Formation mechanism of epitaxial palladium-platinum core-shell nanocatalysts in a one-step supercritical synthesis

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ABSTRACT

The scarcity of platinum group metals provides a strong incentive to optimize the catalytic activity and stability e.g. through nanoalloys or core-shell nanoparticles. Here, time-resolved X-ray total scattering and transmission electron microscopy characterization are used to study the formation of platinum-palladium core-shell nanoparticles under solvothermal conditions. It is shown that Pd rapidly forms small (5 - 10 nm), disordered primary particles, which agglomerate and crystallize when reaching 20 - 25 nm. The primary Pd particles provide nucleation sites for Pt, and with extended reaction time the Pd cores become fully covered with Pt shells. The observed core-shell material is surprising when considering the Pt-Pd phase diagram and relative surface energies, but it can be rationalized through the kinetics of precursor conversion. To bridge the gap between

scientific studies and industrial demand for large-scale production, the synthesis process is successfully transferred to a continuous flow supercritical reactor providing a simple scalable and green process for production of bimetallic nanocatalysts.

1. INTRODUCTION

Platinum-based materials are efficient catalysts in many important chemical processes. These include oxidation or reduction of simple molecules such as carbon monoxide, water, oxygen, methane, methanol, hydrogen and NO_x; but also extend to more specialized steps in advanced organic or polymeric reactions.^[1] This is the basis for the widespread use of platinum-based materials, *e.g.* in automotive catalysts, fuel cells and steam reforming. However, the platinum group metals are characterized by their very low abundance. This means that increasing demand, caused by population growth and widespread use of advanced technology, is challenging to meet. Thus, there is a strong incentive to increase the catalytic efficiency, and this ultimately relies on gaining a fundamental atomic scale understanding of the materials, and their synthesis.

An obvious approach to enhance the efficiency of a heterogeneous catalyst is to increase the number of active sites. This can be done by increasing the surface/bulk ratio through nanoscaling, and by exposing specific facets *e.g.* with controlled particle morphologies.^[2] A more specialized approach is to enhance the intrinsic activity for a given process, *i.e.* to optimize the adsorption, diffusion and desorption properties for relevant reactants. This approach relies on synthesis of multicomponent structures such as alloys, overlayers, or introduction of dopants or vacancies in the structure. All of these features alter the electronic landscape of the surface, and allow for tailoring of the catalytic properties. Theoretical DFT studies have been widely used to provide

chemisorption energies and reaction barriers for various molecules.^[3] A large number of metal or alloy surfaces and surface features have been studied to confirm experimental findings and to predict possible new catalysts. The theoretical studies provide a guidance for the experimentalists to synthesize tailored nanomaterials with optimized properties for a given catalytic process. However, it remains a severe challenge to develop synthesis methods that are environmentally benign, cost-effective and allow for large-scale production.

Decrease of catalytic activity over time (ageing) can be caused by diminishing catalytic surface area due to particle growth, poisoning of the catalyst and/or evaporation/dissolution of catalytic material. In many applications the operating conditions are harsh with elevated and varying temperatures as well as corrosive chemicals. Degradation of material *e.g.* because of dissolution to some extent can give catalysts with high surface areas and, consequently, activities.^[4] However, highly tailored but thermodynamically unstable materials are vulnerable and their use is restricted to low-temperature applications.^[5] Strategies for stabilization exist though, *e.g.* through formation of alloys, protective layers, or bifunctional heterostructures. These effects have been reported for Pt stabilized by Pd, Cu, or Au.^[6] Further favoring the use of Pd are experimental and theoretical studies, which have found improvement in the intrinsic catalytic properties for the oxygen reduction reaction.^[7]

Many different protocols exist for synthesis of platinum-based nanoparticles. Among the more exotic are bacteria-mediated growth,^[8] helium droplet synthesis,^[5c] galvanic replacement in electrochemical cells,^[9] framework-templated growth *via* reduction at ambient conditions,^[10] and microfluidic flow synthesis.^[11] However, the most widespread synthesis method in scientific literature is solvothermal synthesis. This is performed using autoclaves,^[4a, 5d, 6b, 12] microwave setups,^[13] flow reactors,^[14] or reflux setups.^[4b, 5a, 5b, 6a, 6c, 6f, 7b-d, 15] It is possible to reach the

supercritical domain with the use of autoclaves and microwave reactors as they are constructed to sustain high pressure, while reflux syntheses take place at ambient pressure. This restricts the reaction temperature to the boiling point of the solvent, and the synthesis is therefore dependent on highly reactive precursors, reducing agents and/or long reaction times. As a consequence, toxic solvents and reducing agents are often used in reflux synthesis. Metal nanoparticles can also be synthesized by calcination of precursor-impregnated carrier material.^[16] This method is simple, suitable for large-scale production, and capable of producing very small particles. However, it suffers from relatively crude parameter control, high energy consumption, difficulty in producing metastable structures, and limited choice of capping agents due to thermal decomposition.

Synthesis of core-shell particles adds another layer of complexity since the order and position of materials precipitation have to be controlled. This is typically met by using a stepwise method; *e.g.* by synthesizing the core initially, and using this as a seed for the shell.^[7b] Clearly, a rapid one-step synthesis route, as presented in this study, is to be preferred, lowering time consumption and use of equipment. One of the main challenges in catalysis is to bridge the gap between scientific literature and industrial application. Much progress has been made in the field of catalytic metal particles but the reported synthetic routes suffer from small batch sizes, toxicity of the chemicals used, time consumption, and high cost to name a few.

The present study relies on an attractive alternative. Bondesgaard *et al.* found that ethanol is oxidized to ethanal in supercritical conditions, and thereby acting as a reducing agent.^[17] Metallic Pt and Pd can thus be synthesized without toxic reducing agents when using an ethanol-acetone mixture as solvent:

$$M = [Pt, Pd]$$

Here, we report a simple one-step synthesis route for Pd-Pt core-shell particles. Three different reactors have been used: A spiral autoclave reactor,^[18] an *in situ* solvothermal reactor,^[19] and a large-scale flow reactor.^[20] All reactors provide very rapid heating and relatively short reaction time (seconds - minutes). The flow reactor represents a route for large-scale production, the *in situ* cell in the present case provide 1-second time resolution information about the nucleation and growth mechanism, and the spiral reactor can produce samples for TEM analysis at specific reaction times. The two latter are thus highly suited for studying the nucleation and growth. Detailed information on nucleation and growth allows for tailoring of synthesis parameters such as reaction temperature and residence time, in order to obtain specific products.

2. Results and Discussion

2.1 Nucleation and Growth

To understand how core-shell particles form in one step from a single homogeneous precursor, time resolved X-ray scattering and TEM analyses were performed. Figure 1 summarizes the early stages showing stacked diffractograms and selected STEM-EDS images. Before heating is commenced, Bragg peaks from the suspension of reactants (metal acetylacetonates) are observed (data not shown). As heating starts (time = 0), these peaks disappear. Analysis of the Pair Distribution Functions (PDFs) obtained from the first few seconds suggests that all reactant are present as solvated metal-acetylacetonate monomers, Figure 1a (see also Supporting Information for details). Then Bragg peaks from a face centered cubic (fcc) crystal phase appear and grow. This, seemingly, occurs in two steps with high growth rates at times 0-1 min. and 3-4 min. STEM-

EDS maps reveal that the first step corresponds to precipitation of Pd particles with small amounts of Pt on the surface (Figures 1b and 1c). The coverage increases until a full shell with facets is obtained for most particles (Figure 1 d).

Figure 1. Time resolved X-ray scattering. Red lines correlate with the characterization results: a) obs-calc curve from PDF-fitting indicating presence of solvated monomers prior to nucleation, (b, c, d) STEM-EDS maps showing the distribution of Pd (green) and Pt (red) during nucleation and growth. All scale bars are 30 nm for ease of comparison.

Particles prepared with short reaction time (< 3 min.) are agglomerates of primary particles and they are clearly distinguishable with bright field TEM, Figure 2. The primary particles are

irregular non-faceted and thus appear only partially crystalline. Lattice- or Moire fringes are observed in small regions but not spanning entire particles.

At longer reaction times (> 4 minutes), two types of particles are observed: Faceted core-shell particles with sizes around 20 nm and smaller (5-10 nm) disordered particles of either Pd or Pt (Figures 2 and 3). For the larger particles, sharp transitions between the Pd core and the Pt shell are observed, and the orientation of these reflect the particle facets. Lattice fringes are found to span entire particles when using high resolution TEM (HR-TEM), demonstrating an epitaxial relationship between core and shell (Figure 3). A variety of shapes such as cubes, prisms, and cuboctahedra are observed, which are all well known for fcc metal nanoparticles. Further TEM images and particle size histograms can be found in the supporting information (SI1 – SI9).

Figure 2. Bright field TEM image of the sample prepared with a reaction time of 40 seconds (left). Agglomerates of primary particles display regions with lattice- or Moire fringes; the magnified

regions show examples of these. Right shows a high angle annular dark field STEM image of the sample prepared with a reaction time of 30 min.

Figure 3. Particles synthesized with a reaction time of 30 min. imaged using high-resolution TEM (top) and STEM-EDS (bottom). Magnified rectangles show lattice fringes.

2.2 In Situ Experiments

X-ray total scattering *in situ* experiments were performed to monitor global sample development with a good time resolution. Figure 4 summarizes results from sequential PDF refinements of data from the experiment performed at 260 °C (only 16 minutes of reaction time is shown for clarity;

the full data range can be found in the supporting information, SI19). The reaction temperature was reached at reaction time zero, and PDFs were modelled using a single fcc phase with site occupancies corresponding to the nominal composition (25% Pd and 75% Pt) and spherical crystallite morphology. This is a relatively crude model since the ratio between Pd and Pt varies with reaction time (Figure 1), and a range of different particle morphologies are present. However, it represents a sample average and is suitable to extract general structural information.

The plots in Figure 4 can be divided into three regions. The scale factor rapidly increases in the first minute due to formation of Pd primary particles. This is followed by a region of more moderate increase where the Pd reactant is depleted and reduction of Pt^{2+} occurs at a lower rate (based on the TEM observations). Finally, after 10 minutes, the experiment stabilizes. Here a slightly decreasing scale factor is observed, which presumably is due to sedimentation of particles out of the center of the X-ray beam. The unit cell parameter increases throughout the experiment and asymptotically approaches 3.900 Å. An increasing trend driven by precipitation of Pt (unit cell length of 3.9239 Å at 20 °C^[21]) after precipitation of Pd (unit cell length of 3.8907 Å at 22 °C^[21]) was expected, and the end-value is in good agreement with the values reported for Pt_3Pd by Raub *et al.*^[22] and Darby *et al.*^[23] The unit cell parameter at very short reaction time is slightly larger than what is reported for pure Pd, but this may be due to surface relaxation of the structure^[7b] and the presence of small amounts of Pt.

Figure 4. Results from sequential PDF refinements of *in situ* data with a synthesis temperature of 260 °C. Left shows the scale factor (black) and the unit cell parameter (red); right shows size (green) and U_{iso} (brown).

A rapid increase in the crystallite size is observed between 2.5 and 4 min. This matches with a drop in the U_{iso} parameter, which is a measure of the spread of electron density in the modelled structure caused by thermal motion of atoms or disorder. Structural changes from disordered particles toward crystalline particles would imply an increase in size of the coherently scattering domains as well as more ordered atoms, resulting in an increase in the size parameter and a decrease in U_{iso} . A change from agglomerates of primary particles to faceted particles was observed with TEM between 2 min. and 6 min. of reaction time, supporting that the primary

particles merge and become fully crystalline in this time period. Although U_{iso} decreases significantly when the full r -range is analyzed, a constant or slightly increasing trend is observed when only nearest-neighbor peaks are included. This suggests that the local atomic packing is maintained, but that long range ordering occurs. A transition from a random closed packed structure to an ordered fcc structure complies with these findings, and is believed to occur when the primary particles merge (see the supporting information, SI17, for an extended discussion). Both the scale factor and the unit cell parameter change steadily without sudden kinks in the same region. Examples of experimental and modelled PDFs before and after the rapid increase in size are shown in Figure 5.

Figure 5. Experimental PDFs (red), modelled PDFs (black), and difference curves (blue) from the experiment performed at 260 °C with reaction times of 1 min. 40 s. and 8 min. 20 s. respectively.

Comparing the different characterization techniques, a discrepancy in “size” is evident between PDF refinements and TEM, especially at longer reaction times. Different effects contribute to this; most important is the instrumental resolution limit in the PDF technique, which is severe for

particles above 10 nm in these experiments. Furthermore, only a single “average” size has been used in the modelling, while the TEM analysis shows the presence of binary size distributions with ratios between large and small particles that vary with synthesis time (discussed in the supporting information, SI10). The PDF peak intensities will decrease more rapidly with r when a binary size distribution is present, and thus force a premature termination of the PDF “size”-convolution function. Furthermore, some of the particles observed in TEM are not single crystals, but instead consist of multiple subunits with strained interfaces –*e.g.* shown in Figure 6.

Figure 6. A core-shell particle imaged using both dark-field TEM (left) and high-angle annular dark field STEM (right). The coherently scattering domains seen with DF-TEM only constitute a fraction of the entire particle.

A second *in situ* experiment was performed with a reaction temperature of 310 °C, i.e. 50 °C higher than the previously described experiment. The results are summarized in Figure 7. The scale factor follows the same trend as observed at the lower reaction temperature of 260 °C, but much faster with the maxima being reached within one minute. The same can be said about the unit cell parameter, but this stabilizes at a lower value; around 3.895 Å compared with 3.900 Å. Whether this is caused by more pronounced surface relaxation effects due to the larger amount of

small particles, enhanced templating effects in the crystallization of Pt on Pd, or by experimental uncertainty is unknown. However, a combination of these effects is likely to account for the observed difference. Surprisingly, the crystallite size stabilizes at a lower value around 6.2 nm in the high temperature experiment compared with 9.4 nm in the 260 °C experiment. Approximately one minute into the synthesis, a rapid increase in apparent size appears simultaneously with a drop in the U_{iso} value. This is followed by a period of steady, almost linear, increase in size and decrease in U_{iso} . Finally, all modelled parameters stabilize after ca. 11 minutes of synthesis. The dynamics of precipitation may provide an explanation for the smaller average crystallite size at higher reaction temperature. At 310 °C the thermal energy is sufficient to induce crystallization of Pt primary particles without prior agglomeration. This stabilizes the individual small particles and thus decreases the gain in energy from agglomeration/ripening, which ultimately slow down the average particle growth.

Figure 7. Results from sequential PDF refinements of *in situ* data obtained with a synthesis temperature of 310 °C.

2.3 Reaction Mechanism

Based on the experimental results presented above, the following steps in the solvothermal synthesis of Pd-Pt core-shell nanoparticles from acetylacetonate reactants are suggested (Figure 8):

- (1) Dissolution of $\text{Pt}(\text{acac})_2$ and $\text{Pd}(\text{acac})_2$ to square planar monomers

- (2) Precipitation and agglomeration of disordered Pd primary particles
- (3) Nucleation of Pt on the surface of Pd agglomerates
- (4) Crystallization of agglomerates
- (5) Growth of Pt shell

Figure 8. Formation mechanism of Pd-Pt core-shell nanoparticles from acetylacetonate precursors in solvothermal synthesis.

The different steps are not separated in time, i.e. they occur simultaneously with rates that depend on the reaction temperature. At the higher reaction temperature of 310 °C crystallization of primary particles is presumed to occur earlier in the process.

The cause for the formation of primary particles with a disordered structure upon reduction of the metal reactants is most likely a relatively high energy barrier for crystallization. The reaction temperature is high enough to destabilize the solvated acetylacetonate complexes and reduce the metal via oxidation of supercritical ethanol. However, it is not sufficiently high to overcome the crystallization energy barrier and metal atoms assemble in an arrangement that will have structural similarities with random closed packing. Only when the primary particles agglomerate to reach a certain size they can overcome the energy barrier for crystallization.

What drives the formation of Pd-Pt core-shell particles? Is the obtained structural motif thermodynamically stable, or a consequence of the kinetics involved? From literature it is known that Pd has a lower surface energy than Pt.^[24] Also, a miscibility dome exists for the bulk Pt-Pd system, which gives rise to splitting into regions rich in either Pt or Pd with approximate stoichiometries of 9:1 at temperatures around 300 °C.^[25] Based on this, a reversed core-shell pattern with a Pt rich core and a Pd rich shell is to be expected if the atomic diffusivity is sufficiently high. The present results clearly show that this is not the case, and Pd is confined in the particle core with no change observed even at extended synthesis times (up to 50 minutes). Low diffusivity is rationalized by the synthesis temperature, which is more than 1400 °C lower the melting point of Pt₃Pd.^[25] Thus, kinetics account for the structural motif since reduction of Pd(acac)₂ to metallic Pd precedes the reduction of Pt(acac)₂. This difference in metal ion reducibility is not understood from the higher reduction potential of Pt²⁺ compared to Pd²⁺ (1.188 V vs. 0.915 V in aqueous solution^[26]). *In situ* measurements on single metal precursor solutions indeed show formation of metallic Pd at temperatures around 100 °C lower than Pt (SI16). Thus, kinetics drive the formation of the observed nanostructures, and these are stable at the reaction temperatures and times used in this study. Interestingly, Tao *et al.* synthesized bimetallic particles

with a Pd rich shell and pronounced alloying also using acetylacetonate reactants.^[5b] The difference in core-shell pattern must be ascribed to solvent (1,4 butandiol vs. ethanol-acetone), atmosphere, and heating rate. The study also found significant diffusion of Pd towards the surface of Pd-Re core-shell particles under operating conditions (300 °C and cycles of alternating oxidizing and reducing atmosphere), whereas the Pt-Pd particles remained stable. In the present study no changes were observed in the core shell particles after 50 minutes reaction time at 260 °C, but exposure to reactive gasses may facilitate diffusion enabling Pd to migrate to the surface.

Flow Synthesis for Large Scale Production

Flow synthesis was tested as a strategy for upscaling the production of Pd-Pt core-shell particles while maintaining high heating rates and good parameter control as in the spiral reactor and *in situ* experiments. A higher reactor temperature of 310 °C was used in order to convert the reactants despite a short residence time (approx. 15 seconds). The product was characterized using powder X-ray diffraction and TEM. Figure 9 shows a STEM-EDS map of the obtained particles and diffractograms after Rietveld refinement. The resulting particles resemble the previously described nanostructures very well. They consist of a Pd core covered by a Pt shell as well as smaller particles of pure Pt. The Pt shell is localized at the center of particle facets and is generally thinner than observed for the particles synthesized with the spiral reactor. This is probably caused by the short reaction time and turbulent conditions in the flow reactor, which may hinder steady diffusion. The relatively large amount of very small Pt particles indicate that longer reaction times are needed for growth of thick Pt shells *via* Ostwald ripening.

Figure 9. Analysis of the products from flow synthesis. STEM-EDS shows larger core-shell particles and smaller particles of pure Pt (top). The obs-calc diagram obtained after Rietveld refinement (bottom).

Inspired by the TEM analysis, a two-phase model was used for the Rietveld refinements: a minor phase consisting of smaller particles of pure Pt and a major phase consisting of larger particles of 90:10 atom% Pd:Pt. Attempts to refine a single phase gave significantly worse fits as residual peak intensity occurred towards low scattering angles (SI18). The microstructure was analyzed *via* peak broadening, and it is in good agreement with the results from TEM. Thus, the crystallite sizes were found to be 24.6 nm and 4.3 nm for the major and minor phase respectively.

The peak-shape parameters of the major phase indicated pronounced strain, refined to a value of 0.25%. Furthermore, the unit cell parameters of the major phase and minor phase were 3.8987 (1) Å and 3.9266 (6) Å, respectively matching the lattice parameters of Pt_{0.1}Pd_{0.9} and pure Pt.^[21-23] A mass distribution of 72 % major phase and 28 % minor phase was obtained. Further details on the refinements can be found in the supporting information (SI12).

The skewed binary size distribution with large amounts of small particles and low coverage of Pt on Pd supports the hypothesis that primary particles of Pt are stabilized *via* crystallization when a reaction temperature of 310 °C is used. No small uncovered crystals of pure Pd are observed; instead, the Pd cores were relatively large, suggesting that the crystallization energy barrier is large for Pd and that the tendency to agglomerate prior to crystallization is increased at the higher reaction temperature.

For all synthesis methods, the degree of alloying in core-shell particles is challenging to quantify. The atomic radii of Pd and Pt are very similar and previous studies on the crystallography of the system show discrepancies in the deviations from Vegard's law.^[22-23] Adding to the crystallographic uncertainty is nanoscale effects such as surface relaxation and strain. TEM shows clear and sharp transitions between core and shell with high contrasts, indicating very limited amounts of alloying. This, together with the epitaxial relationship between core and shell, would imply that particles are strained in the interface, and parametrization of peak shapes in the measured diffractograms indeed indicate a substantial amount of strain in the core-shell particles from all experiments. The study by Radosavkic *et al* supports the feasibility of no or very little alloying.^[27] Deposition of Pt on Pd (111) in ultra-high vacuum resulted in a surface alloy for the first two monolayers, but this alloy splits up in elementally pure layers upon deposition of more layers. These results are promising with respect to synthesis of thermally stable particles with tuned

catalytic properties through strain-engineering. Zhang *et al.* and Adzic *et al.* showed how the catalytic efficiency of O₂ reduction is significantly increased when using Pt monolayers on Pd nanoparticles compared to pure Pt nanoparticles.^[6d, 9b] Bai *et al.* synthesized cubic Pd-Pt core-shell nanoparticles, and demonstrated their superior catalytic activity toward hydrogen evolution compared with particles of pure Pt. However, all these studies suffer from relatively long and complex synthetic routes. Here, a simple and environmentally benign method for large-scale production of Pd nanoparticles with tunable Pt coverage is presented. This is an important step towards bridging the scientific research and real-world applications of platinum group metal nanoparticle catalysts.

3. Conclusions

We have unraveled how epitaxial Pd-Pt core-shell nanoparticles are formed from acetylacetonate reactants in a stepwise manner using solvothermal synthesis. Primary particles of Pd are formed first, and they agglomerate and act as nucleation sites for Pt. When a certain agglomerate size is reached, the primary particles merge and form a crystalline particle. A Pt shell is formed around the Pd core, and this shell grows with reaction time. A binary size distribution is present with extended reaction time, consisting of agglomerated larger particles and non-agglomerated primary particles. Increasing the reaction temperature increases the fraction of small particles and thus causes a decrease of the average crystallite size. Formation and agglomeration of primary particles prior to crystallization is an example of non-classical nucleation and growth.^[28] A high-energy barrier for crystallization of metallic Pd and Pt is believed to be the cause of this behavior.

The extent of alloying in the synthesized core-shell particles is very limited based on TEM and STEM-EDS. However, HR-TEM showed an epitaxial relationship between core and shell. This is highly desirable with respect to tuning of the catalytic properties via strain-engineering. In situ experiments resolved the reaction with 1 second between consecutive data sets, and relevant reaction times for synthesis of specific products can be based on this information.

Flow synthesis was tested as a strategy for upscaling to industrial scale production. The findings from batch synthesis were confirmed despite the different reactor designs and residence times. The synthesis route is considered environmentally benign since no reducing agents are used, the solvents have low toxicities and moderate synthesis temperatures are applied compared to furnace based techniques. Additionally, the synthesis is simple and rapid since only one precursor solution is needed and the conversion occurs in one step with short reaction time.

The present results suggest a strategy for industrial scale production of tailored bimetallic nanocatalysts. The fine parameter control in flow synthesis opens possibilities for synthesis of products with desired properties, and time-resolved characterization methods provide a fundamental understanding of the underlying formation mechanisms.

4. Experimental Section

A precursor solution consisting of 3.75 mM Pt(acac)₂ (Alfa Aesar, >48 wt% metal) and 1.25 mM Pd(acac)₂ (Sigma Aldrich, >99 %) in 50:50 vol% ethanol (96 %):acetone (analytical) was used for the spiral reactor experiments and flow experiment. For the *in situ* experiments the concentrations of Pt(acac)₂ and Pd(acac)₂ were raised to 0.10 M and 0.033 M, respectively, in order to increase

the signal to noise ratio. The reactants were not fully soluble at these higher concentrations and therefore a suspension was used.

Spiral reactor experiments were performed by injecting 1.8 ml of precursor into a coil of 1/16" steel tubing. This was sealed and pressurized to approx. 70 bar. The coil was heated by immersing it into an oil bath at 260 °C, which caused build-up of pressure to around 250 bar within 4 seconds. After a chosen synthesis time, the coil was removed from the oil bath immersed into water at room temperature to quench the reaction. The following reaction times were used: 0.2, 0.33, 0.67, 2, 6, 10, 15, 30, 50 min. The products were flushed into vials, diluted with ethanol to a total volume of 8 ml and applied to TEM grids after ultrasonication.

In situ X-ray scattering experiments were carried out using an updated version of the instrument described by Becker et al.^[19a] The basic layout and working principles are identical to the initial reactor version. Thus, a precursor solution was injected into the reaction capillary and pressurized to 250 bar *via* tubing connected to a HPLC pump. Data acquisition was initiated and after one minute at room temperature, the temperature was increased to the desired temperature using a hot air blower. Temperature calibration and heating profiles were obtained prior to the actual experiment using a k-type thermocouple placed inside a reaction capillary; see supporting information for further details and heating profiles (SI15). Experiments were performed at beamline P02.1, Petra III at DESY.^[29] A wavelength of 0.2072 Å and sample to detector distance of 195 mm resulted in a q-range of 0.4 Å⁻¹ to 24 Å⁻¹. Dioptas 0.3.1 was employed for integration,^[30] and xPDFsuite was used for background subtraction, corrections, normalization and Fourier transformation to obtain PDFs.^[31] Sequential refinements were performed in the program PDFgui. Refinement details can be found in the supporting information (SI14).

Flow synthesis was carried out using the reactor described by Hellstern *et al.*^[20a] The precursor and ethanol (96%) was pumped into the reactor in two separate lines, both with a flow rate of 15 ml/min. The ethanol solvent passed through hot tube zones at 450 ± 1 °C before the two lines were mixed. After mixing, the flow continued through a reactor zone with a temperature of 310 ± 1 °C. This ensured a residence time in the heated part of the reactor of around 15 seconds for the precursor; assuming a solvent density of 0.3 g/cm³. Finally, the product was cooled and passed through a pressure regulator valve. The product suspension was diluted with ethanol and applied to a TEM grid. Additionally, the product was decanted after sedimentation and dried to a powder at ambient conditions.

PXRD data was measured on a Rigaku Smartlab diffractometer using Cu K α_1 radiation in Bragg-Brentano geometry. Rietveld refinements were carried out using the FullProf software package;^[32] details of the refinement and a full parameter list are given in the supporting information (SI12).

TEM analysis was performed using an aberration-corrected FEI Talos F200X microscope operated at 200 kV. Contrast and brightness were adjusted after acquisition for TEM and STEM images. STEM-EDS elemental mapping was performed with the integrated Super-X system, using a smoothening map filter in the Bruker Esprit software. Grids of type C-foil on 200 mesh Cu were acquired from TED Pella inc.

Supporting Information

Supporting information contains additional electron microscopy images, discussions of the observed particle sizes and structural disorder in the primary particles, and details of Rietveld and PDF refinements. It is available from the Wiley Online Library.

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