Nanoparticles

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Stabilization of 200-Atom Platinum Nanoparticles by Organosilane Fragments

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Nanometer-sized materials have attracted remarkable academic and industrial research interest due to their specific properties (e.g. electronic, optical, and magnetic) and their potential applications ranging from microelectronics to catalysis.[1–5] In particular, the precise control of their size by means of the synthesis itself allows a precise direction of their physical and chemical properties. One of the ultimate goals is to bridge the gap between the molecular and metallic states by establishing a direct correlation between particle size and these properties in a range of particle size at the border between molecular "clusters" and "metallic particles".[6]

Nanoparticles can be defined as isolated particles whose size varies between 1 and 100 nm. These particles are usually stabilized by the addition of a support, a surfactant, a polymer, or an organic ligand to the reaction mixture in order to prevent undesired aggregation and metal precipitation. Nanoparticles of various metals (gold, palladium, platinum, ruthenium, etc.) with diameters in the nanometer range can be prepared using various organic compounds as stabilizers.[7–22] It has been shown that ionic liquids are also able to stabilize platinum nanoparticles of 2 or 4 nm size. These stabilized particles are synthesized by simple decomposition of $[Pt_2(dba)_3]$ (dba = dibenzylideneacetone) under molecular hydrogen in the presence of cyclohexene in imidazolium ionic liquids.[23] The synthesis and characterization by X-ray crystallography of the "molecular cluster" $[Pt_{38}(CO)_{44}]^{2-}$ showed that carbonyl ligands associated with negative charge are able to stabilize an ensemble of 38 platinum atoms.[24,25]

Recently, Pelzer et al.[6] showed that the treatment of a pentane solution of [Ru(cod)(cot)] (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) under 3 bar H_2 in the presence of octylsilane yields soluble 2 nm ruthenium nanoparticles stabilized by direct $Ru_3(\eta^3\text{-}{\equiv}Si\text{–alkyl})$ bonds. We report herein that the decomposition under mild conditions (3 bar hydrogen at 20 °C) of the organometallic platinum precursor $[Pt(dba)_2]$ in the presence of *n*-octylsilane ($n\text{-}C_8H_{17}SiH_3$) also leads to a stable colloidal solution from which small nanoparticles of about 200 atoms with a very narrow size distribution can be extracted.

The stabilizing ligands are attached to the particles as $\equiv Si(n\text{-}C_8H_{17})$ with formation, analogous to related ruthenium particles, of direct $Pt_3(\eta^3\text{-}{\equiv}Si)$ bonds. The presence of the octylsilyl moiety has been checked by elemental analysis, infrared spectroscopy (IR), and synchroton-radiation-based X-ray photoelectron spectroscopy (XPS). This example shows the importance of $\eta^3\text{-}{\equiv}Si$ silyl ligands to stabilize nanoparticles of noble metals during crystal growth.

For all performed analyses, ungrafted ligand was removed after reaction by precipitating the particles with cold pentane and washing them several times with pentane before drying them for 24 h. The purified powder was stored under inert atmosphere. The results of the elemental analysis are summarized in Table 1 and show the resulting ratios of Si and Pt depending on the initial values. For $H_3SiC_8H_{17}$/Pt ratios of 0.2 and 0.5 equivalents, all of the introduced silicon ligands remain grafted on the particles after washing, while in the case of 1.0 equivalent not all of the ligand could be grafted, which indicates a maximum coverage.

Table 1: Elemental analysis of the nanoparticles.

Product	Pt [%]	Si [%]	Si/Pt
$H_3SiC_8H_{17}/Pt = 0.2$	65.29	2.02	0.21
$H_3SiC_8H_{17}/Pt = 0.5$	61.43	3.39	0.48
$H_3SiC_8H_{17}/Pt = 1.0$	49.98	3.8	0.53

In the IR spectra (see the Experimental Section and Figure S1 in the Supporting Information) recorded for the platinum nanoparticles stabilized with 1.0, 0.5, and 0.2 equivalents $H_3SiC_8H_{17}$ in comparison to the free ligand, we observed characteristic bands of alkyl CH_2 and CH_3 groups at 2800–3000 cm^{-1}: ν_{as} CH_3 can be observed at (2960 ± 10) cm^{-1}, ν_{as} CH_2 at (2925 ± 10) cm^{-1}, and ν_{sym} CH_3 and CH_2 at (2870 ± 10) and (2855 ± 10) cm^{-1}, respectively. δ_{asym} CH_3 could be seen at 1463 cm^{-1}. The absence of a characteristic peak of the Si–H group at 2100 cm^{-1} indicates the loss of all the hydrides during the grafting of Si onto the Pt surface.[26]

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Consequently, these results suggest the existence of ≡Si(n-C_8H_{17}) fragments grafted to the metal surface.

Transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX) analysis (see the Experimental Section) gave evidence of the presence of crystalline Pt particles and confirmed the elemental contents. The platinum nanoparticles stabilized by 0.2 equivalents of $H_3SiC_8H_{17}$ present an elongated shape, while particles stabilized with 0.5 and 1.0 equivalent of $H_3SiC_8H_{17}$ are spherical and about 2 nm in diameter (Figure 1). Presumably, the lowest ligand concentration cannot assure a good crystal growth process with stabilization of spherical shape. Agglomeration of smaller particles leads to elongated aggregates. Despite the significantly higher starting Si/Pt ratio, the particles obtained with Si/Pt = 1.0 result in Si/Pt = 0.53 and are slightly larger than those obtained with Si/Pt = 0.5; neither of these types of particles seems to change shape. Interestingly, the obtained nanoclusters are remarkably crystalline. On the TEM image, the lattice fringes are very well visible and the distances undoubtedly fit a face-centered cubic (fcc) platinum packing (Figure 2). Small variation at the outermost border may indicate the presence of covalent Pt–Si bonds.

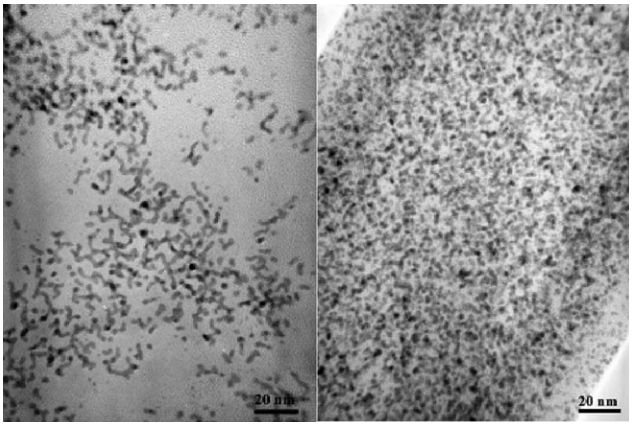


Figure 1. TEM picture of platinum nanoparticles prepared with 0.2 (left) and 1.0 equiv (right) octylsilane fragments.

Metallic particles were modeled assuming a cuboctahedral shape.[27] The number of surface platinum atoms (Pt_s) and total platinum atoms (Pt_t) for particles with $N_{edge} = 2$–4 are reported in Table 2. Knowing the density (ρ_{Pt}) and the molecular weight (M_{Pt}) of platinum, we can then determine the apparent diameters (d) of each platinum particle as a function of N_{edge} [Eq. (1), N_A is the Avogadro number]:

$$d = 2\,[(3\,M_{Pt}\,Pt_t)/(4\pi N_A\,\rho_{Pt})]^{1/3} \tag{1}$$

Table 2: Values of Pt_s, Pt_t, and the resulting diameter d for N_{edge} varying from 2 to 4.

N_{edge}	2	3	4
Pt_t	38	201	586
Pt_s	32	122	272
d [nm]	1.03	1.80	2.57

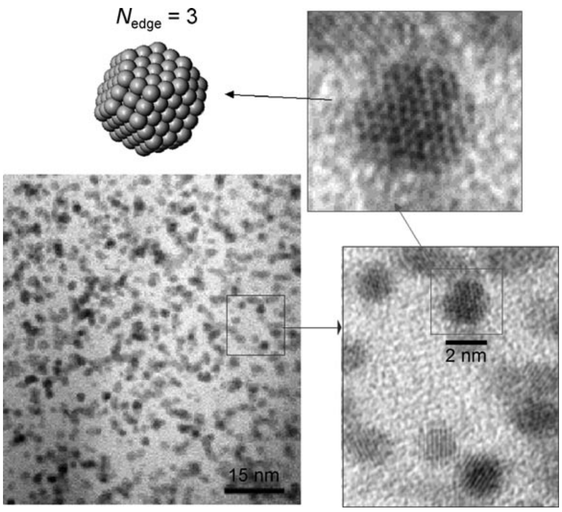


Figure 2. TEM pictures of platinum nanoparticles (Si/Pt = 0.5) with ≡Si(n-C_8H_{17}) fragments. The particles contain ca. 201 platinum atoms and fit well with a cuboctahedral particle shape with $N_{edge} = 3$.

Thus, a particle with a diameter of 1.8 nm is composed of 201 platinum atoms with $N_{edge} = 3$. For Si/Pt = 0.5 equiv, the particle's shape fits well with a cuboctahedral particle of 201 atoms (three edge atoms), as seen in Figure 2.

A size histogram of nanoparticles (Si/Pt = 0.5), established from three different images by counting more than 200 particles (Figure 3) has a narrow distribution of (1.8 ± 0.3) nm, which is quite remarkable for an unsupported Pt colloid. The so-called dispersion of these particles, defined as the number of surface platinum atoms divided by the number of total platinum atoms ($Pt_s/Pt_t = 122/201$; Table 2) is 0.61. Since the number of ≡Si(n-C_8H_{17}) fragments per platinum atom is 0.48 (Table 1), we can conclude that the coverage of the particles by the ≡Si(n-C_8H_{17}) fragments is close to 0.8 Si/Pt_s.

Furthermore, the presence of Pt–Si bonds has been substantiated by synchroton-radiation-based XPS (see the Experimental Section). The Pt 4f core levels of the platinum nanoparticles are shown in Figure 4.

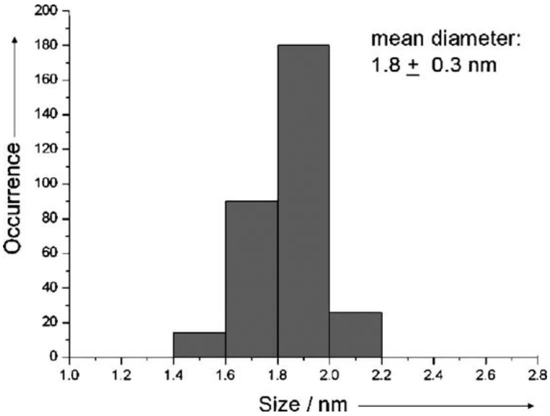


Figure 3. Size histogram of platinum nanoparticles prepared with 0.5 equiv octylsilane fragments.

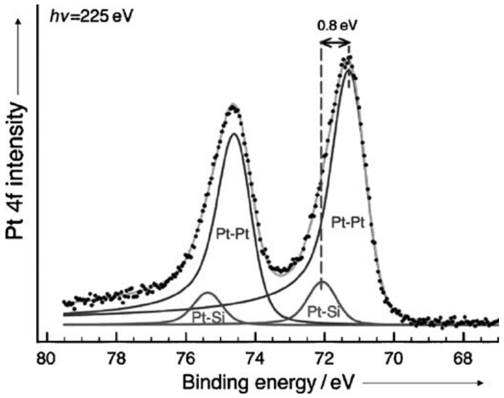
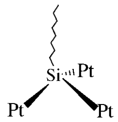


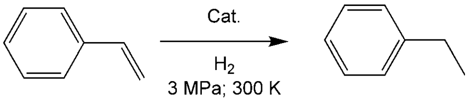
Figure 4. Platinum 4f core level XP spectra of platinum nanoparticles stabilized by octylsilane fragments. The photon energy was 225 eV, resulting in a surface sensitivity of less than 1 nm.

The platinum 4f doublet was fitted using two peaks with an energy separation of 3.3 eV and an intensity ratio of 0.75 after the subtraction of a linear background. The asymmetric peaks of pure platinum (Pt–Pt) were fitted using the convolution of Doniach–Sunjic (Lorentzian) and Gaussian functions with an asymmetry parameter $\alpha = 0.16$. The second phase convolution showed a binding-energy shift of 0.8 eV relative to Pt–Pt, which confirms the formation of covalent Pt–Si bonds.[28] A much smaller asymmetry of the core levels ($\alpha = 0.05$ instead of $\alpha = 0.16$) has been assumed for the Pt–Si phase to account for the well-known decrease in asymmetry for alloys or diluted metals.[29] The intensity ratio of signals from atoms with Pt–Pt bonds to those with Pt–Si bonds is about 9–10, although the intensity of the signal from Pt–Pt species might be slightly underestimated owing to the strong asymmetry of the Pt–Pt peak. At room temperature, we can observe from the XPS measurements only one species, namely Pt–SiC_xH_y. The presence of a PtO_x phase can be excluded, as such compounds typically show a binding-energy shift of more than 1.5 eV.[30]

Interestingly, the presence of organosilane moieties at the platinum surface does not prevent platinum from exhibiting activity in catalytic hydrogenation. Catalytic activity (see the Experimental Section) of these platinum nanoparticles for the hydrogenation of styrene to ethylbenzene (Scheme 1) was studied at 300 K under 3 MPa hydrogen in a 100 mL reactor.

Complete conversion of styrene into ethylbenzene was achieved with greater than 99 % selectivity within 120 min and with an initial turnover frequency (TOF) of 36 s^{-1} (based on the total number of surface platinum atoms). This activity is much greater than that that observed with platinum particles stabilized by 4-hexadecylaniline (selectivity > 99 % to ethyl benzene and TOF of about 10 s^{-1} at 350 K under 1.4 MPa of hydrogen).[31] This increase in activity may be related to the physical affinity of these hydrophobic nanomaterials for hydrophobic reagents (styrene) or to the ligand effect of a triply bridging octylsilyl group in the vicinity of the exposed platinum atoms. The surface structure is likely to have the exposed surface platinum atoms ready to achieve a catalytic cycle of hydrogenation.





Scheme 1. Hydrogenation of styrene by octylsilane-stabilized platinum nanoparticles.

In conclusion, the presence of $H_3Si(n\text{-}C_8H_{17})$ during the formation of Pt nanoparticles leads to a very narrow distribution of particle size of 2 nm, with particles containing approximately 200 atoms and $N_{\text{edge}} = 3$ atoms. The presence of silicon alkyl species on the metal surface was confirmed by IR spectroscopy, elemental analysis, and TEM with EDX. Pt–Si bonds next to the Pt–Pt core could be revealed by X-ray photoelectron spectroscopy. Even if the silane ligand is present on their surface, the Pt nanoparticles are still highly active in the hydrogenation of styrene to ethylbenzene with 99 % selectivity.

Experimental Section

Elemental analyses were performed at the Laboratoire de Synthèse et Electrosynthèse Organométalliques, UMR 5188 CNRS, Dijon, France for carbon and hydrogen and at the Service Central d'Analyse, Département Analyse Elémentaire, CNRS, Vernaison, France for silicon and platinum. Samples were prepared under argon and the elemental analyses were carried out without contact with air.

Infrared spectra were collected on an FTIR Nicolet 550 apparatus. The dry solid was mixed with KBr and compressed into a disk before acquisition of spectra.

Transmission electron microscopy with EDX examination of the samples was performed using a Philips CM200 TEM (LaB6) electron microscope to establish the size distributions and the crystallinity of the particles. The microscope was operated at an accelerating voltage of 200 kV and gave a nominal structural resolution of 0.19 nm. Samples were dispersed in dried and degassed pentane in a glove box and deposited on a holey carbon copper grid. All samples were transferred to the microscope inside a special vacuum transfer holder under inert atmosphere before examination.

For XPS investigations three drops of the Pt/SiC_8H_{17} solution were deposited onto a stainless steel sample holder, and the solvent was removed from the sample under vacuum. The high-pressure XPS endstation designed and constructed at the FHI was used for these studies. Details of the setup are described elsewhere.[32,33] Monochromatic radiation of the U49/2-PGM2 beamline at the synchrotron radiation facility BESSY (Berliner Elektronenspeicherringgesellschaft für Synchrotronstrahlung m.b.H.) served as a tunable X-ray source.

The catalytic tests were performed using *n*-heptane as solvent in an autoclave (Parr Instrument Company, USA), and the reaction was monitored by GC (column: KCl on alumina).

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