



MAX-PLANCK-GESELLSCHAFT

Angew. Chem. Int. Ed. 50 (2011) 5170-5173



Stabilization of 200-Atom Platinum Nanoparticles by Organosilane Fragments

K. Pelzer^{a*}, M. Hävecker^a, M. Boualleg^b, J.-P. Candy^b, J.-M. Basset^{b,c}

^a Fritz-Haber-Institute of the Max Planck Society, Department for Inorganic Chemistry, Faradayweg 4-6, D-14195 Berlin, Germany.

Present address: Laboratoire Chimie Provence UMR 6264, Universités d'Aix-Marseille I, Bâtiment Madirel, Campus St. Jérôme, 13397 Marseille Cedex 20, France.

^b C2P2-LCOMS, UMR CNRS-CPE 5265, 43 bd du 11 Novembre 1918, 69100 Villeurbanne, France.

^c KAUST Catalytic Center, Thuwal, Saudi Arabia

* Corresponding author: e-mail pelzer@fhi-berlin.mpg.de,

Received 27 December 2010; Article first published online: 19 April 2011; Published 23 May 2011

Abstract

Three's a charm: Platinum nanoparticles of 2 nm diameter and containing approximately 200 atoms covered with *n*-octylsilyl groups (see picture, right; Pt blue, Si red, C gray, H turquoise) form when [Pt(dba)₂] (dba=dibenzylideneacetone) decomposes in the presence of *n*-octylsilane. The particles adopt a cuboctahedral structure with an edge length of three atoms.

Keywords: Heterogeneous catalysis; platinum

Nanometer size materials have attracted a remarkable academic and industrial research interest due to their specific properties (e.g. electronic, optical and magnetic) and their potential application 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 goal is to bridge the gap between molecular and metallic state via the access to direct correlation between particle size and these properties in a range of particle size which is just at the border between molecular “clusters” and “metallic particle”.^[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 are now currently 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 in size. This is achieved by a simple decomposition of [Pt₂(dba)₃] (dba = dibenzylideneacetone)

under molecular hydrogen in the presence of cyclohexene in imidazolium ionic liquids.^[23] The synthesis and characterization by X-ray of the “molecular cluster” [Pt₍₃₈₎(CO)₄₄]²⁻ showed that carbonyl ligands associated with anionic charge are able to stabilize an ensemble of 38 platinum atoms.^[24, 25]

Recently, Pelzer et al.^[6] have shown that the treatment of a pentane solution of [Ru(cod)(cot)] (cod=1,5-cyclooctadiene; cot=1,3,5-cyclooctatriene) under 3 bar of H₂ in presence of octylsilane yields soluble 2 nm ruthenium nanoparticles stabilized by direct Ru₃(η⁻³(≡Si) bonds. We report here, that the decomposition under mild conditions, (3 bar hydrogen at 20 °C), of the organometallic platinum precursor [Pt(dba)₂] in presence of *n*-octylsilane (n-C₈H₁₇-SiH₃) leads also to 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 ≡Si(n-C₈H₁₇) with formation, as in the case of ruthenium, of direct Pt₃(η⁻³(≡Si) bonds. The presence of the octylsilyl moiety has been checked by elemental analysis, infrared spectroscopy (IR) and by synchrotron-radiation based X-ray photoelectron spectroscopy (XPS). This example shows

Table 1 Elemental analysis of the nanoparticles

Product	Pt/%	Si/%	Si/Pt
H ₃ Si-C ₈ H ₁₇ /Pt = 0.2	65.29	2.02	0.21
H ₃ Si-C ₈ H ₁₇ /Pt = 0.5	61.43	3.39	0.48
H ₃ Si-C ₈ H ₁₇ /Pt = 1.0	49.98	3.8	0.53

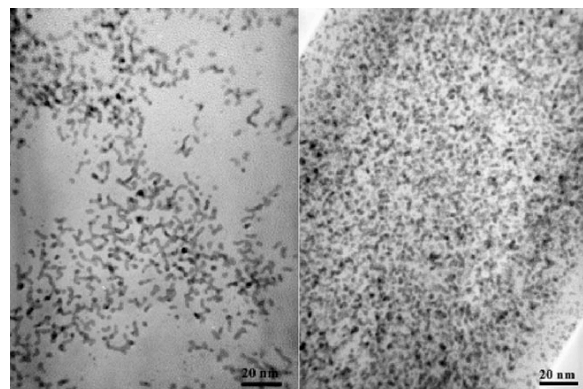


Figure 1. TEM picture of platinum nanoparticles prepared with 0.2 (left) and 1.0 equiv (right) octylsilane fragments.

the importance of $\eta^{-3}\equiv\text{Si}$ silyl ligands to stabilize nanoparticles of noble metals during the process of crystal growth.

For all performed analysis, ungrafted ligand has been removed after reaction by precipitating the particles with cold pentane and by several washing cycles before drying for 24 hours. The purified powder was constantly stored under inert atmosphere. The results of the performed elemental analysis are summarized in Table 1 and show the resulting ratios of Si and Pt depending from the initial values. For H₃Si-C₈H₁₇/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.

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 H₃Si-C₈H₁₇ in comparison to the free ligand, we observed the presence of characteristic bands of alkyl CH₂ and CH₃ groups between 2800-3000 cm⁻¹: $\nu_{\text{as}} \text{CH}_3$ can be observed at (2960 ± 10) cm⁻¹, $\nu_{\text{as}} \text{CH}_2$ at (2925 ± 10) cm⁻¹, $\nu_{\text{sym}} \text{CH}_3$ and CH₂ at (2870 ± 10) cm⁻¹ and respectively at (2855 ± 10) cm⁻¹. $\delta_{\text{asym}} \text{CH}_3$ 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 hydrogen during the grafting of Si on the Pt surface.^[26] Consequently, these results suggest the existence of $\equiv\text{Si}(\text{n-C}_8\text{H}_{17})$ fragments grafted on the metal surface.

Transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX) analysis evidenced the presence of very well crystalline Pt particles and confirmed the elemental contents. The platinum nanoparticles stabilized by 0.2 equivalents of H₃Si-C₈H₁₇ present an

elongated shape while particles stabilized with 0.5 and 1.0 equivalent of H₃Si-C₈H₁₇ are spherical and about 2 nm in diameter (Figure 1). Presumably, the lowest ligand concentration cannot assure a good crystal growth process with stabilisation of spherical shape. Agglomeration of smaller particles lead to elongated aggregates. Independently of the starting Si/Pt ratio, the particles with Si/Pt = 1.0 resulting in the Si/Pt = 0.53 are slightly larger than the ones obtained with Si/Pt = 0.5 and does not seem to change in shape. Interestingly, the nanoclusters obtained are remarkably crystalline. On the TEM image, the lattice fringes are very well visible and the distances are fitting 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.

Metallic particles were modelled assuming a cubo-octahedral shape.^[27] The number of surface platinum atoms (Pt_s) and total platinum atoms (Pt_t) for particles with N_{edge} varying from 2 to 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]:

$$d = 2 \cdot [(3 \cdot M_{\text{Pt}} \cdot \text{Pt}_t) / (4 \cdot \rho_{\text{Pt}} \cdot N_{\text{A}} \cdot \text{Pt}_s)]^{1/3} \quad (1)$$

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

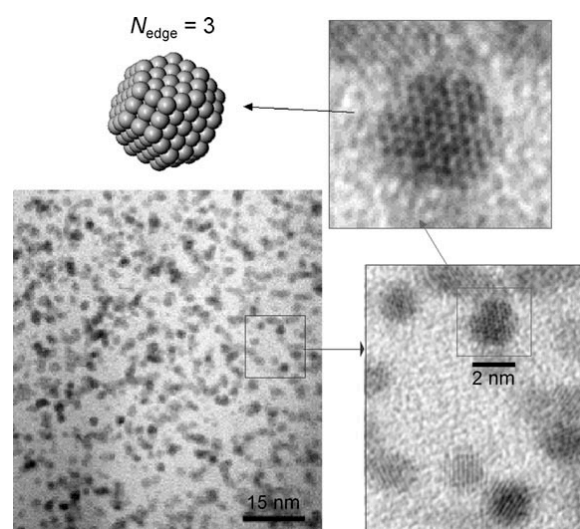


Figure 2. TEM pictures of platinum nanoparticles (Si/Pt=0.5) with $\equiv\text{Si}(\text{n-C}_8\text{H}_{17})$ fragments. The particles contain ca. 201 platinum atoms and fit well with a cubo-octahedral particle shape with $N_{\text{edge}}=3$.

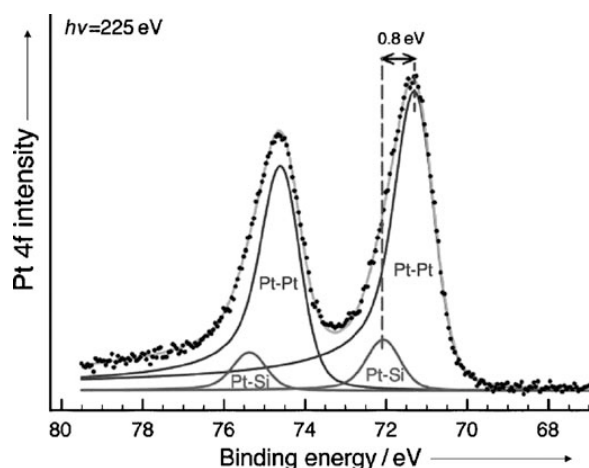


Figure 4. Platinum 4f core level XP spectra of platinum nanoparticles stabilized by octylsilane fragments. The photon energy was 225 eV, resulting in a surface sensitivity of less than 1 nm.

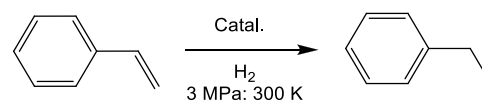
(1.8 ± 0.3) nm, which is quite remarkable for an unsupported Pt colloid. The so-called dispersion of these particles, defined as the number of surface platinum atoms per total platinum atoms ($Pt_s/Pt_t = 122/201$; Table 2) is 0.61. Since the number of $\equiv\text{Si}(\text{n-C}_8\text{H}_{17})$ fragments per total platinum atom is 0.48 (Table 1), we can conclude that the coverage of the particles by the $\equiv\text{Si}(\text{n-C}_8\text{H}_{17})$ fragments is close to 0.8 Si/ Pt_s .

Furthermore, the presence of Pt-Si bond has been substantiated by synchrotron radiation based XPS. The Pt 4f core levels of the platinum nanoparticles are shown as Figure 4.

The platinum 4f doublet was fitted using two peaks with energy separation of 3.3 eV and intensity ratio 0.75 after the subtraction of a linear background. The asymmetric peaks of pure platinum (Pt-Pt) were fitted using the convolution of Doniach-Sunjić (Lorentzian) and Gaussian functions with an asymmetry parameter $\alpha = 0.16$. The second phase convolution showed a BE 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 Pt-Pt / Pt-Si bonds is about 9-10, although the Pt-Pt intensity might be slightly underestimated due to the strong asymmetry of the Pt-Pt peak. At room temperature, we can only observe from the XPS measurements one species namely Pt/Si-C_xH_y. The presence of a PtO_x phase can be excluded since these compounds show typically a binding energy shift of more than 1.5 eV.^[30]

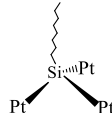
Interestingly the presence of surface organosilane moieties at the surface of platinum does not prevent platinum from exhibiting catalytic hydrogenation. Catalytic activity of these platinum nanoparticles for the hydrogenation of styrene to ethylbenzene (Scheme 1) was studied at 300 K under 3 MPa of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

Complete conversion of styrene into ethylbenzene was achieved with > 99 % selectivity within 120 min and with an initial TOF of 36 s^{-1} (based on the total number of surface platinum atoms). This activity is much greater than 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 with respect to hydrophobic reagents (styrene) or the ligand effect of a triply bridging octylsilyln group in the vicinity of the exposed platinum atoms. The surface structure is likely to have the surface exposed platinum atoms ready to achieve a catalytic cycle of hydrogenation.



Scheme 1 Hydrogenation of styrene by octylsilane stabilized Pt nanoparticles

In conclusion, the presence of $\text{H}_3\text{Si}(\text{n-C}_8\text{H}_{17})$ during the formation of Pt nanoparticles leads to a very narrow distribution of particle size of 2 nm containing approximately 200 atoms with $N_{\text{edge}} = 3$ atoms. The presence of silicon alkyl on the metal surface was evidenced by

 infrared 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, those 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 Élémentaire, 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/SiC₈H₁₇ 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 Elektronenspeicherungsgesellschaft 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).

References

- [1] J. H. Fendler, *Chem. Mat.* **1996**, *8*, 1616.
- [2] Z. L. Wang, *Adv. Mater.* **1998**, *10*, 13.
- [3] V. L. Colvin, M. C. Schlamp, A. P. Allvisatos, *Nature* **1994**, *370*, 354.
- [4] C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, P. P. Edwards, *Chem. Soc. Rev.* **2000**, *29*, 27.
- [5] G. Schmid, *Cluster and Colloids, From Theory to Application*, VCH Weinheim, **1994**.
- [6] K. Pelzer, J.P. Candy., G. Godard, J.M. Basset, *Nano particles and Catalysis, Vol. 18* (Eds.: D. Astruc), Wiley_VCH, **2007**, pp 553-620.
- [7] H. Boennemann, R. M. Richards, *Eur. J. Inorg. Chem.* **2001**, *10*, 2455.
- [8] H. Boennemann, G. Braun, G. B. Brijoux, R. Brinkman, A. S. Tilling, K. Seevogel, K. Siepen, *J. Organomet. Chem.* **1996**, *520*, 143.
- [9] A. C. Templeton, W. P. Wuelfing, R. W. Murray, *Acc. Chem. Research* **2000**, *33*, 27.
- [10] G. Schmid, B. Corain, *Eur. J. Inorg. Chem.* **2003**, *17*, 3081.
- [11] M.-C. Daniel, D. Astruc, *Chem. Rev* **2004**, *104*, 293.
- [12] G. Schmid, V. Mailhack, F. Lantermann, S. Peschel, *J. Chem. Soc., Dalton Trans.* **1996**, *5*, 589.
- [13] J. Fink, C. J. Kiely, D. Bethell, D. J. Schiffrin, *Chem. Mat.* **1998**, *10*, 922.
- [14] S. Chen, R. W. Murray, *Langmuir* **1999**, *15*, 682.
- [15] P. Ohara, J. R. Heath, W. M. Gelbart, *Angew. Chem., Int. Ed.* **1997**, *36*, 1078.
- [16] B. A. Korgel, D. Fitzmaurice, *Adv. Mat.* **1998**, *10*, 661.
- [17] C. Petit, A. Taleb, M. P. Pileni, *J. Phys. Chem. B* **1999**, *103*, 1805.
- [18] F. Dassenoy, K. Philippot, T. Ould Ely, C. Amiens, P. Lecante, E. Snoeck, A. Mosset, M.-J. Casanove, B. Chaudret, *New J. Chem.* **1998**, *22*, 703.
- [19] K. Naka, M. Yaguchi, Y. Chujo, *Chem. Mat.* **1999**, *11*, 849.
- [20] S. Gomez, K. Philippot, V. Colliere, B. Chaudret, F. Senocq, P. Lecante, *Chem. Commun.* **2000**, 1945.
- [21] A. Badia, L. Cuccia, L. Demers, F. Morin, R. B. Lennox, *J. Am. Chem. Soc.* **1997**, *119*, 2682.
- [22] R. H. Terrill, T. A. Postlethwaite, C.-h. Chen, C.-D. Poon, A. Terzis, A. Chen, J. E. Hutchison, M. R. Clark, G. Wignall, et al., *J. Am. Chem. Soc.* **1995**, *117*, 12537.
- [23] C. W. Scheeren, G. Machado, S. R. Teixeira, J. Morais, J. B. Domingos, J. Dupont, *J. Phys. Chem. B* **2006**, *110*, 13011.
- [24] A. Ceriotti, N. Masciocchi, P. Macchi, G. Longoni, *Angew. Chem., Int. Ed.* **1999**, *38*, 3724-3727.
- [25] P. Chini, G. Longoni, V. G. Albano, *Adv. Organomet. Chem.* **1977**, *14*, 285.
- [26] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Ed*, Wiley, **1997**.
- [27] R. Van Hardevelt, R. Hartog, *Surf. Sci.* **1969**, *15*, 189.
- [28] J. Cechal, T. Sikola, *Surf. Sci.* **2006**, *600*, 4717.
- [29] S. Hüfner, G.K. Wertheim, J.H. Wernick, *Solid State Comm.* **1975**, *17*, 417.
- [30] C.D. Wagner, J.F. Moulder, L.E. Davis, W.M. Riggs in *Handbook of X-ray photoelectron spectroscopy*. Perkin-Elmer Co., Eden Prairie, MN, **1993**. pp. 76–181.
- [31] S. Mandal, P.R. Selvakannan, D. Roy, R.V. Chaudary, M. Sastry, *Chem. Commun.* **2002**, 3002.
- [32] H. Bluhm, M. Hävecker, A. Knop-Gericke, M. Kiskinova, R. Schlögl, M. Salmeron, *MRS bulletin* **2007**, *7*, 602.
- [33] E.M.Vass, M.Hävecker, S. Zafeiratos, D. Teschner, A. Knop-Gericke, R. Schlögl, *J. Phys.: Condens. Matter*, **2008**, *20*, 184016.