

Assembly and Activation of Supported Cobalt Nanocrystal Catalysts for the Fischer-Tropsch Synthesis

T. W. van Deelen,^a H. Su,^{bc} N. A. J. M. Sommerdijk,^{bc} and K. P. de Jong^{*a}

a. 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

b. Laboratory of Materials and Interface Chemistry & Center for Multiscale Electron Microscopy, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO box 513, 5600 MB, Eindhoven (The Netherlands).

c. Institute of Complex Molecular Systems, Eindhoven University of Technology, PO box 513, 5600 MB, Eindhoven (The Netherlands).

Electronic Supplementary Information

Experimental Procedures

Synthesis of Co and CoO Nanocrystals

The synthesis of Co-NC was based on the method reported by Iablokov et al.¹ In this method, the introduction of elements that might ultimately affect the catalytic performance, such as phosphorus or sodium, was avoided. The synthesis was performed under N₂ atmosphere on a Schlenk line. Typically, 65 mg of oleic acid (Sigma-Aldrich, 90 %, technical grade) was transferred to a 100 mL 3-necked flask equipped with a cooler and two septa and evacuated at 373 K for 30 min. After flushing several times with N₂, 7.5 mL of 1,2-dichlorobenzene (Sigma-Aldrich, 99 %, anhydrous) was inertly transferred to the flask and the mixture was heated to 447 K under 750 rpm magnetic stirring. Meanwhile, 270 mg dicobalt octacarbonyl (Acros Organics, 95 %, stabilized) was dissolved in 1.5 mL 1,2-dichlorobenzene in a glass vial inside a glovebox. Then, the cobalt precursor was rapidly injected into the flask containing the mixture at 447 K and 750 rpm magnetic stirring. The reaction was continued for 20 minutes and quenched afterwards using a water bath. Optionally, for low-temperature (LT) oxidized nanocrystals (NC), the Co-NC were exposed to air at 298 K under 650 rpm magnetic stirring for 1 h by removing one septum in order to oxidize the NC to CoO. Subsequently, the colloidal suspension of CoO-NC was divided over two glass centrifuge tubes, both were filled up to 20 mL with 2-propanol (Sigma-Aldrich, >99 %, LC-MS Chromasolv) and centrifuged at 2200 G for 20 min. The supernatant was decanted and the precipitated colloids were redispersed in 0.5 mL n-hexane (Acros Organics, 99+ %) per tube using sonication. Again, the tubes were filled to 20 mL with 2-propanol, then centrifuged at 2200 G for 20 min and the supernatant was decanted. This washing cycle was repeated 2 times more and finally the NC were redispersed in 2 mL toluene (Acros Organics, 99+ %, extra pure) and stored in a glass vial.

Deposition of Co and CoO Nanocrystals on Carbon Nanotubes

The support, CNT (Baytubes c150 HP), was first sieved to a fraction of 75-150 μm . Co- and CoO-NC (10 wt% Co) were emplaced on CNT by wet impregnation at elevated temperature under nitrogen atmosphere on a Schlenk line.² To this end, 500 mg CNT was transferred to a 100 mL 3-necked flask equipped with a cooler, septum and glass plug. 5 mL 1-octadecene (Sigma-Aldrich, 90 %, technical grade) was mixed with the colloidal suspension (in toluene) and added to the CNT under 400 rpm magnetic stirring. The suspension was degassed at 373 K for 30 min during which the toluene evaporated, flushed several times with nitrogen and heated to 473 K for 30 min. After cooling down to room temperature, ~20 mL acetone was added to the suspension and the supernatant was decanted. The precipitated catalyst was washed six times by first adding 2 mL n-hexane followed by 6 mL acetone and decanting of the supernatant. Finally, the catalyst was dried at 333 K for 1 h in static air, at 393 K for 3 h in static air and at 353 K for 3 h under vacuum. Afterwards, the catalyst was again sieved to a fraction of 75-150 μm .

High-Temperature Oxidative Treatment of CoO-NC/CNT

A batch of LT-oxidized CoO-NC on CNT was treated at high temperature in an oxidative environment. First, 100 mg of catalyst was loaded in a U-shaped quartz reactor and 37.5 mL·min⁻¹ of 20 vol% O₂ in N₂ was led through the catalyst in fixed bed mode. The catalyst was heated to 523 K for 2 h with 2 K·min⁻¹ and was afterwards cooled again to room temperature.

Characterization

A cryogenic transmission electron microscopy (cryo-TEM) sample of the suspension of metallic Co-NC under inert atmosphere was prepared using a vitrification robot (FEI Vitrobot Mark III). To prepare the sample, 3 μL of sample was applied on a 200 mesh, lacey carbon-coated Cu grid inside an environmental chamber at 298 K with 99 % relative humidity of toluene. The grid was blotted with filter paper for 3 s and then vitrified by rapidly plunging the grid into liquid nitrogen (77 K). The total vitrification procedure took less than 10 s in order to minimize the contact time with air and to avoid oxidation of the Co-NC. Cryo-TEM was performed on a TU/e CryoTitan (FEI) operating at 300 kV using low electron dose rates of 37 e⁻·Å⁻²·s⁻¹ at the magnification used. The crystal structure of the NC was analyzed using low dose selective area electron diffraction (LDSAED).

Transmission electron microscopy (TEM) was performed using a Tecnai 12 (FEI) operating at 120 kV. A sample of a CoO-NC suspension was prepared by dropcasting the colloidal suspension in hexane on a 200 mesh, carbon-coated Cu grid. In the case of CNT supported catalysts, the powder was first suspended in 2-propanol by sonication and subsequently dropcasted on a 200 mesh holey carbon-coated Cu grid. The particle sizes were manually determined using iTEM software and at least 200 particles were analyzed to obtain a statistical analysis.

The reported diameters of all Co_xO_y particles were converted to their equivalent metallic cobalt diameter and were surface averaged ($D[3,2]$). Reduced and passivated samples were corrected for a 3 nm CoO layer.

High-resolution transmission electron microscopy (HR-TEM) was carried out on a Talos F200X (FEI), equipped with a high-brightness field emission gun and operated at 200 kV. Sample preparation was identical to that of TEM.

X-ray diffraction (XRD) was performed using a Bruker D2 Phaser using Co radiation (K_{α} , $\lambda = 1.789 \text{ \AA}$). The diffractograms were analyzed and fitted using Bruker's Eva and Topas software. The reported crystallite size was calculated using the Scherrer equation after fitting the full scan from $20\text{-}100^\circ 2\theta$ and analysis of the $\epsilon\text{-Co}$ [221], CoO [111] and Co_3O_4 [311] peaks.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was measured on a SPECTRO ARCOS and samples were prepared by cobalt extraction in aqua regia.

Thermogravimetric analysis–mass spectrometry (TGA-MS) was carried out on a PerkinElmer Pyris 1 TGA. Approximately 5 mg sample was pre-dried at 323 K under N_2 and subsequently analyzed while heating to 1073 K with $10 \text{ K}\cdot\text{min}^{-1}$ under a flow of 25 vol% H_2 in N_2 .

Catalytic Performance

The performance of the catalysts was evaluated using an Avantium Flowrence 16 parallel reactor setup. Stainless steel, plug-flow reactors were first loaded with a mixture of 15-50 mg of catalyst and 100 mg SiC diluent. Then, the catalysts were reduced *in situ* at 623 K for 8 h ($1 \text{ K}\cdot\text{min}^{-1}$) in 25 vol% H_2 in He at 1 bar. Subsequently, the reactors were cooled to 453 K and the pressure was increased to 20 bar under H_2 flow. Finally, synthesis gas with $\text{H}_2/\text{CO} = 2 \text{ v/v}$, 5 vol% He as internal standard and $\text{GHSV} = 2350\text{-}7850 \text{ h}^{-1}$ was introduced and the reactors were heated to 493 K with $1 \text{ K}\cdot\text{min}^{-1}$. The reaction products were analyzed online with an Agilent 7890A GC. The hydrocarbon products were separated on an Agilent J&W PoraBOND Q column and analyzed by a FID. The permanent gasses were separated on a ShinCarbon ST column and quantified using a TCD.

The activity was reported as CO conversion, defined as $X_{\text{CO}} = (\text{mol}_{\text{CO, in}} - \text{mol}_{\text{CO, out}}) \cdot \text{mol}_{\text{CO, in}}^{-1}$, and as cobalt time yield and turnover frequency. For the TOF calculation, the surface averaged cobalt diameter of the spent catalysts from TEM was used to determine the metallic surface area, assuming spherical particles. From the metallic surface area, the number of surface cobalt atoms was derived using a cobalt cross sectional area of 0.0662 nm^2 per atom.³ Furthermore, the selectivity towards C_1 to C_4 hydrocarbons was calculated as $S_{\text{C}_n} = \text{mol}_{\text{C}_n} \cdot n \cdot (\text{mol}_{\text{CO, in}} - \text{mol}_{\text{CO, out}})^{-1}$, where n is the carbon number (1-4) of the product. The selectivity to C_{5+} was defined as $S_{\text{C}_{5+}} = 1 - S_{\text{C}_{1-4}}$.

Results and Discussion

Electron diffraction of Co- and CoO-NC

Electron diffraction was performed on NC both untreated and after LT-oxidation. The electron diffraction pattern of the untreated NC was measured under cyro conditions using the TU/e CryoTitan microscope and the LT-oxidized NC under regular conditions using the Tecnai 12 microscope. The assignment of the diffraction pattern to a specific cobalt phase is given in Table S1.

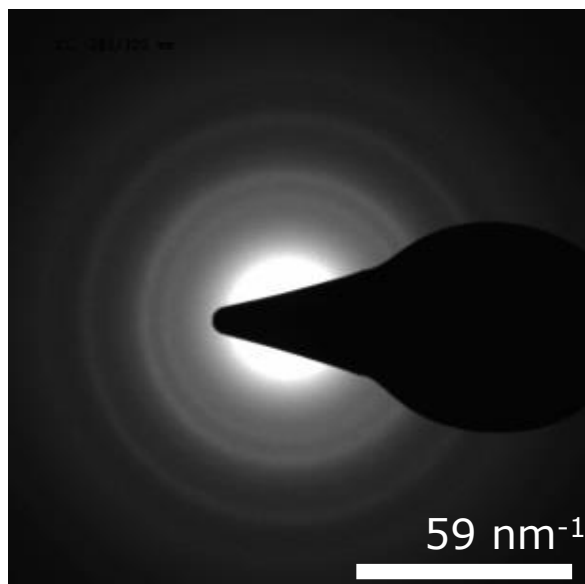


Figure S1. Electron diffraction pattern of CoO-NC.

Table S1. Experimental d-spacing values for Co- and CoO-NC and reported values for the reference materials. Only the d-spacings with a relative intensity above 10 % are given.

Co-NC d (Å)	ϵ -Co reference ⁴ d (Å)	ϵ -Co reference ⁴ h k l	CoO-NC d (Å)	CoO reference ⁵ d (Å)	CoO reference ⁵ h k l
2.07	2.04	2 2 1	2.52	2.46	1 1 1
1.95	1.94	3 1 0	2.18	2.13	2 0 0
1.89	1.85	3 1 1	1.52	1.51	2 2 0
1.23	1.2	5 1 0	1.26	1.28	3 1 1
-	1.13	5 2 0	1.04	1.23	2 2 2

TEM of Co1/CNT

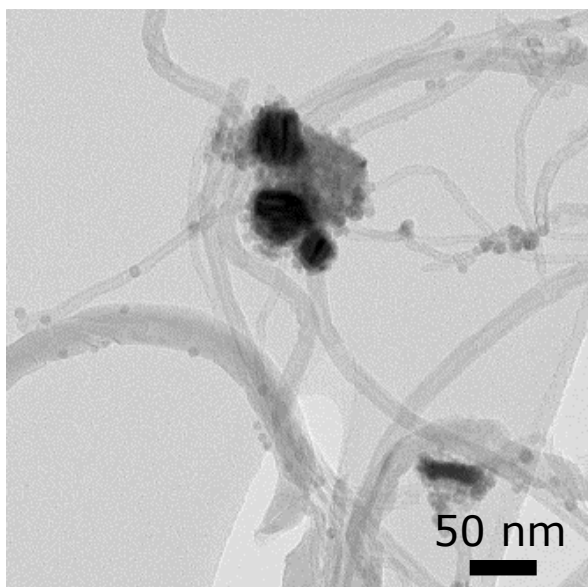


Figure S2. TEM of Co1/CNT after drying and exposure to air.

XRD of Co/CNT Catalysts

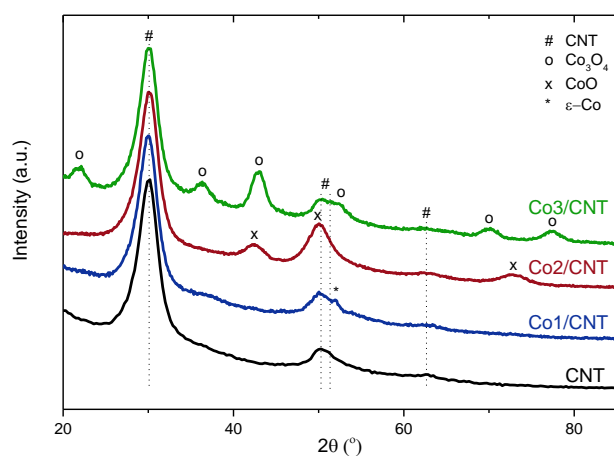


Figure S3. XRD patterns of pristine CNT and the Co/CNT catalysts after various oxidative treatments.

Particle Size Analysis of Co2/CNT and Co3/CNT

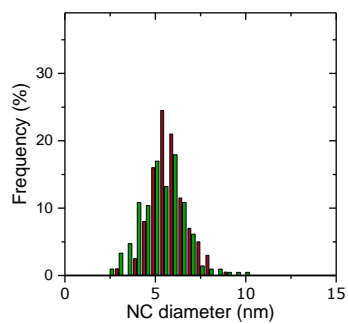


Figure S4. Particle size distributions of Co2/CNT (red) and Co3/CNT (Green).

TGA of Co3/CNT

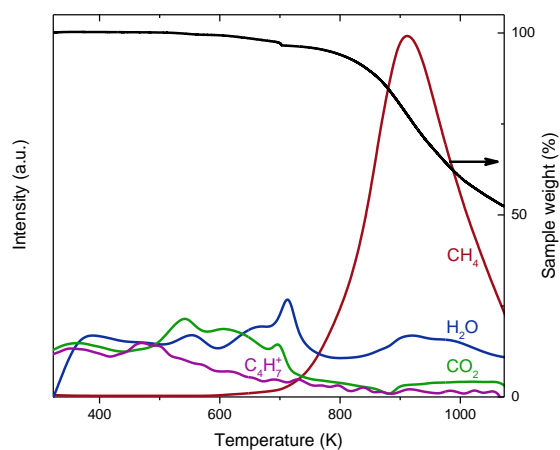


Figure S5. Combined TGA and MS results of Co3/CNT in 25 vol% H₂ with a heating ramp of 10 K·min⁻¹.

Fischer-Tropsch Synthesis Activity

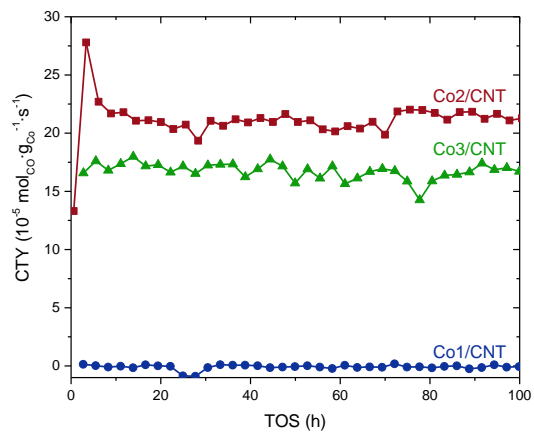


Figure S6. Cobalt time yield during the first 100 h time-on-stream at 20 bar, 493 K, H₂/CO = 2 v/v, GHSV = 2350-7850 h⁻¹

Spent Catalysts

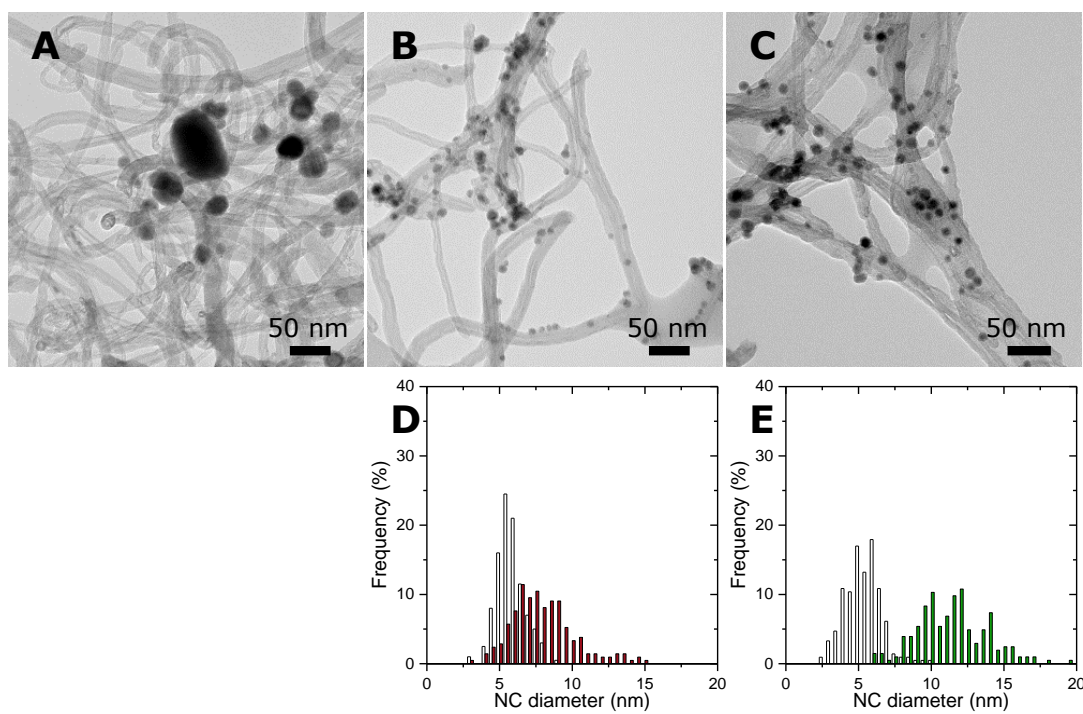


Figure S7. TEM analysis of the spent catalysts. TEM of the spent catalysts of A) Co1/CNT, B) Co2/CNT and C) Co3/CNT after more than 100 h TOS and the cobalt particle size distributions of the fresh (open fill) and spent (solid fill) of D) Co2/CNT and E) Co3/CNT.

Reported Turnover Frequencies

The turnover frequencies that were used as a comparison were recalculated from publications by Herranz et al.⁶ and by Delgado et al.⁷ Their catalysts, testing conditions and units to express the TOF differed from ours, which made recalculation necessary. The results of which are given in Table S2.

Herranz et al. synthesized CoO-NC using a similar $\text{Co}_2(\text{CO})_8$ decomposition method as reported here, but in the presence of both oleic acid and trioctylphosphine oxide (TOPO) as surfactants. The NC were deposited on silica with a BET surface area of $300 \text{ m}^2\text{-g}^{-1}$. The catalytic tests were performed under methanation conditions at 1 bar, 513 K and $\text{H}_2/\text{CO}/\text{Ar} = 3/10/20 \text{ v/v/v}$. The TOF values were derived from Figure 5, in which the TOF was defined as the number of CO molecules converted per number of Co atoms at the surface per second. According to the unit indicated, the values should be multiplied by a factor 10^3 , but the resulting TOF would be unrealistically high and lead to CO conversion levels of 10^5 - 10^6 %. Rather, we assumed the multiplication factor to be 10^{-3} . The TOF at 493 K was derived from the values TOF at 513 K. To this end, the Arrhenius equation and the experimentally determined activation energy ($105 \text{ kJ}\cdot\text{mol}^{-1}$) were used to correct for the temperature difference. Unfortunately, it is not straightforward to correct for the effect of different reaction pressures and feed compositions. Especially at higher pressure, approximately a twofold increase in TOF can be expected.⁸

The NC by Delgado et al. were prepared through reduction of cobalt chloride by sodium borohydride as a reducing agent in the presence of polyvinylpyrrolidone (PVP) as surfactant. Subsequently, the NC were emplaced on TiO_2 P25. The applied FT conditions were 20 bar, 513 K and $\text{H}_2/\text{CO} = 2 \text{ v/v}$ and the TOF values were reported in mol CO converted per mol Co surface atoms per hour. These values were first divided by $3600 \text{ s}\cdot\text{h}^{-1}$ to obtain a TOF per second and afterwards recalculated for a reaction temperature of 493 K using again the Arrhenius equation. A typical activation energy of $100 \text{ kJ}\cdot\text{mol}^{-1}$ was assumed.

The significant discrepancy between the TOF reported here and those reported previously for LT- or non-oxidized NC-based catalysts was remarkable, because those catalysts were rather comparable to ours, in particular the discussed Co/ SiO_2 catalysts. Although the cause was not established, the most significant difference appeared to be in the choice of surfactants. Only oleic acid was used as a surfactant in our NC synthesis, whereas also TOPO was used by Herranz et al. TOPO reportedly poisons the catalytic activity in CO_2 hydrogenation¹ and therefore, a similar poisoning effect could have occurred as well in FT. In the case of Delgado et al., boron from the reducing agent, NaBH_4 , remained in the catalysts and probably affected the catalytic performance considerably.

Table S2. Turnover frequencies reported in literature for LT- or non-oxidized NC-based catalysts. The TOF were converted to the same units and to the same reaction temperatures.

Herranz et al. ⁶			Delgado et al. ⁷			
Average particle diameter (nm)	TOF at 513 K (10^{-3} s^{-1})	TOF at 493 K (10^{-3} s^{-1})	Average particle diameter (nm)	TOF at 513 K (h^{-1})	TOF at 513 K (10^{-3} s^{-1})	TOF at 493 K (10^{-3} s^{-1})
3.0	0.6	0.2	1.8	19	5.1	2.0
4.2	0.8	0.3	2.6	13	3.5	1.4
4.6	1.0	0.4	5.2	6.6	1.8	0.7
5.3	0.8	0.3	7.0	2.1	0.6	0.2
10	1.9	0.7	-	-	-	-

References

- 1 V. Iablokov, S. K. Beaumont, S. Alayoglu, V. V. Pushkarev, C. Specht, J. Gao, A. P. Alivisatos, N. Kruse, G. A. Somorjai, *Nano Lett.*, 2012, **12**, 3091.
- 2 M. Casavola, J. Hermannsdörfer, N. de Jonge, A. I. Dugulan, K. P. de Jong, *Adv. Funct. Mater.*, 2015, **25**, 5309.
- 3 R. C. Reuel, C. H. Bartholomew, *J. Catal.*, 1984, **85**, 63.
- 4 S. Sun, C. B. Murray, *J. Appl. Phys.*, 1999, **85**, 4325.
- 5 C. Petit, Z. L. Wang, M. P. Pileni, *J. Phys. Chem. B*, 2005, **109**, 15309.
- 6 T. Herranz, X. Deng, A. Cabot, J. Guo, M. Salmeron, *J. Phys. Chem. B*, 2009, **113**, 10721.
- 7 J. A. Delgado, C. Claver, S. Castillón, D. Curulla-Ferré, V. V. Ordomsky, C. Godard, *Appl. Catal. A Gen.*, 2016, **513**, 39.
- 8 J. P. den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen, K. P. de Jong, *J. Am. Chem. Soc.*, 2009, **131**, 7197.

Author Contributions

T.W.v.D. synthesized, characterized and tested the catalysts and drafted the manuscript. H.S. performed the cryo-TEM measurements and N.A.J.M.S. devised the cryo-TEM measurements. K.P.d.J. contributed to experiment design, data analysis and manuscript writing.