Supplementary Material for

"Morphological Impact on the Reaction Kinetics of Size-Selected Cobalt Oxide Nanoparticles"

Stephan Bartling, Marga-Martina Pohl, Karl-Heinz Meiwes-Broer, and Ingo Barke

Crystal structure of cobalt oxide particles

In Figure 1 of the main text two RHEED images with the corresponding averaged intensity profiles are shown. The depicted structures are identified as CoO (NaCl structure) and Co$_3$O$_4$ (spinel structure) using conventional powder diffraction theory and bulk-like crystallographic structures. The expected positions and relative intensities of CoO and Co$_3$O$_4$ are calculated with the software PowderCell 2.3$^{51}$ in order to identify strong peaks. The height of the first calculated peak in each graph is normalized to the corresponding experimental one. Before reduction the averaged intensity curve (Figure S1a) of the 6 nm clusters can be explained by Co$_3$O$_4$ with a spinel structure and the characteristic double peak at 4.0 Å$^{-1}$ and 4.4 Å$^{-1}$. After the reaction the RHEED pattern significantly changes, with a strong peak at 4.2 Å$^{-1}$ originating in the CoO structure (Figure S1b).

![Figure S1: Averaged intensity curves obtained from RHEED images before (a) and after (b) reduction experiment.](image)

The first dashed peak at 2.5 Å$^{-1}$ contains artifact contributions from the electron gun. The colored vertical lines indicate the calculated positions and relative intensities for Co$_3$O$_4$ (blue) and CoO (red). In (a) the RHEED intensity curve can be explained by particles consisting of Co$_3$O$_4$ whereas at the end of the reaction treatment in (b) the crystal structure of CoO is present.

Size distribution and stability of deposited Co particles

As stated in the manuscript the oxidized nanoparticles (CoO and Co$_3$O$_4$) are extremely stable and can be exposed to air for extended periods of time. To determine the size of our clusters atomic force microscopy (AFM) measurements are performed after the initial oxidation and are shown in Figure S2 with the corresponding size distributions. In all cases well separated and randomly distributed nanoparticles are visible in the AFM images.
Figure S2: Distributions of cluster heights (top) obtained from AFM images of the three investigated particle sizes. The black line represents the mean size and the light gray area the standard deviation of the distribution. The representative 2x2 µm² AFM images (bottom) show well separated randomly distributed particles.

Reaction kinetics for various cluster sizes

To describe solid state reactions complex reaction models are available in literature taking into account diffusion processes and the dimensionality of solid objects. In case of nanoparticles where the reaction is mainly triggered by the surface and influenced by the large surface to volume ratio typically simple models like first-order or pseudo first-order kinetics are applicable. However for the nanoparticles reaction observed in this experimental regime (low pressure, temperatures up to 540 K) slow reaction rates are found which can be well approximated with zero-order kinetics. After an introduction period and before completion of the conversion the reaction rates are independent of concentration and thus can be fitted with straight lines as shown in the manuscript in Figure 2 leading to the Arrhenius plot in Figure 3. The oxidation and reduction experiments have also been carried out for the other cluster sizes (6 nm, 10 nm, and 18 nm). The corresponding Arrhenius plots are displayed in Figure S3 for oxidation reaction and Figure S4 for reduction to obtain the apparent activation energies \( E_a \) as the slope of the curves which are discussed in detail in the manuscript.
We can exclude that the reaction kinetics is not dominated by higher orders because (i) the evolution of the CoO fraction for extended periods of time at constant pressure and temperature shows a linear behavior and (ii) saturation effects set in rather suddenly at CoO fractions close 1 or 0. Smaller contributions of higher order kinetics do not result in significantly different activation energies. We verified this for the extreme case of pure first order kinetics which resulted in a ≈20% variation of the obtained value.

The remaining dominating systematic uncertainty is the exact composition of the two reference spectra (see Figure 1 in the main text). Based on comparisons with powder diffraction calculations and XANES data (see Ref. 39) we estimate the maximum contribution of other phases to be below 10%. This results in a similar relative error of the ratio between CoO and Co₃O₄ as well as for the reaction rates. However, the resulting activation energy is much less affected (<2%) because variations in the reference compositions predominantly results in vertical shift of the Arrhenius line with little effect on the slope. The statistical error from the linear regression (see Table I) therefore dominates the total error of the activation energy.

Figure S3: Arrhenius plots for the oxidation of 6 nm (a), 10 nm (b) and 18 nm (c) CoO clusters to Co₃O₄. The apparent activation energy is given by the slope of the fitted line and discussed in detail in the main text.
**Figure S4:** Arrhenius plots for reduction of 10 nm Co$_3$O$_4$ clusters to CoO. The apparent activation energy is given by the slope of the fitted line and discussed in the main text.

The observed reactions (oxidation and reduction) are mainly driven by temperature induced diffusion processes and the presence of the reaction gases (H$_2$ or O$_2$). In the case of high temperatures the reaction rates can be limited by the availability of the reaction gases (*i.e.* gas pressure). The temperatures used here to determine the reaction kinetics are chosen such that the reaction gas pressure is not a limiting factor.

In Figure S5 the evolution of particle composition is shown for the reduction (a) and oxidation (b) reaction of the large 18 nm clusters. The extracted slope for each temperature step is plotted in the corresponding Arrhenius graphs in Figure 3 in the main text and Figure S3c, yielding the apparent activation energies for the two reactions of the same nanoparticle sample.

**Figure S5:** Evolution of particle composition for 18 nm clusters during the reduction of Co$_3$O$_4$ to CoO (a) and oxidation back to Co$_3$O$_4$ (b). The corresponding Arrhenius plots are shown in Figure 3 in the manuscript and Figure S3c, respectively.
Crystallite sizes for 6nm and 10nm particles

A distinct change in cluster morphology for the large clusters is seen by TEM in Figure 4 in the main text and Figure S7. The quantification of the observed split-up of the 18 nm particles into smaller sub-crystals is done by RHEED. For this purpose the evolution of the peak width of the characteristic CoO (220) peak at 4.2 Å⁻¹ is evaluated after each oxidation/reduction cycle in Figure 5 of the manuscript. Because for 6 nm and 10 nm clusters a constant peak width is observed they are used as references to determine the crystallite size of the 18 nm particles in Figure 6 in the main text using the Scherrer equation.

In Figure S6 the corresponding crystallite sizes are calculated for the 6 nm and 10 nm clusters after the second oxidation reduction/reduction cycle revealing a constant crystallite size during the whole treatment. The large error bars of the 10 nm clusters are mainly caused by the instrumental peak width which impedes measuring larger crystallite sizes.

**Figure S6:** Crystallite size obtained from peak width measurements. Using the Scherrer equation and the peak width of 6 nm and 10 nm clusters after the first oxidation/reduction cycle as references the crystallite size is calculated for all subsequent cycles. The error bars for the first data points are not shown because these values are used for calibration. The third data point for 10 nm clusters is missing because of incomplete reduction. During the whole treatment the derived crystallite sizes are constant.
Figure S7: Additional STEM HAADF images of 6 nm (a), (b) and 18 nm (c), (d) Co cluster deposited on SiO$_2$ membrane TEM grids after the first oxidation to Co$_3$O$_4$. As stated in the main text smaller particles are compact monocrystallites, larger ones consist of smaller sub-crystallites.

References