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Surface Science

Principles and Current Applications

With 196 Figures



Adsorption on Epitaxial Oxide Films as Model Systems for Heterogeneous Catalysis

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Abstract. We have studied the interaction of Pt with $\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$ and the adsorption of CO on the platinum covered oxide as a function of Pt coverage for deposition temperatures of $T \approx 100$ K and $T \approx 300$ K. At 300 K the platinum forms a twodimensional layer, which is partially ordered whereas for preparation at 100 K no order within the metal deposit could be observed. On the Pt deposits prepared at room temperature CO dissociation occurs, in contrast to non dissociative CO adsorption on Pt single crystals. With TDS (Thermal Desorption Spectroscopy) an unusual CO desorption signal is observed at $T \approx 150$ K. Upon annealing at elevated temperature the Pt seems to diffuse into the oxide film or through the oxide film into the NiAl substrate.

1. Introduction

Oxide surfaces are interesting research objects for different reasons. From a more basic point of view oxides represent a class of materials which is quite different from metals. Whereas at least for the transition metals the electronic properties are well known today this is not the case to this extent for oxides. Even for one of the most studied oxides, NiO, there have been controversial discussions about the electronic structure only a few years ago [1, 2, 3]. This is connected with the fact that oxides are ionic materials and one has to deal not only with delocalized but also with localized electronic levels so that multi electron effects may be quite important [4, 5, 6].

Apart from this basic interest in oxides there is also a more practical interest. Oxides play an important role in catalysis as support materials or as catalytically active components of catalysts and therefore their interaction with gases and metals has been an object of research for a long time [7, 8]. Most of these studies, however, deal with oxide powders. Due to experimental problems one has begun to study well defined oxide surfaces only a few years ago [9, 10, 11]. One problem is that oxides are usually insulators and therefore they tend to charge which hinders the application of electron spectroscopy. For this reasons we study oxide films of limited thickness which do not charge.

Al_2O_3 is a typical support material in catalysis. We have prepared thin Al_2O_3 films by oxidation of NiAl(110). In a previous study we have investigated the electronic and geometric structure of this film [12, 13]. The surface is

chemically quite inert as indicated by CO desorption temperatures between 38 K and 65 K [14, 15]. In this paper we present results of electron spectroscopic studies for platinum deposits on this oxide film. In addition, the adsorption of CO on such Pt deposits has been studied. Platinum interacts strongly with the alumina film, destroying the long range order of the oxide even for coverages far below a monolayer [16]. At least two different types of platinum sites exist on the surface as indicated by CO adsorption experiments. As deduced from TDS, the first type of site is to be assigned to metallic Pt. The nature of the other type of site is not fully understood yet. It leads to a CO desorption temperature of $T \approx 150$ K and is only observed for Pt deposition at room temperature. We tentatively assign it to Pt which has changed its charge state or to oxide sites which are electronically modified by the interaction with Pt. For Pt deposition at $T \approx 300$ K also decomposition of CO is observed.

2. Experimental

The experiments have been performed in three different UHV chambers. All chambers contain equipment for LEED (Low Energy Electron Diffraction), AES (Auger Electron Spectroscopy), TDS and residual gas analysis with a quadrupole mass spectrometer, and crystal cleaning with an ion gun. The sample holders allow for cooling down to $T \approx 90$ K and sample heating by electron impact or heat radiation. One chamber is equipped with an HREELS (High Resolution Electron Energy Loss Spectroscopy) spectrometer which is capable of resolutions down to about 5 meV. The other one contains a XPS (X-ray Photoelectron Spectroscopy) spectrometer. The XPS spectrometer is equipped with a monochromatized X-ray source and an unmonochromatized X-ray tube. The third chamber contains an electron monochromator and a rotatable electron analyzer for angular resolved EELS (Electron Energy Loss Spectroscopy) and ARUPS (Angle Resolved Ultraviolet Photoelectron Spectroscopy). The NiAl(110) samples were cleaned by standard sputtering and heating sequences. After cleaning the oxide film was prepared by admitting 1200 L ($1 \text{ L} = 10^{-6} \text{ Torr} \times \text{sec}$) of oxygen at elevated temperature ($T \approx 550$ K) with subsequent annealing to $T \approx 1200$ K as described elsewhere [12]. The quality of the resulting thin oxide film was checked by LEED. For the final oxide layer a manifold of sharp LEED spots with low background intensity was observed, indicative of a well ordered oxide structure. The metal films were produced by a metal evaporation source as described elsewhere [17]. Thickness control was established by a quartz microbalance. For this purpose the evaporation rate of the metal source was determined by evaporating a thick film of platinum. This value was used to calculate the evaporation time needed to prepare a platinum film with a given thickness.

3. Results and Discussion

3.1. Pt/Al₂O₃(111)/NiAl(110)

In a previous study we have established a structural model for the thin aluminium oxide film on NiAl [12]. According to this model the structure of the oxide film is similar to that of γ -Al₂O₃(111) with the surface most likely covered by oxygen ions. It has a thickness of two Al-O bilayers which corresponds to 5 Å. Due to the large unit cell of the oxide film a multitude of spots is observed in the LEED pattern. The film is chemically rather inert with respect to adsorption of CO as alluded to in the introduction [14], so that adsorption of CO on the pure oxide did not occur in the investigations presented here which have been performed at temperatures $T \geq 100$ K.

Evaporation of a small amount of platinum results in a destruction of the long range order of the film. In the LEED pattern a strongly increased background intensity and a strong reduction of the intensity of the oxide spots is observed [16]. Upon evaporation of 0.5 ML of platinum the intensity of the specularly reflected electron beam in an HREELS experiment decreases by two orders of magnitude and the elastic beam is spread out over a large angular

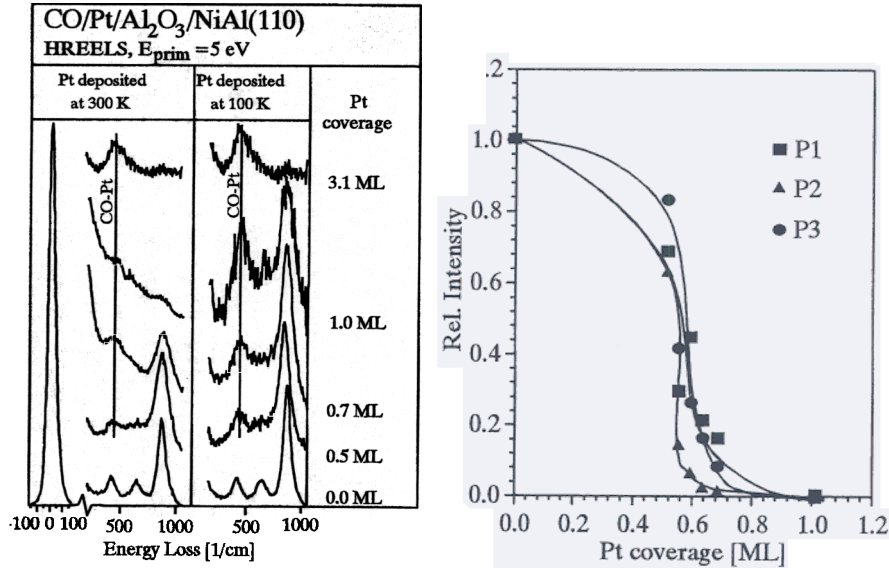


Fig. 1: Left: Series of HREELS spectra for CO/Pt/Al₂O₃(111)/NiAl(110) as a function of coverage. The two sets of spectra show data taken for different substrate temperatures during evaporation. Right: Intensity of the Al₂O₃ phonons as a function of Pt coverage for a substrate temperature of 300 K during evaporation.

range [18]. All these data are indicative of a strong interaction of platinum with the aluminium oxide film. For Pt layers with thicknesses of several monolayers which have been deposited at $T \approx 500$ K a hexagonal LEED pattern is observed, indicative of the formation of Pt(111) [16].

In fig. 1 (left panel) a set of HREELS spectra is shown for CO on a platinum covered Al_2O_3 film as a function of the Pt coverage. The two sets of spectra show data for deposition temperatures of $T \approx 100$ K and $T \approx 300$ K, respectively. Obviously the oxide phonons are damped when Pt is deposited onto the oxidized surface. However, whereas the phonons are nearly fully suppressed at a platinum coverage of 0.8 ML for deposition at room temperature, they are still quite intense for deposition at $T \approx 100$ K. This points towards differences in the structures of the Pt layers.

In the right panel of fig. 1 the intensity of the oxide phonons vs. Pt coverage is depicted for platinum deposition at room temperature. As is obvious from these data, the intensity of the phonons strongly decreases in the coverage range between 0.5 and 1 monolayer of platinum. Similar results have been obtained in other studies where metal deposition on dielectric substrates was investigated [19, 20]. The phonon damping may be explained by dielectric theory as to be due to the interaction between the oxide phonons and the plasmons within the metal overlayer [19]. This theory requires the first Pt layer to form a continuous film or at least a film consisting of small, highly dispersed clusters distributed over the surface so that the free spaces between the clusters are rather small since otherwise the phonon intensity should not be quenched at a coverage of about one monolayer. STM (Scanning Tunneling Microscopy) data of 0.1 ML of Pt on $\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$ support this type of growth mode, i.e. they show the formation of small and rather flat Pt islands [21]. For Pt

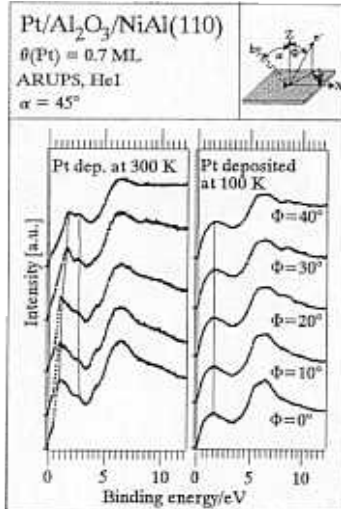


Fig. 2: ARUPS data of 0.7 ML Pt/ $\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$ taken as a function of the detection angle. Left: Pt deposition at $T \approx 300$ K. Right: Pt deposition at $T \approx 100$ K

deposited at $T \approx 100$ K the growth mode must be different as indicated by the less pronounced damping of the oxide phonons. This may be due to a hindered diffusion of Pt atoms at this temperature which might suppress the formation of the small islands observed for a deposition temperature of $T \approx 300$ K.

The differences between the Pt growth modes for deposition at $T \approx 100$ K and $T \approx 300$ K are also documented by ARUPS spectra. Two sets of data taken at temperatures of $T \approx 100$ K and $T \approx 300$ K, respectively, are shown in fig. 2. A Pt valence emission is found near to the Fermi level where Al_2O_3 has no electronic states. As may be seen from these data there is dispersion of the electronic levels of Pt as a function of the detection angle when Pt is deposited at $T \approx 300$ K. This means that for deposition at room temperature the Pt layer must be at least partially ordered. No dispersion of the Pt bands is observed for Pt deposition at $T \approx 100$ K so that in this case the Pt deposit must be less ordered.

In fig. 3 (left panel) two sets of HREELS spectra are shown. This figure compares spectra taken at the respective deposition temperatures with spectra

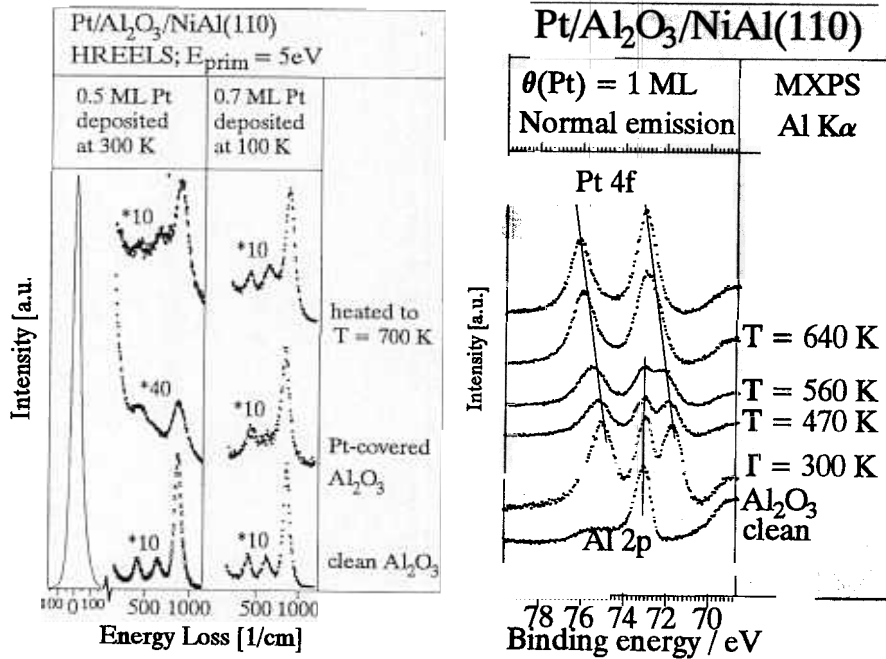


Fig. 3: Left: Comparison of HREELS spectra of Pt/Al₂O₃(111)/NiAl(110) taken at Pt deposition temperature with spectra taken after annealing at $T \approx 700$ K. Right: XPS data of 1 ML of Pt on Al₂O₃(111) on NiAl(110) taken after annealing at different temperatures.

recorded after annealing at $T \approx 700$ K for deposition temperatures of $T \approx 100$ K and $T \approx 300$ K. In both cases the intensities of the substrate phonons recover after the annealing process which means that something must have happened to the Pt layer. The XPS data shown in the right panel of fig. 3 display the Pt 4f levels of 1 ML of Pt after annealing at different temperatures. These levels do not vanish when the layer is annealed at elevated temperatures so that the platinum can not be desorbed. The binding energy shift may indicate that the Pt atoms change their charge states upon annealing. ISS (Ion Scattering Spectroscopy) data (not shown here) indicate that the amount of Pt at the surface decreases upon annealing. TDS data which will be discussed in the following section show that the CO coverage also decreases. We suppose that the platinum migrates into the oxide or through the oxide into the NiAl substrate.

3.2. CO/Pt/Al₂O₃(111)/NiAl(110)

In fig. 4 a set of TDS spectra for CO/Pt/Al₂O₃(111)/NiAl(110) is compared with data for two different Pt single crystal surfaces [22, 23]. Most of the CO desorbs in the temperature range between $300 \text{ K} > T > 550 \text{ K}$ from the Pt covered oxide film. Desorption peaks in this temperature range are to be attributed to CO which bonds to metallic platinum. The fine structure of these peaks is due to different bonding sites which might include bonding to defects,

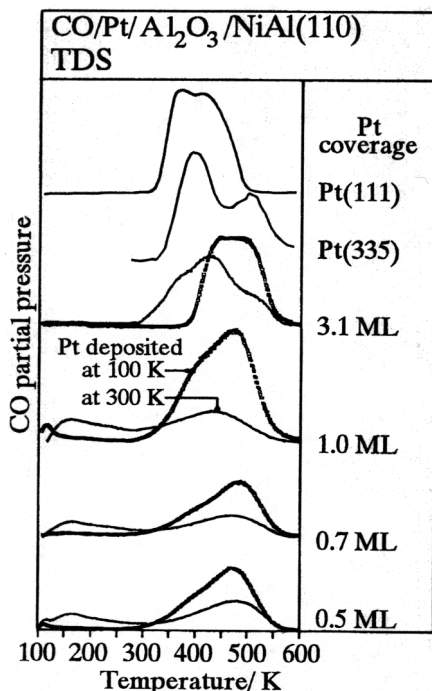


Fig. 4: Comparison of TDS spectra of CO on Pt/Al₂O₃(111)/NiAl(110) with spectra of CO on Pt single crystal surfaces. For each Pt deposition on the oxide surface spectra for two different deposition temperatures are shown.

steps and regular Pt(111) sites [18, 22, 23]. For Pt deposited at $T \approx 300$ K the structures between $300 \text{ K} > T > 550 \text{ K}$ are weaker and some additional desorption at lower temperature is observed. The small desorption peak at $T \approx 110$ K in the spectrum for a Pt coverage of 1 ML is to be attributed to CO_2 desorption.

Additionally, for a Pt deposition temperature of $T \approx 300$ K a CO desorption signal at $T \approx 150$ K is observed. This result may be compared with CO desorption spectra from transition metal oxides. It is often observed that CO desorbs from these oxide surfaces in the temperature range between $100 \text{ K} > T > 200 \text{ K}$ [24, 25]. Therefore, a possible explanation for the signal at $T \approx 150$ K might be that part of CO bonds to oxide sites which are modified by the interaction with Pt or to Pt atoms which have changed their charge state. Further information may be deduced from the data shown in fig. 5. This figure displays series of CO desorption spectra as a function of Pt coverage. In each case the first desorption spectrum is compared with the second one from the same layer. The high temperature CO desorption signals in the second spectra are weaker than in the first spectra. This may be explained as to be due to migration of Pt

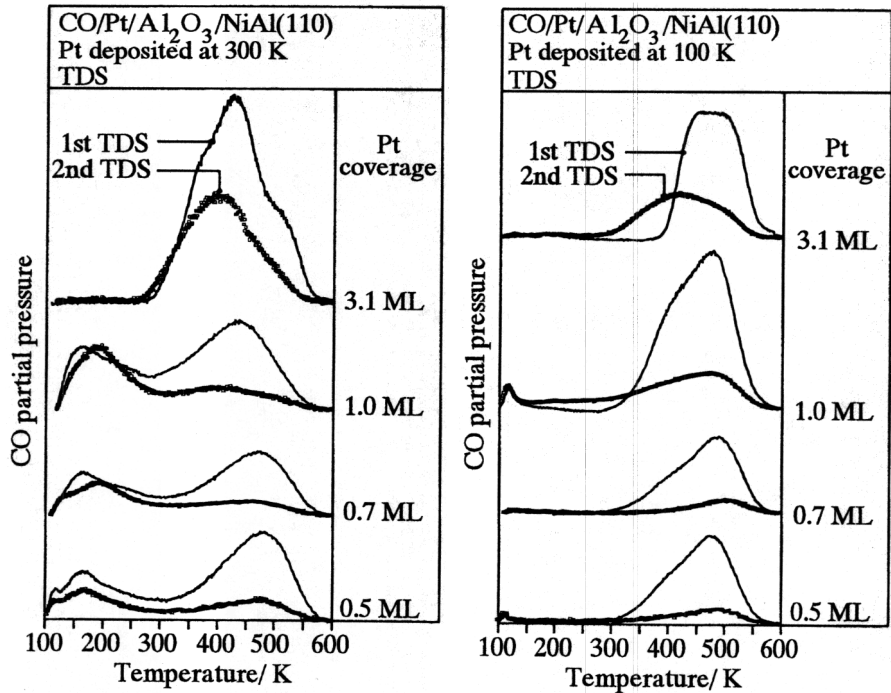


Fig. 5: Series of TDS spectra of CO on Pt/ $\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$ for Pt deposition temperatures of $T \approx 100$ K (left panel) and $T \approx 300$ K (right panel). In each case the first desorption spectrum is compared with the second one.

into the oxide layer or through the oxide layer into the NiAl compound during the heating process needed to record the first spectrum. A comparison of the data in the two panels reveals that the intensities of the desorption peaks at $T \approx 150$ K are not much different for the first and the second desorption spectra. This indicates that the number of adsorption sites leading to this peak is not considerably influenced by the annealing process. In particular, these sites can not be generated by heating a layer which has been deposited at $T \approx 100$ K to $T \approx 700$ K as concluded from the data shown in the right panel of fig. 5.

When CO is adsorbed on Pt which was deposited at $T \approx 300$ K, decomposition of part of the carbon monoxide occurs. This is illustrated in fig. 6. The spectrum at the bottom displays the C1s level of CO adsorbed at $T \approx 120$ K on 0.8 ML Pt/Al₂O₃(111)/NiAl(110) prepared at room temperature. The second spectrum displays the C1s level after annealing at $T \approx 800$ K. Since CO is desorbed at this temperature, the remaining signal must be due to the C1s level of carbon generated by CO dissociation. A comparison with the spectrum at the bottom shows that most of the CO is already dissociated at room temperature. The situation is different when the Pt is deposited at $T \approx 120$ K. In this case most of the CO remains in its molecular form as indicated by a comparison with the spectrum of the C1s level of CO on a thick Pt film (top) which offers preferentially Pt(111) sites. As discussed in the previous paragraphs, CO desorption from Pt which was deposited at room temperature leads to a desorption signal at $T \approx 150$ K. This signal is not observed when the Pt film is prepared at $T \approx 100$ K. One might speculate that there is a connection between the dissociation of CO and the adsorption site which leads to CO desorption at $T \approx 150$ K.

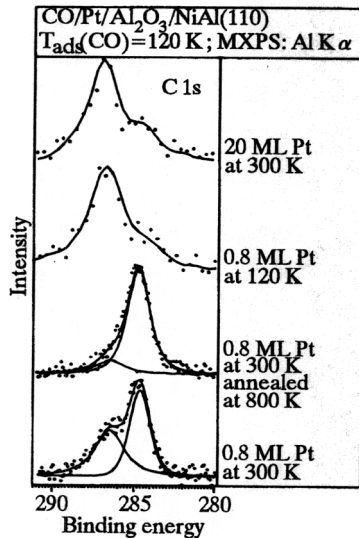


Fig. 6: C1s-XPS spectra of CO/Pt/Al₂O₃(111)/NiAl(110) taken under different conditions

4. Summary

In this paper we have shown that platinum on $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$ represents a system with interesting properties. Pt interacts strongly with the oxide film, thereby destroying the long range order within the film. The Pt/ Al_2O_3 system exhibits an unusual adsorption behaviour with respect to CO when Pt is deposited at room temperature. Besides bonding of CO to metallic Pt, also a bonding state, which leads to desorption at $T \approx 150$ K, is observed. Also, dissociation of CO takes place, in contrast to nondissociative CO adsorption on bulk Pt. These properties and the good applicability of electron spectroscopy at all temperatures make the Pt/ $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ a promising model system for a catalyst. Further studies, including the interaction of NO and CO on this system will be performed in near future.

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG), the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie.

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