

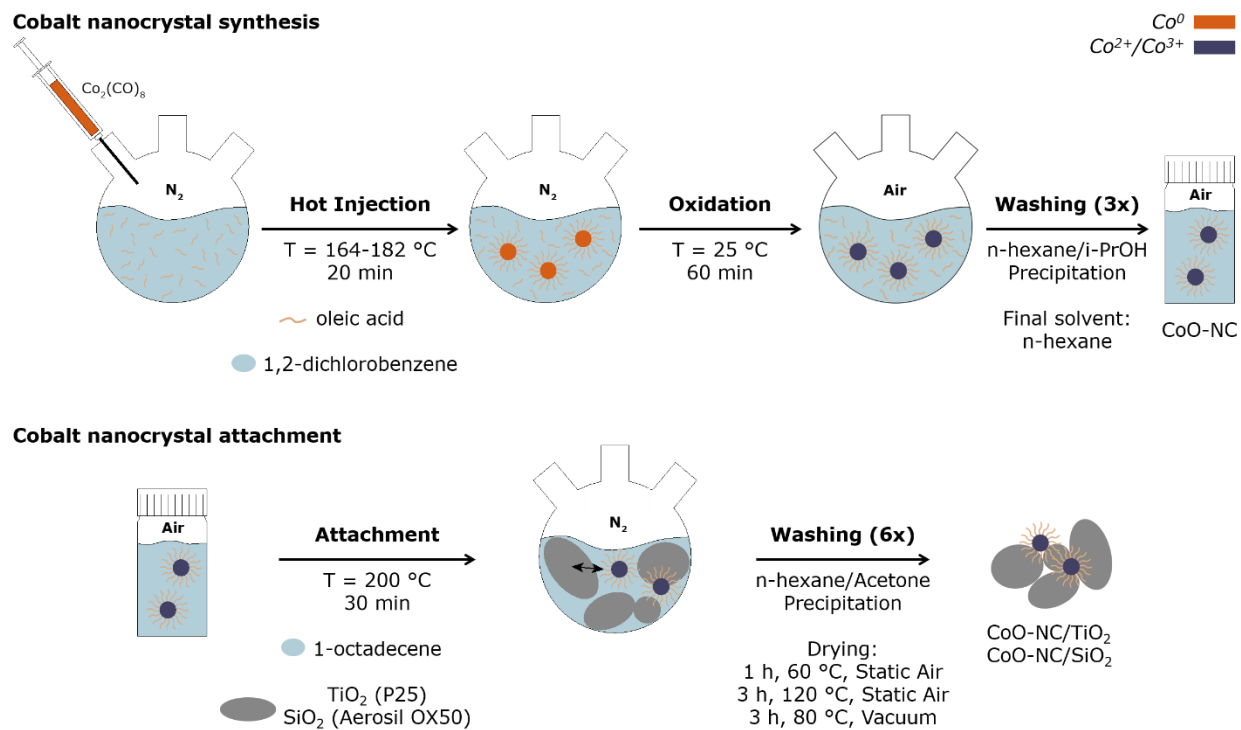
# Supporting Information

## Preparation of cobalt nanocrystals supported on metal oxides to study particle growth in Fischer- Tropsch catalysts

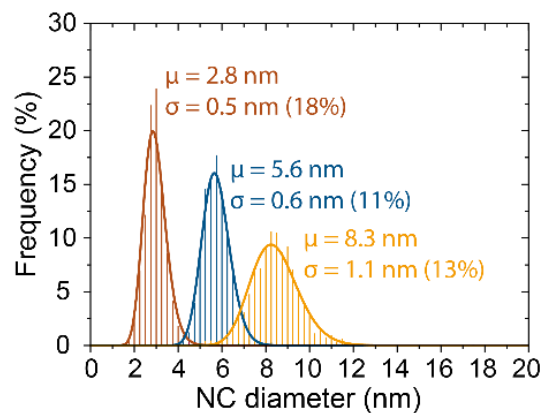
*Tom W. van Deelen, Jelle J. Nijhuis, Nynke A. Krans, Jovana Zečević, Krijn P. de Jong\**

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht  
University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

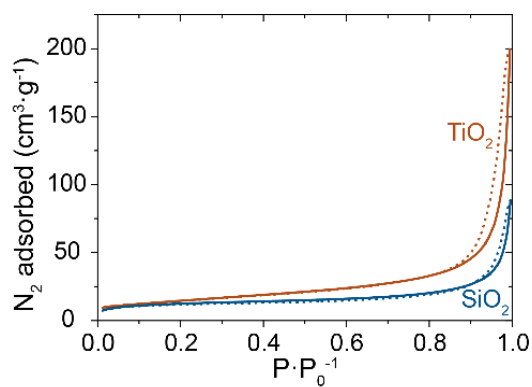
\*E-mail: k.p.dejong@uu.nl



**Figure S1.** Schematic illustration of the catalyst synthesis procedure.



**Figure S2.** Histograms and lognormal distributions of Co-NC that were later attached to SiO<sub>2</sub>.

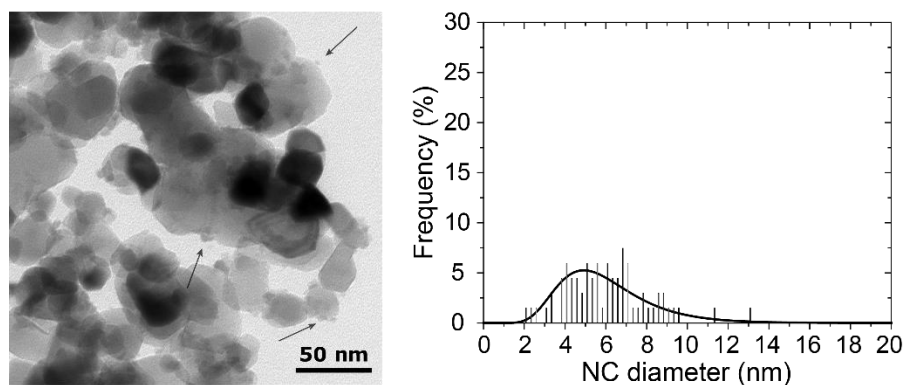


**Figure S3.** N<sub>2</sub>-physisorption isotherms of the bare supports, TiO<sub>2</sub> and SiO<sub>2</sub>.

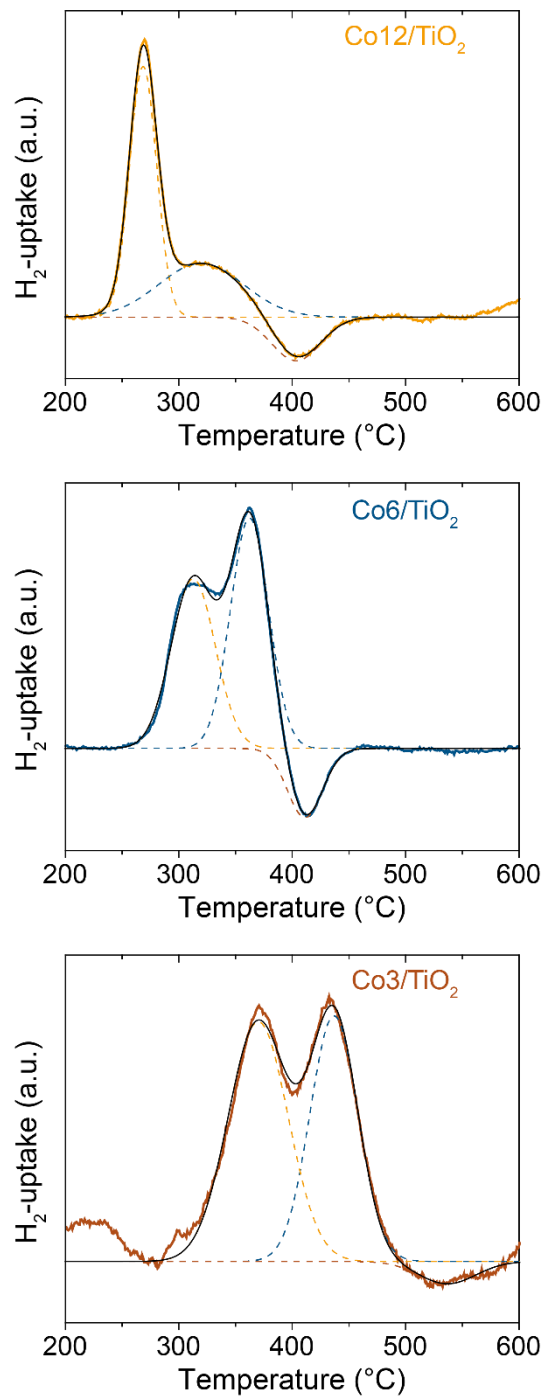
**Table S1.** N<sub>2</sub>-physisorption results of the bare supports, TiO<sub>2</sub> and SiO<sub>2</sub>.

Support	S <sub>ABET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	Pore volume (mL·g <sup>-1</sup> ) <sup>a</sup>
TiO <sub>2</sub> P25	53	0.31
SiO <sub>2</sub> Aerosil OX50	43	0.14

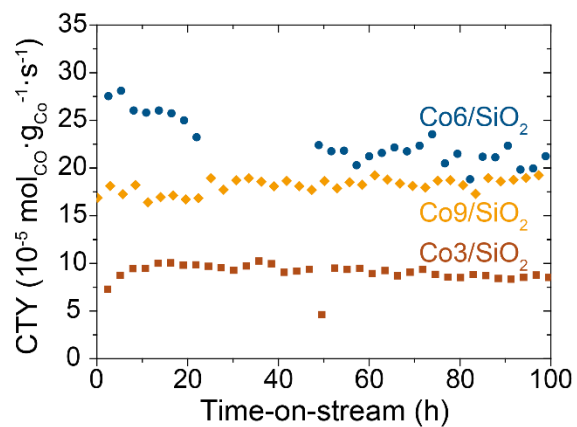
<sup>a</sup> Determined at P/P<sub>0</sub> = 0.995



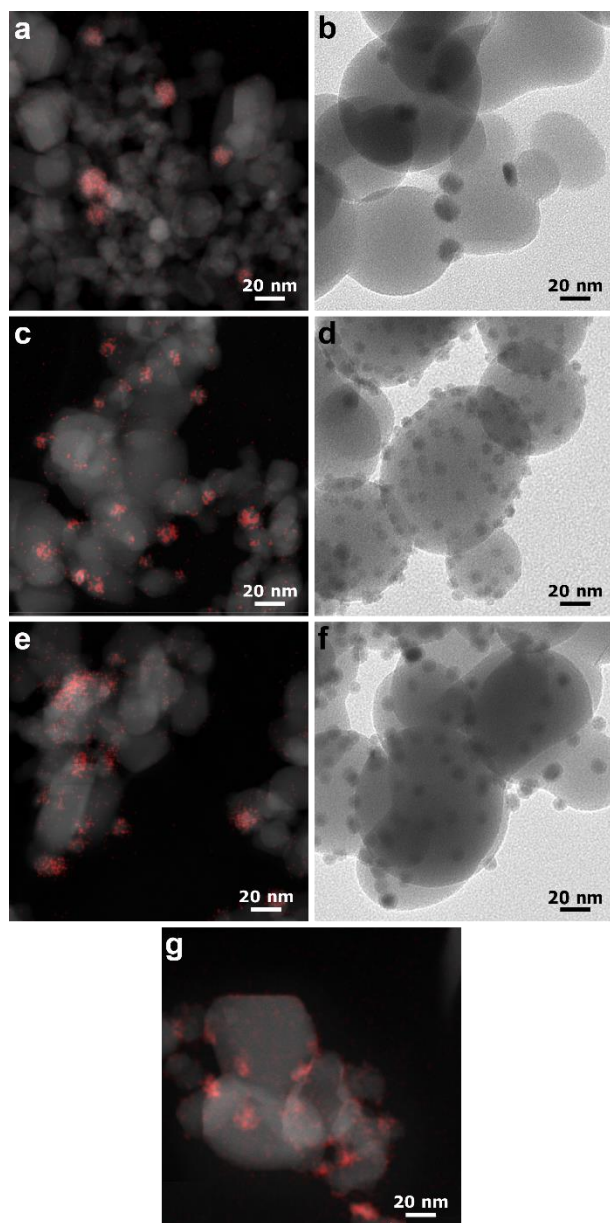
**Figure S4.** TEM analysis of pristine IWI-Co/TiO<sub>2</sub> after heat treatment in N<sub>2</sub>. TEM image (left) with the arrows indicating several Co<sub>3</sub>O<sub>4</sub> particles and the corresponding histogram and lognormal distribution (right).



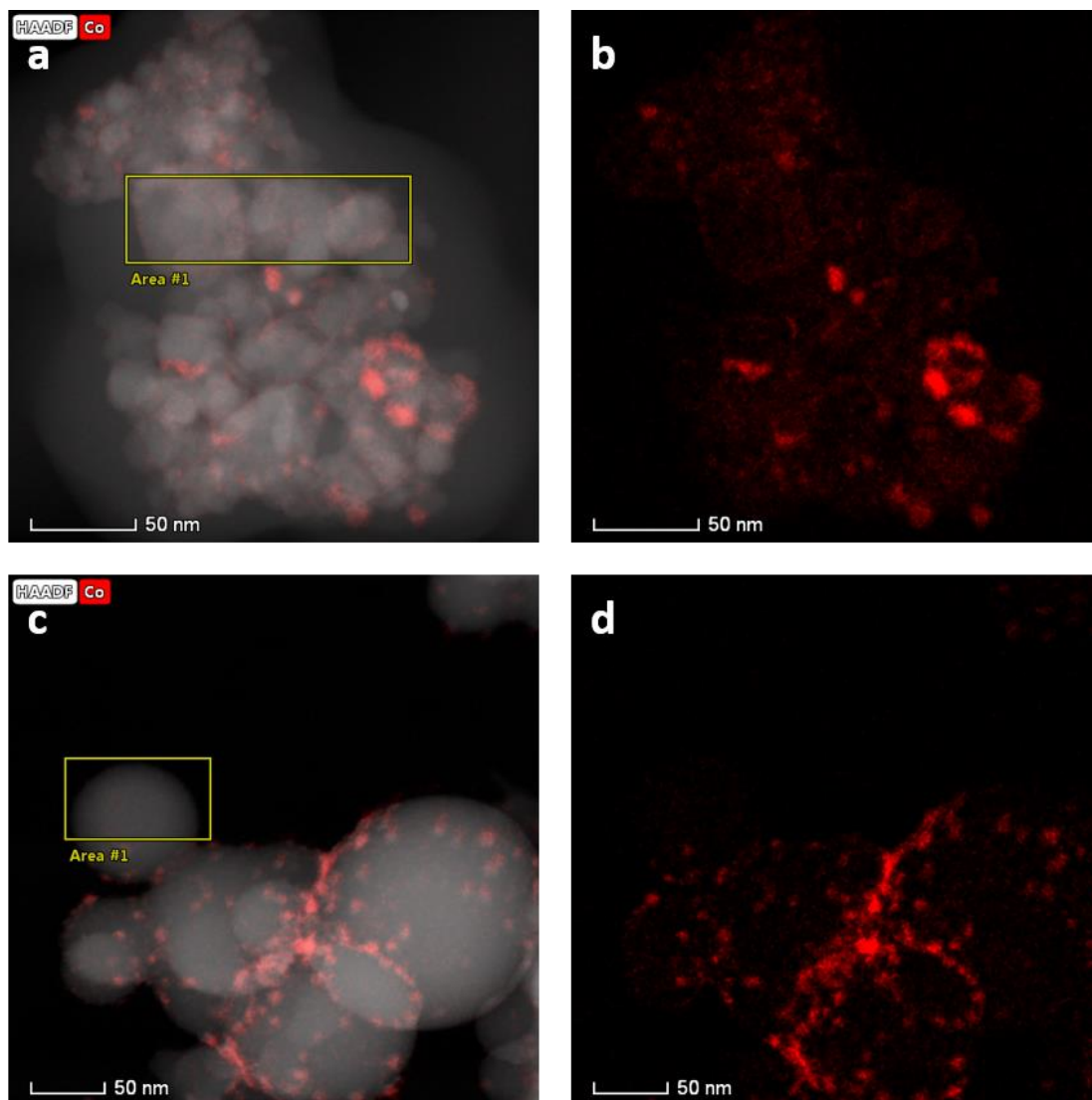
**Figure S5.** Deconvolution of the TPR profiles of the Co/TiO<sub>2</sub> samples. Three Gaussian contributions (dashed colored lines) were combined to give the overall fit (black solid line) to the experimental data (solid colored lines).



**Figure S6.** Cobalt-weight-based activity of the SiO<sub>2</sub>-supported Co-NC against time-on-stream. FT was performed at 20 bar, 220 °C, 2 H<sub>2</sub>/CO (v/v), GHSV = 1500-10750 h<sup>-1</sup> and X<sub>CO</sub> = 15-30 %.

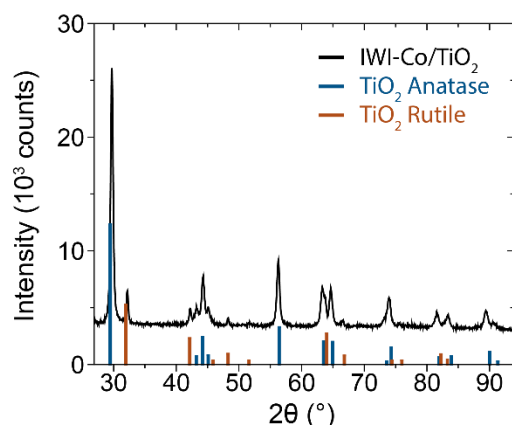


**Figure S7.** Overview of the samples after catalysis. HAADF-STEM-EDX of spent Co/TiO<sub>2</sub> samples are in the left column (Co in red) and TEM of the SiO<sub>2</sub>-supported samples is in the right column. (a) Co<sub>3</sub>/TiO<sub>2</sub>, (b) Co<sub>3</sub>/SiO<sub>2</sub>, (c) Co<sub>6</sub>/TiO<sub>2</sub>, (d) Co<sub>6</sub>/SiO<sub>2</sub>, (e) Co<sub>12</sub>/TiO<sub>2</sub>, (f) Co<sub>9</sub>/SiO<sub>2</sub> and (g) IWI-Co/TiO<sub>2</sub>.

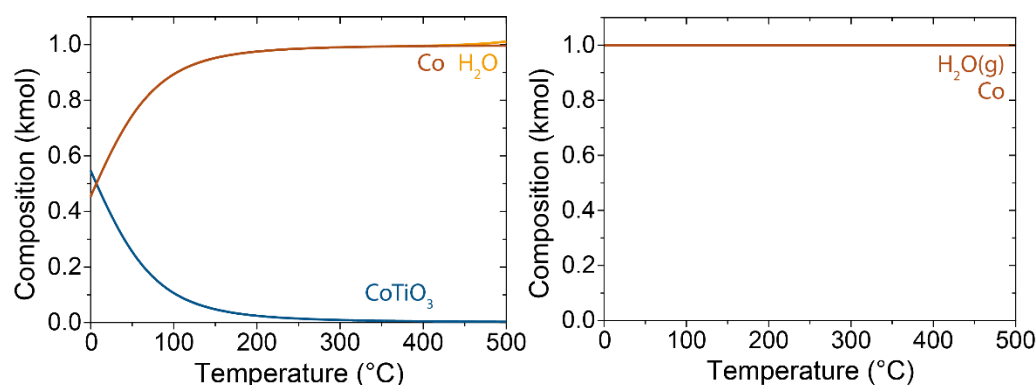


**Figure S8.** Quantification of the cobalt content in the support of the reduced Co/TiO<sub>2</sub> samples. HAADF-STEM-EDX map of (a) Co<sub>3</sub>/TiO<sub>2</sub> and (c) Co<sub>3</sub>/SiO<sub>2</sub> both after reduction (Co in red) and (b,d) the same location with only the Co signal from EDX, respectively. Parts of the samples without any visible particles are highlighted as Area #1.

The cobalt content in the support was determined using the ratio between the Co, O and Ti/Si signals in the highlighted area obtained by quantification of the EDX spectra using FEI Velox software. The same was done for the complete field of view and gave the total Co content, so both in the support and in the NC. The difference between the two represented the amount of Co residing in the NC. The results of multiple EDX maps (4-13) was averaged.



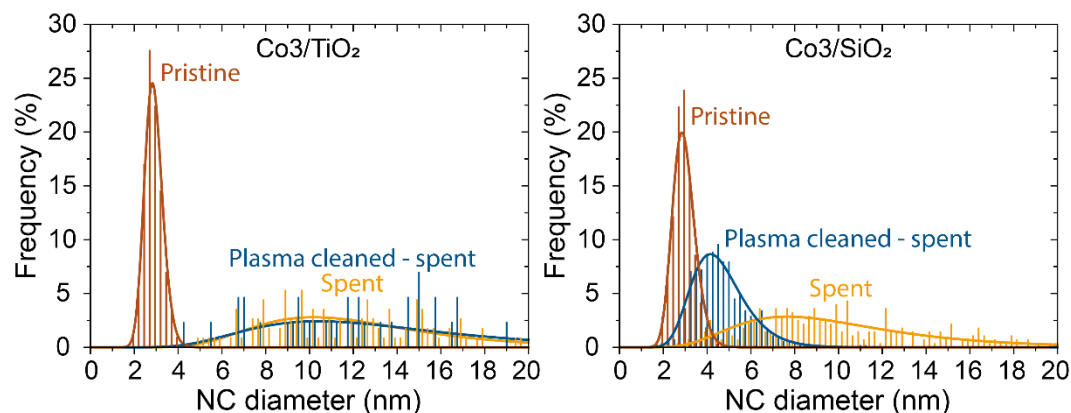
**Figure S9.** Diffractogram of reduced and passivated IWI-Co/TiO<sub>2</sub> as measured by XRD. The expected diffractions for TiO<sub>2</sub> in the anatase and rutile phase are provided. No cobalt phases were apparent.



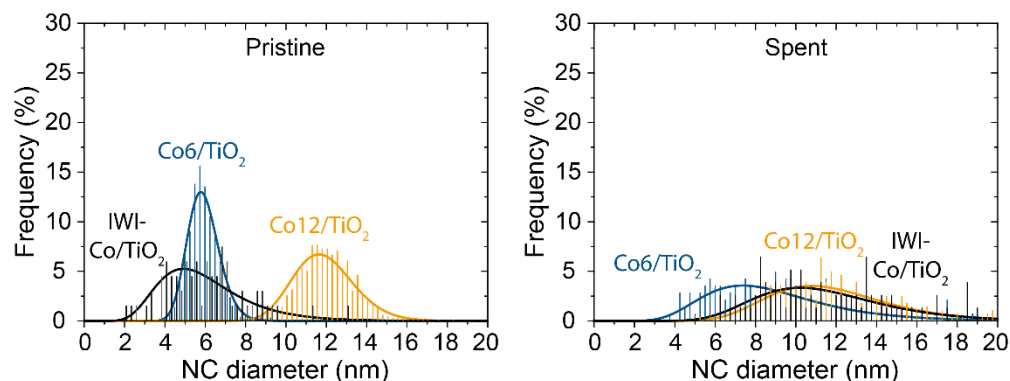
**Figure S10.** Thermodynamic equilibrium composition calculations on the formation of mixed metal-support compounds of Co/TiO<sub>2</sub> (left) and Co/SiO<sub>2</sub> (right). Equilibrium calculations based on the Gibbs free energy were performed with HSC Chemistry 7.1 software using 1 kmol CoO(s), 100 kmol TiO<sub>2</sub>(s) or SiO<sub>2</sub>(s) and 100 kmol H<sub>2</sub>(g) as starting compounds and a constant number of atoms and pressure (1 bar). All available solid Co, CoO<sub>x</sub>, Ti, TiO<sub>x</sub> and TiH<sub>x</sub> and mixed Co-TiO<sub>x</sub> species in the database (or the Si analogues) were included as possible reaction products together with gaseous H<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub>. A large excess of H<sub>2</sub> and TiO<sub>2</sub> or SiO<sub>2</sub> with respect to CoO was selected to keep the partial pressure of H<sub>2</sub>O formed upon reduction of CoO low, in line with the experimental conditions during reduction in a plug flow reactor.

Based on these calculations, it is thermodynamically possible to form small amounts of cobalt titanates in a reducing environment at the relevant temperatures, whilst cobalt silicates are not stable under the same conditions. N.B. H<sub>2</sub> and the supports are outside of the scale of the plots.

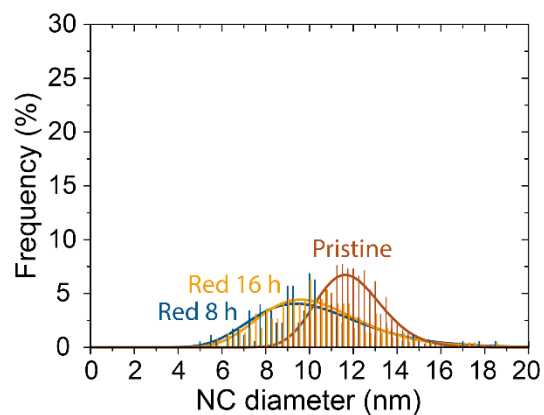




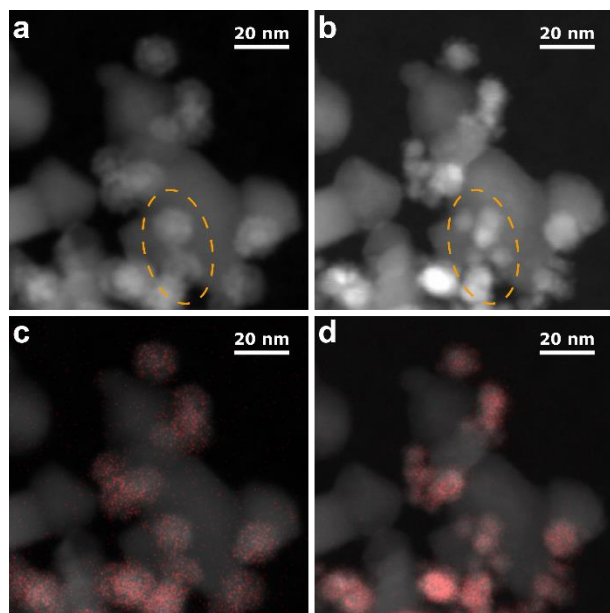
**Figure S11.** Effect of ligand removal on the particle growth in Co3/TiO<sub>2</sub> (left) and Co3/SiO<sub>2</sub> (right). The histograms and lognormal distributions are shown for the catalysts in the pristine, spent and cleaned and then spent state. Ligands were removed by plasma cleaning for 8 h prior to reduction and catalysis. No effect was observed on the particle size after catalysis on TiO<sub>2</sub> but it did reduce the sintering in Co3/SiO<sub>2</sub>.



**Figure S12.** Sintering behavior of IWI-Co/TiO<sub>2</sub> after >100 h on stream at 20 bar, 220 °C, 2 H<sub>2</sub>/CO. The histograms and lognormal distributions of the IWI-Co/TiO<sub>2</sub> before (left) and after catalysis (right) are shown together with the histograms and lognormal distributions for the NC-based Co6/TiO<sub>2</sub> and Co12/TiO<sub>2</sub> samples as comparison.



**Figure S13.** Effect of prolonged reduction on the particle growth in Co12/TiO<sub>2</sub>. The histograms and lognormal distributions are shown for Co12/TiO<sub>2</sub> in the pristine state and after reduction at 350 °C for 8 and 16 h. Prolonged reduction did not influence the final particle size.



**Figure S14.** The size evolution of individual Co-NC in Co12/TiO<sub>2</sub> during reduction. (a) HAADF-STEM and (c) HAADF-STEM-EDX images of pristine Co12/TiO<sub>2</sub>. (b) HAADF-STEM and (d) HAADF-STEM-EDX images of the same locations after reduction at 350 °C for 8 h. Co is depicted in red. The highlighted area contains two particles that disintegrated during reduction and formed multiple smaller particles.