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Coarsening of Pt clusters on amorphous carbon substrates

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Motivation

Deposition of metal clusters and their rearrangement on substrates
Fundamental issues:
- strong dependence of physical and chemical properties of clusters on the cluster size
- fabrication of nano-devices with new properties

Pt clusters in catalysis:
- high catalytic activity for hydrogen-dissociation and hydrogen-oxidation at low temperature
  (P. Costamagnam and S. Srinivasan, J. Power Sources 102 (2001) 242)
- electrocatalysts on carbon material in proton-exchange membrane fuel cells

Problem: progressive loss of active surface area due to cluster coarsening

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Study of the stability and time evolution of the cluster-size distribution at different temperatures and dominant coarsening mechanisms

Basic mechanisms of coarsening: mass transport via surface diffusion of
- whole clusters – dynamic coarsening or Smoluchowski ripening (SR)
- atomic constituents – surface Ostwald ripening (OR)

Theory of Ostwald Ripening (OR)

Coarsening of cluster ensembles due to the tendency to lower the total free energy of the system by redistribution into fewer and larger clusters

Coarsening via surface OR based on the Gibbs-Thomson effect
- growth of large clusters on the expense of small clusters

The kinetics of the OR is discussed in terms of two different limiting cases [1]:
- Diffusion-limited kinetics
- Reaction- or attachment-limited kinetics

The power laws for the average cluster radius $\bar{R}(t)$ in case of the mass transport performed through the contact perimeter between cluster and substrate [1]:

diffusion-limited case $\bar{R}^4(t) = \bar{R}^4(0) + K_d\, t$

reaction-limited case $\bar{R}^3(t) = \bar{R}^3(0) + K_r\, t$

K_d, K_r constants.

[1] B.K. Chakraverty, J. Phys. Chem. Solids 28 (1967) 2401.

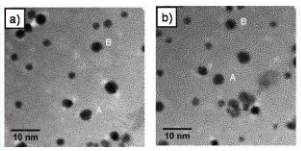
Experimental Details

Samples prepared by electron-beam vapour deposition of Pt on 10 nm thick commercial amorphous carbon (a-C) substrates

Annealing in a standard oven at temperatures of 200 °C, 250 °C, 300 °C on air

TEM in a Philips CM200 FEG/ST electron microscope at 200 keV electron energy and Titan³ 80-300 at 300 keV

Effect of Electron Beam Illumination



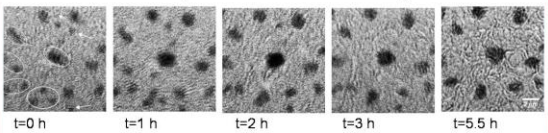
t'=0 s — after t'=25 min 30 s continuous illumination

Largest change between inter-cluster distances $d_{A\text{-}B}$
⟶ $v_{A\text{-}B} = 2.9 \cdot 10^{-3}$ nm/s

No measurable change of Pt-cluster radii during the first 20 min

No effect of the electron-beam illumination on the cluster coarsening within the time necessary to record a TEM image (about 2 s)

In-situ TEM Study of Pt-cluster Coarsening at 470 °C



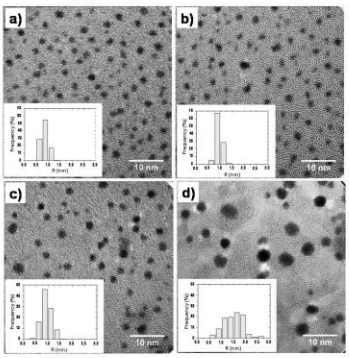
t=0 h | t=1 h | t=2 h | t=3 h | t=5.5 h

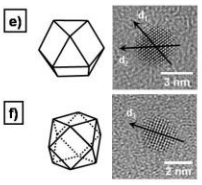
Two different coarsening regimes with time:
- t < 2 h : coarsening by SR and surface OR
- t > 2 h : coarsening mainly by OR (SR negligible)

Surface Ostwald Ripening of Pt clusters

Kinetics of the surface OR during the second growth regime

TEM images of Pt clusters with histograms of cluster-radius distribution after annealing at 200 °C for (a) 2 h, (b) 15 h and after annealing at 300 °C for (c) 2 h and (d) 15 h.

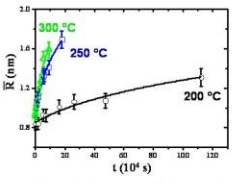




Clusters composed of elemental Pt:
lattice-fringe distances along to
d_1=0.227±0.009 nm (e)
d_2=0.199±0.011 nm (e)
d_3=0.198±0.010 nm (f)
correspond to
$d_{(111)}$=0.227 nm and
$d_{(200)}$=0.196 nm
in bulk *fcc* Pt (a=0.3925 nm)

Pt clusters with *fcc* cuboctahedral structure: (e) in the [110]- and (f) [100]-zone axis: schematic views and typical TEM images

Average Pt-cluster radius $\bar{R}(t)$ as a function of time and temperature with fit of the experimental data assuming diffusion-limited kinetics of surface OR

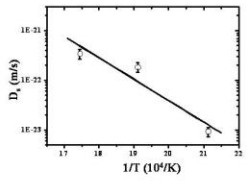


Significant increase of $\bar{R}(t)$ described by the power law: $\bar{R}(t) \sim t^{1/4}$ corresponding to the diffusion-limited kinetics of surface OR.

K_d values obtained from the fit curves
⟶ calculation of the surface mass-transport diffusion coefficient D_s

$$D_s = \frac{45 \ln(L)\, \varphi(\theta)\, k_B\, T}{8\, \omega^2\, \gamma\, n_0} K_d$$

ω : Pt atomic volume 1.5·10⁻²⁹ m³
n_0 : number of sites on the Pt-cluster surface 1.3·10¹⁹ m⁻²
L : constant screening distance (expressed in units of R) 2.5
γ : Pt-surface energy 3.0 Jm⁻²
k_B : Boltzmann constant
T : corresponding absolute temperature
$\varphi(\theta)$ = 0.56 for Pt clusters with *fcc* cuboctahedral structure



Arrhenius-type dependence of $D_s(T)$

$$D_s = D_0 \exp\left(-\frac{E_d}{k_B T}\right)$$

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activation energy for the surface diffusion Pt atoms on a-C
E_d = 0.85 ± 0.09 eV/atom

Conclusions

Significant increase of the average Pt-cluster radius with time after annealing at 200 °C, 250 °C and 300 °C

In-situ annealing at 470°C demonstrates the presence of two growth regimes:
- t < 2 h : cluster coarsening by SR and surface OR
- t > 2 h : coarsening mainly due to surface OR (SR negligible)

In the second growth regime:
- Surface OR with diffusion-limited kinetics
- Steady-state conditions with the mass transport performed through the contact perimeter between cluster and substrate

Arrhenius-type dependence of the surface mass-transport diffusion coefficient $D_s(T)$ with an activation energy for the surface diffusion of Pt atoms on a-C substrate
E_d = 0.85 ± 0.09 eV/atom

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