Structural characterization of a model catalyst: Pt/Al₂O₃/NiAl(110)

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Abstract

By using STM, LEED and ISS we have studied the condensation of Pt on clean NiAl(110) and on a thin ordered Al₂O₃ film grown on NiAl(110). On Al₂O₃/NiAl(110) and up to a coverage of one monolayer Pt forms highly dispersed two-dimensional islands with an average diameter of 10–30 Å whose density increases with the coverage. For higher Pt coverage the formation of three-dimensional Pt clusters is observed. Annealing of the Pt-covered surface leads to a diffusion of Pt into the oxide film. On clean NiAl(110) and up to one monolayer we found two-dimensional growth of Pt the density of the islands remaining approximately constant.

Keywords: Aluminum oxide; Clusters; Growth; Low index single crystal surfaces; Nickel; Platinum; Scanning tunneling microscopy; Surface structure, morphology, roughness, and topography

1. Introduction

Dispersed metals supported by oxide surfaces are of great importance in heterogeneous catalysis. In order to provide a better understanding of the catalytic properties of such metal/oxide surfaces well defined model systems have to be prepared and investigated.

Recent work characterizing the electronic and geometric structure of a thin Al₂O₃ film grown on a NiAl(110) substrate [1] has shown that this oxide film may be used as a model support for metal/support catalysts. The oxide film has a thickness of only 5 Å, corresponding to two layers of Al and O atoms.

It combines the advantage of non-charging during electron spectroscopy measurements with a high degree of order which is important for the use of structure sensitive methods like low-energy electron diffraction (LEED), atomic force microscopy (AFM) or scanning tunneling microscopy (STM). After studying the adsorption behavior of the clean Al₂O₃ film [2] the next step on the way to a model catalyst is the deposition of metals on this surface. First high resolution electron energy loss spectroscopy (HREELS), angle-resolved photoelectron spectroscopy (ARUPS), X-ray photoelectron spectroscopy (XPS), spot profile analysis (SPA)-LEED and thermal desorption spectroscopy (TDS) results [3,4] of Pt deposition on Al₂O₃/NiAl(110) indicate the formation of small (20 Å diameter) highly dispersed Pt clusters in the submonolayer range. It was

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concluded from SPA-LEED measurements that heating of the surface should lead to the growth of distorted parts on the oxide film, until at 800 K the undistorted oxide structure reappears.

The aim of the present experiments using STM, ISS and LEED is to give more insight into the growth of Pt on the Al₂O₃ film and its behavior in annealing cycles. For comparison and to clarify some experimental problems due to imaging of thin oxide films in STM, Pt has been deposited on clean NiAl(110) as well. The latter results will be summarized briefly.

2. Experimental

The experiments have been performed in an UHV system equipped with STM, ISS, AES and LEED (for details see Ref. [5]). In situ preparation of the NiAl(110) surface consisted of sputtering (Ar⁺, 500 eV) and heating (1200 K) by electron bombardment, until the LEED pattern showed a sharp 1 × 1 structure and ISS and AES indicated a clean surface. The oxide film was prepared as reported in the literature [1]. Dosing the NiAl crystal with 1200 L O₂ at elevated temperature (550 K) and annealing to 1150 K leads to the formation of a well ordered Al₂O₃ film as demonstrated by a sharp LEED pattern displaying the oxide superstructure. Pt was evaporated from a filament with a deposition rate of around 0.3 monolayers (ML) per min. We studied Pt coverage in the range of 0.1–6 ML on the oxidized surface and 0.1–1 ML on the clean NiAl(110) surface. The deposition rate was calibrated by analyzing STM measurements of Pt/NiAl(110) surface. For the STM measurements constant current topographies (CCT) have been recorded.

3. Results

3.1. Pt / NiAl(110)

Because Pt is miscible in NiAl under the conditions used during the sample preparation the step/terrace structure and the atomic arrangement of the clean NiAl(110) surface was controlled before each experiment by means of STM and LEED.

3.2. Pt / Al₂O₃ / NiAl(110)

Concerning the interpretation of the measured CCTs from Pt/Al₂O₃/NiAl(110) one has to consider the voltage dependence of imaging the oxide
film by STM. As reported previously [6], only for sample bias voltages $U \geq 4$ V the electronic contributions of the oxide film leads to a height change of the tip upon scanning of an oxidized part of the surface. For gap voltages $U \leq 4$ V no significant height change is visible. Due to this effect a
voltage-dependent shape of the Pt islands is expected and actually found in the measurements.

Figs. 2a and 2b show the same part of the surface using different sample bias voltages (three identical features are marked by A, B and C). In Fig. 2a which was acquired with \( U = 4 \, \text{V} \) the measured height of the clusters is typically \( 1.7 \, \text{Å} \), whereas the height of the clusters in Fig. 2b obtained with \( U = 2 \, \text{V} \) is about \( 5 \, \text{Å} \). In addition, the Pt coverage seems to have increased with decreasing voltage. This can be explained by the voltage dependence of the CCTs of the oxide film. In Fig. 2a the oxide film is discernible as a weak structure of lines. The tip essentially measures the height difference between oxide and Pt islands while scanning over the surface. In Fig. 2b the tunneling current is mainly provided by the electrons of the NiAl substrate. Therefore, the tip measures the height difference between the NiAl substrate and the surface of the Pt islands. Under these conditions the broadening of the islands is the result of a blunt tip. For a flat tip (diameter of the apex larger than the height of cluster plus oxide) the parts of the tip away from the apex contribute significantly to the tunneling current and lead to the apparent enlargement of the Pt islands. As a result, only the measurements taken with \( U \geq 4 \, \text{V} \) provide a reasonable impression of the Pt coverage of the oxidized NiAl(110) surface.

In Fig. 3 the oxidized NiAl(110) surface after deposition of 0.1 ML Pt is displayed. The oxide film is visible as a line structure which is formed by a hexagonal arrangement of protrusions in a distance of nearly \( 10 \, \text{Å} \). In this coverage range, Pt deposition leads to the formation of small highly dispersed clusters similar to those observed on the clean NiAl(110) surface. The measured height of the Pt clusters is between \( 1.5 \, \text{Å} \) for the small and \( 4 \, \text{Å} \) for the larger ones. Their diameter is about \( 10-30 \, \text{Å} \). Considering the electronic effects as discussed above, it is estimated that the monatomic islands contain 20–50 atoms. In comparison to a previous STM study of Ag/Al\(_2\)O\(_3\)/NiAl(110) [7] where Ag clusters were only found on step edges, the random distribution of Pt indicates the presence of a stronger interaction between Pt and the oxide film and a smaller diffusion length. Another interesting point is the fact that neither in measurements with negative (Fig. 3) nor with positive (Fig. 2a) sample bias voltage a distortion of the oxide structure in the vicinity of the islands can be observed, whereas the SPA-LEED results have led to the conclusion that the oxide structure is distorted by Pt. More specifically, a surprisingly small amount of Pt leads to a marked weakening of the oxide LEED spots whereas in STM the characteristic line pattern of the oxide is apparently not changed. One possible reason for this discrepancy could be that the influence of Pt on the electronic structure of the Al\(_2\)O\(_3\) film as probed by STM (essentially the surface layer) and LEED (extending somewhat into the bulk) is different.

The behavior of the Pt-covered Al\(_2\)O\(_3\)/NiAl(110) surface after annealing cycles is demonstrated in the ISS spectra (Fig. 4). Annealing Pt/Al\(_2\)O\(_3\)/NiAl(110) to higher temperatures (up to 800 K) leads to a drastic decrease of the observed Pt peak. This means that the area of the Pt covered parts of the surface must be reduced. Since the temperatures are too low for desorption of Pt [8], one has to consider two alternative explanations for this effect. (a) The cluster size could increase or (b) Pt diffuses into the oxide (or through the oxide into the bulk). STM measurements of the heated surface (not shown here) provide no evidence for the formation of large Pt clusters. Instead, a decrease of the Pt coverage and a reappearing of the oxide structure is found. At 800 K
a nearly clean Al₂O₃ film is visible again. This observation indicates a diffusion of Pt into or through the oxide. Although the final state of the heating process is in agreement with the SPA-LEED results, the discrepancy remains that STM does not show a change of the oxide structure during annealing.

In summary, we have described the general growth mode of Pt on a clean and an oxidized NiAl(110) surface. For coverage up to 1 ML on both substrates a two-dimensional growth of the Pt deposit was found. On the oxidized surface small Pt clusters are observed in the entire range, whereas on clean NiAl(110) Pt tends to the form larger islands with increasing coverage. Pt deposition of more than 1 ML on the oxide film leads to the formation of three-dimensional islands.

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