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TEM investigations of the sintering behavior of noble metal nanoparticles

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Introduction

Catalytic nanoparticles

- Many industrial applications, e.g. cleaning automobile exhaust gas and production of chemicals and pharmaceuticals
- In high-temperature catalytic processes:
  - ➜ Loss of catalytic activity of the active metal phase due to sintering or thermal deactivation
- Goal: better understanding of the nanoparticle transport kinetics
  - ➜ Enhancement of the stability of catalytic particles

Microscopical analysis

- *Ex-situ* TEM: investigations after several steps of annealing at temperatures between 100 °C and 800 °C
- *In-situ* TEM: investigation of samples heated from room temperature to an annealing temperature between 100 °C and 800 °C under high vacuum at a frequency of 1 image per minute

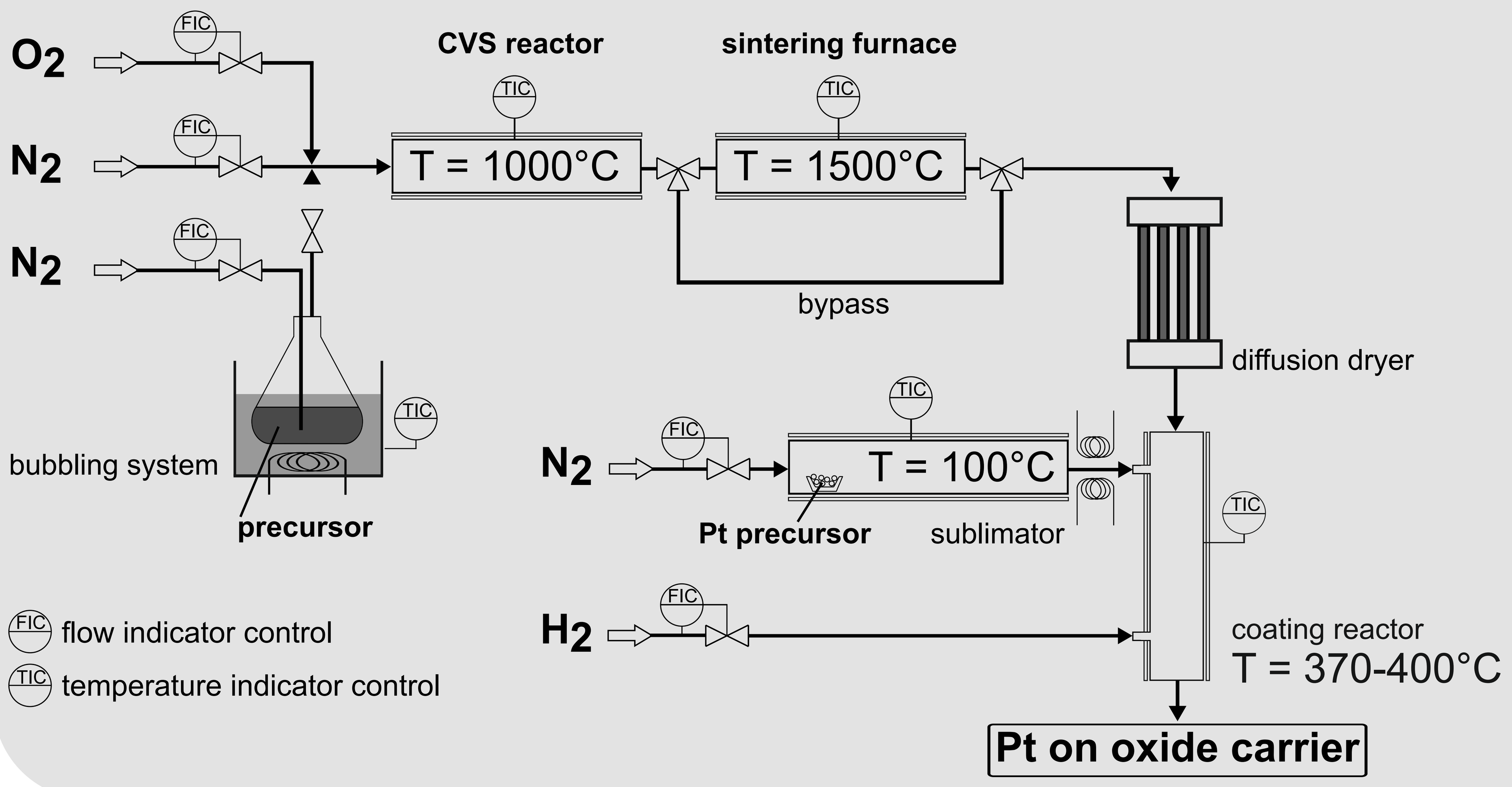
Model system

- Pt nanoparticles on globular carrier particles of Al_2O_3, TiO_2, and SiO_2
- Subsequent deposition of carriers and Pt nanoparticles on Si_3N_4 TEM grids with a foil thickness of 20 nm

Sample preparation

Chemical vapor synthesis (CVS) of metal-organic precursors [1]

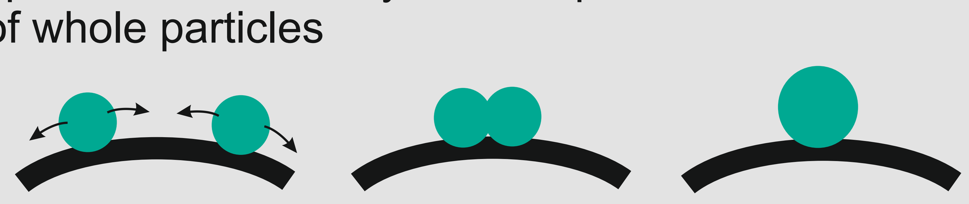
- Preparation of oxide carrier particles by first metal-organic precursor in CVS reactor at 1000 °C and following sintering and drying at 1500 °C
- Deposition of Pt nanoparticles by second precursor at 400 °C



Theory of the surface particle ripening

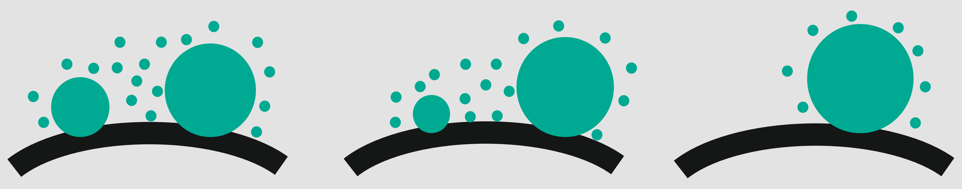
Smoluchowski ripening [2,3]

- Controlled by Brownian motion of nanoparticles
- Dependent on particle size, density and temperature
- Coalescence of whole particles



Ostwald ripening [3,4]

- Concentration of atoms in the vicinity of particles determined by Gibbs-Thompson effect, atom concentration ~1/r (r: particle radius)
- Diffusion-controlled process
- Transport of single metal atoms through vapor phase and/or along surface
- Growth of bigger particles at the expense of smaller ones energetically advantageous



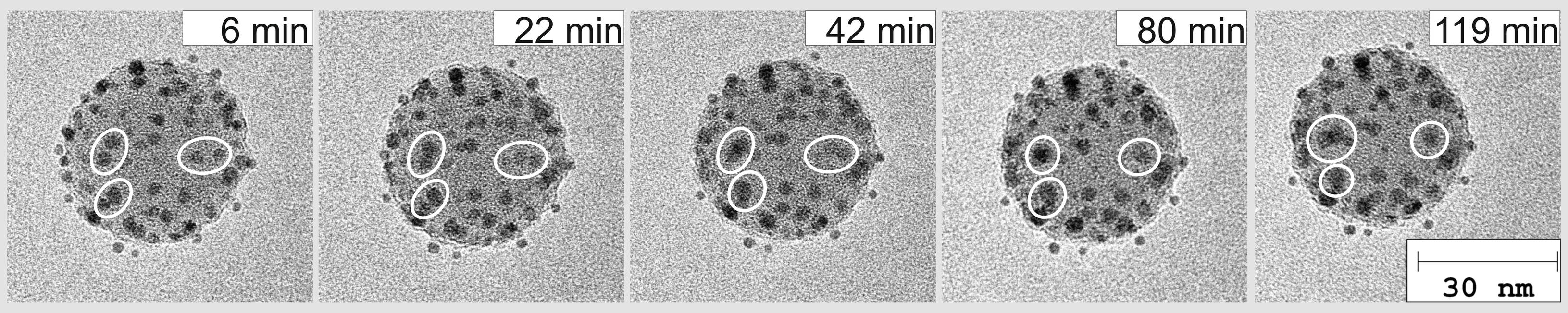
References

[1] A. Binder et al., Appl. Catal. A 396 (2011) p. 1-7.
[2] M. Smoluchowski, Z. Phys. Chemie 92 (1918) p. 129-168.
[3] P.J.F. Harris, Int. Mat. Rev. 40 (1995), p. 97-115.
[4] E. Ruckenstein et al., J. Catal. 29 (1973) p. 224-245.

Results

***In-situ* investigations**

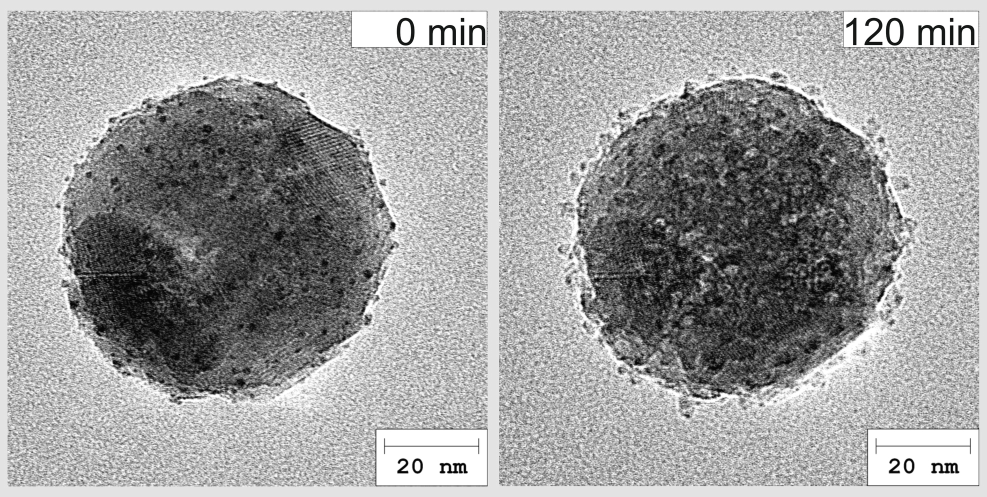
- Pt nanoparticles on SiO_2 carrier at 100 °C



➜ High mobility of single Pt nanoparticles

➜ Coarsening by simultaneous Smoluchowski and Ostwald ripening

- Pt nanoparticles on Al_2O_3 carrier at 23 °C



- Modification of the carrier surface under the influence of the 200 kV electron beam in TEM

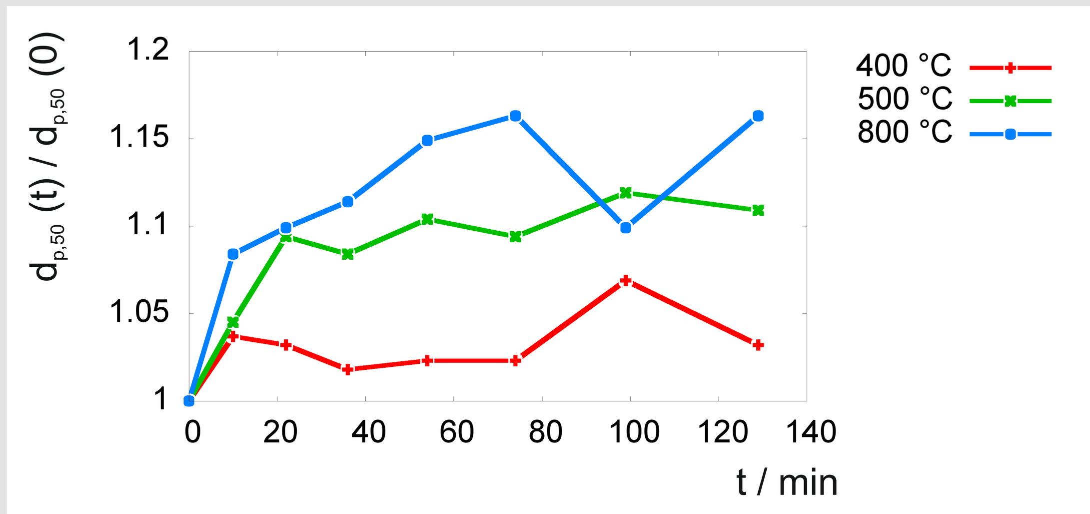
➜ Ostwald ripening dominant

***Ex-situ* investigations**

- Pt nanoparticles on Al_2O_3 carrier
- Annealing at temperatures between 400 °C and 800 °C for up to 130 min
- Determination of the median particle diameter from particle size distributions
- Particle size distributions fitted to a logarithmic normal distribution $f(d_p)$

$$f(d_p) = \frac{1}{\sqrt{2\pi}\, d_p \ln(\sigma_g)} \cdot \exp\left(-\frac{(\ln d_p - \ln d_{p,50})^2}{2\,(\ln \sigma_g)^2}\right)$$

d_p particle diameter
σ_g geometric standard deviation
$d_{p,50}$ median diameter



Median particle diameter normalized with the initial median diameter as a function of annealing time

- Increase of median diameter with increasing temperature and annealing time
  - ➜ Fast increase at small annealing times due to Smoluchowski ripening
  - ➜ Dominant Ostwald ripening for annealing times larger ~20 min

Conclusions and outlook

- *In-situ* TEM study of Pt nanoparticles on SiO_2 carriers at 100 °C: coarsening by simultaneous Smoluchowski and Ostwald ripening
- *In-situ* TEM study of Pt nanoparticles on Al_2O_3 carriers: dominant Ostwald ripening at room temperature (influence of the electron beam irradiation to be clarified)
- *Ex-situ* TEM study of Pt nanoparticles at temperatures between 400 °C and 800 °C: Smoluchowki ripening for annealing times smaller than 20 min, Ostwald ripening at larger times
- *Ex-situ* TEM is an appropriate method for revealing the ripening mechanisms of platinum nanoparticles on carrier particles
- Further studies required for characterization of the nanoparticle coarsening process and surface properties, e.g. at longer annealing periods

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