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TEM investigations of the sintering behavior of noble metal nanoparticles

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Supported catalysts such as Pt or Pd deposited on an oxide carrier like, e.g., silica are widely used in chemical industry today. However, sintering of the noble metal nanoparticles (NPs) results in severe deactivation of the active metal phase. To enhance the stability of the catalyst particles, a comprehensive understanding of the kinetics of NP growth is crucial. For Pd NPs Binder and Seipenbusch [1] proposed three different mechanisms of ripening, based on the theoretical description by Wynblatt and Gjostein [2, 3]. According to literature [4] the dominant factors for particle growth at low temperatures or short times are surface migration, collision, and coalescence of particles of nearly equal size. This process as illustrated in Fig. 1a is also known as Smoluchowski ripening. Smoluchowski ripening is competing with the process of Ostwald ripening, where an atomic transport from small particles to larger ones takes place resulting in a reduction of the total surface energy of the system. This interparticle transport was described by Wynblatt and Gjostein [3] and is sketched in Fig. 1b. Goal of the present research was to investigate the influence of annealing temperature on the contact angle between NP and surface of the carrier material, surface-migration velocity, and surface-collision frequency of the NPs. This would gain insight into the deactivation process of the active phase of supported noble metal catalysts.

Pt NPs supported on Al_2O_3, TiO_2, and SiO_2 carrier particles were chosen as model system to study the sintering behavior at temperatures from 100°C to 800°C. The Pt/carrier particle systems were fabricated in the gas phase by chemical vapor synthesis (CVS) and metal-organic chemical vapor deposition (MOCVD) at atmospheric pressure. The size distribution and number density of Pt NPs were controlled by the concentration of Pt precursor and the partial pressure of O_2 in the gas phase during the CVS process. Pt/Al_2O_3 and Pt/SiO_2 nanostructures were deposited on Si_3N_4 grids with a foil thickness of 20 nm for transmission electron microscopy (TEM). The NPs were characterized *ex-situ* after annealing in nitrogen atmosphere and *in-situ* in the microscope. For the *in-situ* TEM measurements, Pt/Al_2O_3 and Pt/SiO_2 samples were heated from room temperature to the desired annealing temperature (100 °C to 800 °C) under high vacuum in a Philips CM200 FEG/ST transmission electron microscope. TEM bright-field (BF) images were taken at a frequency of $1min^{-1}$ to determine the surface-migration velocity and contact angle between the noble metal NPs and the support.

Smoluchowski ripening was observed both for *ex-situ* and *in-situ* heat treatment. The change of Pt-NP size distribution at different temperatures and the average surface-migration velocity were measured. Fig. 2 shows exemplarily the results of the Pt/SiO_2 system examined *ex-situ* after intervals of two hours of annealing at 600 °C in an N_2 atmosphere. Annealing of Pt catalyst NPs on SiO_2 carrier particles results in a measurable increase of NP sizes, which can be observed in the TEM images given in Fig. 2. Histograms of the relative frequency distribution q_0 of NP sizes after the corresponding annealing times are also illustrated in Fig. 2. The relative frequency is given by $q_0=n_i/(N\cdot\Delta x_i)$ where n_i denotes the number of NPs within a distinct size interval with a width Δx_i (here 0.5 nm) and N the total number of NPs. A significant shift of the maxima from about 2.5 nm (0 h) towards larger particle sizes of about 4.5 nm (8 h) can be observed, which demonstrates the ripening process of the catalyst NPs. The analysis of the contact angle between Pt and silica from high-resolution TEM images is subject of current investigations.

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Figure 1. Schemes describing the processes of a) Smoluchowski ripening and b) Ostwald ripening.

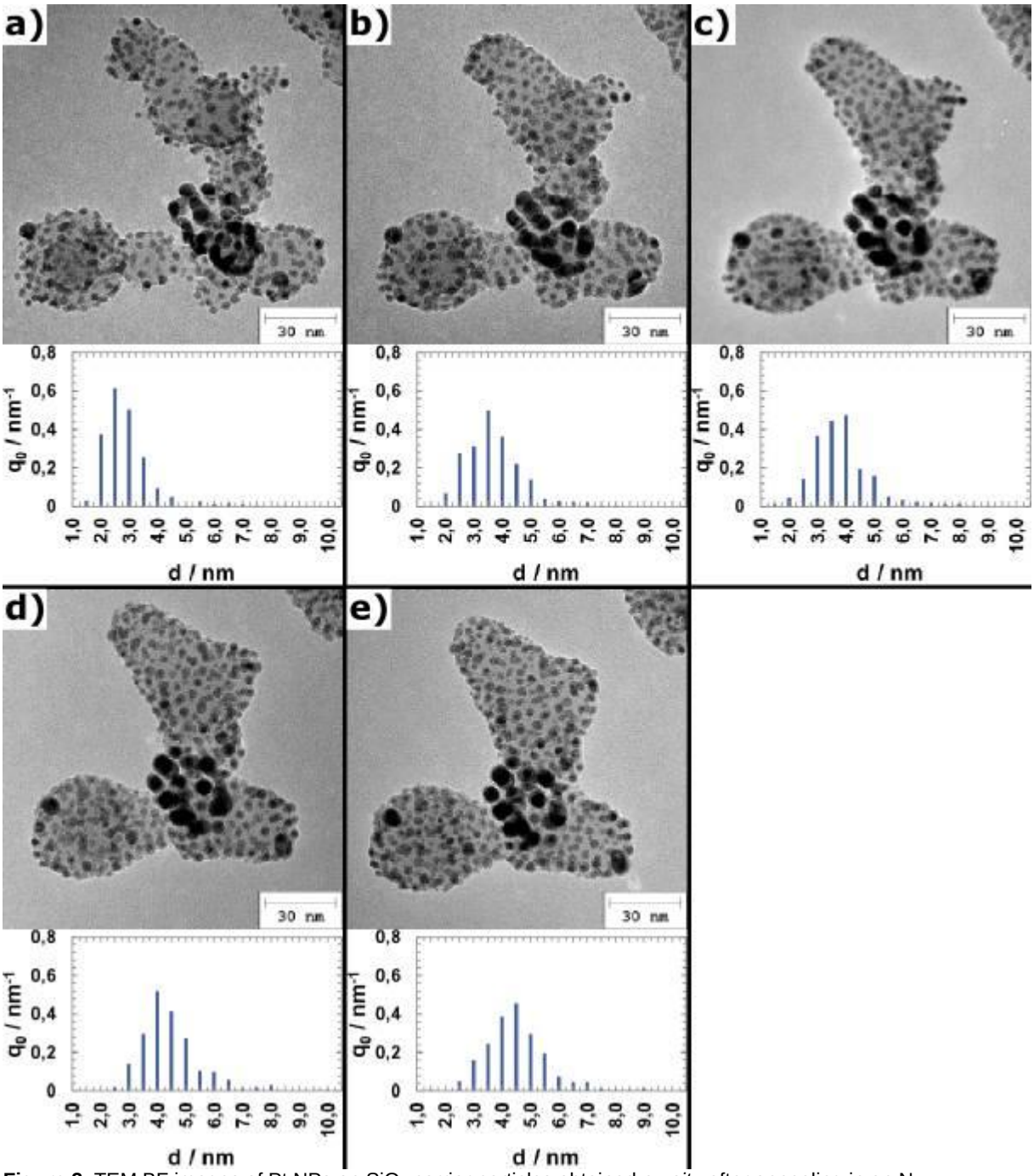

Figure 2. TEM BF images of Pt NPs on SiO_2 carrier particles obtained *ex-situ* after annealing in an N_2 environment at 600°C and corresponding frequency distribution of NP sizes after (a) 0 h, (b) 2 h, (c) 4 h, (d) 6 h, and (e) 8h.