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The structure of Pt-aggregates on a supported thin aluminum oxide film in comparison with unsupported alumina: a transmission electron microscopy study

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Abstract

Platinum has been deposited from the vapor onto a sample consisting of a thin aluminum oxide film grown on a NiAI(110) substrate wedge. At the tip of the wedge small γ -alumina crystallites are formed which have also been platinum decorated. The size distribution of the Pt aggregates on the thin aluminum oxide film is almost identical to the one found for the support-free alumina crystallites. It is also identical to the size distribution observed with STM under UHV conditions in earlier experiments [Th. Bertrams et al., Surf. Sci. 331–333 (1995) 1515]. The present structural analysis reveals that after Pt decoration the structure of the substrate remains unchanged. The Pt forms flat, epitaxial islands on both substrates. The nearest neighbor distances within the platinum aggregates have been determined for the supported oxide as a function of particle size. For large particles with radii greater than 20 Å the nearest neighbor distance of bulk Pt is observed. In the case of the smallest particles with radii close to 10 Å a contraction of up to 10% is detected. The contraction of the interatomic distance appears not to be isotropic. The observed Moiré patterns comply with the assumption that the substrate lattice underneath the Pt aggregates does not change. © 1997 Elsevier Science B.V.

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1. Introduction

Transmission electron microscopy (TEM) has in the past played, and still plays, a major role in the characterization of dispersed metal catalysts with respect to morphology and atomic structure. Several reviews on this subject have been published, and it is obvious that the impact of the method on heterogeneous catalysis is enormous

* Corresponding author. Fax: (+49) 30 8413 4101; e-mail: freund@fhi-berlin.mpg.de [1–4]. The numerous TEM studies of Pt/Al_2O_3 aimed at catalytic applications [1,2,5,6] have revealed a substantial effect of both the nature of the substrate and the preparation conditions on micro-morphology and stability of the Pt. No information on the precise lattice spacings was obtained in these studies. A recent nano-diffraction study of the system [7] revealed strong epitactic effects leading to a perfectly parallel alignment of Pt[110] with Al_2O_3 [110]. Again, no lattice parameter was stated. Owing to the ratio of the lattice parameters of Pt and alumina in the (110) direction only minor distortions are expected (the length of

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the [220] lattice vector of Pt (11.04 Å) is similar to that of the [110] lattice vector of γ -Al₂O₃ (11.18 Å)). All these experiments were, however, carried out with fully hydroxylated substrate surfaces of ill-defined structure.

In recent years, efforts have been undertaken to approach modeling of heterogeneous catalysts from a somewhat different angle: well-structured oxide surfaces have been prepared and metal aggregates have been deposited by various methods, including metal vapor deposition and pyrolysis of compounds deposited using the CVD method [8-11]. The oxide supports have been prepared as oxide single crystals or as epitaxially grown oxide films [12]. The latter have the advantage of allowing electron spectroscopic methods and scanning tunnelling microscopy (STM) to be applied without charging of the surface. Also, cooling to low temperature represents no obstacle in those studies [13]. In fact, structural studies via electron scattering (LEED, low energy electron diffraction) and STM have been performed on the clean [12,14] and adsorbate-covered surfaces, as well as on substrates onto which metal aggregates have been deposited [8-11]. The morphologies of Ag, Pd, Rh and Pt deposited upon a thin very well-ordered Al_2O_3 film prepared via oxidation of a NiAl(110) single crystal have been studied by reciprocal- and real-space structural methods [10]. In view of the wide knowledge on metal deposits derived via TEM on real catalysts on the other hand, it is rather appropriate to try to study a thin-film-based model system by TEM. To this end one has to make sure that the samples which have been prepared under ultrahigh vacuum (UHV) conditions "survive" transport into the typical non-UHV environment of TEM. We have shown in an earlier study [15] that the thin Al₂O₃ film remains unchanged after having undergone this treatment. In the present paper we also find this to be true for small Pt deposits on the thin alumina film. The TEM data presented here allow us to further deduce interatomic distances within the metal deposits. We have chosen Pt as the deposited metal in the present case because Pt is known to sustain transport through a gas atmosphere more easily than Ag, Pd and Rh, which we have mentioned above.

2. Experimental

The experiments were performed in a Hitachi 8100 200 keV transmission electron microscope. Sample preparation was similar to that reported in Refs. [16,17]. Briefly, a rather thin NiAl single crystal surface was used. A thin alumina film was prepared on top of the NiAl(110) single crystal according to a well-known recipe after the crystal had been ion-milled to form a small hole. Pt was evaporated onto the oxide surface from a filament using deposition parameters as tested before in LEED and STM studies [18,19], and the amount of Pt was controlled via a quartz microbalance. During evaporation the substrate temperature was held at 300 K and, if not otherwise stated, the sample was not annealed after Pt deposition. According to Refs. [20,21] the thickness of the deposited clusters is about one monolayer. Thick films (about 20 Å) exhibit the LEED pattern of Pt(111) [18], whereas for the orientation of thin films no data are available yet.

The form of the sample is shown schematically in Fig. 1. A wedge is formed near the hole which exposes the supported alumina film, as well as an unsupported oxide film where all the support material has been removed in the sputtering process [22]. This sample has also been heated to above room temperature to study the thermal behavior of the metal deposits. The particular shape of the present sample allows direct comparison of the thermal behavior of the metal deposits on the supported film with the respective behavior on the unsupported film.

3. Results and discussion

Fig. 2 shows a TEM picture of an area of the wedge near the hole taken at room temperature.



Fig. 1. Schematic drawing of the oxidized wedge.



Fig. 2. Transmission electron micrograph of the region near the edge of the wedge. $\theta_{\text{Pt}} = 0.7$ monolayers. $T_{\text{deposition}} = \text{room temperature}$.

It covers a region of several hundred angströms along the hole which shows up as the uniformly illuminated area. The wedge exhibits two types of area. The darker regions correspond to those parts where the NiAl(110) is present underneath the alumina film, the lighter regions represent areas where the support-free alumina is exposed to the electron beam. The dark spots which are images of the deposited Pt aggregates are more-or-less uniformly distributed over the wedge. On the NiAl(110) support the alumina film shows up in the TEM images via clearly resolved Moiré patterns. Their analysis and the procedures to recover the structural parameters have been discussed in detail in our previous paper dealing exclusively with the clean substrate [15]. In this former publication [15] we have also alluded to the orientation of the Moiré fringes and its correlation with domain and antiphase domain boundaries within the oxide film.

The length scales within the images have been calibrated using the well-resolved pattern of the NiAl (100) planes. This allows us to determine the sizes of the Pt deposits on the support-free and the supported alumina films. Fig. 3 shows histo-

grams based on the evaluation of several hundred clusters observed on many images equivalent to the one shown in Fig. 2. The size distributions peak near 20 Å diameter of the clusters, independent of whether the supported or the unsupported alumina is considered, thus ensuring that at room temperature the oxide-metal interface does not influence the aggregate formation at the oxidevacuum interface. As will be pointed out later, this situation changes upon heating of the system to above 400 K.

Fig. 4 shows a TEM micrograph where some of the deposited clusters clearly exhibit Moiré fringes. In the lower right part of the figure one cluster is shown on an expanded scale. The imaging conditions were chosen such that the NiAl lattice spacing in the [100] direction, i.e. 2.87 Å, shows up as marked in the figure and, in addition, the Moiré pattern of the Pt cluster is seen. Its periodicity a_M is indicated in Fig. 4. How from such a pattern, information about the cluster may be extracted is explained in Ref. [15]. One problem to solve was that we had to find an appropriate combination of Pt and NiAl(110) lattice vectors being responsible for the Moiré patterns. This was achieved by



Fig. 3. Histogram of aggregate sizes for Pt on support-free oxide (a) and on the supported oxide film (b) at room temperature. $\theta_{\rm Pt} = 0.7$ monolayers. $T_{\rm deposition} =$ room temperature.

considering a low index reflection of the NiAl lattice and calculating the corresponding Pt reciprocal lattice vector from the k-vector of the NiAl reflection and the Moiré periodicity and orientation. Assuming a basically undistorted Pt lattice, the combination of NiAl reflection and computed Pt reciprocal lattice vector was accepted as being

responsible for the Moiré pattern if the length of the Pt reciprocal lattice vector was similar to a vector expected for bulk platinum. If this was not the case then the calculation was repeated for another reflection of the NiAl substrate. This led to unambiguous results, since for only one combination we obtained physically acceptable values. Since the orientation of the Pt lattice with respect to the NiAl substrate varied somewhat for different clusters, we got different Moiré periodicities and orientations for different clusters; the smallest Moiré periodicity observed in our data was 7.3 Å. However, in all cases we found that the Moiré pattern should be due to scattering of the electron beam by a vector of NiAl(111)-type with subsequent scattering by a (220)-type reciprocal lattice vector of the platinum clusters. This situation is depicted schematically in Fig. 5. This figure also illustrates how, from the observed Moiré periodicities and their angle with respect to the substrate, the Pt lattice constant may be calculated. However, it must be clear at this point, that such a calculation only holds quantitatively under the above simplifying assumption that the Pt lattice is not distorted. We shall provide evidence in the following that this assumption may, as expected, not necessarily be fully appropriate. Nevertheless, we investigate the results of such a simple calculation in Fig. 6 applied to many aggregates, where the Pt lattice constant is plotted vs. particle diameter. Assuming a basically cubic lattice for the clusters the lattice constant may be converted into a Pt nearest neighbor distance. The vertical scales on the right of Fig. 6 refer to this parameter. Interestingly, at around 30 Å particle diameter the lattice constant is close to the bulk Pt value, whereas upon reduction of size close to 10 Å the lattice constant continuously decreases to a maximum decrease of about 10%. This is a large decrease, and it would certainly allow one to rationalize why, in some studies, small Pt aggregates have been found to exhibit remarkable chemical properties, such as the ability to dissociate CO [18]. While this strong reduction in interatomic distance needs further experimental corroboration, we state at this point that the habit of the Pt aggregates found in the TEM study is fully in agreement with the STM results reported by Bertrams et al. [19] for the



Fig. 4. Transmission electron micrograph of platinum clusters on supported oxide. $\theta_{Pt} = 0.7$ monolayers. $T_{deposition} = room$ temperature. In the lower right part of the figure the marked cluster is exhibited on an expanded scale.



Fig. 5. Reciprocal lattice of NiAl(110) (\bullet) and reciprocal (220)-type lattice points of γ -Al₂O₃ (\bigcirc). Also, the intersection of the (220) Ewald sphere of γ -Al₂O₃ with the NiAl(110) reciprocal lattice plane is shown.

same system. This provides further evidence that comparability between the STM results gained under UHV conditions and the TEM results after transport through air can be established. If this is true then we may use the TEM findings to state that the small Pt aggregates do exhibit strong structural modifications compared with bulk Pt. Indeed, the smaller interatomic distances may point towards a partly reduced electron density on the Pt aggregates which would also be consistent with the chemical shifts observed in photoelectron spectra [18,23]. While those are rather qualitative statements, it should be possible to substantiate both the reduction in the lattice constant and the interatomic distances by looking at electron diffraction diagrams.

Fig. 7 shows two electron diffraction diagrams taken with the electron microscope for two different preparations. We have chosen sample areas with rather uniform particle size distributions containing some hundred clusters in the regime hit by the electron beam. Three different types of reflection are visible: (i) intense spots due to the NiAl(110) substrate arranged in a rectangular manner; (ii) weak reflections of the aluminum



Fig. 6. Pt lattice constant and Pt–Pt interatomic distance as a function of the diameter of the Pt deposits (particle size) as determined from the TEM pictures. The ends of the horizontal bars give widths and lengths of the clusters, whereas the vertical bars are the errors of the calculated lattice constants assuming that the error in the determination of the Moiré period is 10% and that of the angle between Moiré and substrate *k*-vectors is 5%. $T_{deposition} =$ room temperature.

oxide $(\gamma$ -Al₂O₃ 440) which are arranged on the broken black line; (iii) reflections which are only visible when Pt clusters are on the surface. The latter reflections (Pt 220) are found on the two white semicircles in Fig. 7 which have different radii due to the reasons explained below. The amounts of platinum evaporated onto the surface correspond to uniform layer thicknesses of 0.2 Å and 0.7 A for the left- and the right-halves of the figure respectively. According to our evaluations, this gives rise to maxima in the particle size distributions at 12 Å and 22 Å. These values transform into lattice constants of about 3.55 Å and 3.85 Å (see Fig. 6). The two diagrams shown in Fig. 7 are joined in the middle to demonstrate that the NiAl reflexes reside in exactly the same positions, whereas the circles on which the Pt reflections are positioned (broken lines) exhibit large differences in radii. The radii in the present case correspond to lattice constants of 3.59 Å and 3.92 Å if the simple cubic lattice is used as reference. These values are near to the values obtained from the maxima of the particle size distributions.

At this point we note that the sixfold symmetry of the distribution of Pt-derived intensity in the diffraction patterns indicates that the [111] direction of the clusters is oriented along the surface normal, as has also been found for 20 Å thickness Pt films on $Al_2O_3/NiAl(110)$ [18,23].

Fig. 8A shows two electron diffraction diagrams of the region around the NiAl 200 reflection taken from different areas of the sample ($\theta_{Pt} = 0.2 \text{ mono-}$ layers). The broad, due to experimental misalignments, non-spherical NiAl substrate spots are accompanied by less intense Pt-220-derived features. The observed splitting of the Pt features in separate spots can be due to several reasons. Firstly, different clusters exhibit different lattice constants and thus lead to a variation of the distance between the Pt and the NiAl spot (see Fig. 7). This is the case for the two parts of Fig. 8A, as indicated by the broken lines. Secondly, varying angular alignments of the clusters with respect to the substrate may lead to spots at different positions on a circle centering at the position of the undiffracted beam. This is the case for the group of Pt reflections in the lower panel of Fig. 8A.

Fig. 8B represents a densitometer trace through the substrate and the Pt spots giving a more detailed impression of the relative widths of the spots. In particular, the profiles of the Pt spots indicate asymmetries. These asymmetries are indicative of the above-mentioned non-cubic symmetry of the Pt deposits. This becomes more evident when the background intensity of the substrate is subtracted, as shown in Fig. 8C. Although this discussion deals with very small effects, so that we cannot completely rule out that experimental misalignments are at least partly responsible for the observed effects, we consider it as a hint that the Pt aggregates are not completely isotropic in structure. This, in turn, is a hint towards a pronounced Pt-substrate interaction leading to an epitaxial growth of flat Pt islands, as was revealed and discussed in detail on the basis of the STM investigations performed in UHV [17]. Significant distortions of the Pt lattice upon interaction with a wellordered carbon support have been reported in earlier TEM studies [1]. These distortions led to a loss of the cubic symmetry of the Pt lattice. No



Fig. 7. Electron diffraction diagrams for two samples of Pt deposits with different average size. The diagrams are joined in the middle and the circles on which the Pt reflections are located are indicated. The larger circle on the left side corresponds to smaller clusters. Left: $\theta_{Pt} = 0.2$ monolayers. Right: $\theta_{Pt} = 0.7$ monolayers. $T_{deposition} = room$ temperature.

distortions were found in the earlier studies after supporting the Pt on a disordered hydroxylated carbon surface, indicating the pronounced influence of chemical substrate modification on the particle morphology and structure. Another hint towards a considerable cluster–substrate interaction is the form of the clusters. For Pt clusters weakly interacting with the substrate three-dimensional decahedral or icosahedral structures have been observed [24], whereas in the present case the clusters are two-dimensional with thicknesses of about one monolayer.

There is basically no difference in the appearance of the Pt aggregates on the supported and the unsupported alumina films, as far as size distribution and growth behavior at room temperature are concerned. However, as soon as the temperature increases to 700 K a phenomenon is observed which was also found under UHV conditions [19]: the Pt aggregates vanish from the surface via diffusion through the oxide layer into the substrate, where Pt can be detected after the oxide layer has been removed. On the support-free alumina film this process did not occur, as can be clearly seen in Fig. 9, where a sample was annealed at 700 K and most of the Pt has disappeared from the supported alumina film. On the unsupported film, however, the Pt deposits are clearly visible, although their distribution and size have also been changed.



Fig. 8. (A) Close-up of electron diffraction diagrams near the substrate diffraction spots. $\theta_{Pt}=0.2$ monolayers. $T_{deposition}=$ room temperature. (B) Densitometer trace through the substrate and Pt deposit spots. (C) Densitometer trace of the Pt deposits spots after subtraction of intensity of the substrate spot.

4. Summary and conclusion

The present study has revealed that Pt deposits on a thin alumina film exhibit a size distribution and habit after imaging with TEM under non-UHV conditions very similar or even identical to the same properties revealed in an earlier STM study under UHV conditions. We conclude from



Fig. 9. Transmission electron micrograph of a region near the edge of the wedge. Left: before annealing. Right: after annealing at 700 K. $\theta_{\rm Pt} = 0.7$ monolayers. $T_{\rm deposition} =$ room temperature.

this that the TEM results are also relevant for the STM studies. The TEM study allows us to determine the average Pt-Pt interatomic distances in the clusters if we assume that the Pt lattice is cubic. We find that there is a contraction of the Pt-Pt distance by about 10% from the bulk value when the size of the particles is reduced from about 30 Å to close to 10 Å. This contraction of the lattice parameter is evident from a Moiré analysis, as well as from electron scattering results. It would not be surprising if this strong decrease in the interatomic distances, which in its determined size does depend somewhat on the preassumption of dealing with cubic Pt, were correlated with a change in the chemical properties of the particles. In this respect the observation that smaller Pt particles deposited on an alumina film may dissociate CO could receive support.

It is relevant at this point to realize that the size distribution of Pt aggregates is identical on the supported film and on the unsupported alumina layer. It is also important to realize that upon increase of the substrate temperature Pt migrates into the NiAl substrate, whereas it stays on the surface in the case of the unsupported alumina film. The former observation had also been made under UHV conditions.

In conclusion, we report on a novel aspect of strong metal-support interaction which is made possible by the all-UHV preparation of the sample. Avoiding the complex alumina-water interface as supporting surface leads to an intimate contact between metal and oxide support with measurable structural consequences for small metal particles. With increasing particle size (Fig. 6) the lattice distortion at the metal-oxide interface gradually vanishes. The resulting internal strain/stress no longer gives rise to a fluctuation in position of the diffraction spots but affects their profiles (Fig. 8). The mediating influence of a hydroxyl-terminated substrate on the magnitude of metal-support interaction prevents the observation of this effect in conventionally prepared Pt/Al₂O₃ catalyst samples.

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