



SiO₂-supported Pt particles studied by electron microscopy

D. Wang^{a,*}, S. Penner^b, D.S. Su^a, G. Rupprechter^c, K. Hayek^b, R. Schlögl^a

^aDepartment of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

^bInstitut für Physikalische Chemie, Leopold-Franzens-Universität, A-6020 Innsbruck, Austria

^cDepartment of Chemical Physics, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

* Corresponding author: e-mail wangdi@fhi-berlin.mpg.de, phone +49 30 8413 4482, fax +49 30 8413 3155

Abstract

Regularly grown Pt particles supported by amorphous SiO₂ were heated in hydrogen at 873 K after an oxidising treatment. The morphological and structural changes were studied by electron microscopy. Platinum silicides Pt₃Si with L1₂ (Cu₃Au) structure, monoclinic Pt₃Si and tetragonal Pt₁₂Si₅ were identified after the treatment. The mechanisms of coalescence of the particles and the formation of irregular large particles are suggested. A topotactic structural transformation accompanied with the migration of Si from the substrate to the particles are suggested to take place during Pt₃Si formation.

Keywords: Platinum silicide; Strong metal–support interaction; Electron diffraction; High–resolution electron microscopy

Introduction

Supported catalysts usually show activities and selectivities depending strongly on the treatment conditions. Due to the complexity of industrial catalysts consisting of randomly oriented and irregularly shaped metal particles on large–surface area porous supports, it is difficult to apply ultrahigh vacuum–compatible methods and electron microscopy to a “real” catalyst. Therefore, well–oriented and regularly shaped metal particles were grown on planar thin supports as initial state, and the structural changes in a chemical environment during activation or reaction were characterized by electron microscopy [1-6]. The changes in the particle structure after reductive treatments have been explained previously by the approach to a hydrogen–induced equilibrium shape [1].

In addition, a strong metal–support interaction has also been frequently observed in supported metal catalysts. Various mechanisms were proposed to explain this interaction, such as decoration of the metal surface by species derived from the support, electron transfer from the support, and intermetallic compound formation [7-10]. Apart from the interac-

tions of reducible metal oxides (*e.g.* TiO₂) with the supported metals, increasing evidence for similar phenomena, involving nonreducible oxides such as silica and alumina, was also reported. The formation of intermetallic compounds (Ni₃Si, Pd₂Si, Pd₃Si, Pd₄Si, Pt₂Si, Pt₃Si, etc.), has been observed after prolonged heating at high temperatures in H₂ [11-14]. Moreover, after heating Pt–SiO₂ at 840 K in H₂, a Pt₃Si phase with the cubic Cu₃Au structure was identified as intermediate to the monoclinic Pt₃Si, which appeared after additional heating at 1020 K in H₂ [15].

In the present work, the morphology of silica–supported Pt particles and their interaction with the support during the treatment in hydrogen at 873 K are investigated by transmission electron microscopy. A mechanism of the metal–support interaction is proposed upon the experimental observations.

Experimental

Pt particles were deposited at 623 K by electron beam evaporation at a pressure of 10⁻⁶ mbar on vacuum–cleaved

(001) NaCl single crystals. They were then covered with a thin supporting film of amorphous silica. Subsequently, the NaCl was dissolved in distilled water and the films were mounted on gold grids [2, 3]. After an oxidising treatment in O₂ at 673 K for 1 h, the reduction is performed with hydrogen gas at 873 K for 1 h. The morphology and structure of the samples were then examined using a Philips CM200 FEG microscope and were compared to the as-prepared state.

Results

The low-magnification electron microscope image in Fig. 1a shows the as-grown Pt particles and in b, that after treatment. The as-prepared Pt particles exhibit regular shapes,

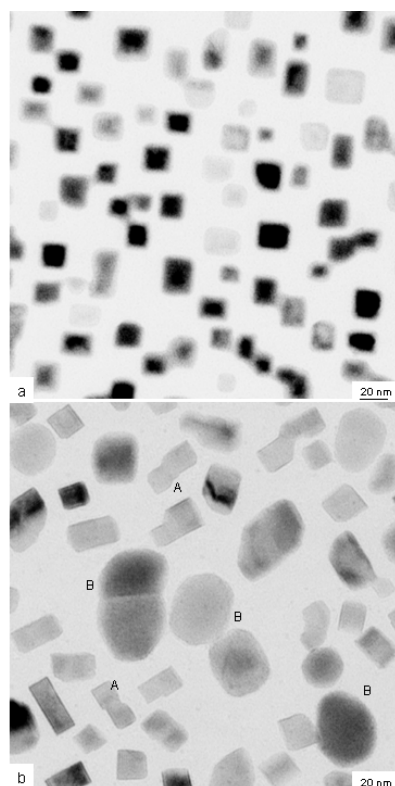


Fig. 1. Low-magnification image of Pt supported on SiO₂ (a) before and (b) after the treatment in H₂ at 873 K.

most of them being squares with edges parallel to each other. The size of the particles amounts to 8–15 nm. The electron micrograph of the particles after the treatment reveals a significant change in the morphology. A considerable amount of particles coalesce, leading to the formation of rectangular or irregular large particles (about 20 nm in size). These particles are randomly oriented.

The selected-area diffraction patterns of the sample before and after the treatment are shown in Figs. 2a and b, respectively, which give further information about the structure modification. The pattern in Fig. 2a is identical to the pattern of the [001]-oriented single crystal Pt, i.e., all the as-grown particles exhibit the same orientation. This is simply due to the epitaxial growth of the Pt particles on the (001) NaCl.

Comparatively, the diffraction pattern of the sample after the treatment shows a series of rings together with some diffuse, but distinct spots.

Calibrated by the electron diffraction pattern of Pt before the treatment, the interplanar distances d ($\pm 1\%$) are calculated from rings and diffuse spots in Fig. 2b and are listed in Table 1. The diffraction intensities corresponding to the posi-

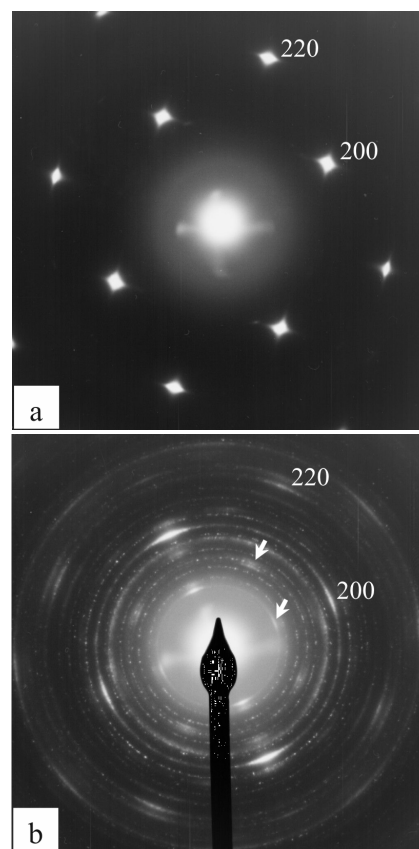


Fig. 2. Electron diffraction patterns of Pt supported on SiO₂ (a) before and (b) after the treatment in H₂ at 873 K.

tions of the Pt (200) and (220) reflections can still be distinguished upon a series of rings. This indicates that for some particles the original Pt [001] zone and azimuth orientation were preserved, while for some other particles changes in the crystal orientation also took place. Interestingly, additional spots are found corresponding to the positions of the (100) and (110) reflections (denoted in Fig. 2b by arrows), which are forbidden diffractions for the face-centered cubic structure. Comparing the d values of all the rings and diffuse spots with those of the reported Pt silicide, which are also shown in Table 1, we found that the structural changes can be attributed to the formation of Pt₃Si (cubic), Pt₃Si (monoclinic), and Pt₁₂Si₅ (tetragonal). Among them, cubic Pt₃Si was reported to have an L12 (Cu₃Au) structure with space group $Pm\bar{3}m$, and its lattice parameter $a=3.88$ Å, decreases by only 1 % with respect to that of Pt, $a_0=3.92$ Å. The structure of monoclinic Pt₃Si with space group $C2/m$ and lattice parameters $a=7.702$ Å and $b=c=7.765$ Å and $\beta=88^\circ 11'$ is also closely related to that of Pt. Therefore, the appearance of the forbidden diffractions (100) and (110)

Table 1 Measured interplanar distances *d* compared with those of Pt₃Si (cubic) Pt₃Si (monoclinic), Pt₁₂Si₅ and Pt

<i>d</i> (Å)	Pt ₃ Si (cubic)		Pt ₃ Si (monoclinic)		Pt ₁₂ Si ₅ (tetragonal)		Pt	
	<i>d</i> (Å)	(<i>hkl</i>)	<i>d</i> (Å)	(<i>hkl</i>)	<i>d</i> (Å)	(<i>hkl</i>)	<i>d</i> (Å)	(<i>hkl</i>)
3.91	3.88	(100)	3.88	(002)				
3.45					3.48	(301)		
3.00					3.01	(420)		
2.76	2.75	(110)	2.78	(202)	2.76	(331)		
2.69			2.69	($\bar{2}02$)				
2.46								
2.36			2.36	(113)	2.36	(222)		
2.20			2.21	($\bar{2}22$)				
2.13					2.13	(620)		
1.96	1.94	(200)					1.96	(200)
1.81			1.80	(313)	1.82	(003)		
1.50			1.50	(115)				
1.38	1.37	(220)	1.39	(404)			1.39	(220)
1.31								
1.18	1.17	(311)					1.18	(311)

correspond to these two structures. Most of the other rings correspond to either monoclinic Pt₃Si or Pt₁₂Si₅.

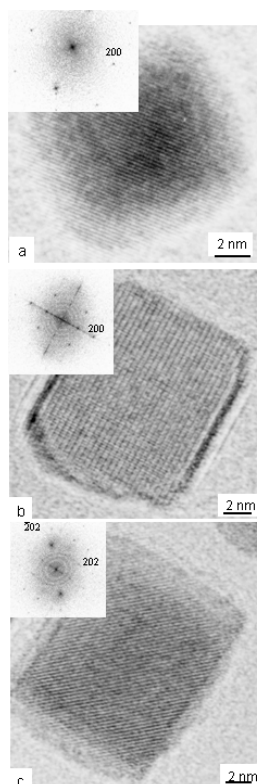


Fig. 3. The high-resolution images of particles (a) before the treatment, (b) showing Pt₃Si with L12 structure and (c) showing monoclinic Pt₃Si, after the treatment. The corresponding Fourier transforms are inserted, respectively.

The high-resolution images of one particle before the treatment and of two particles after the treatment are shown in Figs. 3a–c, with their Fourier transforms inserted. It is obvious that the lattice fringe in Fig. 3b, which corresponds to the L12 structure of cubic Pt₃Si, has a double periodicity compared to that in Fig. 3a. The lattice fringe in Fig. 3c is more likely to correspond to the ($\bar{2}02$) planes of monoclinic Pt₃Si, which can be deduced either from the period of the fringes or the symmetry in the Fourier transform of the image, since the primary vectors are not perpendicular to each other. The image is taken along the (010) projection of monoclinic Pt₃Si.

Discussion

The present study provides valuable information about the mechanism of the Pt/SiO₂ interaction in a reductive gas at high temperatures. The suggested mechanism involves the dissociative adsorption of hydrogen on Pt particles, reduction of SiO₂ through atomic hydrogen, and the migration of Si atoms into the Pt particles [14]. This leads to the formation of the intermetallic phase Pt₃Si with a Cu₃Au structure, which is also confirmed by the present work. However, other mechanisms may be involved in the Pt/SiO₂ reaction. A detailed observation of the electron micrograph in Fig. 1b reveals two different kinds of particles with a striking contrast: particles consisting of two coalesced parts (A) and large particles with irregular forms (B). For the first kind of particles, it is possible that the atomic hydrogen reduces the SiO₂ surface to a thin suboxide SiO_x phase, on which the Pt particles at the temperature of 873 K become highly mobile. This facilitates the coalescence of neighboring Pt particles

(10 – 15 nm in size), accompanied with the migration of Si atoms into the Pt particles.

The B kind particles in Fig. 1b are formed through melting and recrystallisation. Since the dissociative adsorption of H₂ on Pt particles is an exothermal reaction, a large amount of heat will be liberated and can result in a local increase of the temperature, causing the coalesced particles to melt and recrystallise, forming the large irregular particles. This local high temperature may also explain the appearance of the monoclinic Pt₃Si phase, which was reported earlier to occur only at 1020 K [15]. The observed tetragonal Pt₁₂Si₅ could also be the heating result of the exothermal reaction.

In addition, diffuse reflections in Fig. 2b corresponding to the (100), (110), (200) and (220) reflections of Pt indicate that the base plane and azimuth orientations of some particles are preserved during the reduction treatment. Inspection of the structure of Pt, cubic Pt₃Si and monoclinic Pt₃Si reveals that the [001] zone of the cubic Pt₃Si and the [010] zone of the monoclinic Pt₃Si correspond to the [001] zone of Pt. It suggests that a topotactic structural transformation from Pt to either cubic or monoclinic Pt₃Si took place on some particles and this process involves the migration of Si into the Pt particles. The Si atoms are available either due to the further reaction of the Si suboxide with hydrogen or due

to the decomposition of the suboxide at high temperature. All suggested processes (coalescence, melting and recrystallisation, and Si migration) lead to the flattening of the as-grown half octahedral Pt particles, which was confirmed in Ref. [16].

Conclusions

The Pt particles supported by silica show a strong metal–support interaction in H₂ at 873 K, following the oxidising treatment. This results in the formation of Pt₃Si with L12 (Cu₃Au) structure, monoclinic Pt₃Si and tetragonal Pt₁₂Si₅. The present observations confirm the mechanisms of metal–support interaction, involving the dissociative adsorption of H₂ on Pt particles, the reduction of silica to suboxides, the coalescence, melting and recrystallisation of particles, and the migration of Si into the particles.

Acknowledgement

This work was in part supported by the Austrian Science Foundation (Project S 8105).

References

- [1] T. Wang, C. Lee, L.D. Schmidt, *Surf. Sci.* 163 (1985) 181.
- [2] G. Rupprechter, K. Hayek, L. Rendón, M. Jose-Yacamán, *Thin Solid Films* 260 (1995) 148.
- [3] G. Rupprechter, K. Hayek, H. Hofmeister, *J. Catal.* 173 (1998) 409.
- [4] A.S. Eppler, G. Rupprechter, E.A. Anderson, G.A. Somorjai, *J. Phys. Chem. B* 104 (2000) 7286.
- [5] G. Rupprechter, H.J. Freund, *Top. Catal.* 14 (2001) 1.
- [6] P.J.F. Harris, *Surf. Sci.* 185 (1987) L459.
- [7] S.J. Tauster, S.C. Fung, R.L. Garten, *J. Am. Chem. Soc.* 100 (1978) 170.
- [8] G.C. Bond and R. Burch, in: *Catalysis*, Vol. 6, by G.C. Bond and G. Webb (Eds.), Royal Society of Chemistry, London, 1983.
- [9] G.L. Haller and D.E. Resasco, *Adv. in Catalysis* 36 (1989) 173.
- [10] R. Burch, in: *Hydrogen Effects in Catalysis*, Z. Paal, P.G. Menon (Eds.), Marcel Dekker, New York, 1988, Chapter 13.
- [11] R. Lamber, N. Jaeger, G. Schulz-Ekloff, *Surf. Sci.* 227 (1990) 268.
- [12] R. Lamber, N. Jaeger, G. Schulz-Ekloff, *J. Catalysis* 123 (1990) 285.
- [13] W. Juszczyk, D. Lomot, J. Pielaszek, Z. Karpinski, *Catal. Lett.* 78 (2002) 95.
- [14] R. Lamber, *Thin Solid Films* 128 (1985) L29.
- [15] R. Lamber, N. Jaeger, *J. Appl. Phys.* 70 (1991) 457.
- [16] S. Penner, D. Wang, D.S. Su, G. Rupprechter, R. Podlucky, R. Schlögl, K. Hayek, *Surf. Sci.*, accepted.