TEM investigations of the sintering behavior of noble metal nanoparticles

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Introduction
Catalytic nanoparticles
Several 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 Al₂O₃, TiO₂, and SiO₂
Subsequent deposition of carriers and Pt nanoparticles on Si₃N₄ TEM grids with a foil thickness of 20 nm

Sample preparation
Chemical vapor synthesis (CVS) of metal-organic precursors
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
- Controlled by Brownian motion of nanoparticles
- Dependent on particle size, density and temperature
- Coalescence of whole particles

Ostwald ripening
- Concentration of atoms in the vicinity of particles determined by Gibbs-Thompson effect, atom concentration \( \propto \frac{1}{r} \) (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

Results

In-situ investigations
- Pt nanoparticles on SiO₂ carrier at 100 °C
  - High mobility of single Pt nanoparticles
  - Coarsening by simultaneous Smoluchowski and Ostwald ripening

Ex-situ investigations
- Pt nanoparticles on Al₂O₃ carrier at 23 °C
  - Modification of the carrier surface under the influence of the 200 kV electron beam in TEM
  - Ostwald ripening dominant

Goals of the study
- Better understanding of the nanoparticle transport kinetics
- Enhancement of the stability of catalytic particles

Sample preparation
- Chemical vapor synthesis (CVS) of metal-organic precursors
- Preparation of oxide carrier particles
- Deposition of Pt nanoparticles

Theory of the surface particle ripening
- Smoluchowski ripening
- Ostwald ripening
- Combination of the two processes

References

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