Electron Spectroscopy Studies of Small Deposited Metal Particles

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The Al_2O_3/NiAl(110) system with and without Pd clusters on the surface has been studied using photoemission of both core and valence levels. Pd has been deposited under various conditions, and changes in the spectra due to differences in growth modes are discussed. The C 1s spectra for CO adsorbed on deposited Pd clusters of increasing size can be viewed as showing the evolution from a deposited carbonyl-like species to CO adsorbed on a metallic surface. Heating of CO-saturated clusters to 300 K leads to desorption of more than half of the CO, which allows for a stronger interaction between the remaining molecules and the Pd clusters.

1. INTRODUCTION

Small metal particles usually exhibit electronic properties which strongly differ from those of the bulk material and often involves interesting changes in the interaction with adsorbates. This has for a long time been utilized in the manufacturing of supported heterogenous catalysts, of which aluminium oxide with deposited particles of noble metals like Pd, Pt and Rh is one of the most important examples. In order to find ways to optimize the performance of the catalysts or develop cheaper catalysts, a detailed understanding of the elementary processes is necessary. This has motivated the use of electron spectroscopies, which are especially well suited for studies of surface processes involving adsorbates. In particular, photoemission of core and valence levels has proven to be most useful. This is because of the high surface sensitivity, and, in the case of core level studies, the atomic selectivity due to the strong localization of the core hole and the well-separated ionization energies for different elements. Moreover, if the resolution of the core level spectra is high enough, information can be obtained not only about the chemical state of the adsorbate (e.g. if dissocitation takes place or not), but also detailed information

regarding adsorption geometries, interaction strengths etc. [1]. There are also other core level techniques that can provide most valuable complementary information about the adsorbate properties, such as X-ray Absorption Spectroscopy (XAS) and Deexcitation Electron Spectroscopy (DES) [1].

Unfortunately, the metal/Al_2O_3 catalysts used in industry are difficult to study with these techniques. The surface is disordered and, since Al_2O_3 is an insulator, charging effects occur and the possibility for cooling is limited. However, these problems can be circumvented if instead an oxide film grown upon a metal substrate is used. For example, it has been found that a thin, well-ordered Al_2O_3 film can be grown on the surface of a NiAl(110) single crystal, and extensive studies about the properties of this alumina film have been carried out, e.g. refs. [2,3].

In this contribution we present core and valence photoemission data for the Al_2O_3/NiAl(110)-system with and without metal particles on the surface. Pd has been deposited under various conditions, and changes in the spectra due to differences in growth modes are discussed. Of special interest is the interaction of the Pd particles with CO.

2. EXPERIMENTAL

The valence photoemission measurements were carried out at the TGM3 beamline at BESSY Synchrotron Radiation Center (Berlin) using a hemispherical analyzer rotable in two orthogonal planes. The photon energy was 42 eV and the total resolution was 0.3 eV. The core level spectra were recorded at Beamline 22 at MAX-lab at Lund University, Sweden, using a modified Zeiss SX700 plane grating monochromator in conjunction with a large hemispherical analyzer [4]. The C 1s spectra were recorded at a photon energy of 380 eV with a total resolution of 0.3 eV. The Al 2p spectra were measured with a photon energy of 150 eV and 0.1 eV resolution.

The preparation of the clean NiAl(110) surface and the subsequent formation of the Al_2O_3 film has been described elsewhere [2]. The evaporation rate of the metals was calibrated using a quartz microbalance.

3. RESULTS AND DISCUSSION

3.1. The alumina film

Several electron spectroscopies have been employed in order to elucidate the geometrical structure of the alumina film formed upon NiAl(110). Photoemission and Auger data yields an estimation of a film thickness of about 5 Å [2]. The chemical inertness of the surface points to an oxygen terminated surface, and LEED together with angular resolved photoemission shows that the oxygen atoms form a quasi-hexagonal structure [2]. EELS data suggest that the structure of the oxide film is similar to either γ-Al_2O_3(111) or α-Al_2O_3(0001), where, in the case of bulk alumina, the main difference between the two structures is the positions of the aluminium atoms [2]. In the first case, the Al-atoms occupy both tetrahedal and octahedral sites, whereas only octahedral sites are occupied in the latter case. However, there are no results so far where the positions of the Al-atoms in the thin Al_2O_3 film on NiAl(110) are unambigously determined.

Fig. 1 shows high resolution Al 2p spectra for three different emission angles, which have been normalized to the broad peak centered at 75.0 eV. This peak has been identified as emission from the
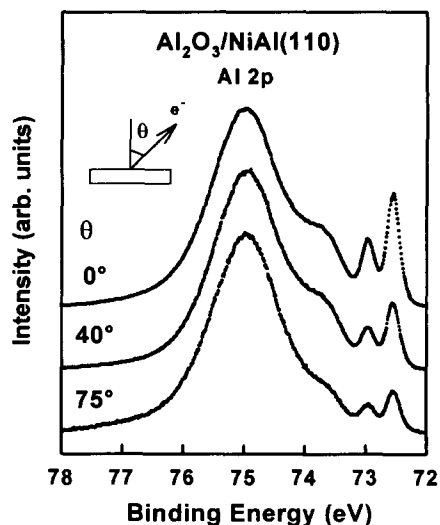

Figure 1. Al 2p spectra for three different emission angles.

oxide, whereas the narrow peaks at 72.55 and 72.95 eV are assigned to Al $2p_{3/2}$ and $2p_{1/2}$ from the NiAl(110) substrate, respectively. The weak shoulder on the low binding energy (BE) side of the oxide peak could be caused by an interface layer of Al-atoms between the oxide and the substrate, as suggested in ref. [2]. The presence of an interface has been put forth in an STM study of the same system [3]. Moreover, in a study of the oxidation of Al(111), a feature was observed at exactly the same binding energy, which was convincingly assigned to an interface layer [5]. The intensity variations observed in Fig. 1 supports this interpretation, since the intensity of the shoulder more follows the intensity of the substrate.

3.2. Deposition of Pd

The initial characterization of the Pd growth was carried out using SPA-LEED (spot profile analysis), STM and TDS [6]. The results for sample temperatures of 90 and 300 K show a 3D growth mode in both cases, but the islands formed at lower temperature are considerably smaller. For large amounts of Pd deposited at 300 K, crystallites with preferentially (111)-facets are formed, giving rise to a diffuse hexagonal LEED pattern. In order to investigate how the differences in growth mode are manifested in the electronic structure, valence
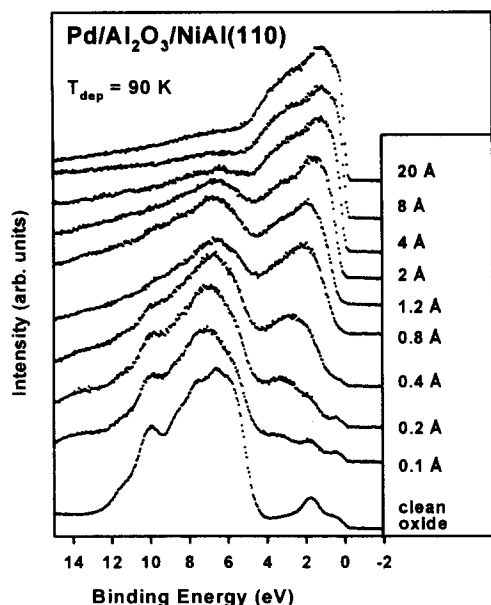
Figure 2. Valence photoemission spectra for Pd
deposited on Al_2O_3/NiAl(110) at 90 K. The
features at 0-3 eV in the clean oxide spectrum are
due to emission from NiAl(110), whereas the O 2p
states for the oxide appear between 4 and 13 eV.

Figure 3. Valence photoemission spectra for Pd
deposited on Al_2O_3/NiAl(110) at 300 K.

photoemission spectra were recorded for both the
situations and these are presented in Figs. 2 and 3.

Starting with the growth at 90 K (Fig. 2), we
observe already at 0.1 Å Pd a new feature emerge at
a BE of about 3.5 eV, which can be attributed to Pd
4d states. It gradually moves towards lower binding
energies and eventually develops into a broad band
reaching down to 5 eV and with a considearble
intensity close to E_F, as expected for bulk Pd. It is
worth noting that a significant increase in the
intensity at E_F is not observed until an exposure of
0.8 Å Pd is reached.

Turning next to the growth at 300 K (Fig. 3),
significant differences are observed for the lower
coverages: instead of a rather well-defined peak as
in the 90 K case, the Pd induced states appear more
as an evenly distributed increase of the intensity in
the BE region 0-4 eV, with no evident shift towards
lower BE:s for increasing exposure. This feature
becomes apparent for exposures exceeding 0.1 Å. At
higher coverages, the situation becomes more and
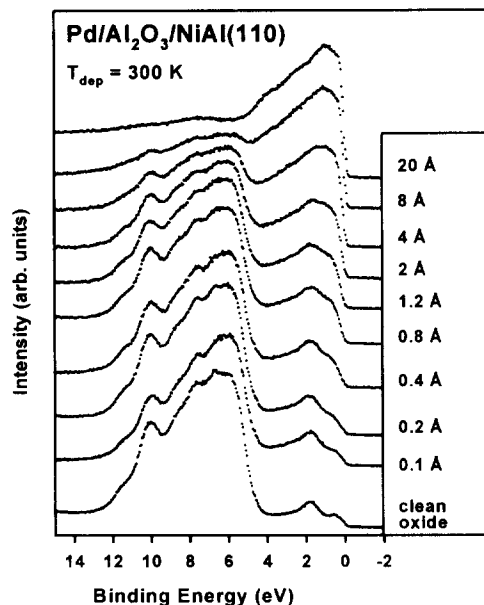more similar to the low temperature growth.

However, the relative intensity of the 4d states, as
compared to the O 2p emission from the oxide, is in
all cases considerably lower than in the 90 K-
spectra.

The differences in the Pd 4d states as a
function of exposure is a consequence of the
different growth modes for the two temperatures. If
larger islands are formed, the particles will exhibit
metallic properties, such as a broad valence band, at
lower exposures, thereby explaining the differences
in shape of the 4d feature. Furthermore, shifts
towards higher BE:s for decreasing size is typical for
supported clusters, e.g ref. [7]. This shift is found to
be largest for small clusters. Since the clusters
formed at 90 K are much smaller than than those
formed at 300 K, this will result in a more prominent
shift towards higher BE for low exposures. Other
factors, which can contribute, but are difficult to
verify, are small differences in the local ordering
within the cluster and/or in the interaction with the
oxide. Moreover, formation of larger islands also
means that a smaller part of the oxide is covered,
which explains the lower relative Pd intensity for the
300 K growth. The valence photoemission spectra
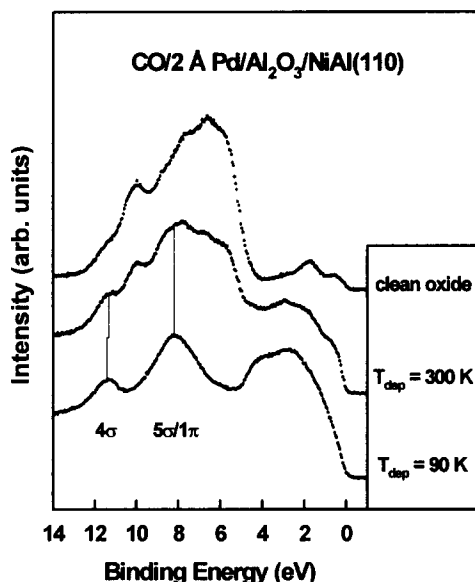are thus consistent with the SPA-LEED results.

CO/2 Å Pd/Al$_2$O$_3$/NiAl(110)

Intensity (arb. units)

clean oxide

T$_{dep}$ = 300 K

T$_{dep}$ = 90 K

4σ   5σ/1π

14 12 10 8   6   4   2   0

Binding Energy (eV)

Figure 4. Valence photoemission spectra for CO/2 Å Pd/Al$_2$O$_3$/NiAl(110) for the two different deposition temperatures.

Further support for these findings is obtained when comparing the situations when the particles are saturated with CO. In Fig. 4, valence photoemission spectra for three different situations, apart from the clean oxide, are presented; the two spectra in the middle show the valence region for 2 Å of Pd deposited at 90 K and 300 K, respectively, and thereafter dosed with 20 L CO at 90 K. It is easy to see that the relative intensity of the CO induced states, 4σ and 5σ/1π, is much higher when Pd is deposited at 90 K than for 300 K. This is again an effect of the different cluster sizes, since the presence of a large number of small clusters allows for a higher degree of CO-Pd coordination than a surface with few, large clusters.

In order to investigate the properties of the adsorbed CO in more detail, high resolution core level spectra have been recorded. Fig. 5 show C1s spectra for 30 L CO adsorbed on increasing amounts of Pd: 0.2 and 2 Å deposited at 90 K and 12 Å deposited at 300 K. The spectrum at the top shows a CO (2x2) overlayer on Pd(111), formed by saturation at 90 K, and recorded with slightly higher resolution than the others (from ref. [8]). Most

apparent in Fig. 5, however, is the continuous decrease in binding energy for increasing Pd amounts, accompanied by a decrease in shake-up intensity.

Starting with the 0.2 Å situation, an average island size of about 5 Å can be estimated with the use of SPA-LEED [6]. The UP data in Fig. 2 suggest that no broad metallic-like 4d band is formed. Pd 3d spectra show that upon CO adsorption all Pd atoms are coordinated to CO molecules [9]. Thus, based on the lack of metallic properties and the high degree of Pd-CO coordination, the small CO saturated particles can be considered as similar to carbonyl molecules deposited on the oxide surface. In fact, the satellite/main peak intensity ratio is close to what has previously been observed in the C 1s spectra for different carbonyls [10].

Adsorption of CO on the islands formed after an exposure of 2 Å Pd (average size 10 Å) represents an intermediate situation, where the islands are more metallic. Finally, when adsorbing CO on a deposit of 12 Å, we have reached the situation of CO-metal adsorption. The spectrum is found to be identical to the spectrum obtained for CO/Pd(111), thereby confirming the presence of crystallites largely dominated by (111)-facets for large amounts of Pd. The spectra in Fig. 5 can thus be envisaged as a demonstration of how a carbonyl-like species gradually transform into the CO/metal case.

Heating of the 0.2 and 2 Å situations to 300 K was performed, and the resulting spectra are presented in Fig. 6, together with the spectrum for CO/Pd(111) (√3x√3) (from ref. [8]). Based on the changes in the peak intensities, it can be estimated that the heating leads in both cases to desorption of about 60 % of the CO molecules. The C 1s lines for the heated species are narrower and have lower binding energies. By comparing Figs. 5 and 6, it can be concluded that this peak was not present before the desorption. The lower binding energies and the decreased shake-up intensities points to a species interacting more strongly with the Pd-atoms. The change in linewidth could be caused by a decrease in the number of different CO-adsorption sites. This has been observed for CO/Pd(111), where the (2x2) phase, formed by saturation at 90 K, consists of molecules adsorbed in both hollow and on-top positions, whereas in the (√3x√3) situation only
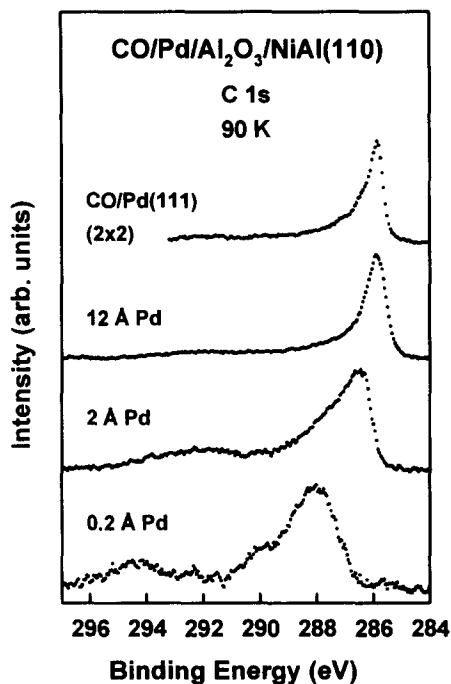
Figure 5. C 1s spectra for CO adsorbed on clusters of increasing size compared to CO/Pd(111) (2x2).

Figure 6. C 1s spectra for CO adsorbed on two different cluster sizes after heating to 300 K compared to CO/Pd(111) ($\sqrt{3}$x$\sqrt{3}$).

hollow sites are occupied [11,12]. The ($\sqrt{3}$x$\sqrt{3}$) phase exhibit significantly narrower C 1s line as compared to the (2x2) structure due to the decreased number of adsorption geometries. Moreover, the decreased coverage also induces a shift towards lower BE for the molecules adsorbed in hollow sites. Hence we conclude that desorption of parts of the overlayer from the clusters allows for a stronger CO-Pd interaction for the remaining molecules, which probably are adsorbed in one preferential, highly coordinated site.

However, it is important to point out that desorption of large amounts of CO takes place at much lower temperatures for the cluster than for the (111) surface, as shown by TDS [6]. Thus, the molecules forming the saturated overlayer bond more weakly to the Pd atoms. This is also reflected in the increased shake-up intensity for the supported clusters observed in Fig. 5, since stronger satellites are normally found for weakly bonded adsorbates [13].
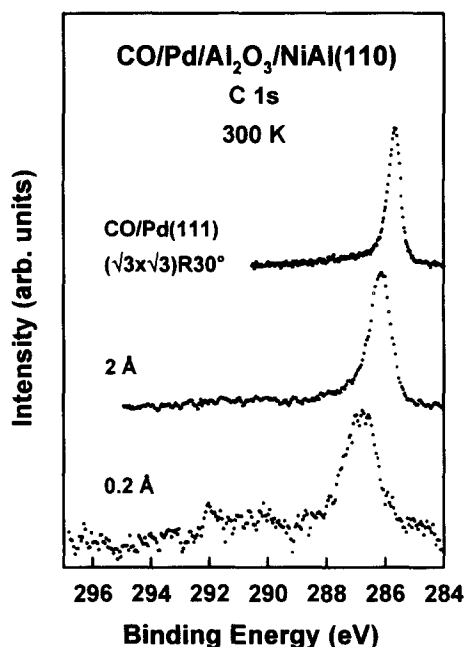
Heating to higher temperatures has been found

to result in desorption of the remaining CO molecules, accompanied by diffusion of Pd into the oxide [6,14].

4. CONCLUSIONS

We have studied the Al_2O_3/NiAl(110) system with and without Pd clusters on the surface, employing photoemission of both core and valence levels. The Al 2p spectra supports the previously suggested existence of an interface layer of Al atoms between the oxide and the NiAl(110) substrate. Differences in the Pd growth modes for 90 K and 300 K were found to induce characteristic changes in the Pd 4d peak, and differences in island sizes is furthermore reflected in the uptake of CO. C 1s spectra for CO adsorbed on deposited Pd clusters of increasing size can be viewed as showing the evolution from a deposited carbonyl molecule to CO adsorbed on a metallic surface. The formation of crystallites with (111) facets is confirmed by a comparison with CO/Pd(111) spectra. Heating of

CO-saturated Pd clusters to 300 K leads to desorption of more than half of the CO, allowing for the remaining molecules to interact more strongly with the Pd atoms.

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