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Metal–oxide interaction for metal clusters on a metal-supported thin alumina film

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Abstract

The interaction between deposited metal clusters and a thin model alumina film grown on NiAl(110) have been studied using X-ray absorption spectroscopy (XAS) and core and valence photoelectron spectroscopy. A lower limit for the fundamental gap of the supported alumina film is determined, and found to be slightly lower than that of alumina surfaces. O 1s XAS shows that new states appear in the fundamental gap upon metal deposition. Al 2p X-ray photoelectron spectra from the alumina film are also sensitive to metal deposition, whereas spectra from Al atoms at the substrate–oxide interface appear unaffected. The present data demonstrate the existence of gap states in the pristine film, and we discuss the effects of these states for the properties of this film as a model oxide substrate.

Keywords: Alumina; Metal clusters; Metal–oxide; Thin film; X-ray absorption spectroscopy

Metal particles on an oxide support constitute a type of system commonly used in catalytic applications. For such systems it is often the metal particles which are the primary catalytic surface, though it is well established that the oxide support can also play an important role for the chemical characteristics. Both selectivity and reactivity for different processes can change because of the metal–oxide interaction. For example, the interaction of CO and H_2 with supported Rh has been shown to change for different oxide supports [1,2]. An improved understanding of the metal–oxide interaction can therefore help the further development of such systems [3], and has implications for a number of other applications as well [4,5].

One film which is interesting for model studies is that produced by oxidation of NiAl(110) at moderately elevated temperatures. This film has been shown [6–8] to have a structure (in the plane of the surface) reminiscent of bulk α- or γ-Al_2O_3, and is thin enough to be useful for electron spectroscopy studies. The best model for the structure of this film thus far consists of two layers each of Al

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and O atoms, with O at the surface and Al at the oxide/substrate interface [6]. Various studies of molecules adsorbed on this surface, e.g. electron spin resonance [9] and adsorbate core level autoionization [10], show that the surface has a very weak electronic interaction with such adsorbates, as expected for an insulator. The interaction has not been tested for adsorption of metal particles, however, for which it could be significantly stronger. Another important aspect yet to be studied is that of adsorbate-induced changes within the oxide film.

With these considerations in mind, we have studied the metal particle–oxide support interaction for small Pd and Rh particles deposited on a model alumina support. The analytical techniques used were X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and valence photoelectron spectroscopy (PES). The chemical specificity of XAS allows us to focus on the new states formed by the metal–oxide interaction at the oxygen atomic sites. We find states in the fundamental gap of the thin alumina film for the clean film, and find that many more such states are induced by the presence of metal particles on the film. XPS shows that Al atoms in the oxide film are affected by the deposition of metal particles, whereas those which are located at the oxide/substrate interface appear to be essentially unaffected. We furthermore discuss the use of this film as a model alumina film in studies of catalysts.

The experiments were carried out at Beamline 22 at the Swedish synchrotron facility MAX-Lab in Lund. The beamline was based on a modified Zeiss SX-700 monochromator. The analysis chamber contained a large hemispherical electron energy analyzer for photoelectron spectroscopy and a multichannel plate with a retarding grid for XAS measurements by detection of secondary electrons [11]. For the O 1s XAS data presented below, the retarding grid was set at 430 eV. The absolute photon energies were determined using photoemission spectra excited by first- and second-order radiation. The thin oxide film used here was produced through oxidation of a clean NiAl(110) crystal. The crystal was held at 525 K and exposed to 6×10^{-6} Torr of O_2 for 10 min. The film produced in this way was then annealed to 950 K for 3 min. Further details of this oxidation process have been given elsewhere [6].

Pd was evaporated at a sample temperature of 300 K using a Knudsen cell and the evaporation rate was monitored using a quartz microbalance. The Rh deposition was done at a sample temperature of 90 K, using a commercial evaporator (Focus EFM 3) based on electron bombardment and which allows evaporation from a rod. This evaporator had previously been calibrated using a quartz microbalance, giving the nominal film thickness. During evaporation the sample was put on a retarding potential to avoid effects due to ions produced in the evaporation source which are accelerated towards the sample. After deposition the metal coalesces into size-distributed islands. Studies of the geometric structure [12–14], electronic structure [15–17], and CO adsorption characteristics [14,18–20] of these particles have been described previously. In this paper we will use the nominal film thickness to denote the different depositions; the relationship of this to particle size is given in the relevant figure captions, with recent corrections to previous size calibrations for Rh discussed in Ref. [14].

We begin by discussing the properties of the pristine aluminum oxide film, and compare PES data to XAS data in Fig. 1. The valence spectrum is characterized by two sets of peaks, one group between 0 and 4 eV below E_F, and one between 5 and 12 eV. Similar valence data have been presented previously and compared to the clean substrate [6], showing that the low-energy Ni d state-derived peaks are the only structure present before the oxide forms. The more deeply bound group is therefore assigned to the valence states of the oxide film, and as pointed out previously [6], strongly resembles data for bulk samples [21,22]. This assignment is also consistent with the angle-dependence of the two signals [6].

The XA spectrum of the pristine alumina film exhibits a large double-peak in the photon energy range between 535 and 544 eV. Our data are quite similar to previous measurements [22–25] on bulk α-Al_2O_3 in the shape of this structure. One should note that the details of the shape of the main structure in the data are dependent on the relative

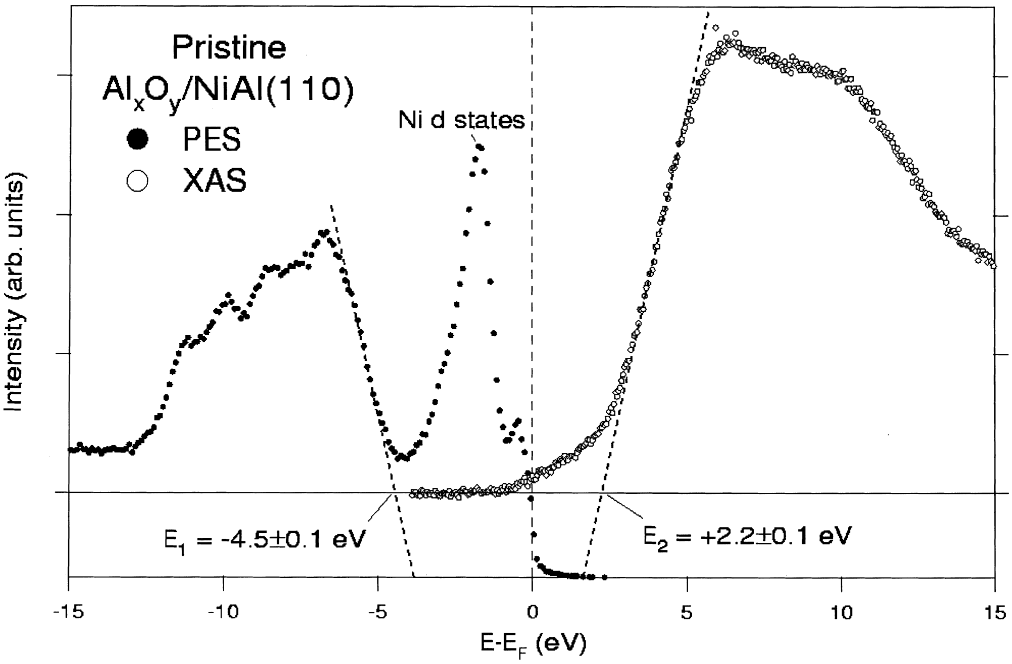

Fig. 1. Valence photoelectron and O 1s XA spectra for the pristine aluminum oxide film on NiAl(110).

orientation of the polarization of the radiation and the surface, both within and outside the plane, with moderate variations in the relative intensities of the two subpeaks. However, the basic structures are independent of the relative orientation. The position of the leading edge of this structure is lower than for bulk samples by about 3 eV, judging from the halfway position at ~535 eV in our data and ~538 eV for bulk α-Al_2O_3.[1] The width of the double-peak is quite similar for our sample and bulk α-Al_2O_3. This structure has been attributed to orbitals formed by the hybridization of O 2p orbitals and Al 4s, Al 4p and Al 3d orbitals [22]. It is, however, premature to use the similarity in the shape of the spectra for the thin alumina film as a structural indicator, due to the light polarization questions described above.[2]

We attribute the shifted O 1s threshold to 535 eV mentioned immediately above to the pinning of the gap of the present alumina film to the Fermi level (E_F) of the metallic substrate, combined with a moderate reduction of the bandgap from the value for thick samples. The gap at the surface of α-Al_2O_3 was found to be between ~7 and 8 eV in recent measurements [22], depending on the surface reconstruction, compared to bulk values near 9 eV.

For our data, we note that the O 1s binding energy for oxygen atoms closest to the substrate of 531.2 eV [26] (indicated in Fig. 2) coincides with the onset of a gradual intensity build-up below the main edge. This intensity build-up is in line with the existence of gap states induced by the proximity of the metal interface, and investigated theoretically for several systems [4]. We therefore associate the observed XAS onset with these 'inner' oxygen atoms. The coincidence of the onset of these states with the O 1s binding energy strongly suggests that the core hole is charge transfer screened in the XPS process, so that this binding energy represents E_F in the XAS data (see e.g.

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[1] We use the term 'bulk' somewhat loosely, since a surface structure dependence in O 1s XAS has been observed for α-Al_2O_3 [22]. It is also important to note that the calibration of the bulk data is of variable quality; nevertheless all data show similar edge positions.

[2] For a detailed discussion of the differences between α- and γ-phases relevant to the present case, see Ref. [6].

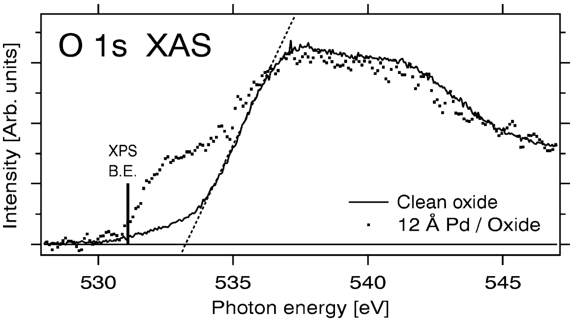

Fig. 2. O 1s XA spectra recorded before and after deposition of Pd at 300 K. The Pd particles produced contained an average of ~2000 atoms [12,16].

Ref. [27]). Thus, the screening upon core ionization of the 'inner' oxygen layer in this sense resembles that of a chemisorption system, as could have been expected. The O 1s binding energy for the 'outer' (surface) oxygen atoms is slightly higher (532.5 eV), which, due to the difficulty of differentiating between XAS features related to the two types of oxygen atom, makes it impossible to draw conclusions regarding the screening properties or upper gap edge of this layer from the present data.

Using the information above, we re-express the energy scale of Fig. 2 relative to E_F, shown on the right-hand side of Fig. 1. If we adopt the typical approach of using the asymptote of the strongly-sloping part of the alumina conduction band in our spectrum to identify the band edge, also shown in the figure, we place this at $E_F+2.2\pm0.1$ eV. For the occupied states, we find using the same simple measurement[3] that the alumina-induced states begin at $E_F-4.5\pm0.1$ eV. This gives a value of ~6.7 eV for the electronic gap for the supported alumina film, in good agreement with the reflection electron energy loss data of Ref. [28]. This value has to be considered a lower limit at present, for two reasons: (1) there are two oxygen layers, which could have different 'local' gaps due to the different chemical environments; (2) an excitonic state could be formed at the XAS threshold in this system, as is often the case in XAS of insulators, thus making the XAS-determined threshold lower than expected from the ground state electronic structure. However, the exciton question has been studied and ruled out [24] for bulk alumina based on the lack of sharp structures or resonant core hole decay spectra at the onset, suggesting that the present determination is likely not significantly affected by an excitonic effect. We assume that substrate-induced gap states are filled above the valence band edge to pin E_F at the observed ~2.2 eV below the conduction band edge.

Fig. 2 shows the O 1s XA spectra of the alumina film before and after Pd deposition. In the XA spectra recorded after metal deposition a new component emerges on the low photon energy side of the absorption peak with an onset at ~531 eV. We assign this new component to unoccupied states formed from the combination of O 2p states and Pd d states. The latter are also reflected in photoelectron spectra [15], and are strong near E_F. We note that the metal-induced intensity shown here and in the Rh spectra presented below decreases towards E_F. This supports the identification made above of that energy as E_F. Furthermore, it should reflect a decreasing O 2p character of these states with increasing separation from the alumina conduction band, consistent with theoretical studies for these states. In particular, the case of Nb/Al_2O_3 has been modeled, and the qualitative trends observed here are consistent with the results of those calculations [4,29]. A study of work function changes induced by Pd particles adsorbed on bulk α-Al_2O_3 found an increase in the work function with cluster deposition, and interpreted this in terms of charge transfer from the oxide to the metal particles within a simple dipole model [30]. We find this conclusion unjustified by the present results, considering that the basic positions of the XAS peaks are unchanged, and we do not detect new intensity at photon energies below the previous threshold as, e.g., observed for intercalated graphite [31]. We discuss alternative explanations for the work function changes elsewhere [17].

The O 1s XAS show similar changes in gap

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[3] To estimate the position of the baseline for the oxide-induced states in the photoelectron spectrum, a step function is assumed to be centered at E_F, overlaid by a small peak due to the Ni d band. We have estimated the step function plateau as shown. This estimate of the occupied bandgap edge is strongly supported by the data of fig. 8 in Ref. [6].

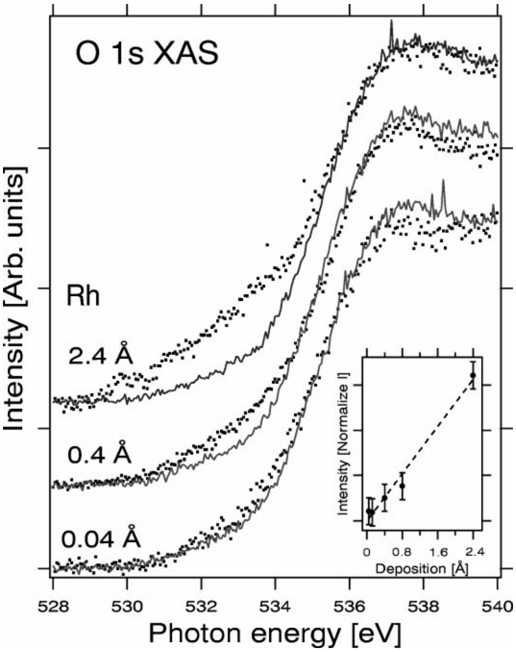

Fig. 3. O 1s XA spectra recorded before and after deposition of the indicated nominal film thickness of Rh at 90 K. The thicknesses indicated are related to average particle size as follows [13,14]: 2.4 Å, ~120 atoms; 0.4 Å, ~25 atoms; 0.04 Å, ~8 atoms. Inset: intensity of the metal-induced states normalized to the cross-section at 560 eV.

state population upon deposition of Rh, as shown in Fig. 3. Both the position and the width of the metal-induced band are the same within small error margins. We observe that the intensity of the new component due to the deposited metal increases with the amount of deposited metal. XAS data for deposited Ir also show the appearance of new states in the alumina gap. One issue which arises in analyzing the intensity of the metal-induced gap states in XAS is the surface sensitivity of the measurements. It is almost certain that our data, taken in the partial yield mode as noted above, do not reflect the states of the particle–oxide interface in the middle portion of the contact area (for relatively thick three-dimensional particles, i.e. those with more than several hundred atoms), but highly emphasize the states near the edges of the particles, as well as the uncovered areas of the oxide. Thus the present results should be taken as qualitative indicators of the effects of metal deposition on the oxide electronic structure.

The cluster–support interaction can also be observed using XPS. Fig. 4 shows a series of Al 2p core level spectra recorded before and after Rh deposition. As can be seen in the figure, the large peak with a binding energy of ~75 eV (associated with the outermost Al atoms [26]) shifts towards lower binding energy upon metal deposition. The magnitude of this shift as a function of nominal film thickness is summarized in the inset. A similar effect is also seen in O 1s XPS, where the component identified with surface oxygen atoms shifts towards lower binding energy upon metal deposition. Since these measurements are also surface sensitive, the same limitations as regards probing the central region of the cluster–oxide interface which we discussed for O 1s XAS apply. As in the O 1s XA spectra, these qualitative effects in XPS are common to Rh, Pd and Ir deposits.

The observed binding energy shifts can be due to a combination of several factors. Redistribution of charge within the alumina which could be expected to accompany the bonding to the adsorbed metal is one likely contribution. Another factor which should be considered is that the deposited metal will change (presumably enhance) the electronic screening for the oxide surface atomic layers, which would be expected to decrease the binding energies, as observed. It is noteworthy that metal deposition on the alumina film has no measurable effect on the binding energies of either the Al 2p peak associated with the interface atoms (feature at 73.6 eV seen in Fig. 4) [6,15,26], or the O 1s peak associated with subsurface O atoms bonded directly to the metal substrate (via the interface Al atoms) [26]. We attribute this to the excellent charge transfer screening afforded to atoms in those locations by the proximity of the substrate, which should be negligibly affected by adsorption onto the oxide surface as long as the oxide structure is not significantly perturbed. The fact that the effects of metal bonding on the oxide electronic structure decay very rapidly with distance from the interface is in agreement with qualitative trends from calculations [4]. Overall, these data show that the electronic structure of the outer oxide layer approaches that of the inner with increasing metal coverage.

As noted initially, the alumina film studied here

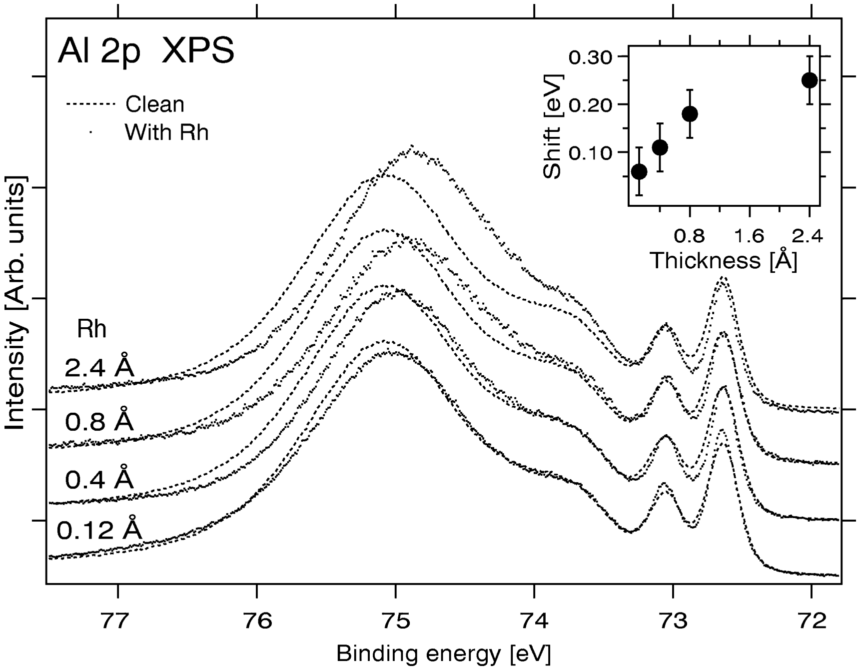

Fig. 4. Al 2p XP spectra recorded before and after deposition of the indicated nominal film thickness of Rh at 90 K. The dotted lines are spectra after metal deposition and the dashed lines show the spectra of the pristine oxide film. The thicknesses indicated are related to average particle size as follows [13,14]: 2.4 Å, ~120 atoms; 0.8 Å, ~45 atoms; 0.4 Å, ~25 atoms; 0.12 Å, ~12 atoms. Inset: summary of binding energy shifts of the large peak near 75 eV associated with the outer Al atomic layer [26] as a function of the quantity of deposited Rh.

has characteristics of insulating Al_2O_3. This could be expressed in terms of tunneling probabilities for electrons from the substrate to reach adsorbed species, which has been shown to correspond to tunneling times significantly longer than 1 fs [9,10,16]. However, it seems clear that by putting enough metal onto the surface, one could induce enough gap states to qualitatively change this characteristic, and there are indications from XPS that this may occur [17]. This suggests a need to study supported alumina films of controlled thickness, in order to eliminate uncertainties in applying results of such studies to, e.g., real catalysts or ceramic/metal interfaces. At the same time, the limited thickness of the alumina film studied here has enabled us to access the oxide electronic density-of-states more simply, providing to our knowledge the first experimental snapshot of this quantity near the interface with a metal. And, as noted above, further studies aimed at understanding the role of surface sensitivity in the present XAS measurements are required to more accurately characterize the particle–oxide interaction.

To summarize, we have shown that for the ordered alumina film which can be reliably produced on NiAl(110) [6–8], the bandgap is reduced from 8 eV at the surface of bulk α-Al_2O_3 to (a lower limit of) about 6.7 eV, with a continuum of defect states extending from the conduction band edge (and presumably the valence band edge) to E_F. E_F is found to be pinned ~2 eV below the conduction band edge.[4] The density of gap states increases with metal deposition. Atoms which can be identified with the outer layers show shifted core level binding energies, whereas atoms associated with the interface are negligibly affected, suggesting an evolution of the oxide electronic structure as a function of separation from the

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[4] After submitting this work, we were alerted to theoretical work which is in qualitative agreement with our results for the pristine oxide electronic structure [32].

metallic support which is in qualitative agreement with recent calculations.

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