Interaction of platinum colloids with single crystalline oxide and graphite substrates: a combined AFM, STM and XPS study

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The interaction of platinum colloids encapsulated by an organic shell (Pt-col) with oxide (sapphire, quartz) and graphite single crystal substrates was investigated by AFM, STM and XPS. When dipped into aqueous colloid solutions at 20°C, Pt-col particles and excess shell molecules are adsorbed onto these substrates. After annealing in vacuum at 500°C the organic shell around the Pt colloids is decomposed for all supports used, and atomic force microscopy (AFM) images showed individual, sphere-shaped species on the alumina support, which are randomly distributed over the surface. They are attributed to Pt articles encapsulated by a carbonaceous shell. Oxidation in air at 650°C removes this coating and leads to sintering of platinum. For the graphite support, after annealing in vacuum at 500°C, large Pt particles are found that are stabilized by step edges on the graphite surface. This observation and the smaller amount of Pt adsorbed on carbon supports signal a stronger interaction of the Pt colloid with the oxide substrates.

Keywords: scanning tunnelling microscopy; atomic force microscopy; platinum colloids; model catalysts

1. Introduction

Usually noble metal catalysts are prepared by impregnation of the support material using metal salt solutions, followed by drying, calcination in air and reduction in hydrogen. Another prospective way for their preparation involves the immobilization of metal colloids. These colloids can be coated with an organic shell which prevents them from agglomeration [1,2]. In these particles the metal is already in the reduced state and heating at modest temperatures could lead to a highly dispersed metal phase on the surface with a narrow size distribution.

Recently, various types of transition metal colloids protected by tetraalkylammonium groups have been synthesized [2]. Transmission electron microscopy (TEM) images showed sphere-shaped, nanometer-sized particles with a sharp, uniform size distribution [3]. The interaction of these colloids with different supports, their evolution during thermal as well as red-ox treatments are of interest for the preparation of heterogeneous catalysts. In addition to conventional catalyst preparation using highly dispersive support materials, the study of single crystal surfaces with the new techniques of scanning probe microscopies (AFM, STM) can reveal information about the interaction of the active metal with support surfaces, e.g. adsorption in basal planes or surface defects like step edges, kinks, adatoms or holes, which otherwise hardly can be obtained. Furthermore, sintering and redispersion of the active metal, e.g. in dependence of the present gas phase, can be studied without being perturbed by sinter processes of the support material. Moreover, the mechanic force acting from the scanning tips in AFM opens the possibility to probe the binding forces between the metal surface species and the support.

In this letter, we present first results of a study on the interaction of platinum colloids with oxide (sapphire, quartz) and graphite single crystal surfaces, by atomic force and scanning tunneling microscopies (AFM, STM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The AFM images were obtained on a home-built microscope [4], operated in contact mode, with a laser beam deflection detection system and a maximum scan range of $1 \times 1\ \mu m^2$. The microscope is located in an ultra high vacuum (UHV) chamber equipped with standard facilities for surface preparation and characterization. A commercial Si-cantilever (Park Sci. Instrum.) with a spring constant of 0.03 N/m was used. The atomic resolution of the AFM was verified on graphite. STM images were obtained in air, with a tungsten tip and in constant current mode. The home-built microscope was described in detail elsewhere [5].

XPS spectra were recorded with a hemispherical analyser (Fisons Instrum.) using non-monochromized Mg K_α radiation and pass energies of 10 or 50 eV. The binding energy scale was calibrated with the Au $4f_{7/2}$ line (83.8 eV). For quantitative evaluations, atomic sensitivity factors (ASF) were used as given in the literature [6].

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The platinum colloid was prepared using the general method described elsewhere [2]. $N(C_{12}H_{25})(CH_3)_2$-$(CH_2)_3SO_3$ (here denoted as SB_{12}) molecules form the organic shell around the Pt particles [3]. An elemental analysis of the colloid powder by inductively coupled plasma optical emission spectroscopy (ICP-OES) revealed 15 wt% platinum content. The concentration of the colloid solution used for deposition was 0.7 g/ℓ for all supports under study.

The substrate materials were prepared as follows: A (11$\bar{2}$0)-oriented ("a-plane") polished sapphire single crystal (Kelpin) was cleaned with nitric acid, trichloroethane, acetone and water followed by annealing in air at 1400°C for 12 h. The (01$\bar{1}$0)-oriented single-crystalline quartz sample ("Y-cut") was cleaned in a similar manner, except for the final annealing step which was performed at 700°C. Highly oriented pyrolytic graphite samples (HOPG, Institute of Nuclear Physics, Novosibirsk) were cleaved by razor blades or adhesive tapes before deposition.

Prior to deposition, the sample surfaces were checked by XPS and, in the case of oxide substrates, by AFM. The supports used for these measurements contained only negligible amounts of contaminations such as carbon and oxygen and exhibited atomically flat terraces. The deposition of the Pt-col was performed at room temperature by dipping the samples into the Pt-col solution for 10 min. Subsequently, the samples were removed from the solution with their surface being vertically oriented in order to prevent the formation of drops on the surface.

3. Results and discussion

After depositing the Pt-col onto the HOPG surface the following elements were detected by XPS: Pt $(4f)_{7/2}$: 71.4 eV, S (2p): 168.2 eV, Cl (2p): 198.5 eV, N (1s): 403.0 eV, O (1s): 531.8 eV. Additionally, a clearly resolved shoulder on the C (1s) signal at 284.2 eV indicates another form of carbon (denoted as C^*). The binding energy of C^* was estimated to be 285.7 eV based on a deconvolution of the signal using Gaussian functions. For comparison, the XPS spectrum of graphite dipped in an aqueous solution of SB_{12} (ca. 1 g/ℓ) was also recorded. The binding energies of the S (2p), N (1s), O (1s) and C^* lines were found to be almost identical to those of the adsorbed Pt-col. However, in this case the Cl (2p) line was not detected. (Probably, the Cl^- ions are an impurity introduced from the synthesis of the colloid from $PtCl_2$ [2].) The ratios of the normalized areas of the S, O, N and C^* lines were calculated within an accuracy of 10% to be $S:O:N:C^* = 1:4:0.9:17$, and $1:3.3:1:18$ for samples treated with Pt-col and SB_{12}, respectively (see table 1). These values are close to the stoichiometric composition of SB_{12} molecules. Hence, the SB_{12} molecules are most likely adsorbed as intact entities. The Pt : S and hence the Pt : SB_{12} ratio was found to be about 0.07, which is only one third of the value of 0.2 determined in XPS measurements of the pure Pt-col powder. Therefrom, we conclude that during deposition excess SB_{12} molecules are also adsorbed on the graphite support, in addition to those connected with the platinum particles. Coadsorption of excess SB_{12} is supported also by annealing experiments (at 500°C under UHV conditions): A sample having only SB_{12} adsorbed on the surface shows only a very weak carbon signal in the XPS (5% of the original value after deposition) and exhibits an unchanged surface in AFM images. In contrast, on the sample with adsorbed Pt-col a significant amount of carbon, about 20% of the original value, remains present on the surface after annealing. AFM images of this sample exhibit dots on the surface which are interpreted as Pt particles encapsulated by the

Table 1
Pt-col on HOPG (dipped in 0.8 g/ℓ Pt-col in aqueous solution)

	Pt (4f)	S (2p)	N (1s)	O (1s)	Cl (2p)	C^* (1s)
HOPG						
binding energy (eV)	–	–	–	–	–	284.1
HOPG + SB12						
atomic ratio	0	1.0	1.1	3.8	–	17
binding energy (eV)	–	168.2	403.0	531.8	–	285.6
HOPG + SB12/500°C						
atomic ratio	–	–	–	–	–	–
HOPG + Pt-col						
atomic ratio	0.04	1.0	1.0	4.1	0.3	17
binding energy (eV)	71.4	168.2	403.0	531.8	198.5	285.7
HOPG + Pt-col/500°C						
Pt signal enhancement by	1.5					
binding energy (eV)	71.3	–	–	–	–	–

remaining carbon. The 20% of remaining carbon is close to what would be expected for the SB_{12} molecules in the shell around the Pt colloids.

The XPS investigations of the oxide samples were complicated by electrostatic charging of the nonconductive oxides. Therefore the binding energies were referred to the Si (2p) and Al (2p) lines of quartz and sapphire at 103.5 and 74.7 eV, respectively. The binding energy values of The S (2p), N (1s) and C (1s) lines differed slightly from those obtained on graphite by ±0.4 eV. The normalized XPS area ratios were determined to $S:N:C = 1.0:1.1:17$, and $1.1:1.0:17$, for quartz and sapphire, respectively, i.e., similar to the data for the graphite support. For the oxide samples the amount of surface oxygen arising from the deposition procedure cannot be determined precisely, nor is this possible for the Pt (4f) line for the alumina support. The position of the Pt $(4f)_{7/2}$ line on silica samples (71.3 eV), was found to be identical to that on the HOPG substrate. Comparing the data obtained on oxide and graphite supports, we find also for the other elements a close similarity in the XPS peak positions (vide supra). This suggests that on all supports the Pt-col particles adsorb without destruction of the organic shell. There is a significant difference, however, in the total Pt coverage: The absolute intensities show that on the oxide supports three times more Pt-col is adsorbed than on the graphite surface.

The AFM images of the 15 wt% Pt-col adsorbed on sapphire and quartz at room temperature, as well as STM images of Pt-col covered graphite samples, showed structureless "foggy" features. On the other hand, monolayer or higher steps of the graphite or oxide substrate were clearly resolved on these images. Furthermore, the working mode of the scanning probe microscopes was often unstable, presumably due to adsorbed species sticking to the tip and their subsequent moving with the tip. These observations can be explained by assuming that at room temperature the Pt colloids are loosely bound to the support surface and can be transferred to the scanning tip (and reverse). The same may hold true for the adsorbed excess SB_{12} molecules.

Individual Pt-colloid species on these samples were clearly resolved only after annealing the supported samples in vacuum. This treatment led to the decomposition of the organic shell as evidenced by XPS: only Pt and C lines were detected besides those originating from the supports. Fig. 1 shows an AFM image of a Pt-col coated sapphire sample, obtained after heating in UHV for 30 min at 400 and 800°C, respectively. The height of the sphere-shaped features is around 32 Å, which is very close to the average platinum particle size of 28 Å determined from TEM images [3]. Their average diameter in contrast is found to be 105 ± 20 Å, i.e., much larger than one would expect for individual spherical Pt colloid particles. Hence, the particles are rather flat, with an aspect ratio (height-to-diameter ratio) of about 0.3. The lateral dimensions (not heights) of surface features observed by AFM depend significantly on the radius of the tip curvature. Using a simple geometrical model of a hard spherical tip [8], one can calculate the factor of the apparent increase of the particle diameter. For an estimate, we applied this model to step edges on the same images, which gave a tip radius of about 50 Å. Using a similar

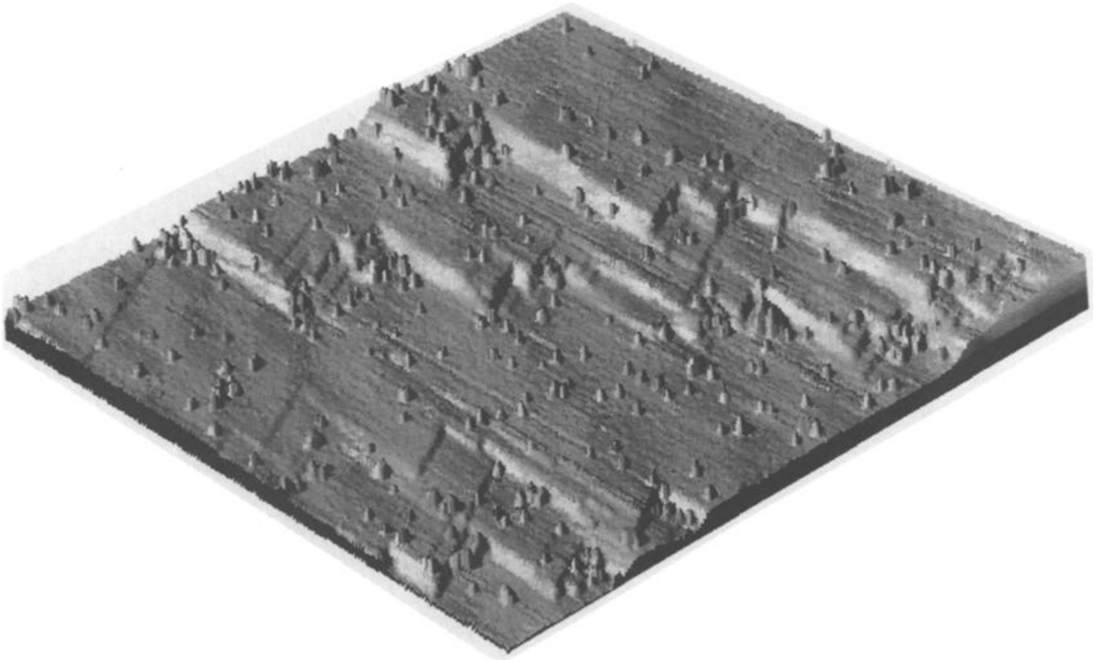

Fig. 1. AFM image (8.000 Å × 8.000 Å) of sapphire coated with Pt/SB_{12}-colloid particles (32 Å high), after annealing in UHV at 400 and 800°C for 30 min.

tip, a spherical particle of 32 Å in diameter and height would be imaged as a flat disk-like particle with a diameter of 112 Å. This value is in excellent agreement with our AFM observations (fig. 1). Therefore, the surface features observed by AFM are attributed to individual Pt colloid particles which are randomly distributed on the surface and exhibit a narrow size distribution. An agglomeration of Pt particles can be ruled out.

The situation is quite different for the graphite samples. STM images of vacuum annealed (500°C) 15 wt% Pt-col/HOPG samples (fig. 2) always showed irregularly shaped particles with average sizes of about 70 Å, located near the steps of the graphite surface. Therefore, on the graphite surface, diffusion and subsequent sintering of Pt colloid particles occurs during heating at 500°C. A comparable decoration of steps was also observed in STM studies of metal clusters evaporated on HOPG [9]. These observations indicate that the interaction of Pt colloids with oxide supports is stronger as compared to graphite. This is in accordance also with the higher Pt concentration observed for the oxide supports (vide supra). Based on XPS measurements of annealed samples, which showed that carbon was still present on the oxide surfaces, the Pt particles could still be encapsulated by a carbonaceous shell. In order to remove carbon contaminations, usually oxidative treatments are used. Indeed, subsequent heating of the annealed Pt–sapphire sample in air, at 650°C for 90 min, leads to a considerable loss of more than 90% of the carbon intensity. AFM images, recorded after this treatment step, showed sintering of the particles during this treatment (fig. 3). The smaller particles seen in fig. 3 have dimensions of 300 to 500 Å in diameter and 50 Å in height, the larger ones are 1000 to 1200 Å in diameter and 160 Å high. Sintering is confirmed by XPS which shows a reduction in the Pt intensity by a factor of 4 due to the metal sintering. Thus, under these conditions the highly dispersed state of the platinum could not be stabilized.

4. Conclusions

The interaction between Pt colloids with an organic shell and single-crystalline graphite and oxide substrates has been investigated by scanning probe microscopies and XPS. After deposition at room temperature, by dipping the support into Pt-col solutions, the surfaces are covered by Pt colloid particles and excess molecules of the organic shell. Annealing in vacuum at 500°C leads to the decomposition of the organic material. AFM images of annealed samples show individual spherical particles on the sapphire surface that were attributed to Pt particles encapsulated by a carbonaceous shell. The platinum particles are randomly distributed over the sapphire surface. Oxidation in air at 650°C removes this shell and leads to agglomeration of the particles. Contrary to this, on graphite supports sintering already occurs after annealing in UHV at 500°C and the Pt particles are stabilized by step edges. In conjunction with the higher Pt concentration on oxide surfaces, these observations indicate a stronger interaction of the Pt-col with the oxide as compared to the graphite surface.

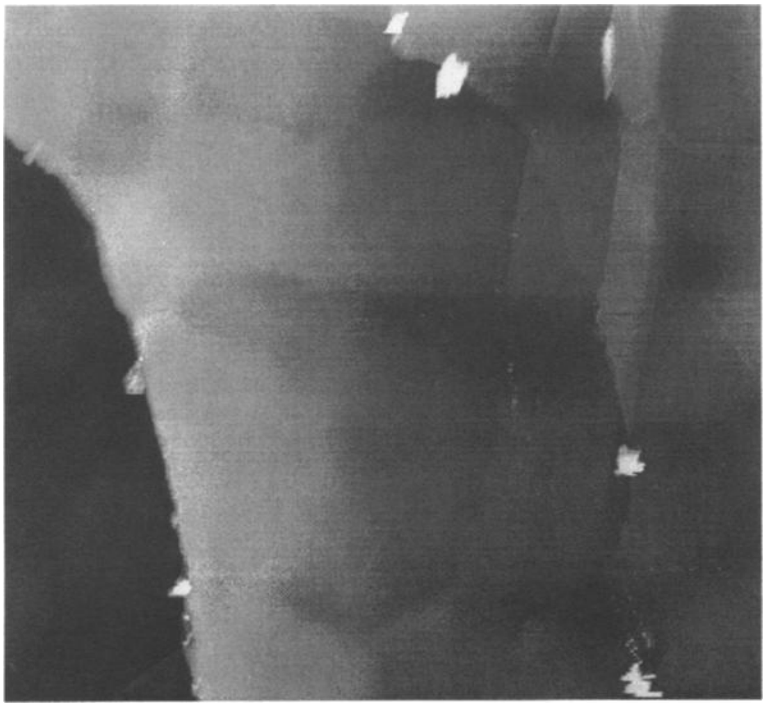

Fig. 2. STM image (10.000 Å × 10.000 Å) of HOPG coated with Pt/SB_{12}-colloid particles (70 Å high), after annealing in UHV at 500° C for 30 min.

Fig. 3. AFM image (8.000 Å × 8.000 Å) of sapphire coated with Pt/SB_{12}-colloid particles (50 to 60 Å high), after annealing in UHV and subsequent calcination in air at 650°C for 90 min.

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