

From Pt molecules to nanoparticles: *in-situ* (anomalous) small-angle X-ray scattering studies

H.-G. Haubold^a*, T. Vad^a, N. Waldöfner^b and H. Bönemann^b

^a Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany, ^b Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim an der Ruhr, Germany

Anomalous small angle X-ray scattering was employed to monitor in situ the formation of colloidal Pt particles by the reaction of Pt(acac)₂ and Al(CH₃)₃ in solution. An intermediate complex molecule was found to decompose to form stable Pt particles of 1.2 nm diameter with a monomodal particle size distribution. A network like correlation in the particle positions tends to build up by organic spacer molecules between stabilizing aluminum–organic shells.

Keywords: Nanoparticles; ASAXS; anomalous dispersion; colloids

1. Introduction

The preparation of noble metals in form of small nanoparticles by wet chemical reactions plays a crucial role in the production of effective finely dispersed catalysts or more recently, in the field of chemical nanotechnology to synthesize nanocrystal superlattices from these materials (Conolly & Fitzmaurice, 1999). One of the key questions for the chemists is the knowledge of their particle size distributions in the solution of the reactants. Ex situ studies of samples, which are removed from the solution of the reactants are often of limited value, since changes can occur during the washing and drying procedures. To achieve in situ information on the formation of Pt nanoparticles in solution, anomalous small-angle X-ray scattering (ASAXS) was employed to monitor in situ the formation of colloidal Pt particles and to examine their particle size distributions.

2. Experimental

We studied the formation of platinum nanoparticles by a wet chemical synthesis. The preparation method was a reductive stabilization of nanoparticles with aluminum-trialkyls, which was developed recently by Bönemann and co-workers (Bönemann *et al.*, 1999), Fig. 1.

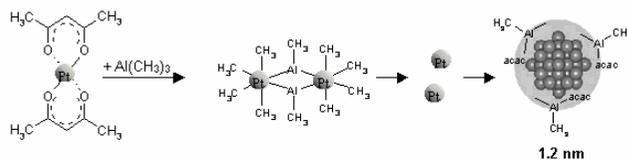


Figure 1

Reaction path of the reductive stabilization of Pt nanoparticles with a protective organic shell.

From the combination of NMR, XANES and EXAFS spectroscopy, one retrieves the formation of an intermediate organometallic molecule with two platinum atoms (Bönemann *et al.*, 2002) as the initial step in the reaction. This binuclear platinum complex is rather

unstable and decomposes into zerovalent platinum atoms, which then nucleate to small nanoparticles. We performed an ASAXS experiment to study this particle formation in situ.

For the in situ SAXS/ASAXS experiment, Pt-acetylacetonate Pt(acac)₂ was dissolved in toluene and a solution of trimethylaluminum Al(CH₃)₃ in toluene was then added under argon atmosphere. The reaction mixture was transferred to a sealed capillary tube and quenched to -78 °C. The samples were prepared at the MPI in Mülheim and brought to the JUSIFA beamline at the Hamburg Synchrotron Radiation Laboratory HASYLAB-DESY, where the measurements were performed at room temperature.

The SAXS measurements were performed with synchrotron radiation from the storage ring DORIS at the small-angle scattering beamline JUSIFA (Haubold *et al.*, 1989, <http://www.fz-juelich.de/iff/personen/H.-G.Haubold>). This beamline is especially designed for anomalous scattering studies at a low parasitic background scattering from the experimental setup.

The total amount of platinum in the capillary sample was 0.07 mg Pt per cm² sample surface. The measurements were performed with a 0.1×0.1 cm² size of the primary X-ray beam, i.e. with the low platinum amount of only 0.7 µg. For this measurement, a low parasitic background turned out to be mandatory.

3. Results and discussion

Small-angle scattering cross sections were measured in situ after reaction times *t* between 0.8 up to 63 h at room temperature, Fig. 2.

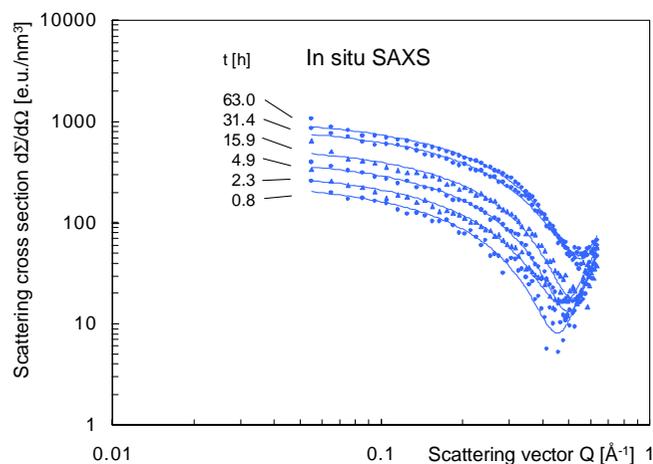


Figure 2

In situ SAXS scattering cross sections at an X-ray energy $E_1 = 11.46$ keV after increasing reaction at room temperature.

With increasing reaction time, the scattering intensity increases by half an order of magnitude, whereas the overall shape of the scattering curves remains essentially unchanged. This indicates that an increasing amount of nanoparticles is formed with equal sizes during the course of the reaction. This interpretation, however, is not unambiguous, since there is an unknown scattering contribution from the organic molecules in the solution.

To get rid of this unknown scattering contribution, we used two X-ray energies for our measurements: $E_1 = 11.46$ keV and a second energy $E_2 = 11.54$ keV, both in the pre-edge energy region of the L₃

X-ray absorption edge of platinum. Here, by anomalous scattering (Cromer & Liberman, 1981), the atomic scattering amplitudes of the platinum atoms are reduced by about 10% and the scattering contributions from Pt structures become energy dependent, whereas background scattering contributions as from the organic molecules remain unaffected and can be subtracted out (Haubold *et al.*, 1994, 1995, 1996, 1999).

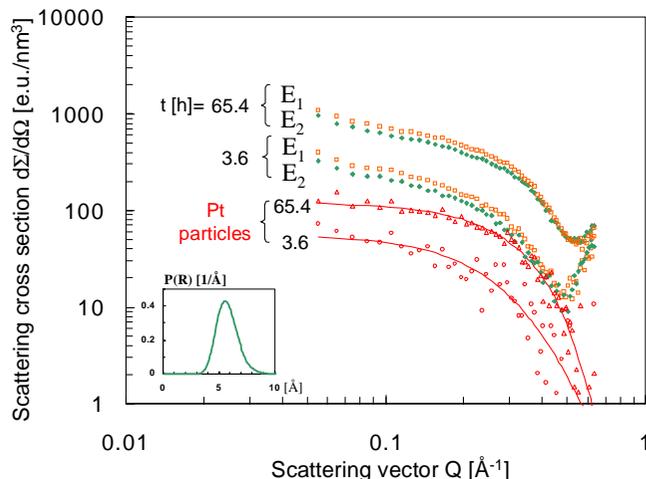


Figure 3
In situ ASAXS small-angle scattering cross sections for reaction times 3.6 and 65.4 h at two X-ray energies $E_1 = 11.46$ keV and $E_2 = 11.54$ keV in the pre-edge region of the L_3 X-ray absorption edge of Pt atoms. Fitted difference cross sections of Pt nanoparticles with mean radii $\langle R \rangle = 5.8$ Å and a monomodal lognormal particle size distribution (insert).

The resulting ASAXS difference scattering cross sections $d\Sigma/d\Omega(E_1) - d\Sigma/d\Omega(E_2)$ thus reflect the separated scattering from Pt structures unambiguously. A fit is given in Fig. 3 for spherical platinum particles in a homogeneous matrix with organic molecules. Their scattering contrast in this 2-phase model is $n_{Pt}f_{Pt} - n_m f_m \approx n_{Pt}f_{Pt} - f_m$ and f_{Pt} and f_m are the atomic form factors of matrix and platinum atoms, n_{Pt} and n_m are their number densities. The scattering cross section for spherical particles with radii R then writes

$$d\Sigma/d\Omega(Q) = c |n_{Pt}f_{Pt} - n_m f_m|^2 \int V^2(R) P(R) F^2(Q, R) dR$$

Here, Q is the modulus of the scattering vector, $= 4\pi \sin\theta/\lambda$ with $2\theta =$ scattering angle and $\lambda =$ wavelength of the X-rays, $V(R)$ is the volume and $F(Q, R)$ the form factor of the particles

$$F(Q, R) = 3 [\sin(QR) - QR \cos(QR)] / (QR)^3$$

For the particle size distribution $P(R)$ a mono-modal lognormal size distribution is used with a width σ

$$P(R) = [(2\pi)^{1/2} \sigma R]^{-1} \exp[-\ln^2(R/R_0)/(2\sigma^2)]$$

The particle concentration c can be expressed by the amount of platinum in particles, denoted as m_{particle} per sample surface. Their concentration then writes $c = m_{\text{particle}} / (\rho_{Pt} \langle V \rangle D)$; ρ_{Pt} is the density of metallic Pt in the particles, $\langle V \rangle = \int V(R) P(R) dR$ is their mean volume and D the sample thickness.

From the fit one concludes, that platinum atoms nucleate into small particles with mean radii $\langle R \rangle = \int R P(R) dR = 5.8$ Å and a rather narrow monomodal lognormal particle size distribution (Fig. 3, insert). A summary of all time-resolved ASAXS results is given in

Fig. 4 for the mean particle radius $\langle R \rangle$ and the mass fraction $m_{\text{particle}}/m_{\text{total}}$ of Pt atoms transformed into particles.

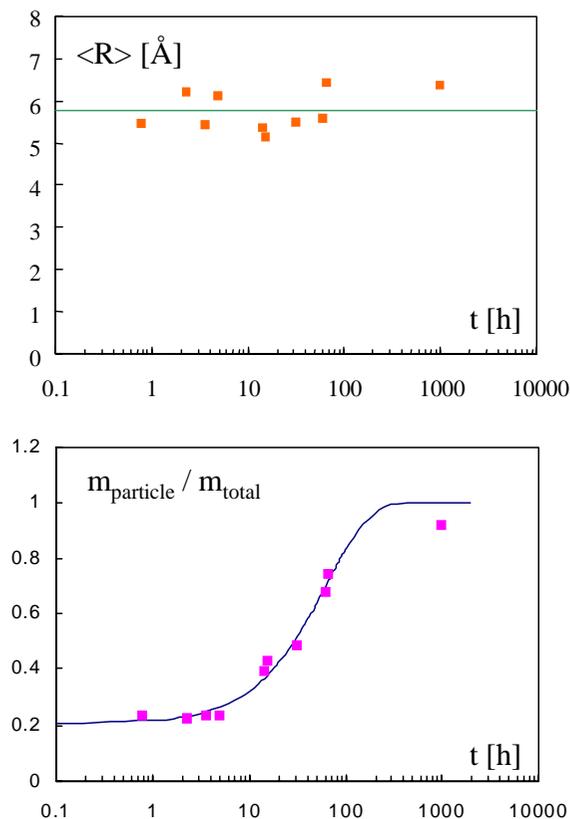


Figure 4
Time dependence of the mean particle radius $\langle R \rangle$ and mass fraction $m_{\text{particle}}/m_{\text{total}}$ of Pt atoms transformed into particles.

The amount of Pt in the particles m_{particle} was retrieved from the small-angle scattering data as measured quantitatively in absolute units. The total amount of Pt in the sample was determined by X-ray absorption from a comparison of the measured jump $\Delta(\mu D)_{\text{exp}}$ of the absorption at the Pt- L_3 X-ray absorption edge with the tabulated value $\Delta(\mu/\rho)_{Pt}$ of platinum atoms

$$m_{\text{total}} = \Delta(\mu D)_{\text{exp}} / \Delta(\mu/\rho)_{Pt}$$

Pt particles with a 1.2 nm size contain 53 atoms. This number is the second in the row of the “magic numbers” 13, 55, 147 ... of atoms, which build up energetically favorable icosahedra with closed complete outer shells of atoms (Echt *et al.*, 1981). This indicates that a complete outer shell of Pt atoms is required for the formation of a closed protective organic shell around the particle with about 53 Pt atoms. This shell is able to stop the nucleation process of platinum atoms into the particle, which is a basic requirement for the synthesis of mono-disperse particles with a narrow size distribution.

The mass fraction of platinum which nucleated into particles during the experiment is $x = (m_{\text{particle}}/m_{\text{total}} - 0.206) / (1 - 0.206)$; the initial amount $m_{\text{particle}}/m_{\text{total}} = 0.206$ had nucleated prior to the start of the measurement and is subtracted. With increasing reaction time, an exponential time dependence $x = 1 - \exp(-t/t_0)$ is found and given in Fig. 4 (solid line). Fig. 5 gives the fit for the fraction $(1-x) = \exp(-$

t/t_0) with a characteristic time $t_0 = 62.4$ h, i.e. the amount of Pt atoms in the precursor molecules which had not yet clustered into particles. After the half time of this reaction $t_{0.5} = t_0 \sqrt{\ln 2} = 52$ h, 50% of the bi-nuclear intermediates are decomposed.

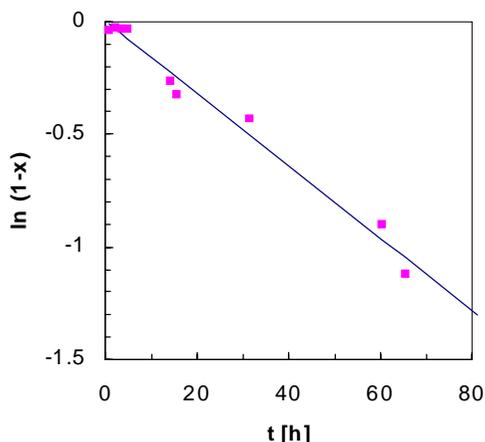


Figure 5
Fraction (1-x) of Pt atoms in precursor molecules. Fit of the exponential time decrease $(1-x) = \exp(-t/t_0)$, $t_0 = 62.4$ h.

The decomposition rate of the precursor molecules is $d(1-x)/dt = (-1/t_0)\exp(-t/t_0) = (-1/t_0) [1-x(t)]$ and decreases linearly proportional with the number $[1-x(t)]$ of not yet decomposed precursor molecules. The characteristic time of this thermally activated process can be expressed by its activation energy U : $d(1-x)/dt \sim [1-x(t)] \exp(-U/kT)$. The integration $\int [1-x]^{-1} dx \sim \int dt \exp(-U/kT)$ then yields the observed time dependence $\ln[1-x] \sim t \exp(-U/kT)$ or $[1-x] = \exp(-t/t_0)$, $1/t_0 \sim \exp(-U/kT)$ as given in Fig. 5 for the fraction (1-x) of Pt atoms in the precursor molecules.

The nucleation rate depends linearly on the amount $[1-x(t)]$ of intermediate precursor molecules in the solution. The rate controlling step for the nucleation is the thermally activated decomposition of the unstable bi-nuclear precursor molecules. The time for the subsequent diffusion of the decomposed single Pt atoms into the particles is on a much shorter time scale and has no significant influence on the nucleation rate. If this diffusion was the time determining process, the first order kinetics would not have been observed. This is in agreement with the results from three other samples (Waldöfner, 2002), from which the amount of methane was measured which accompanies the thermal decay of the intermediate precursor molecules and is a direct measure of the amount of decomposed molecules. A combination with the half times from these measurements at higher temperatures yields activation energy of about 1 eV for the decomposition of the bi-nuclear complex.

In another experiment, ASAXS was successfully applied to characterize metal-organic networks, which are formed by cross-linking the aluminum-organic-stabilized platinum nanoparticles with the bifunctional spacer molecule hydroquinone (Bönnemann *et al.*, 2002). The preparation pathway for this self-organizing arrangement is given in Fig. 6.

The reactive nature of the Al-CH₃ groups in the organic shell at the surface of the Pt particles allows protonolytic reactions with OH groups of substituents, such as the diol hydroquinone, to occur. If the substituent is bifunctional like hydroquinone, the shells of two particles can be interconnected. Hydroquinone acts then as a spacer

molecule between the particles. As the particles are covered with reactive Al-CH₃ groups, this leads to the formation of a 3-D cross-linked nanoparticle network. ASAXS was used here to separate the scattering of the Pt particles from background contributions, to analyze the inter-particle correlation, and to establish the build up of an inter-particle distance, which corresponds to both the thickness of the shells and the length of the connecting hydroquinone spacer molecules.

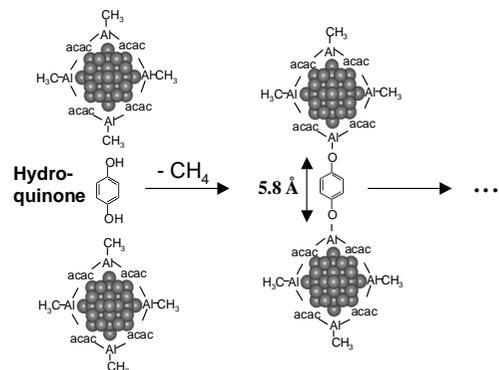


Figure 6
Principle of the synthesis of the protonolytic crosslinking mechanism for Pt particles with reactive aluminum-organic protecting shells.

The synthesis was performed with 0.5g aluminum-organic-stabilized Pt colloid, dissolved in 500 ml dry tetrahydrofuran (thf). 5 mmol spacer molecule, dissolved in 200 ml thf, was added dropwise to the colloidal solution at room temperature. For the measurement the precipitated particle network was filtered and washed out in thf.

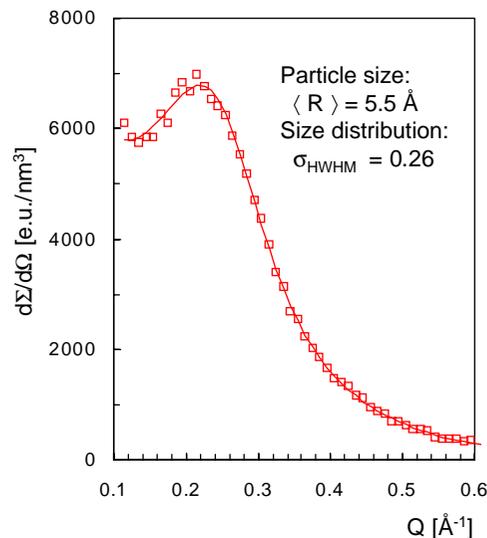


Figure 7
ASAXS scattering cross section of cross-linked Pt particles. Particle connection by organic hydroquinone spacer molecules (Vad *et al.*, 2002).

The ASAXS cross section, Fig. 7, from a contrast variation experiment at the Pt-L₃ X-ray absorption edge establishes a correlation peak at about $Q = 0.22 \text{ \AA}^{-1}$. Because of the Q -dependence of the particle form factor and their size distribution, its position at Q

$\approx 2\pi/d$ reflects the inter-particle distance d only approximately. The fitted curve with a log-normal particle size distribution gives an inter-particle distance $d = 21 \text{ \AA}$ and a mean particle radius 5.5 \AA . With the thickness 2 \AA of the surrounding shell from an ASAXS measurement of directly connected colloid particles without any spacer molecule in a dried colloid, one obtains a spacer length $21 - 11 - 4 = 6 \text{ \AA}$, consistent with the expected 5.8 \AA , which results from a molecular modeling calculation (SYBYL, 2000).

4. Conclusion

In-situ time-resolved and ex-situ ASAXS experiments allow very direct studies of the formation of metal colloids in molecular solutions. The use of anomalous scattering from the metal atoms allows a separation of the superimposed small angle scattering contributions from particles and the organic molecules in the solvent. Applied to the wet chemical synthesis of Pt colloids by reductive stabilization with aluminum-trialkyls, the nucleation of Pt nanoparticles with a rather narrow size distribution could be established from binuclear platinum complex molecules in a toluene solution.

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