Interaction of oxygen with PtRh(100) studied with STM

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Abstract

The adsorption of oxygen at 500°C on a Pt$_{80}$Rh$_{20}$(100) single crystal surface was studied using UHV-STM and Auger electron spectroscopy. Images were taken of the p(3 x 1) phase; of a mixed phase with p(2 x 2), c(2 x 2) and (3 x 3) units; and of rhodium oxide patches. Possible models for these structures involving surface reconstruction are presented. Exposure of the p(3 x 1)O/PtRh(100) to H$_2$ at room temperature led to the conversion to the p(1 x 1) substrate structure. The ordering and composition of this substrate structure after reduction is discussed. © 1997 Elsevier Science B.V.

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1. Introduction

Fundamental knowledge of oxygen adsorption on the surfaces of transition metals is of great importance to the understanding of catalytic oxidation processes. Oxygen island formation and oxygen-induced reconstruction are examples of processes which may significantly influence the course of oxidation reactions [1]. Scanning tunneling microscopy (STM) is a highly suitable technique to image such phenomena [1–9]. The present paper treats the adsorption of oxygen on the (100) surface of the PtRh alloy. This alloy is the active component in the formulation of many automobile exhaust three-way catalysts (TWC) with various oxidic compounds like CeO$_2$ as promotor/co-catalyst. Under operating conditions, the TWC is exposed to changes in the gas phase composition varying from oxidizing to reducing at high temperatures. In this respect, it is important to know how easily the surface of the PtRh alloy itself is oxidized and reduced.

The oxidation and reduction of supported PtRh have been studied by various authors [10–12]. The general conclusion of these studies is that the presence of Pt facilitates the decomposition of Rh$_2$O$_3$, but it is not agreed on whether Pt has a positive or negative influence on the formation of rhodium oxide. Various studies of oxygen adsorption on PtRh single crystal surfaces [13–17] clearly point towards an oxygen-induced segregation of rhodium to the surface, whereas on clean PtRh, the surface is enriched in Pt [18–22] with the second layer being enriched in Rh [21]. The high Rh surface concentration under oxidizing conditions makes it probable that the PtRh(100) sur-
face, the subject of this paper, resembles the Rh(100) surface in certain aspects of its behavior towards oxygen. At low coverages on Rh(100), oxygen is reported to adsorb in a p(2×2) phase [23–27], which, at higher coverages, shifts into a phase that was originally [25] designated as (2×2)p2gg and which was later [27] shown to be (2×2)p4g using STM: the low-energy electron diffraction (LEED) pattern of the latter structure coincides with the LEED pattern of the two domains of the (2×2)p2gg. The c(2×2) phase that is observed by various authors [23,26,27] is believed to be a transition phase between the primitive (2×2) and the p4g phase [27]. Furthermore, a p(3×1) [24,28] and a (2×8) structure [29] have been found on Rh(100). Formation of Rh2O3 on the Rh(100) surface at elevated pressures was reported in Ref. [30] and on a Rh field emitter tip in [31,32]. The interaction of oxygen with a rhodium field emitter tip was extensively studied [33] and the oxide formation was reported to be surface structure dependent.

In a recent publication, the oxygen-induced p(3×1) reconstruction on Pt85Rh15(100) was studied in more detail [38]. This reconstruction was found after exposing the clean p(1×1) surface to 10⁻⁴ torr O₂ at about 600K and has been proposed to consist of Rh–O–Rh chains, flanked by rows of Pt atoms. In the present paper, a STM/AES study is presented of the various oxygen adsorption structures and surface oxidation on the PtRh(100) surface.

2. Experimental

In the work presented in this paper, the (100) surface of a Pt85Rh15 single crystal has been studied. The surface was extensively cleaned in vacuum by sputtering (1 keV Ar⁺) and annealing (cycles 600–850°C) until no contaminating species such as Si could be detected with Auger electron spectroscopy (AES). Oxygen was adsorbed at room temperature as well as at 500°C at pressures between 5×10⁻⁸ and 1×10⁻⁷ mbar. The vacuum system consisted of two chambers: (1) a preparation chamber with a base pressure of 1×10⁻¹⁰ mbar in which all annealing, sputtering and most of the adsorption procedures took place; and (2) a STM/AES/LEED chamber in which the pressure during measurements was 2×10⁻¹¹ mbar. The scanning tunneling microscope used in this study was a commercial Omicron micro-STM which has been provided with additional vibration damping: the STM head itself is supported by a viton stack and the entire vacuum system has been suspended in a combined spring–elastomer system as is described in Ref. [34]. A tungsten tip was used and the sample bias was always negative.

3. Results

In an earlier publication, the chemical resolution of the Pt85Rh15(100) surface with STM was reported [22] as is shown in Fig. 1(a). The clean surface after annealing between 600 and 850°C was found to be composed of 64% of platinum with formation of small rhodium and small platinum ensembles. The same surface was used in the study reported in this paper.

In Fig. 1(b and d), two stages of oxygen adsorption at elevated temperatures are shown. The phase in Fig. 1(b) was prepared by exposure to 23 Langmuir of O₂ (1 L = 1.3×10⁻⁶ mbar s) at 500°C and subsequent cooling in 5×10⁻⁸ mbar O₂ for 5 min. The repeating units here are (3×3) squares with a center that has an apparent height 0.25 Å lower than the rest of the cell. Furthermore, small areas of p(2×2) and c(2×2) can be seen in Fig. 1(b). A part of this figure is cut out and modeled in Fig. 1(c).

In Fig. 1(d), an image of a full p(3×1) phase is shown. The p(3×1) ordering was confirmed using LEED. This p(3×1) phase was prepared by admitting 23 L O₂ at 500°C and cooling to room temperature in 5×10⁻⁸ mbar O₂ (cooling time 20 min). Furthermore, two domains of this phase were imaged of which the domain boundary was nicely resolved, as can be seen in Fig. 2. It was determined that any bright spot in a certain row R in the image has an (n+½) lattice distance (n ∈ ℤ) to any perpendicular row crossing the produced row R, implying that these spots are located on
Fig. 1. STM images (100 x 100 Å) of a Pt$_{50}$Rh$_{50}$(100) surface. (a) Clean surface; Rh appears with the greatest apparent height and has a 36% surface concentration. A certain degree of demixing of Pt and Rh atoms can be observed. $V_{\text{sample}} = -0.5$ mV; $I = 0.47$ nA. (b) Oxygen adsorption: 23 L O$_2$ at 500°C + shortly cooling in O$_2$. $V_{\text{sample}} = -0.5$ mV; $I = 1.71$ nA. (c) The structural units of the image in Fig. 1(b). (3 x 3) Units with dark centers appeared, which are probably the elements of a reconstruction from which the p(3 x 1) develops. In the model, gray circles represent the O atoms and the grid indicates the substrate lattice with the four-fold hollow sites of the fcc(100) surface at the intersections. (d) Oxygen adsorption: 23 L O$_2$ at 500 C + cooling to RT in O$_2$ leads to a p(3 x 1) structure. Lines A and B refer to the corrugation profiles in Fig. 3. $V_{\text{sample}} = -4$ mV; $I = 0.46$ nA.
Fig. 2. The p(3 × 1) reconstruction of the Pt$_{50}$Rh$_{50}$(100) surface after exposure to oxygen at 500°C. Two domains appeared of which the boundary was nicely resolved. Using the lines in the image, it can be determined that the spots with greatest apparent height are located at bridge positions. Image size 100 × 97 Å. $V_{\text{sample}} = -2$ mV; $I = 1.03$ nA.

the two-fold sites of the fcc(100) surface. To illustrate this, three lines have been drawn in the image. The two parallel lines run over the rows in the left domain and through the positions between the bright spots of the rows in the right domain. The perpendicular line connecting the parallel lines has the length of nine substrate lattice distances: consequently, the shortest distance from a bright spot to one of the two parallel lines is for instance $9 + \frac{1}{2}$, $10 + \frac{1}{2}$, $11 + \frac{1}{2}$ etc. to go short: $n + \frac{1}{2}$. The distance between two neighbouring bright spots exactly matches the atom–atom distance in the (1 × 1) lattice. In Fig. 3(a and b), the respective corrugation profiles of lines a and b, indicated in Fig. 1(d), point out that there is a 25–30 pm corrugation in the rows themselves and a 30–40 pm apparent height difference perpendicular to the rows. The p(3 × 1) phase was also found after exposing the clean surface to 68 L O$_2$ at 300°C.

After exposing the clean surface to 68 L O$_2$ at 500°C, patches with a more- or less-hexagonal pattern were observed. An example of this is shown in Fig. 4. These patches had a greater apparent height than their surroundings and the correlation length inside the quasi-hexagonal pattern was 3.07 Å (± 0.08). These presumed islands of rhodium oxide were found in coexistence with the p(3 × 1) phase and seemed to be primarily located at its domain boundaries. They could not be imaged at low tunneling resistance and did not

Fig. 3. Corrugation profile of: (a) line A in Fig. 1(d); (b) line B in Fig. 1(d).

Fig. 4. Patch of rhodium oxide on the Pt$_{50}$Rh$_{50}$(100) surface after exposure to 68 L O$_2$ at 500°C. Image size 100 × 40 Å. $V_{\text{sample}} = -38$ mV; $I = 1.14$ nA.
disappear during the reduction procedures described in the next paragraph.

After exposing this surface with coexisting phases to 1.5 L H₂ at room temperature, the characteristic row structure of the p(3 x 1) phase had disappeared but the rhodium oxide patches were still present. In general, exposing the p(3 x 1) phase to H₂ at room temperature resulted in the restoration of the p(1 x 1) substrate lattice. Auger electron spectra, taken after this reduction procedure, indicated that Rh was present in excess in the top layers of the crystal as was expected.

In Fig. 5, an STM image of this reduced surface is shown. Small areas of low apparent height are present and there are clear apparent height differences between the substrate metal atoms. However, it is not possible to attribute chemical species to high or low apparent heights as was performed in Ref. [22]. In that paper, Pt was reported to have a lower apparent height in STM images than Rh on a clean PtRh(100) surface. The histogram of the image in Fig. 5 does not show two discrete levels of apparent height which is necessary to be able to speak of chemical resolution.

Images were found of a (√2 x √2)R45° structure. This phase was found after exposing the clean surface to 4.6 L of oxygen at room temperature. The same structure was reported in [27] and interpreted as either the c(2 x 2) or the (2 x 2)p4g phase of oxygen on Rh(100). It was not possible to decide whether the substrate lattice had reconstructed in this adsorption structure.

4. Discussion

The peculiar dark squares in the image in Fig. 1(b) have to our knowledge never been mentioned in literature before. For the interpretation, the fact that this structure coexisted with the p(2 x 2) and c(2 x 2) [Fig. 1(b)] phase is quite helpful.

The square units in Fig. 1(b) are (3 x 3) with respect to the substrate metal lattice. In Fig. 1(c), the framed area in Fig. 1(b) is presented schematically and the positions of the oxygen atoms are indicated. Oxygen is supposed to occupy four-fold hollow sites and appears as a black hole in the STM image because of a locally reduced density of states near the Fermi level. In the p(2 x 2) patches, the apparent height of the metal atoms is decreased less than in the c(2 x 2) patches, which is explained by the fact that in the c(2 x 2) every metal atom has two oxygen neighbours, whereas in the p(2 x 2) it only has one oxygen neighbour. Within the dark squares, four oxygen atoms surround one substrate metal atom [see model in Fig. 1(c)], creating, locally, a 0.25 Å lower apparent height. This structure with an oxygen coverage of 4/9 will undoubtedly involve some substrate lattice relaxation to stabilize the O–O repulsion, but it is not possible to deconvolute the topographic and electronic contributions to the corrugation in these STM images.

It is plausible to assume that the structure in Fig. 1(b) is a stage in the formation of the p(3 x 1). First, the preparation procedures for the two structures are very much alike, and secondly some images were recorded in which the p(3 x 1) coexisted with cells that strongly resembled the (3 x 3) units in Fig. 1(b). The exposures used to create
these patterns are within the range where in [35], the c(2 × 2)O/Pt_{25}Rh_{75}(100) is reported to change to a p(3 × 1) + p_{4g}(2 × 2) mixed phase at 780K. This transition may consequently very well involve a conversion of the c(2 × 2) unit cell into (3 × 3)-like units followed by a further conversion resulting in the shifted row reconstruction of the p(3 × 1). A structural model of the p(3 × 1) should be based on the following considerations.

From [35], it is known that the p(3 × 1)O/PtRh(100) is characterized by a much higher O:Rh ratio than the c(2 × 2) along with a lower Pt:Rh ratio. This means that there will be a very high rhodium concentration at the surface and that, whereas the c(2 × 2) corresponds to an oxygen coverage of 0.5, the p(3 × 1) should have a much higher oxygen coverage. Actually, the very high O:Rh ratio is an indication for the presence of subsurface oxygen formation. This consequently means that we cannot say anything about the oxygen surface coverage expected for the full p(3 × 1). Subsurface oxygen on rhodium has only been reported for the rougher surfaces like Rh(210) [36] and Rh(711) [44] and for polycrystalline rhodium wires [15] and a rhodium field emitter tip [33]. This indicates that the p(3 × 1) formation involves a significant reconstruction/roughening of the substrate lattice. The electronic influence of the oxygen and of the rearrangement of the metal atoms in the first layer along with the very low Pt concentration in the first layer is probably the reason that no chemical specificity, such as in Fig. 1(a), is observed.

A second point of importance in this matter is the stability of the image. The p(3 × 1) structure could be imaged at tunneling resistances of $1 \times 10^5 \Omega$ and higher without many tip changes, which is unlike the imaging of the c(2 × 2) phase. This makes it reasonable to assume that the oxygen atoms in the p(3 × 1) reconstructed phase are bound in a totally different way than in the c(2 × 2) adlayer. It is much more probable that the adsorption resembles the models presented in [8] for O/Rh(110).

The third point that leads us to a structural model are the values of the apparent height differences. As was already mentioned in Section 3, thecorrugation along the rows was about 25–30 pm, which is quite an ordinary value for metal lattices. The 30–40 pm corrugation in the perpendicular direction can be explained by a small surface relaxation or by added rows and a high electron density in the troughs. As all distances in the images of the p(3 × 1) are multiples of the substrate lattice nearest neighbour distance, an added or shifted row model indeed seems to be the most probable option. Here, it has to be noted again that it is common in scanning tunneling microscopy that oxygen atoms in certain adsorption modes cannot be imaged and appear as black holes.

Fourth, reducing the p(3 × 1) phase with H2 did not lead to step growth or island formation which excludes an added row reconstruction; lifting an added row structure necessarily involves a lot of mass transport. This observation is in accordance with observations by Matsumoto et al. [38]. The fifth point is the observation that the bright spots in the rows of the p(3 × 1) are located at the bridge sites of the substrate lattice.

The models evolving from these considerations are presented in Fig. 6. Every third row on the rhodium rich surface has shifted half a lattice distance. The row shifts are of course induced by the oxygen atoms and there are two models that are consistent with the observations. The first model is model A given in Fig. 6. The oxygen atoms support the shifted rows on either side and there is a very high oxygen coverage of 2/3. With this model it is reasonably easy to understand the growth of the p(3 × 1) from the (3 × 3) units.

The second model given in Fig. 6 implies an oxygen coverage of 1/3 and places the oxygen

![Fig. 6. Structural models of the p(3 × 1)O/PtRh(100) reconstruction. The surface has a high rhodium concentration and the models involve shifted rows of substrate metal atoms.](image-url)
atoms in the troughs between the shifted rows. Now, at close examination and comparison of the images in Figs. 1 and 2, it is observed that the apparent height maxima in the troughs do not have the same position in both images. In Fig. 1(d), one maximum in the troughs lies between two maxima in the bright rows whereas in Fig. 2, the trough maxima lie between two minima in the bright rows. It is very probable that in this case, a different tip conformation causes the imaging of different species, which is not unusual in STM (see, for instance, Ref. [39,40]). This again is a strong argument in favor of the model B presented in Fig. 6: one time the structure between the bright shifted rows could be the metal lattice (Fig. 2), the other time it could be the oxygen [Fig. 1(d)]. The fact that the p(3 x 1) shifted row reconstruction has never been found on the Rh(100) surface points at a possible relationship with the shifted row reconstruction on the clean (100) surfaces of PtNi [41] and PtCo [42]. For those systems, it was shown that the tendency to form shifted rows was clearly related to the Pt concentration.

Treating the p(3 x 1) phase with hydrogen at room temperature results in the restoration of the p(1 x 1) lattice. In the case of an added-row reconstruction, either the steps would have grown by one third of the terrace width or there would have been islands of metal atoms covering one third of the terraces. Neither of these observations were made during or after the reduction which also speaks in favor of the shifted row model.

Close examination of the image in Fig. 5 shows that the regenerated clean surface contains a certain amount of patches with somewhat lower apparent height. These are assumed to be caused by residual oxygen atoms. In addition, it appears that not all metal atoms have the same apparent height. However, the resolution is not good enough to discern two nicely separated levels of apparent height and to be able to decide that either there is some chemical resolution like in Fig. 1(a) or the Pt and Rh in the second layer influences the apparent height in the nearly 100% rhodium top layer.

Next to the p(3 x 1) phase, patches with roughly hexagonal patterns were observed, as shown in Fig. 4. These patches could not be imaged at low tunneling resistances pointing at an oxidic nature. The most commonly found oxide of rhodium below 750°C is Rh2O3, which has a corundum crystal structure [37,43]. The corundum lattice is built up of hexagonally close packed layers of oxygen anions. The rhodium cations are positioned in two third of the octahedral sites but are not exactly centered between the two triangles of oxygen atoms constituting the octahedron. There are two oxygen–oxygen distances within the hexagonal close packed layers, namely 2.62 and 3.14 Å, which are found in a ratio of 1:2.

The average distance of 3.07 Å (±0.08) that is found in the image in Fig. 4 is in reasonable accordance with expectation, but still slightly higher than the average literature value of 2.97 Å. This small deviation is attributed to the non-stoichiometry of top layers of oxides: a higher rhodium cation concentration in the first cation layer is necessary to compensate the excess of negative charge resulting from the unsaturation of the surface anions.

A final word is added referring to the c(2 x 2) patches: it should be noted that on PtRh(100), a much lower oxygen exposure is needed to form these islands than on Pt(100) as can be learned from [6]. Actually, it is close to the exposures used in [27] for c(2 x 2)O/Rh(100) pointing out that the (100) surface of Pt50Rh50 is rhodium-like in the sticking probability of oxygen.

5. Conclusions

The adsorption of oxygen on the (100) surface of PtRh at 300 and 500°C leads to a p(3 x 1) surface reconstruction along with a large rhodium surface segregation. This reconstruction is believed to involve shifted rows of rhodium atoms, stabilized by oxygen. The p(3 x 1) is easily removed with hydrogen at room temperature. A (3 x 3) phase with a probable coverage of 4/9 was found which is believed to be a stage in the formation of the p(3 x 1). Rhodium oxide can be formed on this surface at the relatively low exposures of 68 L.
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