 44.2°2θ was then used to quantify Co, taking into account the contribution at 44.8°2θ of Co₃O₄ if this latter was detected by its typical peak at 65.2°2θ (Eq. 3).

$$\%Co = 100 \times \frac{A_{44.2} - A_{65.2} \times \frac{19}{34}}{A_{Co REF}} \quad (Eq. 3)$$

Where $A_{44.2}$ and $A_{Co REF}$ are respectively the areas at 44.2°2θ on the diffraction patterns of a mixture containing Co phase and of the Co reference. The coefficient (19/34) was determined on diffraction patterns containing only Co₃O₄ as the ratio between the areas of the peak at 65.2°2θ and that at 44.8°2θ.

When the catalyst was not fully reduced after the reduction step (case for 7nm-Co/silica catalyst), the proportion $x\%$ of CoO was determined according to equation 2 and the proportion of Co was then $(100-x)\%$ before treatment. Equation 3 was then replaced by equation 4.

$$\%Co = 100 \times \frac{A_{44.2} - A_{65.2} \times \frac{19}{34}}{A_{Co REF}} \times \frac{100 - x}{100} \quad (Eq. 4)$$

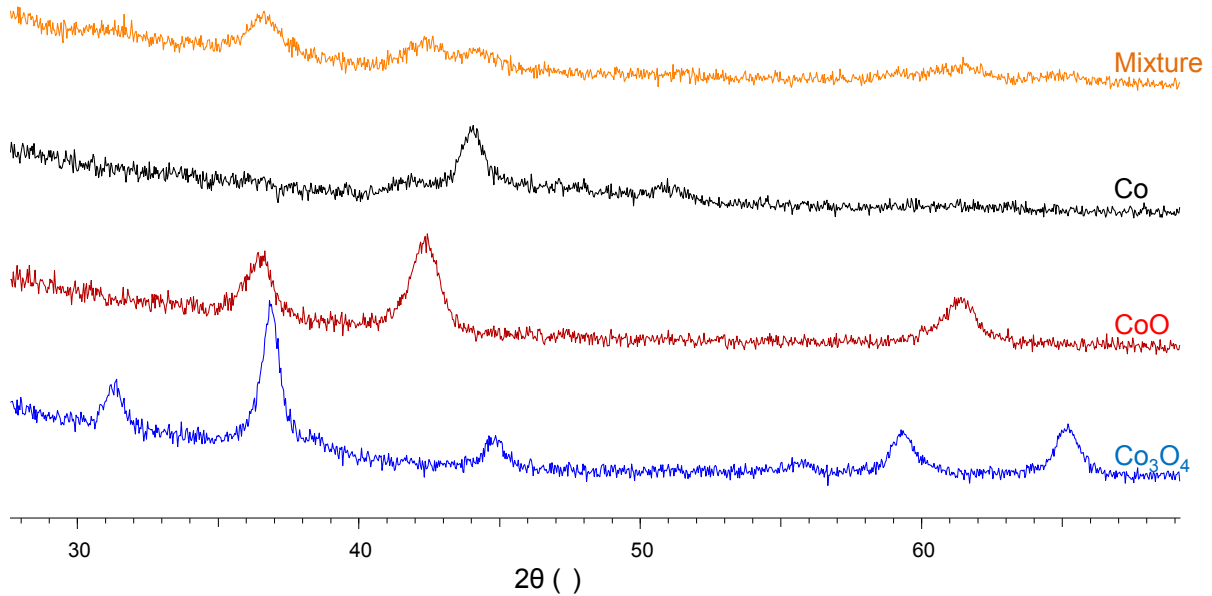


Figure S3. XRD patterns of 12nm-Co/silica catalyst during reduction at 100°C (ref Co₃O₄, blue), 250°C (ref CoO, red), after reduction at 700°C and cooling at 230°C (ref Co, black), and during steam treatment (mixture of Co, CoO and Co₃O₄, orange)