**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, and Krijn P. de Jong*

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

**Supporting Information**

**ABSTRACT:** Colloidal synthesis of nanocrystals (NC) followed by their attachment to a support and activation is a promising route to prepare model catalysts for research on structure-performance relationships. Here, we investigated the suitability of this method to prepare well-defined Co/TiO₂ and Co/SiO₂ catalysts for the Fischer–Tropsch (FT) synthesis with high control over the cobalt particle size. To this end, Co-NC of 3, 6, 9, and 12 nm with narrow size distributions were synthesized and attached uniformly on either TiO₂ or SiO₂ supports with comparable morphology and Co loadings of 2−10 wt %. After activation in H₂, the FT activity of the TiO₂-supported 6 and 12 nm Co-NC was similar to that of a Co/TiO₂ catalyst prepared by impregnation, showing that full activation was achieved and relevant catalysts had been obtained; however, 3 nm Co-NC on TiO₂ were less active than anticipated. Analysis after FT revealed that all Co-NC on TiO₂ as well as 3 nm Co-NC on SiO₂ had grown to ∼13 nm, while the sizes of the 6 and 9 nm Co-NC on SiO₂ had remained stable. It was found that the 3 nm Co-NC on TiO₂ already grew to 10 nm during activation in H₂. Furthermore, substantial amounts of Co (up to 60%) migrated from the Co-NC to the support during activation on TiO₂ against only 15% on SiO₂. We showed that the stronger interaction between cobalt and TiO₂ leads to enhanced catalyst restructuring as compared to SiO₂. These findings demonstrate the potential of the NC-based method to produce relevant model catalysts to investigate phenomena that could not be studied using conventionally synthesized catalysts.

**KEYWORDS:** colloidal synthesis, cobalt nanocrystals, supported catalysts, Fischer–Tropsch synthesis, particle growth, metal–support interaction

**INTRODUCTION**

Metal nanoparticles on a support material are widely applied as heterogeneous catalysts in industrial processes. In order to improve industrial catalyst design, it is a prerequisite to link their structure to their performance which requires well-defined model catalysts. Several nanotechnological techniques have recently been developed that allow the synthesis of catalysts with high control over parameters such as composition, size, or shape of metal nanoparticles.

Among the available techniques, the colloidal synthesis of nanocrystals (NC) is especially promising for the preparation of catalysts. By preforming the NC in solution instead of directly on the support as is custom in conventional synthesis techniques, it is possible to synthesize monodisperse, single crystalline, and size-controlled NC. The vast majority of the research so far focused on noble metal NC even though base metals are very important for catalysis. However, base metal NC are more challenging to utilize in supported catalysts. First, homogeneous attachment of base metal NC on a support can be hindered by magnetic interactions between the NC. Second, removal of the stabilizing ligand shell can be incomplete, blocking active sites and lowering catalytic activity, or harsh treatments are applied that may compromise the well-defined nature of the catalyst. Recently we demonstrated uniform attachment and successful ligand removal for Co-NC supported on carbon nanotubes by applying a mild, low-temperature oxidation to the NC in suspension prior to attachment.

A particular application where NC-based catalysts can contribute to fundamental understanding is the Fischer–Tropsch (FT) synthesis, i.e. the catalytic conversion of synthesis gas (an H₂/CO mixture) into hydrocarbon fuels and chemicals. The cobalt-catalyzed FT reaction is reported to be structure sensitive, related to both cobalt particle size and cobalt crystal structure. So far, most research involving Co-NC for FT concentrated either on slurry-phase FT, in which the unsupported Co-NC remain in suspension, or on Co-NC supported on irreducible oxides (mainly SiO₂ or Al₂O₃). However, reducible oxides such as TiO₂ provide additional opportunities to control the performance of the catalyst, notably by changing the reducibility of the support.

Co/TiO₂ catalysts are not trivial to obtain, since the TiO₂ support oxidizes Co at low temperature. Therefore, we have developed a method to synthesize supported Co-NC on TiO₂ that involved temperature oxidation to the NC in suspension prior to attachment. Moreover, in contrast to previously reported methods, Co-NC can now be supported on TiO₂ by applying a mild, low-temperature oxidation to the NC in suspension prior to attachment.
as TiO₂ are also interesting supports for cobalt-based FT catalysts, for both industry and academia. TiO₂-supported cobalt catalysts can be considered more complex than Co/SiO₂ or Co/Al₂O₃, since TiO₂ can be partially reduced under reaction conditions, leading to special interphase phenomena known as strong metal–support interactions (SMSI). The effects of these metal-TiO₂ interactions remain poorly understood, in part because synthesis procedures for well-defined catalysts are lacking, especially for <10 nm Co particles. TiO₂-supported catalysts with narrow Co particle size distributions can be synthesized using conventional methods, but the control over the average particle size is limited. Furthermore, there are only a few reports of NC-based Co/TiO₂ catalysts, and these either contained boron impurities owing to the synthesis method or the Co-NC were 10 nm or larger. Therefore, it would be highly desirable to expand the applicability of Co-NC to TiO₂ as support.

Here we report the synthesis and catalytic performance of well-defined catalysts containing 3–12 nm Co-NC on TiO₂ and SiO₂ and demonstrate their use as model systems by studying particle growth under FT conditions. The Co-NC were synthesized by a hot-injection method. After low-temperature oxidation, the Co-NC were homogeneously attached to either TiO₂ or SiO₂. Their catalytic performance was comparable to that of Co/TiO₂ prepared by impregnation, except for 3 nm Co-NC on TiO₂, whose activity was substantially lower. The TiO₂-supported Co particles and 3 nm Co-NC on SiO₂ sintered during reduction and/or FT, indicating that both the support and initial NC size affected the stability of Co-NC under reaction conditions. We show that the controlled NC-based methodology enabled the synthesis of size-controlled Co/TiO₂ and Co/SiO₂ with relevant catalytic performance. Their potential as model systems is underlined by investigating NC particle growth, revealing phenomena that are not observed with conventionally prepared catalysts.

#### EXPERIMENTAL METHODS

**Coating Nanocrystal Synthesis.** Cobalt nanocrystals of different sizes were synthesized by a hot injection method based on the literature and our previous work. A schematic summary of the NC synthesis procedure is shown in Figure S1. The supports were TiO₂ (Evonik, Aeroside P25) or SiO₂ (Evonik, Aerosil OX 50), both sieved to a fraction of 75–150 μm. To regulate the final cobalt loading, between 0.4 and 2.5 g of support was suspended in a mixture of the colloidal suspension and 5–31 mL of 1-octadecene (Sigma-Aldrich, 90%, technical grade) inside a 100 mL 3-necked flask. A cooler, glass plug, and septum were connected to the flask, the magnetic stirring was set to 400 rpm, and the suspension was degassed under vacuum at 100 °C for 15 min, during which the n-hexane from the colloidal suspension evaporated. The setup was then flushed, switched to N₂, and heated to 200 °C. The heating was stopped after 30 min at 200 °C, and the solution was cooled to ambient temperature in approximately 30 min. The suspension was divided over two glass centrifuge tubes and centrifuged at 1500 G for 5 min, and the supernatant was decanted. The residue was resuspended and combined in a total of 2 mL of n-hexane, sonicated for 1 min, diluted with 6 mL of acetone, and centrifuged at 1500 G for 5 min, and the supernatant was again decanted. This washing cycle was repeated five times, followed by resuspending the residue in 20 mL of acetone, sonicating for 1 min, centrifuging at 1500 G for 5 min, and the supernatant was again decanted. Afterward, the samples were dried at 60 °C for 1 h in static air, followed by 120 °C for 3 h in static air and 80 °C for 3 h under vacuum. Finally, the samples were sieved to a grain size of 75–150 μm.

**Incipient Wetness Impregnation.** A comparison Co/TiO₂ sample was prepared by incipient wetness impregnation following the procedure by Eschemann et al. First, 2 g of TiO₂ (Evonik, Aeroside P25) was sieved to 75–150 μm and then dried at 80 °C for 1 h under vacuum. The vacuum was released and the TiO₂ was impregnated directly afterward with a pore-filling amount of precursor solution consisting of Co(NO₃)₂·6H₂O (Acrors Organics, 99+%) in Milli-Q water. The solution was added dropwise under magnetic and manual stirring. After the addition, the powder was dried and heat treated in a U-shaped, glass reactor in fluidized bed mode (1 L·min⁻¹ upward flow of N₂). Drying took place at 80 °C for 2 h and was followed directly by a thermal treatment at 250 °C for 2 h, both with 2 °C·min⁻¹. The sample was finally sieved again to a grain size of 75–150 μm.

**Plasma Cleaning.** Optionally, pristine Co-NC samples were plasma cleaned to remove the ligands prior to reduction and FT. Typically, 100 mg of sample was treated for 8 h in a homemade container inserted into a Fischione Model 1020 Plasma Cleaner. The plasma was generated using a 25% O₂ in Ar flow and a 13.56 MHz oscillating electromagnetic field.

**Characterization.** Transmission electron microscopy (TEM) was performed on a Tecnai 12 (FEI), operated at 120 kV, or on a Tecnai 20 (FEI), operated at 200 kV. TEM samples of Co-NC suspensions were prepared by sonication and dropcasting a diluted sample directly on a carbon-coated TEM grid. To prepare a sample of supported Co-NC, the solid
was first suspended in 2-propanol by sonication and then dropcasted on a TEM grid. In the case of samples after catalysis, the samples were washed three times using toluene and 30 min sonication and once using n-hexane to remove the hydrocarbon reaction products before dropcasting on a TEM grid. The sizes of >200 Co particles were determined manually using ImageJ software. All particle sizes are reported as the Sauter mean diameter (volume/surface mean, D[3,2]) of the equivalent metallic cobalt particles, meaning that the measured diameters of (partial) cobalt oxide particles were corrected based on the densities of the oxide and the metal.

Scanning transmission electron microscopy combined with energy-dispersive X-ray spectroscopy (STEM-EDX) was performed in high-angle annular dark-field (HAADF) mode on a Talos F200X (FEI), equipped with a high-brightness field emission gun (X-FEG) and a Super-X G2 EDX detector and operated at 200 kV. Particle size analysis was similar to that of TEM, with the exception that <200 particles were analyzed for some samples, depending on the particle size and cobalt loading.

HAADF-STEM-EDX of the same positions of 12 nm Co-NC on TiO2 before and after reduction was performed using a SiN TEM chip (TEMWindow SN100-A50Q33). After imaging the pristine sample, the SiN TEM chip was transferred to a glass U-shaped reactor, and the sample on the chip was reduced ex situ in 25% H2 in Ar flow at 350 °C for 8 h with 1 °C·min⁻¹ and cooled down afterward under the same atmosphere. Subsequently, the chip was transferred back to the microscope and analyzed again. During the transfer, the sample was exposed to air at ambient conditions.

N2-physisorption of the bare supports was measured at −196 °C on a Tristar 3000 (Micromeritics). The samples were dried in N2 at 300 °C for 14−20 h prior to the analysis.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was carried out on a SPECTRO ARCOS, and the sample was digested in aqua regia to extract the cobalt.

Temperature programmed reduction (TPR) profiles were measured on an Autochem 2920 (Micromeritics). Approximately 100 mg of sample was reduced in 5% H2 in Ar flow from 50 to 800 °C with 5 °C·min⁻¹.

X-ray diffraction (XRD) was performed on a Bruker D2 Phaser, equipped with a Co radiation source (λ = 1.789 Å). The sample was measured between 20 and 100° 2θ with an increment of 0.05°.

**Fischer–Tropsch Synthesis.** The catalytic performance in the Fischer–Tropsch synthesis was investigated using an Avantium Flowrence 16 parallel reactor setup. Stainless steel plug flow reactors of 2.0 or 2.6 mm ID were loaded with 25−110 mg of catalyst (75−150 μm) diluted with 100 mg of SiC (200−425 μm). Prior to reaction, the catalysts were reduced in situ at 1 bar in 25% H2 in He flow at either 350 °C (TiO2-samples) or 500 °C (SiO2-samples) for 8 h with 1 °C·min⁻¹. Afterward, the reactors were cooled to 180 °C and pressurized to 20 bar. At these conditions, the atmosphere was switched to synthesis gas with H2/CO = 2 (v/v) and 5% He as internal standard. Subsequently, the reactors were heated to 220 °C with 1 °C·min⁻¹, and product analysis was started after 1 h. The reaction products were analyzed online using an Agilent 7890A GC equipped with two channels. The first channel contained an Agilent J&W PoraBOND Q column connected to an FID to detect the hydrocarbon products, and the second one consisted of a ShinCarbon-ST column connected to a TCD to analyze the permanent gases.

The catalytic activity was reported as CO conversion (XCO), cobalt time yield (CTY), and turnover frequency (TOF). The TOF was based on the activity and the Sauter mean diameter (D[3,2]) of the spent Co-NC after correction for a 3 nm CoO passivation layer, assuming a cross-sectional area of 0.0662 nm² per cobalt atom. The selectivity (S) to C1−C4 products was defined as S = 100 ·F ·(CO,out)−XCO)⁻¹ with n being the product’s carbon number and F being the flow of the corresponding hydrocarbon or CO. The selectivity to C5ₙ was defined as Sₕₙ = 100 ·S ·CO.

**RESULTS AND DISCUSSION**

**Cobalt Nanocrystal Synthesis.** Well-defined cobalt nanocrystals were synthesized with distinct sizes between 3 and 12 nm and a polydispersity of 11−18% (Figure 1, additional particle size distributions in Figure S2). The Co-NC were designated as CoX, with X denoting the average diameter of the NC. The size of the Co-NC size was regulated by varying the temperature of the hot-injection temperature. The Co-NC size correlated with the synthesis temperature in the range of 170−183 °C and
became less reproducible at lower temperature (Figure 1d). After the synthesis, low-temperature oxidation by air-exposure at ambient conditions was applied to facilitate attachment and activation of the Co-NC. The Co-NC of 3, 6, 9, and 12 nm were attached to TiO₂ or SiO₂, thus omitting the Co-NC of 4 and 8 nm in Figure 1d.

**Cobalt Nanocrystal Attachment.** The Co-NC were attached to titania and silica with comparable specific surface areas (∼50 m²·g⁻¹) but different mesopore volumes (0.3 and 0.1 mL·g⁻¹, respectively) as determined by N₂-physisorption (Figure S3, Table S1). The cobalt loading was adjusted to obtain similar cobalt metal surface areas per unit weight of catalyst in the pristine samples with the aim to avoid major differences in catalyst-weight-based activities during FT (Table 1). Furthermore, the Co-NC on the supports were analyzed with TEM (Figure 2). The Co-NC distribution was uniform over both supports, similar to previous results with a carbon support. In addition, a reference Co/TiO₂ sample was prepared by conventional techniques, in this case incipient wetness impregnation of a cobalt nitrate solution (designated as IWI-Co/TiO₂ details in Table 1 and TEM results in Figure S4). Its average particle size was most comparable to Co6/TiO₂, but the particle size distribution was substantially broader.

The sizes of the Co-NC remained unchanged during the attachment treatment as concluded from TEM (Figure 2). The Co-NC of 3 and 6 nm consisted completely of CoO, while for the 9 and 12 nm Co-NC only an outer layer of CoO was formed and a metallic core with higher contrast was observed. This CoO shell had a thickness of 4.5 nm in the case of Co12/TiO₂, which exceeds the CoO passivation layer of 3 nm that is typically observed upon exposure of metallic cobalt particles to air at ambient conditions. The increased oxidation of the Co-NCs could have occurred during drying at 120 °C, as this is close to the temperature range where Kirkendall effects have been observed. The Kirkendall effect occurs upon oxidation of metals at elevated temperatures and leads to the formation of hollow metal oxide particles.

The reducibility of the Co-NC on TiO₂ samples was investigated by temperature-programmed reduction (TPR, Figure 3a). Two reduction peaks were observed between 250 and 450 °C for all samples next to a negative peak at higher temperatures, which is attributed to the desorption/decomposition of remaining ligands. As expected, the reduction shifted to lower temperatures with increasing particle size, because small oxide particles often display lower reducibility. Furthermore, the total H₂-uptake related to the first two peaks increased with the particle size following the increase in cobalt content. When comparing the total H₂-uptake of the Co-NC/TiO₂ samples normalized to the amount of Co, the H₂-uptake of Co12/TiO₂ was only 89–92% of that of the 3 and 6 nm NC (deconvolutions in Figure S5). This indicated that 10% of the cobalt in Co12/TiO₂ was still present in the core of the NC as metallic cobalt, which was in line with the earlier TEM observation of a metallic core and a CoO passivation layer (Figure 2).

**Fischer–Tropsch Synthesis.** The cobalt-weight-based activity (cobalt time yield, CTY) of the TiO₂-supported samples was evaluated over 100 h on stream (Figure 3b, Table 2). Co6/TiO₂ was the most active after 100 h followed by Co12/TiO₂, which was initially more active but deactivated faster. Co3/TiO₂ was a factor 5 less active per unit weight of cobalt over the entire time range studied. Interestingly, the 6 and 12 nm Co-NC catalysts were similar or even higher in CTY than the IWI-Co/TiO₂ catalyst, indicating that these Co-NC were adequately activated and that relevant catalytic results were obtained with these NC-based model systems.

**Table 1. Characteristics of the Supported Co-NC and IWI-Co Samples**

| Sample       | D(3,2)Co-NC (nm) | Co loading (wt %) | Initial Co surface area (mCo²·g⁻¹) |
|--------------|------------------|------------------|----------------------------------|
| Co3/TiO₂     | 2.9 ± 0.4        | 2.4              | 5.7                              |
| Co6/TiO₂     | 6.0 ± 0.8        | 4.6              | 5.5                              |
| Co12/TiO₂    | 12 ± 1.5         | 8.7              | 5.4                              |
| IWI-Co/TiO₂  | 7.3 ± 2.5        | 6.7              | 6.2                              |
| Co3/SiO₂     | 2.8 ± 0.5        | 3.6              | 6.8                              |
| Co6/SiO₂     | 5.6 ± 0.6        | 6.8              | 9.2                              |
| Co9/SiO₂     | 8.6 ± 1.1        | 9.6              | 7.7                              |

The Sauter mean diameter (± standard deviation) of the Co-NC was analyzed by TEM before attachment and recalculate to the corresponding Co⁰ particle sizes. The Co loading was determined by ICP-OES. Based on these two results, a Co specific surface area of the pristine catalysts was calculated.

**Figure 2.** Overview of the Co-NC attached to a support. The TiO₂-supported samples are in the left column, and the SiO₂-supported samples are in the right column. (a) Co3/TiO₂, (b) Co3/SiO₂, (c) Co6/TiO₂, (d) Co6/SiO₂, (e) Co12/TiO₂, and (f) Co9/SiO₂. The insets are at double the magnification of the original image.

DOI: 10.1021/acscatal.8b03094
ACS Catal. 2018, 8, 10581–10589
as well as the IWI-Co/TiO2, had grown to similar to the others (∼65 × 10⁻³ s⁻¹). Therefore, a TOF similar to the others (∼65 × 10⁻³ s⁻¹) should have been obtained. Instead, the low apparent TOF was ascribed to loss of cobalt from the metal particles to the TiO2 resulting in less metallic surface area available for catalysis. Judging from the decrease in TOF, up to 80% of the cobalt was lost in this manner.

Furthermore, the selectivity toward C₅⁺ products was around 85% for all TiO2-supported samples, except for Co3/TiO2 whose C₅⁺-selectivity was only 57% (Table 2). The catalytic activity of the Co/SiO2 samples was investigated over 100 h on stream at CO conversion levels between 15 and 30% (Figure S6, Table 2). The cobalt-weight-based activities of Co6/SiO2 and Co9/SiO2 were the highest of all investigated catalysts. The 3 nm Co-NC displayed again the lowest activity of the series, yet Co3/SiO2 was a factor 6 more active per unit weight of cobalt than Co3/TiO2. The C₅⁺-selectivities of the SiO2-supported catalysts varied between 76 and 79% and were overall lower than that of most TiO2-supported catalysts (∼85%). This observation corresponds well with earlier findings of TiO2 promoting the C₅⁺-selectivity of cobalt catalysts in FT.⁴⁹

The deactivation and observed differences in activity could be caused by several mechanisms, such as carbon deposition,⁵⁰ metal-support compound formation,⁵¹ or net particle growth.⁵¹ To investigate the occurrence of particle growth in more detail, the spent catalysts were analyzed with TEM (Table 2, Figure 4, Figure S7). All Co-NC supported on TiO2, as well as the IWI-Co/TiO2, had grown to ∼13 nm on average, which was in line with recently reported particle sizes of a Co–Re/TiO2 catalyst after various periods on stream.¹³ On SiO2, the initially 3 nm Co-NC had also sintered to 13 nm, while the 6 and 9 nm Co-NC were stable.

Using the particle sizes of the spent catalysts and the activities at 90–100 h on stream, the surface-specific activities (turnover frequencies, TOF) were calculated (Table 2). The TOF of all TiO2-supported catalysts except Co3/TiO2 was around 65 × 10⁻³ s⁻¹, in line with previous reports. The identical TOF of 6 and 12 nm Co-NC on TiO2 and the IWI-Co/TiO2 catalyst showed that the active cobalt sites were not affected by the presence of residual ligands or other factors specific to the NC-based synthesis method. The apparent TOF of Co3/TiO2 based on the particle size of the catalyst and the end-of-run activity, was only 12 × 10⁻³ s⁻¹ (Table 2). This was remarkable, because the Co particles in Co3/TiO2 had grown outside of the size regime where particle size effects typically cause low activities (<6–8 nm).¹⁴,¹⁵,²² Therefore, a TOF similar to the others (65 × 10⁻³ s⁻¹) should have been obtained. Instead, the low apparent TOF was ascribed to loss of cobalt from the metal particles to the TiO2 resulting in less metallic surface area available for catalysis. Judging from the decrease in TOF, up to 80% of the cobalt was lost in this manner.

### Table 2. Catalytic Performance at 20 bar, 220 °C, and 2 H₂/CO (v/v)b

| sample             | GHSV (h⁻¹) | X_{CO} (%) | CTYa | TOF (10⁻³ s⁻¹) | S₂ (%, C) | S₂₋₅ (%, C) | S₅⁺ (%, C) | D_{[3,2]}spent (nm) |
|--------------------|------------|------------|------|---------------|-----------|-------------|------------|-------------------|
| Co3/TiO2           | 2000       | 4.6        | 1.4  | 12            | 21        | 21          | 57         | 15 ± 5.1          |
| Co6/TiO2           | 3100       | 23         | 11   | 66            | 9.2       | 8.1         | 83         | 11 ± 3.3          |
| Co12/TiO2          | 6900       | 24         | 8.6  | 68            | 8.2       | 5.9         | 86         | 13 ± 4.0          |
| IWI-Co/TiO2        | 7500       | 18         | 8.4  | 68            | 8.7       | 7.0         | 84         | 14 ± 5.9          |
| Co3/SiO2           | 1500       | 25         | 8.5  | 67            | 13        | 12          | 76         | 13 ± 5.5          |
| Co6/SiO2           | 5500       | 16         | 21   | 82            | 14        | 11          | 76         | 6.7 ± 1.4         |
| Co9/SiO2           | 10800      | 21         | 19   | 106           | 13        | 8.7         | 79         | 9.6 ± 2.1         |

a in 10⁻⁵ molCO·s⁻¹·g⁻¹. b The reported data was obtained after 90–100 h on stream. The TOF was based on the end-of-run activity and Co particle size (D_{[3,2]}) of the spent samples. The Sauter mean diameter (± standard deviation) of the Co-NC was analyzed in the spent and passivated state and corrected for the lattice expansion due to the 3 nm CoO passivation layer.
The TOF of the SiO₂-supported catalysts increased with initial particle size (Table 2). In the case of the initially 3 nm Co-NC on SiO₂, the TOF was 67 × 10⁻³ s⁻¹, which was similar to most Co/TiO₂ catalysts and already somewhat higher than previously reported for Co/SiO₂ catalysts. However, the intrinsic activities of 6 and 9 nm Co-NC on SiO₂ were exceptionally high in comparison to the literature. A possible explanation for the different TOF of Co-NC and conventional catalysts could be that the Co-NC approach led to cobalt particles with a higher fraction of hcp Co, which is more active in FT than fcc Co. Alternatively, the Co-NC could have less interaction with the support, because the Co-NC were formed prior to attachment to the support. For example, when comparing the TEM results of spent Co/SiO₂, the grown particles of Co₃/SiO₂ were mainly confined between primary SiO₂ particles where the contact area with the support was maximal (Figure S7). The Co-NC in Co₆/SiO₂ and Co₉/SiO₂, on the other hand, were still distributed uniformly over the support, and as such, a higher fraction of the cobalt surface area would be accessible to reactants.

Overall, the employed NC-based approach to catalyst synthesis yielded well-defined model systems with reasonable control over the initial NC size and relevant catalytic performance. It is therefore anticipated that these model catalysts are suitable to investigate structure-performance relationships, and already some interesting phenomena were observed here, especially on the growth of NC of specific sizes under reaction conditions. These observations will be investigated and discussed in more detail in the next section.

### Sintering of Cobalt Nanocrystals.
To investigate the growth of Co-NC, the particle sizes were analyzed using TEM after reduction as well as after calcination (Figure 4). The 3 nm Co-NC on TiO₂ sintered to particles of 10 nm already during reduction and grew further to 15 nm during FT. The 3 nm Co-NC on SiO₂ ultimately grew to the same extent, but in this case the particles predominantly sintered during FT. The reduction barely affected the particle size of Co₃/SiO₂ even though the reduction was performed at 500 °C.

EDX maps of the reduced and passivated TiO₂-supported catalysts and Co₃/SiO₂ were quantified to investigate the location of Co on the supports (Table 3, see Figure S8 for results and experimental details). Compared to ICP (Table 1), the total cobalt loading from EDX was 30–50% higher on TiO₂ and 50% lower on SiO₂. Therefore, relative differences for one and the same sample were considered more representative than the absolute values.

For the reduced and passivated Co/TiO₂ samples, ∼2.5 wt % of Co was found dispersed in the support and not in particles, regardless of NC size and loading. In the case of Co₃/TiO₂, this amounted to approximately 60% of the total cobalt content from EDX and might be partially responsible for its low CTY. Furthermore, the Co signal in the EDX maps occasionally followed the contours of TiO₂ particles with increased intensity at the surface (Figure S8). This means that a higher Co concentration existed at the surface than in the bulk of the TiO₂ particles. In contrast, only 16% of the Co was found on the silica support for Co₃/SiO₂, and the remaining 84% was still present in Co particles. Consequently, no contours of the support were observed in the Co signal from EDX at locations without any particles (Figure S8). These EDX results show that, during reduction, cobalt migrated to the support more with TiO₂ than with SiO₂, as illustrated in Figure 4c,d. These cobalt species on the support were therefore more prone to sintering. Interestingly, in these earlier studies, growth took place via monomers that were created upon exposure to CO under reaction conditions. For example, in the case of Co/Al₂O₃, cobalt subcarbonyls were proposed as monomers that migrate over the support and give rise to particle growth via Ostwald ripening. However, in our Co₃/TiO₂ sample, a large part of the growth took place already during reduction, so sintering was not induced by CO. When combining these results with the tendency of 60% of the cobalt in the NC to “leach” to the surface of the TiO₂, we propose that different mobile species, possibly cobalt titanates, spread out over the support and cause a few particles to grow large. This hypothesis is in line with thermodynamic calculations (Figure S10), which showed that it is thermodynamically possible to form small amounts of cobalt titanates under reduction conditions, and agrees with previous observations. Notably, Cats et al. observed a thin layer of Co species surrounding TiO₂ particles, albeit in spent and not in reduced catalysts.

On SiO₂, the formation of cobalt silicates during reduction is thermodynamically limited (Figure S10), and the growth of 3 nm Co-NC occurred mainly during FT. The sintering might therefore be ascribed to CO-induced Ostwald ripening as observed before by Kistamurthy et al. or particle migration and coalescence. Furthermore, 8 h plasma cleaning of the pristine samples to remove ligands reduced the particle growth for Co₃/SiO₂ but not for Co₃/TiO₂ (Figure S11). This further confirmed that the mechanism responsible for particle growth is different on both supports even though the final particle size is similar.

The 6 nm Co-NC on TiO₂ did not grow during reduction (Figure 4). The driving force for sintering during reduction was thus less than for Co₃/TiO₂, because of the larger particle size. However, the NC on TiO₂ did grow to 11 nm during FT. Growth of the 6 nm Co-NC was not observed on SiO₂ even after calcination, showing that the Co-NC are less stable on TiO₂ compared to SiO₂. Interestingly, Co₆/TiO₂ had sintered less than IWI-Co/TiO₂ after FT, with final particles sizes of 11 and 14 nm, respectively (Figure S12). Because the average particle

### Table 3. Quantification of the Cobalt Present in the Support and in Particles after Reduction of Co/TiO₂ and Co₃/SiO₂

| sample          | Cₐtot (wt %) | Cₐparticle (wt %) | Cₐsupport (wt %) | Cₐparticle/Coₐtot | Cₐsupport/Coₐtot |
|-----------------|--------------|-------------------|------------------|-------------------|-----------------|
| Co₃/TiO₂        | 3.3          | 1.3               | 2.0              | 0.38              | 0.62            |
| Co₆/TiO₂        | 6.8          | 4.1               | 2.7              | 0.61              | 0.39            |
| Co₁₂/TiO₂       | 11           | 9.2               | 2.2              | 0.81              | 0.19            |
| Co₃/SiO₂        | 2.4          | 2.0               | 0.4              | 0.84              | 0.16            |

“The total Co loading and the fractions of Co in particles and Co in the support were derived from HAADF-STEM-EDX (Figure S8).”

DO: 10.1021/acscatal.8b03094
ACS Catal. 2018, 8, 10581–10589
sizes of both samples were initially comparable while the polydispersity of IWI-Co/TiO₂ was higher, this shows the impact of the width of the particle size distribution on the stability of the cobalt nanoparticles. It nicely illustrates the advantage of the NC-based approach over the traditional synthesis techniques to arrive at more stable catalysts.

On average, 12 nm Co-NC on TiO₂ did not grow, but the particle size distribution did become broader already after reduction (Figure 4). Both smaller and larger particles were thus formed, which implied Ostwald ripening or redispersion of cobalt, possibly via cobalt-ion migration, under reducing conditions. No evidence of Co-NC growth or redispersion was apparent on Co9/SiO₂ indicating that Co mobility was more extensive with the TiO₂ support or the somewhat larger Co-NC sizes. Extending the reduction to 16 h instead of 8 h did not change the particle size distribution of Co12/TiO₂ further (Figure S13). This observation is qualitatively in line with the results of Xaba et al.⁷¹ on titania P25, although their Co particles were substantially larger (~50 nm).

The size evolution of individual Co-NC in Co12/TiO₂ was followed before and after reduction and passivation to investigate the redispersion in more detail (Figure 5). No particles were found that had moved from their original position, indicating low mobility of the Co-NC as a whole and making migration and coalescence unlikely as a pathway for particle growth during reduction. Furthermore, approximately 5% of the particles broke up into multiple smaller particles (Figure 5c,d highlighted area, Figure S14). This redispersion caused an increase in the fraction of 5–8 nm particles, resulting in broadening of the particle size distribution.

Two reasons can be proposed for the disintegration of the NC. First, it might be favorable for certain particles to maximize their contact area with the support, since the interaction between metals and reducible supports such as TiO₂ can lead to dynamic systems under reducing conditions.⁷² Second, the core–shell structure in pristine Co12/TiO₂ could be an intermediate stage of the Kirkendall effect.⁷³ Sasdavian et al.⁴⁵ investigated this effect for Co-NC of different sizes on SiO₂ and reported similar core–shell particles in the case of incomplete oxidation of 29 nm particles. Completely oxidized, hollow cobalt oxide particles of 29 nm disintegrated into multiple smaller particles upon reduction, whereas smaller hollow particles returned to their original size of 11 nm. Based on these results, our 12 nm Co-NC, being similar in size to their 11 nm particles, are not expected to disintegrate upon reduction.

CONCLUSIONS

Here, we investigated the preparation of well-defined TiO₂- and SiO₂-supported catalysts via colloidal synthesis of Co-NC and evaluated their catalytic performance in the Fischer–Tropsch synthesis. The 3–12 nm Co-NC were synthesized by a hot-injection method, oxidized at low temperature to restrict magnetic interactions and subsequently attached to TiO₂ or SiO₂. The catalytic activity of most TiO₂-supported samples was in line with that of a Co/TiO₂ sample prepared by impregnation of cobalt nitrate, proving that relevant catalytic data was obtained with these model catalysts. The cobalt-weight-based activity of 3 nm Co-NC on TiO₂ was 5-fold lower than expected, and this was partially ascribed to loss of cobalt to the support. Furthermore, the TiO₂-supported Co particles and 3 nm Co-NC on SiO₂ sintered, while 6 and 9 nm Co-NC on SiO₂ were stable during reduction and FT. We showed that the interaction between Co(O) and TiO₂ was responsible for the decreased stability of the Co-NC. This study illustrates the promise of synthesizing model catalysts using colloidal techniques, as the high precision in particle size enabled the investigation of effects that have not have been revealed earlier with conventional synthesis techniques.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b03094.

Schematic summary of the catalyst synthesis procedure, additional characterization, and catalytic results (PDF)

AUTHOR INFORMATION

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

ORCID

Tom W. van Deelen: 0000-0002-3666-4576

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

T.W.v.D. and K.P.d.J. acknowledge Shell Global Solutions and The Netherlands Association for Scientific Research (NWO) for funding through the CHIPP framework. N.A.K., J.Z., and K.P.d.J. acknowledge the European Research Council, EU FP7 ERC Advanced Grant no. 338846 for funding. We thank Pasi Paalanen and Łennart Weber (N₂-physisorption), Carlos Hernández Mejia (TPR), and Helen de Waard (ICP-OES) for the measurements indicated.
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