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:

$$S_{CH4} (\%) = 100 \times \frac{n_{CH4}}{(n_{CO})_{in} - (n_{CO})_{out}}$$

The selectivity of C5+ 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

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

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 ($\lambda$ expressed in %):

$$TOF_{corr} (molCO.molCosurf \text{-1}.s^{-1}) = \frac{100 \times X_{CO} \times (n_{CO})_{in} \times M(Co)}{m_{catalyst} \times %Co \times D} \times \frac{100}{\lambda}$$
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 γ-Al₂O₃ were detected and the corresponding diffraction pattern was used as intern reference “100%CoO” (*Figure S1*).

The signals assigned to γ-Al₂O₃ 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 γ-Al₂O₃ used for the catalyst preparation. The diagrams were normalized with respect to the area at 1.41 Å exclusively assigned to γ-Al₂O₃.

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

\[
\%_{\text{CoO}} = 100 \times \frac{A_{1.51} - A_{\text{Alumina REF}}}{A_{\text{CoO REF}} - A_{\text{Alumina REF}}}
\]

Where $A_{\text{Alumina REF}}$ and $A_{\text{CoO REF}}$ are respectively the areas at 1.51 Å on the diffraction patterns of the references γ-Al₂O₃ 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:

\[
\phi = \text{Reduction Degree (\%)} = \%_{\text{Co}} = 100 - \%_{\text{CoO}}
\]

4/ TEM measurements
Figure S2. TEM picture of the Co/alumina catalyst.
**Figure S3.** Reduction degree of the Co/alumina catalyst as a function of time under H$_2$ flow at 500 °C