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Interaction of rhodium with hydroxylated alumina model substrates

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Abstract

In order to investigate how metal growth and metal-oxide interaction depend on the chemical properties of oxide surfaces, we describe a modification procedure which allows the introduction of surface hydroxyl groups on a well-ordered Al_2O_3 film on NiAl(110). The modification – based on deposition of metallic Al and subsequent water exposure – is characterized using LEED spot-profile analysis (SPA-LEED) and high-resolution photoelectron spectroscopy (PES). Upon Al deposition, small aggregates are formed, which are oxidized completely in the final preparation step as verified via PES. The presence of OH-groups is supported by the appearance of additional Al 2p and O 1s surface features. The origin of oxide core and valence level binding energy shifts induced by the modification procedure is discussed.

Growth and metal-substrate interaction of Rh deposited onto the hydroxylated Al_2O_3 film is compared to Rh growth on the nonmodified oxide surface. It is shown that at 300 K nucleation preferentially occurs on modified oxide areas (SPA-LEED). Photoelectron spectroscopy of both oxide and rhodium core levels points to a direct chemical interaction between the metal and surface hydroxyl groups. © 1997 Elsevier Science B.V.

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1. Introduction

Employing suitable model catalysts based on ordered oxide films detailed information on the electronic structure and chemisorption behaviour of supported metal particles can be obtained (see e.g. [1-5]). As reported elsewhere, we have previously performed detailed studies on various noble metal deposits, e.g. Pt [6,7], Pd [8–10], Rh [4,11,12] and Ag [13], supported on an ordered Al_2O_3 film grown on NiAl(110). It was shown that the surface properties of this alumina model substrate are dominated by its termination by a layer of O^{2-} -ions [14,15], leaving the film rather inert towards various simple adsorbates.

Alumina supports used in technical catalysts, however, exhibit much more complex surface structures (see Fig. 1). Their surface properties are determined by coordinatively unsaturated O^{2-} -ions (Lewis basic sites) and Al^{3+} -ions (Lewis acidic sites) in various coordinations (see e.g. [16]). In particular, depending on the preparation procedure, their surface can to a large extent be

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Fig. 1. Schematic representation of various possible surface structures of an alumina support.

covered by OH-groups. For several reasons the presence of hydroxyl groups might be of fundamental importance for the chemical behaviour of these systems: Apart from catalytic reactions which directly involve adsorption on the support, OH-groups were shown to stabilize surfaces of ionic systems which are otherwise thermodynamically unfavourable [17,18]. Further, focussing on supported catalysts, OH-groups are known to mediate strong interactions between the support and the active metal deposited. One of the most prominent examples for such an effect is the CO induced redispersion of Rh particles on alumina [19-24]. IR-spectroscopy results demonstrate that surface hydroxyl groups are vital for this process [22,23].

Therefore, it appears most tempting to establish a preparation procedure introducing OH-groups on the Al₂O₃/NiAl(110) model support, as this would allow to compare growth and metal/ substrate interaction depending on the oxide surface properties. In the first part of this article we will describe such a modification procedure and characterize the geometric structure of the modified surface by SPA-LEED (spot-profile analysis low energy electron diffraction) and its electronic structure via high resolution PES (photoelectron spectroscopy). In the second part we will present first results on the growth and interaction of Rh on the modified surface. Detailed studies on the growth and adsorption behaviour of Rh deposits on the non-modified alumina film will be reported elsewhere [11,12].

2. Experimental

The experiments were performed in two different UHV (ultrahigh vacuum) systems. The LEED spotprofile measurements were carried out in a chamber equipped with a SPA-LEED system (Leybold, specified transfer width 900 Å, effective transfer width limited to 200-300 Å caused by the mosaic spread of the crystal). All intensity profiles shown have been recorded along the [001]-direction of NiAl or along one of the basis vectors of the oxide reciprocal unit cell (see Figs. 3 and 8). The scaling refers to the NiAl reciprocal lattice vector along [110] (1.54 Å^{-1}) , which has been used for k-space calibration of the instrument. Additionally, for thermal desorption measurements the UHV system is equipped with a differentially pumped quadrupole mass spectrometer.

All high resolution PES (photoelectron spectroscopy) experiments were carried out at beamline 22 at the Swedish synchrotron radiation facility MAX-Lab (Lund). Here, the setup contains a modified Zeiss SX-700 monochromator in conjunction with a large hemispherical electron energy analyser. The spectra were recorded at 150 eV photon energy for Al 2p (total resolution 0.1 eV), at 400 eV for Rh 3d (total resolution 0.2-0.5 eV), at 640 eV for O 1s (total resolution 0.4 eV) and at 180 eV for the valence region (total resolution 0.2 eV).

The ordered Al_2O_3 film was obtained as previously reported [14]. For the modification procedure Al was deposited from a home built evaporation source which is based on an alumina crucible resistively heated by a tungsten filament. A quartz microbalance was used for calibration purposes. Typical deposition rates were about 1.0 Å min⁻¹ (1 Å Al corresponds to 6.1×10^{14} atoms cm^{-2}). In order to minimize contamination of the vacuum chamber, a doser tube was used for H₂O exposure. The doser could be positioned directly in front of the sample. Condensation of an H₂O multilayer was checked via photoelectron spectroscopy or the disappearance of the oxide LEED pattern, respectively. Finally, Rh (Heraeus, >99.95%) was deposited using a commercial evaporator (Focus EFM 3) based on electron bombardment and allowing evaporation from a rod. During evaporation the sample was put on a retarding potential to avoid effects caused by ions produced in the evaporation source and accelerated towards the sample. Again, the evaporator was calibrated using a quartz microbalance. The deposition rate for Rh was 1.0 Å min⁻¹ (1 Å Rh corresponds to 7.3×10^{14} atoms cm⁻²).

3. Results and discussion

Aiming at a hydroxylation of oxide surfaces the most straightforward procedure certainly is direct exposure to water vapour. As such a procedure was proven to be successful for various alumina surfaces [25-31], a related experiment appears most natural. However, first experiments with water exposure both at 90 K and at 300 K reveal a rather inert behaviour of the Al₂O₃ film on NiAl(110). This inertness can be understood in terms of the film surface structure. An easy reaction path for dissociative adsorption of H₂O requires the presence of both Lewis acidic and basic sites, which - disregarding the unknown structure of defect sites - are not available for the purely O²⁻-terminated film. Therefore, in our case a hydroxylation requires a suitable chemical modification.

3.1. Preparation and characterization of the modified Al_2O_3 -film

Fig. 2 illustrates the preparation procedure we have applied to introduce OH-groups on the alu-

mina film in spite of its chemical inertness: After preparation of the $Al_2O_3/NiAl(110)$ film (in the following denoted as A), in a first modification step a submonolayer of aluminium metal is deposited at 300 K (situation denoted as B). Afterwards the sample is cooled to 90 K and exposed to H_2O until a multilayer of ice has been formed. On Al single crystal surfaces water is known to dissociate at temperatures between 90 and 160 K [32]. Therefore, upon subsequent annealing to 300 K (situation C), we expect dissociation followed by desorption of non-dissociatively adsorbed water at approximately 170 K.

However, expecting this modification procedure to yield a homogeneously hydroxylated surface, it has to be ensured (1) that Al exhibits a suitable growth mode on $Al_2O_3/NiAl(110)$, i.e. there is no formation of large three-dimensional islands but two-dimensional growth or at least formation of small aggregates and (2) that the deposited Al is entirely oxidized to Al^{3+} during the final preparation step. To check whether this is the case we have performed SPA-LEED and high resolution PES measurements.

3.1.1. SPA-LEED

LEED patterns for the situation A (clean $Al_2O_3/NiAl(110)$, 300 K), B (after deposition of 1 Å Al at 300 K), C (approx. 10 L H₂O at 90 K and subsequent heating to 300 K) and after annealing of C to 1000 K (D) are shown in Fig. 3(a).

The ordered alumina film on NiAl(110) exhibits a complex and characteristic LEED-pattern. As a detailed description can be found in the literature [14,33], no further discussion will be given here. Instead, we will focus on the changes induced by the modification procedure.

Upon Al deposition (B) three effects can be observed. (1) The most obvious change is the strong attenuation of the oxide superstructure spots which, in connection with the increased background, is a result of defect density induced by Al deposition. (2) However, a close inspection of the spot intensities reveals that the damping is not uniform; the relative intensities change significantly. This observation points to a certain degree of ordering within the Al deposits (i.e. it can be thought of as a weak indication of a (1×1)



Fig. 2. Schematic representation of the modification procedure (see text).

superstructure). (3) The diffuse background is not homogeneous, but the appearance of a diffuse shoulder surrounding the (00) spot indicates clustering, i.e. island formation.

After the hydroxylation step (C) the relative spot intensities remain different from A and comparable to B, but the spot to background intensity ratio decreases further. Upon annealing to 1000 K (D) the relative spot intensities of the clean film (A) are restored. However, the increased background level indicates that the defect density remains slightly higher than directly after the initial preparation (A).

More detailed information on the growth behaviour can be obtained via quantitative measurements of LEED spot profiles. In Fig. 3(b) onedimensional (00) reflex profiles in two different scanning directions are shown for situations A to C. Only profiles for one electron energy are displayed, as the shape of the diffuse part exhibits no significant energy dependence. Comparing the profiles before and after Al deposition and after H_2O exposure, a diffuse shoulder in the form of a ring can be identified (the additional structures in the LEED profiles of the non-modified film are caused by higher order oxide and multiple diffraction spots). As mentioned before, such diffuse profiles are characteristic for island formation (see e.g. [34,35]) and can be used to derive quantitative information on, e.g., island sizes and densities (Pt/Al₂O₃/NiAl [6], Pd/Al₂O₃/NiAl [8], Rh/ $Al_2O_3/NiAl$ [11]). The appearance of a rather isotropic shoulder in the form of a ring reveals that there is no strong decoration of oxide defects, but mainly nucleation on regular oxide terraces (in contrast to Rh growth on the non-modified film at 300 K, where defect decoration dominates; see discussion in Section 3.2.1 and [11]). With respect to the determination of island sizes, however, complications arise from the unknown scattering factors of clean and Al covered surface areas (unlike in the noble metal studies mentioned above, scattering from metal islands into oxide superstructure spots is not negligible). Nevertheless, we can still give an estimate of the island density: To a first approximation, this quantity is reflected by the radius of the diffuse diffraction ring. Following a procedure related to the one described in [8] we obtain island densities of 1.1×10^{13} cm⁻² for both situation A and B. Using the Al exposure of 1 Å $(6 \times 10^{14}$ cm⁻²) and assuming a unity sticking coefficient we can estimate an average number of approximately 50 Al atoms per island.

Summarizing the results on the growth behaviour, it is obvious from the SPA-LEED measurements that the Al deposited on the alumina substrate forms a high density of rather small aggregates, covering a large fraction of the oxide surface. Upon dissociative H_2O adsorption the island density and correlation remain nearly unchanged. For such small aggregates it appears reasonable that the Al deposits can be completely oxidized by H_2O exposure. Still, to check whether this is really the case, we have to employ high resolution photoelectron spectroscopy.

3.1.2. Photoelectron spectroscopy

Corresponding photoelectron spectra of the Al 2p and O 1s BE (binding energy) regions for the experimental situations A to C, i.e. for clean Al_2O_3 for Al deposition and after H_2O exposure, are displayed in Figs. 4 and 5, respectively.

The Al 2p spectrum of Al₂O₃/NiAl(110) can be reduced to three components at 72.53 ± 0.01 eV, 73.57 ± 0.03 eV and 74.80 ± 0.03 eV (Al 2p_{3/2}, BEs are average values over 10 preparations). Each component is additionally split because of the spin-orbit interaction (410 meV; for simplicity, only the sums of the spin-orbit split peaks are shown for components 1–3; for the modification-



Fig. 3. (a) SPA-LEED patterns (85 eV) for (A) clean $Al_2O_3/NiAl$, (B) after deposition of 1 Å Al at 300 K, (C) after exposure to H_2O at 90 K and subsequent annealing to 300 K and (D) after annealing to 1000 K. The scan range (dashed box) and the NiAl and oxide (domain a and b) unit cells are indicated in the LEED overview pattern. (b) LEED spot profiles of the (00) reflex for the modified and non-modified film (situations A-C). Scanning directions are indicated in the insets.



Fig. 4. Al 2p photoelectron spectra of the modified and non-modified film (situations A-C) in normal ($\theta = 0^{\circ}$) and grazing ($\theta = 70^{\circ}$) emission. Assignments for the components 1 to 5 are given in the text (for simplicity, only the sums of the spin-orbit split peaks are shown for components 1–3).

induced features 4 and 5 the spin-orbit components and the sums are displayed). The possible origin of these components was discussed in a previous paper [14]. From the angular dependence of relative intensities (in Fig. 4 spectra in normal and grazing emission are shown) and from comparisons with studies on oxygen chemisorption and oxide growth on Al surfaces [36,37] it appears most reasonable to assign component 1 to the NiAl substrate beneath the oxide film, component

2 to an interface layer between oxide and metallic substrate and component 3 to Al^{3+} emission from the oxide. In the corresponding O 1s spectrum the situation is less obvious (see Fig. 5). However, a high BE shoulder is observed, which might be related to a O^{2-} -surface species, as it increases in intensity if we change to grazing emission.

Upon Al deposition (1 Å Al, deposition temperature 300 K, situation B), drastic changes occur in both the Al 2p and the O 1s region: An additional



Fig. 5. O Is photoelectron spectra of the modified and non-modified film (situations A–C) in normal ($\theta = 0^{-1}$) and grazing ($\theta = 70^{\circ}$) emission.

asymmetric component (Fig. 4, component 4) appears at 73.1 eV BE (Al $2p_{3/2}$), which becomes strongly enhanced under grazing emission angles. This Al⁰ signal is found at higher BE with respect to the bulk value (for comparison see e.g. [37]). Such a behaviour is characteristic for metal clusters on poorly conducting supports and – apart from various initial state contributions – is in many cases dominated by the final state Coulomb energy [38,39]. Concerning the asymmetric shape of component 4, there might be contributions caused by the island size distribution determined by the growth process [40] and by the formation of chemically different species (e.g. a partially oxidized species, see the discussion below).

A second effect which can be observed after Al deposition is a large shift of the oxide component in the Al 2p spectrum (component 3) towards higher BE (+470 meV \pm 30 meV). Comparable shifts are observed in the O 1s signal (Fig. 5) as well as in the O 2p valence region (Fig. 6).

There are several possible effects which might cause such adsorbate induced BE shifts. Among

those, however, a shift caused by a direct chemical interaction between the adsorbate and the substrate can be immediately excluded as we are dealing with a rigid shift of both Al and O valence and core levels. Such rigid shifts might be caused by pure final state effects, i.e. changes in the screening of the core hole. However, upon metal deposition one would expect an increased screening caused by the increased polarizability, necessarily resulting in a negative BE shift. This is confirmed if we compare the BE shifts of the Al 2p oxide component after deposition of various noble metals (see Table 1), most of which exhibit a rather weak interaction with the oxide film. These shifts are small and negative and therefore most probably dominated by screening contributions.

One effect which might indeed lead to a large positive or negative BE shift is a change of the electrostatic potential within the oxide film caused by charge rearrangements. On alumina films such effects have been observed for various adsorbates [40-42]. The scenario is schematically illustrated in Fig. 7. Charge transfer from the Al deposit to



Fig. 6. Valence photoelectron spectra of the modified and non-modified film (situations A–C) in normal ($\theta = 0^{\circ}$) and grazing ($\theta = 70^{\circ}$) emission. Additionally, a spectrum before desorption of molecular H₂O is shown.

Table 1 Binding energy shift of the Al 2p oxide component (see Fig. 3, component 3) upon metal deposition on non-modified Al_2O_3 /NiAl(110)

Metal	Growth temperature [K]	Coverage [Å]	BE-shift: Al 2p, oxide component [meV]
Al	300	1.0	$+470 (\pm 30)$
Rh	300	2.0	-60
	90	0.6	-30
	90	2.0	-90
Pd	300	12.0	+20
	90	2.0	-160
Pt	300	1.2	-130

the NiAl substrate or the oxide/NiAl interface leads to a contribution to the electrostatic potential resulting in a positive BE shift. Considering the low work function of Al (in comparison with the noble metals in Table 1), such a charge transfer can be expected. Furthermore, the formation of a partially oxidized Al species cannot be excluded, as mentioned before in connection with the high BE tail of the additional Al 2p component (component 4).

We will now focus on the adsorption of H₂O in

the next preparation step. The formation of an ice multilayer upon H_2O exposure can be confirmed via the characteristic valence band emission of molecular water (1b₂, 3a₁, 1b₁, see e.g. [43]; Fig. 6). Al 2p, O 1s and valence photoelectron spectra after subsequent annealing to 300 K (situation C) and desorption of non-dissociatively adsorbed water are displayed in Figs. 4–6, respectively.

From the Al 2p spectra in grazing emission it is evident that the Al⁰ signal at 73.1 eV BE (component 4, Fig. 4(c)) vanishes completely and a new surface component appears at 76.0 eV BE (Al $2p_{3/2}$, component 5, Fig. 4(c)). Thus, it can be concluded that during this procedure the Al film is oxidized entirely. Moreover, an additional high BE surface component is observed in the O 1s region (533.5 eV BE), as indicated in Fig. 5. Comparable shoulders on the high BE side of the O 1s signal have previously been observed for various types of hydroxylated oxide surfaces (see e.g. [28,29,44,45]).

At this point it should be noted that water adsorption, in contrast to Al deposition, results in no further BE shifts of the Al 2p (component 3) and O 1s signals originating from the oxide film.



Fig. 7. Schematic representation of the influence of the environmental charge distribution on electronic levels for the different preparation steps.

Alluding to the discussion on the metal induced shifts given above, the natural conclusion would be that no further drastic charge redistribution occurs upon proceeding from the Al covered (B) to the hydroxylated surface (C). Again, this is schematically illustrated in Fig. 7. However, it should not be ignored that upon hydroxylation the structure of the alumina film might be subject to strong geometric relaxations which also change the electrostatics of the system.

In many cases, the presence of OH-groups can be verified via their characteristic valence features at about 11 eV (OH 3σ) and 7 eV BE (OH 1π) (see e.g. [43]). In Fig. 6(c) valence spectra for the corresponding situation are shown. Indeed, additional intensity is found in these regions. However, because of drastic changes within the O 2p bands the corresponding signals cannot be unambiguously identified.

Further evidence for the presence of OH-groups can be derived from preliminary thermal desorption measurements, which show a weak and rather broad desorption at m/e=18 in a temperature regime between 400 and 700 K. Desorption spectra of comparable width have been observed for other hydroxylated oxide surfaces [31,46].

Finally, summarizing the results derived from photoelectron spectroscopy, we can conclude that

the deposited Al is entirely oxidized upon H_2O treatment and that there are indications for the formation of OH-groups. Therefore, discussing the interaction of Rh deposits with the modified surface in the following sections, we will assume that there is a significant density of hydroxyl groups present. An unambiguous identification and characterization of these OH groups, however, clearly requires future vibrational spectroscopy studies.

3.2. Growth and interaction of Rh with the modified film

3.2.1. SPA-LEED

Before we will come to the discussion of possible chemical interactions between the Rh deposits and the oxide substrate, we will again use LEED spot profile analysis to acquire a basic understanding of the growth behaviour on the modified film. Fig. 8 shows (00) spot profiles for the hydroxylated film (C) before and after Rh deposition at 300 K (Rh coverages of 2 and 4 Å, respectively). Furthermore, corresponding profiles for Rh growth (4 Å Rh) on the non-modified surface are shown for comparison (growth temperature 300 K).

As a detailed discussion of Rh growth on the non-modified $Al_2O_3/NiAl(110)$ will be given else-



Fig. 8. LEED spot profiles of the (00) reflex before and after Rh deposition on the modified film. Corresponding profiles for Rh deposition on the non-modified film are shown for comparison.

where [11], we will mention only a few points here which are relevant to growth on the modified surface. As the interaction with the oxide is rather weak, nucleation on the non-modified film preferentially occurs at defects. The defect density of the oxide film is dominated by a network of anti-phase domain boundaries [33]. If we proceed to higher coverages, their decoration finally results in a strongly anisotropic correlation of the threedimensional Rh islands growing. This gives rise to an anisotropic diffuse spot profile, as can already be observed comparing the two scan directions in Fig. 8, but which becomes even more pronounced at higher metal coverages.

If we now compare the spot profiles for growth on the hydroxylated film, we find only weak changes upon metal deposition. However, the diffuse profile becomes slightly more intense and the shape of a ring more distinct.

Discussing growth on the modified film, we can hypothetically think of two limiting cases: The first would be a growth mode which is unaffected by the surface modification. In principle, this should result in three contributions to the diffuse reflex

profile. A shoulder caused by the correlation of modified oxide patches, a shoulder due to the metal island correlation, and a third contribution depending on both defect types [47]. The second growth scenario would be a situation where nucleation occurs on the modified oxide patches only, finally resulting in decoration of these areas. As in this case the defect correlation is not seriously affected, only slight changes of the diffuse profiles can be expected. Since the latter possibility appears to be more compatible with the observations, we conclude that growth on the modified surface is indeed strongly determined by the distribution of hydroxylated oxide areas. In the following section we will focus on the electronic structure to decide whether this decoration process is connected with a direct chemical interaction.

3.2.2. Photoelectron spectroscopy

A comparison between Al 2p and O 1s photoelectron spectra before and after deposition of 2 Å Rh (growth temperature 300 K) is shown in Fig. 9. Upon Rh growth two changes occur: (1) the characteristic high BE features in both the Al 2p



Fig. 9. Al 2p and O ls photoelectron spectra ($\theta = 0^{\circ}$) for the modified alumina film before and after deposition of 2 Å Rh (for simplicity, only the sums of the spin-orbit split peaks are shown for components 1-3).

and the O Is spectra disappear and (2) the Al 2p oxide component (component 3) and the O Is signal shift back to lower BE (Al 2p: $\Delta BE = -0.4 \text{ eV}$; O Is: $\Delta BE = -0.3 \text{ eV}$).

As the high BE features in the Al 2p (component 5) and O 1s spectra originate from the hydroxylated oxide patches, which are decorated upon Rh deposition (as shown in the preceding section), the disappearance of the additional features might be the result of either a preferential attenuation caused by the metal particles or of a drastic and specific shift of this component to lower BE. A closer inspection of Al 2p peak intensities, however, reveals that there is hardly any change in the intensity ratio of the NiAl substrate signal (component 1) to the sum of the oxide components (components 3 and 5). Since such a redistribution of intensity within the Al 2p oxide components is not compatible with a preferential attenuation of component 5, we conclude that, indeed, there is a specific interaction between the modified oxide patches and the Rh deposits, resulting in a shift of component 5 to lower BE (and in a coincidence with component 3). Moreover, this interpretation is confirmed by the complete disappearance of the

hydroxyl group-specific high BE feature in the O ls spectrum (see Fig. 9).

As mentioned above, in addition to the disappearance of the high BE features smaller Al 2p and O 1s shifts are observed for the main oxide components, where no direct interaction with Rh can be expected. In line with the discussion in Section 3.1.2, one possible contribution to these shifts might be caused by a change of the electrostatic potential (see schematical representation in Fig. 7). However, since we are dealing with negative shifts, in contrast to the Al film discussed in Section 3.1.2 an additional contribution resulting from increased screening caused by the additional metal layer cannot be excluded.

A possible interaction between substrate hydroxyl groups and Rh should not only affect the substrate but also the Rh core level spectra. Fig. 10 shows a comparison of Rh 3d PE spectra for three different experimental situations, all corresponding to deposition of 2 Å Rh: The BEs (Rh $3d_{5/2}$) are 307.1 eV and 307.3 eV for Rh growth on the non-modified $Al_2O_3/NiAl$ at 300 K and 90 K, respectively, and 307.6 eV for Rh growth on the hydroxylated film (at 300 K).



Fig. 10. Rh 3d photoelectron spectra ($\theta = 0^{\circ}$) for 2 Å Rh deposited on the modified film at 300 K and on the non-modified film at 300 K and 90 K.

The BE differences between different growth temperatures, i.e. growth at 90 K and 300 K, for deposition on the non-modified oxide can be related to differences in the average cluster sizes. As a detailed discussion of the growth and electronic structure of Rh on non-modified Al₂O₃/NiAl is given in separate articles [11,12], here we would like to draw the reader's attention to only one point which is of relevance in the present discussion: For deposition of 2 Å Rh at 90 K on the non-modified oxide film the island density has been estimated to be approximately 2×10^{13} cm⁻² (from LEED spot profile analysis [11]). Growth at 300 K leads to a significantly larger island size, i.e. a smaller island density. If we now assume that the density of Rh islands for growth at 300 K on the modified surface is comparable to the density of hydroxyl islands $(1.1 \times 10^{13} \text{ cm}^{-2})$, see Sections 3.1.1 and 3.2.1) and apply pure cluster size considerations only, we would expect a BE slightly smaller for growth on the hydroxylated film at 300 K as compared with growth on the non-modified surface at 90 K. In contrast to this, we find a significant shift (+0.3 eV) to higher BE.

One possible contribution to this shift might be related to differences in island shape. As the SCLS (surface core level shift) for Rh is known to be rather large (Rh(111): -0.50 eV, Rh(100): -0.62 eV, Rh(110): -0.64 eV, [48]), changes in island shape (resulting in changes of the average coordination number) might contribute to the BE

shifts observed. However, as the SCLS is negative, a positive BE of +0.3 eV would require a drastically increased average coordination number.

It therefore appears more likely that the dominant contribution to the BE shift is caused by a positively charged Rh species, which might be formed upon interaction with the surface hydroxyl groups. This process could be schematically described as:

$${Al^{3+}OH^{-}} + Rh^{0} \rightarrow {Al^{3+}O^{2-}}Rh^{+} + H_{(ad)}$$

We would like to point out that such a mechanism is compatible with all experimental results described above. In particular, it might contribute to a positive Rh 3d BE shift not only via formation of an oxidized Rh species, but also through the evolution of adsorbed hydrogen, which gives rise to adsorbate-induced core level shifts [49] comparable to the one observed in this study.

Thus it can be concluded that the photoelectron spectroscopic results presented in this section, i.e. the disappearance of the characteristic O 1s and Al 2p features and the Rh 3d BE shifts observed, point to a direct chemical interaction between the Rh deposit and the surface hydroxyl groups introduced on the alumina film.

4. Conclusions

We have studied the growth and interaction of Rh with a chemically modified, i.e. hydroxylated,

alumina surface. The modification procedure employed allows us to hydroxylate the surface of a well-ordered Al₂O₃ model support on NiAl(110), which originally is OH-free and O^{2-} -terminated. The procedure is based on the deposition of a submonolayer coverage of metallic Al and subsequent oxidation by water exposure. All preparation steps were characterized using LEED spot-profile analysis and high-resolution photoelectron spectroscopy. A high dispersion of Al can be verified by SPA-LEED (island density of about 1.1×10^{13} cm⁻²), complete oxidation of Al in the final preparation step by PES. Characteristic Al 2p and O Is surface features appear for the modified alumina film. Core and valence level BE shifts within the oxide film observed after Al deposition and H₂O exposure can be related to changes in the charge distribution within the ionic film.

Employing the same experimental techniques, growth and metal-substrate interaction of Rh deposited on the modified Al_2O_3 film were studied. It is shown that at 300 K nucleation of Rh aggregates preferentially occurs on modified oxide areas (SPA-LEED). Photoelectron spectroscopy of both oxide (Al 2p and O 1s) and rhodium (Rh 3d) core levels point to a direct chemical interaction between the metal deposits and the surface hydroxyl groups. Consumption of the hydroxyl groups can be directly monitored via the disappearance of characteristic features in the photoelectron spectra.

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