

Supporting Information

Surface Stabilization Determines a Classical versus Non-Classical Nucleation Pathway During Particle Formation

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A Calculation of the size depending melting point of cobalt particles

The size-dependent particle melting point $T_m(d)$ is determined by the bulk melting point T_{mB} , the surface stabilization γ_A , the specific enthalpy of fusion ΔH_m , the particle diameter d and by the density ρ and also by the surface tension γ of the solid (S) and liquid (L) states.

$$T_m(d) = \frac{4 \cdot T_{mB}}{\Delta H_m \cdot \rho_S \cdot d} \left[(\gamma_S - \gamma_A) - \gamma_L \left(\frac{\rho_S}{\rho_L} \right)^{2/3} \right] \quad (S1)$$

The following values were used for $T_m(d)$ calculation: T_{mB} : 1768 K, ΔH_m : 260 J/g,

ρ_S : 8.89 g/cm³, ρ_L : 7.67 g/cm³, γ_S : 2.8 J/m², γ_L : 1.8 J/m².^[1]

B DSC experiments with dicobalt octacarbonyl

The decomposition temperature of dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) and the subsequent cobalt particle formation were investigated by means of *differential scanning calorimetry* (DSC) using a TA Instruments Q100 heat flow calorimeter. 14 mg of $\text{Co}_2(\text{CO})_8$ was put into an open native oxidized aluminum pan and subjected to a continuous flow of dry nitrogen at 50 mL·min⁻¹, while an empty pan served as a reference. Standard aluminum pans are suitable

for such experiments because the presence of an aluminum oxide coating prevents the formation of an Al-Co-alloy.

The sample was heated from 30 °C to 490 °C at a rate of 10 °C·min⁻¹. The melting and the decomposition of Co₂(CO)₈ was observed in the DSC thermogram. A subsequent cooling and repeated heating cycle produced no further signals implying the irreversibility of the observed processes and suggesting the formation of crystalline cobalt particles.

The particles which were formed during the DSC experiment were subsequently probed by *scanning electron microscopy* (SEM) and *X-ray diffraction* (XRD). The investigations show strongly fused spherical particles with a mean diameter of 22.9±8.1 nm and an fcc- and hcp-cobalt structure with a small fraction of cobalt(II) oxide (Figure S1).

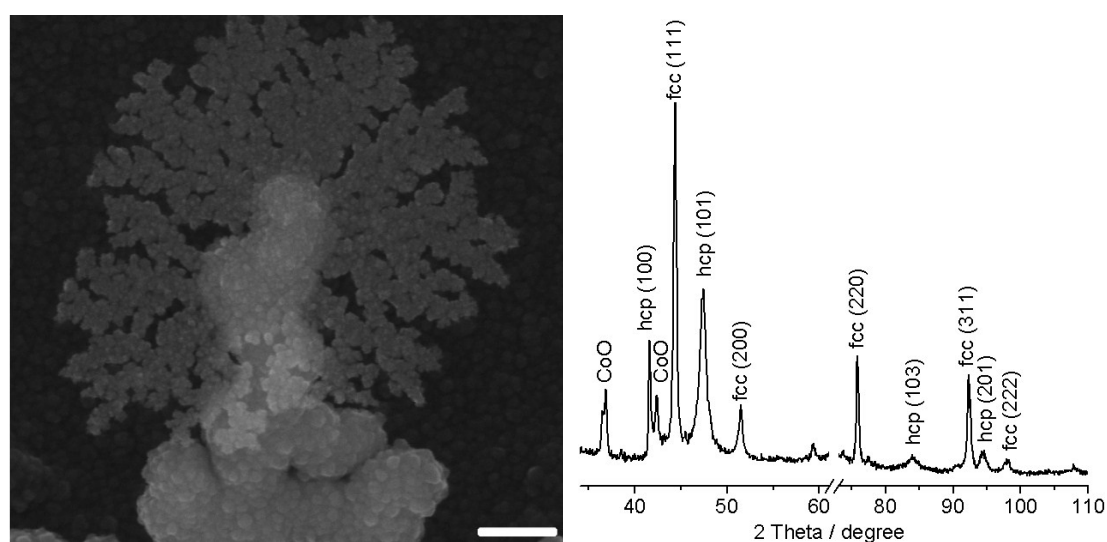


Figure S1. SEM image of cobalt particles formed during the DSC experiment. The scale bars are equal to 200 nm. The XRD measurement shows the typical Bragg reflexes of fcc- and hcp-cobalt allotropes. Additionally, a small fraction of cubic cobalt(II) oxide is observable.^[2]

C XRD- and TEM-investigations of cobalt particles obtained during the synthesis with various Co₂(CO)₈ amounts

The influence of various precursor amounts on particle properties was investigated by

thermolysis of $\text{Co}_2(\text{CO})_8$ in 3 mL squalane without additives at 190 °C for 30 minutes. The carbonyl amounts 0.16 mmol, 0.24 mmol, 0.44 mmol and 0.88 mmol were chosen for the experiments.

Figure S2 shows the TEM and XRD investigations of the obtained particles. The formation of spherical superficially-fused particles were observed in all cases, analogous to the additive-free synthesis at 200 °C (cf. Figure 1 c). All particles show the typical Bragg reflexes of an hcp-cobalt crystal structure: 41.6° {100}, 44.5° {002} and 47.1° {101}.^[2]

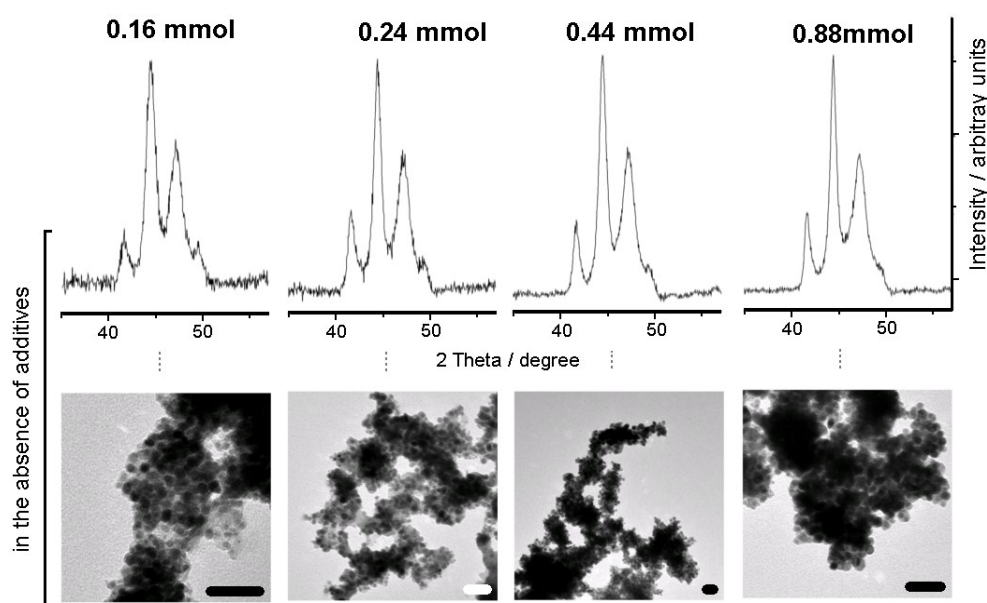


Figure S2. XRD and TEM measurements of cobalt particles that were synthesized by thermal decomposition of $\text{Co}_2(\text{CO})_8$ in the solvent squalane without additives at 190°C. The $\text{Co}_2(\text{CO})_8$ -amount was varied in the different experiments, see labels in top panel. The scale bars in the TEM images correspond to 50 nm.

D Smoluchowski and LaMer fitting

The *Smoluchowski* equation describes the particle growth by an uninhibited and undirected coalescence process of liquid particle precursors.^[3] In this work we used equation (S2) that

has been deduced and used already previously.^[4] Details regarding the equation are given in that work, and only a brief description will be given.

$$r(t) = r(0) \cdot \sqrt[3]{1 + a_f \cdot A(0) \cdot (1 - e^{-kt})} \cdot t \quad (\text{S2})$$

Here, $r(t)$ is the mean droplet radius after the coalescence time t , $r(0)$ is the mean droplet radius at the beginning of coalescence, and a_f is the coalescence coefficient. The droplet formation rate is determined by the initial precursor concentration $A(0)$ and the decomposition rate constant k .

The parameters obtained by fitting the experimental data (Figure 3) with the *Smoluchowski* equation (S2) are given in Table S1.

Table S1. Parameters used for the Smoluchowski fitting (eq. S2) of the experimentally determined particle diameters depending on the precursor concentration $A(0)$ and thermolysis temperature T .

	$r(0)$ / nm	$A(0)$	T / K	k / s ⁻¹	a_f / s ⁻¹	t / s
$d(A(0))$	0.1253	variable	455	$7.35 \cdot 10^{-2}$	$1.90 \cdot 10^{-19}$	705
$d(T)$	0.1253	$2.649 \cdot 10^{20}$ (4 mL 0.11 mol/L)	variable	variable	$1.08 \cdot 10^{-20}$	22608

The $\text{Co}_2(\text{CO})_8$ decomposition rate used for the fitting procedure was measured by extracting small sample volumes (~ 0.2 mL) from the reaction solution at specified time instants and determination of the carbonyl concentration by means of infrared spectroscopy. We observed that carbonyl decomposition follow first-order kinetics with a rate constant of $1.03 \pm 0.11 \cdot 10^{-5}$ s⁻¹ at 110 °C^[5] and $8.0 \pm 2.3 \cdot 10^{-2}$ s⁻¹ at 182 °C. The rate constants at other temperatures were inferred from these values using the Arrhenius equation.

Surfactants like oleyl amine (OA), oleic acid (OS) or tri-*n*-octylphosphinoxide (TOPO) had only a small influence on the decomposition kinetics: $7.74 \pm 1.76 \cdot 10^{-2}$ s⁻¹ with OA

($0.02 \text{ mol}\cdot\text{L}^{-1}$) at $185 \text{ }^\circ\text{C}$ and $1.36\pm 0.11\cdot 10^{-2} \text{ s}^{-1}$ with a surfactant mixture of TOPO ($0.07 \text{ mol}\cdot\text{L}^{-1}$) and OS ($0.03 \text{ mol}\cdot\text{L}^{-1}$) at $185 \text{ }^\circ\text{C}$.^[6]

We note that during the kinetic infrared spectroscopic measurements, we observed a remaining weak carbonyl vibration band at 2059 cm^{-1} after the $\text{Co}_2(\text{CO})_8$ thermolysis in squalane at 110°C . A centrifugation of the reaction solution yields a black sediment in a brown solution. These observations may indicate the formation of higher cobalt cluster aggregates or particles at low temperatures.

The kinetic analysis of $\text{Co}_2(\text{CO})_8$ thermolysis in squalane at 185°C shows that the mean particle volume increases quickly in time at a rate that is directly correlated to the carbonyl decomposition rate (see Figure S3), in agreement with the requirement of the Smoluchowski model of an approximately activation-free coalescence process.^[3]

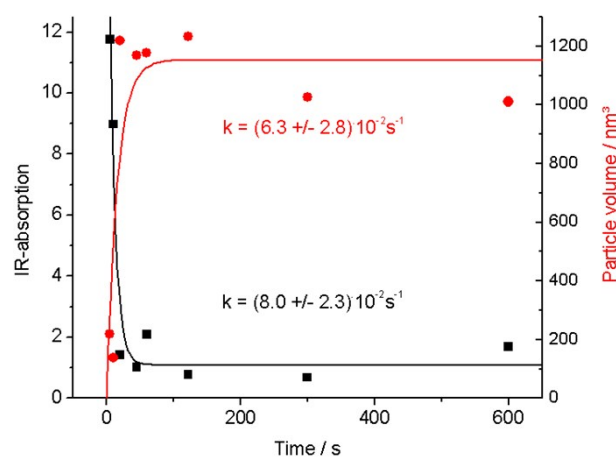


Figure S3. Kinetic analysis of the thermal decomposition of $0.07 \text{ mol L}^{-1} \text{ Co}_2(\text{CO})_8$ in 1,2-dichlorobenzene in presence of 0.03 mol L^{-1} TOPO at 185°C . A direct correlation between the decrease of carbonyl infrared absorption and the increasing mean particle volume is discernible.

According to the *LaMer*-model, the formation of crystalline nuclei takes place in the early stage of phase separation.^[7] Equation (2) describes this nucleus formation processes.^[8]

$$d = \left[A(0) \cdot a \cdot \exp\left(-\frac{16 \cdot \pi \cdot \gamma^3}{3 \cdot k_B T \cdot b^2 \cdot \ln(A(0)/N_{eq})^2}\right) \right]^{-1} \quad \text{with} \quad a = K \cdot (1 - \exp(-k \cdot t)) \quad (\text{S3})$$

Here, $A(0)$ is the initial precursor concentration, N_{eq} is the saturation concentration of the monomers, γ is the surface tension of the nucleus, $k_B T$ is the thermal energy, and a and b are the kinetic and thermodynamic fitting parameters. The kinetic parameter a depends on the decomposition rate constant k , time t and an independent kinetic constant K .

The fitting of the experimental data from Figure 3 with the LaMer equation (2) resulted in the following parameters collected in Table S2.^[9]

Table S2. Parameters obtained from the LaMer fitting (eq. S3) of the experimentally determined particle diameters depending on the precursor concentration $A(0)$ and thermolysis temperature T .

	A(0)	N_{eq}	T / K	γ / J·m⁻²	a (~K) / nm⁻¹	b / J·m⁻³
d(A(0))	variable	3.25 · 10 ¹¹	455	2.8	5.14 · 10 ⁻⁵	4.25 · 10 ⁹
d(T)	2.649 · 10 ²⁰ (4 mL 0.11 mol/L)	3.25 · 10 ¹¹	variable	2.8	1.05	7.64 · 10 ⁹

E References

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- 2 The diffractiongram was measured with a copper X-ray source (K α 1: 1.54056 Å, K α 2: 1.54439 Å). XRD-Reference data from X'Pert High Score (hcp-Co 00-005-0727; fcc-Co 00-015-0806; fcc-CoO 00-048-1719) and from literature V. F. Puentes, K. M. Krishnan, A. P. Alivisatos, *Science (Washington, D. C., 1883-)* 2001, **261**, 2115-2117 (ϵ -Co).
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