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On the thermal stability of metal particles supported on a thin alumina film

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Abstract

The structure of metal (Co, Rh, Pd) particles deposited on a thin alumina film grown on a NiAl(110) substrate were studied as a function of annealing temperature. The results reveal at least three processes to occur upon heating: (a) rearrangement of metal atoms on the particle surface, (b) sintering of the particles, and (c) metal migration into the substrate. The latter process is probably mediated by the defect structure of the oxide film and dominates at higher temperatures. The thermal stability is found to be better for Co, which strongly interacts with the alumina support, as compared to Pd and Rh. Hydroxylation of the alumina film increases Pd and Rh dispersion and shifts processes (b) and (c) to higher temperatures, likely due to a stronger interaction of the metals with the hydroxylated film. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal particles deposited on thin oxide films represent suitable systems for modeling highly dispersed metal catalysts supported on oxides [1– 5]. Previously, we have studied the structure and adsorption properties of various metals deposited on a well-ordered thin alumina film grown on a NiAl(110) substrate aiming at a systematic investigation of structure–activity relationships in catalysis [1,5–7, and references therein]. It has been found that, in many cases, the adsorption on metal particles is governed by their morphology. For example, saturated CO adsorption on small and rough Pd particles leads to a larger fraction of terminally bonded CO while annealed and faceted particles preferentially adsorb CO in highly coordinated (e.g. three-fold hollow) sites [5,8,9].

In principle, the structure of the model system may change upon heating due to a number of processes such as particle surface re-structuring (e.g. faceting) and particle sintering, i.e., growth of larger particles at the expense of smaller ones (see e.g. the review of Gunter et al. [10] and ref. therein). In the case of thin oxide films, metal migration into

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the substrate has to be considered as well [1,11]. Therefore, the thermal stability of the model catalysts becomes an important issue setting a limit to experiments at elevated temperatures.

In the present paper, we report on a comparative study regarding the thermal stability of metal (Co, Rh, Pd) particles deposited on a thin alumina film. The structure of the metal deposits was studied by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED).

2. Experimental

Most of the experiments were performed in an UHV chamber (base pressure below 10^{-10} mbar) equipped with an STM instrument (Omicron), XPS facilities and a LEED optics. LEED intensity data were taken with a spot profile analysis LEED optics (Leybold Heraeus) in another UHV chamber. In order to combine the data obtained in the two chambers, identical preparation recipes were used.

The preparation of the thin alumina film involved two cycles of oxidation of the clean NiAl-(110) surface in 10^{-6} mbar of oxygen at 550 K for 20 min followed by annealing in vacuum at 1140 K for 3–5 min. Pd, Rh, and Co (99.99%, Goodfellow) were deposited on the alumina film with commercial evaporators (Focus, EFM3). Note that, with this kind of evaporators, the sample must be biased with a retarding potential in order to prevent metal ions from being accelerated towards the sample and creating nucleation centers on the surface. The deposition rates were about 0.7 Å min⁻¹ as calibrated with a quartz microbalance. The pressure during metal deposition never exceeded 5×10^{-10} mbar.

The STM images presented in this paper were obtained at room temperature at tunneling voltages of \approx 3.5 V applied to the sample and a current of \approx 0.5 nA.

3. Results and discussion

3.1. Temperature induced processes for Pd, Co and Rh deposits

The nucleation and growth of metal particles on the $Al_2O_3/NiAl(110)$ surface has already been

discussed in previous reviews [1,5]. When deposited at low temperatures (\sim 90 K), the particles are randomly distributed on the support due to nucleation at point defects of the film. At room temperature, on the other hand, Pd and Rh particles are mostly found at domain boundaries and steps of the alumina substrate, whereas Co (as well as Ir, V, and Pt) particles still cover the oxide surface homogeneously. The temperature dependence of the particle nucleation (and growth) can be understood in terms of the different mobility of the metal atoms on the surface. In contrast to Co which is trapped at point defects also at room temperature, Pd and Rh can escape from them under these conditions and reach the line defects, where they are hold more strongly. Taking the preferential nucleation site (point defects vs. line defects) as an indicator of the metal/oxide interaction, it was concluded that the strength of interaction increases in the following direction: Pd < Rh < Co [1].

In order to study the effect of annealing on the morphology of the metal deposits, we have recorded STM images at room temperature after heating the sample to a specified temperature. Fig. 1 shows a series of STM images taken for a Pd overlayer of nominal thickness 0.2 Å deposited at 90 K and then heated to room temperature (a) and to 500-900 K in steps of 100 K (b-f). Upon heating to 500 K, no changes are observed. The particle density starts to decrease when heating to 600–700 K due to preferential disappearance of the smallest particles. Also, the protruding lines corresponding to domain boundaries become more visible (Fig. 1(d)). The particle density further decreases upon heating to 800 K (Fig. 1(e)), but most of the remaining particles appear to be larger. This indicates that sintering of the particles occurs at elevated temperatures. Finally, upon annealing to 900 K, the particles have almost completely vanished, and the surface looks similar to the bare alumina. Note that these temperature induced changes observed for Pd are similar to those we have previously reported for Rh deposits [1].

For Co deposited at 300 K (0.1 Å), a corresponding series of STM images is shown in Fig. 2. After heating to 570 K, only minor changes can be detected by comparing images (a) and (b) in Fig. 2.



Fig. 1. Room temperature STM images of Pd particles deposited on an Al₂O₃/NiAl(110) at 90 K (a), and annealed in vacuum to 500 (b), 600 (c), 700 (d), 800 (e) and 900 K (f), respectively (size: $100 \times 100 \text{ nm}^2$, Pd nominal thickness is 0.2 Å). The image (f) is presented with a differentiated contrast in order to highlight the line defects.

The particles become slightly larger and the particle density slightly decreases. Annealing to 770 K (c) leads to a markedly smaller particle density. In particular, the domain boundaries (weakly protruding lines) and their vicinity seem to be affected by this effect as demonstrated by the large area scan in Fig. 2(c'). Upon heating to 870 K, many particles have disappeared while a few large particles have gained size due to further sintering processes as shown in Fig. 2(d).

Fig. 3 summarizes the data for the particle densities as a function of annealing temperature for Co, Rh and Pd. In all cases, the density starts to decrease at temperatures above 500 K. One can explain this fact by particle sintering at elevated temperatures. However, the total amount of metal



Fig. 2. STM images of Co particles deposited on an alumina film at 300 K (a) and subsequently annealed in vacuum to 570 (b), 770 (c) and 870 K (d), respectively (nominal thickness: 0.1 Å, image size: $100 \times 100 \text{ nm}^2$). The image (c') shows a large area scan (300 × 300 nm²) with inverted contrast enhancing the visibility of the domain boundaries of the support. The pinhole-like features formed on the sample (d) are shown in the inset (size $10 \times 10 \text{ nm}^2$).



Fig. 3. Particle density as a function of annealing temperature for Rh (nominal thickness is 0.05 Å, deposition at 90 K), Pd (0.2 Å, 90 K) and Co (0.1 Å, 300 K) deposits, normalized with respect to the particle density at 300 K.

on the surface strongly decreases upon annealing, too. Moreover, at the highest temperatures studied no particles are observed anymore (cf. (a) and (f) in Fig. 1). Since metals are not desorbing at these temperatures, their migration into the oxide film must be invoked.

This conclusion is also supported by a LEED study performed in order to detect changes in the structure of oxide film caused by annealing of metal deposits. The LEED pattern for $Al_2O_3/NiAl(110)$ is very complex and includes many spots resulting from the specific long range order of the alumina thin film with respect to the metal substrate underneath, as described in detail in Refs. [1,12]. Subsequent metal deposition leads to a simultaneous attenuation of all diffraction spots and increasing background intensity.

Fig. 4 shows the intensity of a selected spot (in fact, all spots behave similarly) as a function of annealing temperature for Pd and Rh particles deposited at 90 K. Starting at 400 K, the diffraction spots are gradually attenuated. Upon heating to 700 K, the LEED pattern has nearly vanished. Obviously, such a behavior cannot be attributed to sintering processes. In this case, the opposite has to be expected, i.e., increasing intensity of the substrate spots since the uncovered fraction of the surface increases due to particle sintering. There-



Fig. 4. Damping of the LEED pattern of the alumina film as a function of annealing temperature (flash to the respective temperatures) in case of Pd (2 Å) and Rh (0.5 Å) overlayers deposited at 90 K. The intensity for the metal-free alumina surface is set to 1. The measurements were performed at 90 K.

fore, we can attribute the perturbation of the longrange order of the alumina film to particle migration into the support upon heating. The question arises how and where this process takes place on the surface.

The STM data presented in Figs. 1 and 2 suggest that, on annealing, particles first disappear near the line defects. Meanwhile, the largest particles are mostly located between the domain boundaries, i.e. on the regular oxide surface. Since sintering processes at elevated temperatures proceed via metal ad-atom diffusion, the diffusing atoms may either stick to a bigger particle or be captured at the line defects, through which they can migrate into the substrate. In other words, it is conceivable that the domain boundaries act as migration channels for the metal atoms. In such a case, particles, which are closer to the line defects, are expected to vanish first, as actually observed in Fig. 2(c').

In the case of Pd (see Fig. 1) and Rh [1], where the surface mobility is relatively high, the temperature induced changes occur earlier than for Co. Note that for Co the interaction with the support is stronger. This may lead to sintering and migration processes proceeding more slowly as compared to Pd and Rh (see Fig. 3). Interestingly, for Co deposits only, STM images reveal numerous surface features, which appear as dark "pinholes" on the surface annealed to 870 K. They are presented with a higher contrast in the inset of Fig. 2(d). Since these features have never been observed on the metal-free surfaces, they are probably created by particles "dissolving" into the support on the spot.

Thus, based on our STM and LEED results, we conclude that metals supported on the thin alumina film may undergo two processes at temperatures above 500 K: (a) particle sintering and (b) migration into the metallic substrate. Both processes seem to occur simultaneously upon heating. It is therefore difficult to discriminate the temperature intervals of each of them.

Apart from these two effects, re-structuring of the particles themselves has to be considered as another process taking place upon annealing. Especially particles deposited at low temperatures exhibiting rough surfaces may be subject to thermally induced ordering. Although such changes could not be followed by STM due to the lack of atomic resolution on these systems, they have been observed in IRAS and XPS studies of CO adsorption on Rh deposits [5].

In this context, our recent TPD study [7] of ethene adsorption on Pd/alumina has to be mentioned as well which revealed strong differences between TPD spectra taken for samples freshly prepared at 90 K and samples pre-heated in vacuum to ~400 K. Again, this effect has been interpreted in terms of surface smoothing upon heating leading to a decreasing number of low coordinated Pd atoms which adsorb ethene molecules in a π geometry (in other words, in on-top sites).

3.2. Effect of support hydroxylation

The pristine alumina film studied above exhibits an oxygen terminated surface, while technical alumina supports are largely covered by hydroxyl groups, which in turn may influence the structure of metal particles and their catalytic performance. Therefore, we have recently initiated studies of metals deposited on hydroxylated alumina films [13,14]. Hydroxylation was achieved by evaporation of sub-monolayer coverages of Al at 300 K



Fig. 5. STM images obtained for Pd particles (nominal thickness: 0.2 Å) deposited at 300 K on a pristine (a) and a hydroxylated (b) alumina film. For sample (b), the preparation involved deposition of 0.2 Å Al at 300 K on the pristine film followed by exposure to 20 L water at 90 K and subsequent heating to 300 K. Diagram (c) shows the particle density as a function of annealing temperature obtained for sample (b) and a sample prepared at 90 K on pristine film (see Fig. 1). Both samples contain the same amount of Pd and exhibit similar dispersions.

followed by saturation exposures of water at 90 K and subsequent heating to 300 K in order to dissociate water. Formation of hydroxyl groups on the surface was confirmed by XPS, IRAS and HREELS [13,14].

It was found that hydroxylation of the oxide film alters the dispersion of Rh particles [14]. In the present paper, we have extended these studies to Pd in order to investigate effects of hydroxylation on the thermal stability of Pd aggregates.

Fig. 5 shows two STM images obtained for Pd (nominal thickness: 0.2 Å) deposited at 300 K on the pristine (a) and the hydroxylated (b) alumina film. The image (a) shows relatively large particles nucleating at the line defects of the pristine film, while the image (b) reveals smaller particles, which homogeneously cover the surface of the hydroxylated film. Again, as in the case of Rh [14], the hydroxylation strongly increases the Pd dispersion. This means that hydroxyl groups result in a stronger metal-support interaction probably involving charge transfer processes [13]. As a result, the Pd diffusivity during nucleation and particle growth on the hydroxylated surface is rather limited as compared to the pristine film.

The diagram (c) in Fig. 5 shows that, upon annealing, the particle density observed for the hydroxylated film starts to decrease at a higher temperature than for the pristine film. The difference of about 100 K between threshold temperatures clearly indicates a higher thermal stability of the Pd particles deposited on the hydroxylated film. It is noteworthy that the positive temperature shift in the density vs. temperature relationship shown in Fig. 5 is very similar to what we have observed above for Co as compared to Pd and Rh on the pristine film (see Fig. 3). This finding strongly indicates that an increasing metal/oxide interaction leads to a higher thermal stability of the metal deposits. A similar conclusion was recently drawn in a study of Cu and V deposits on a thin alumina film grown on $Ni_3Al(111)$ [15].

4. Summary

For different metals (Pd, Rh, Co) deposited on a thin alumina film no apparent changes are observed in the particle size and density upon heating to \sim 500 K. However, surface re-structuring (smoothing) of the metal particles occurs if they have been deposited at low temperatures.

Annealing to 500–900 K results in a strong decrease of the particle density due to particle sintering. In addition, a gradual loss of the support long-range order is observed. This effect is attributed to metal migration into the support. The latter process is probably mediated by the defect structure of the film and plays a dominant role at elevated temperatures.

Hydroxylation of the alumina film strongly increases the metal dispersion and leads to a higher thermal stability due to inhibition of sintering and migration processes.

At this point, it is worthwhile to compare the thermal stability of the model systems and real catalysts supported on bulk alumina. Sintering of metal particles is a well-documented phenomenon for catalysts. Actually, it depends on several parameters such as the metal loading, gas environment, and metal-support interaction (e.g., see [16]). However, the temperatures at which sintering becomes important for technical catalysts is typically much higher than for our model systems. In principle, such a big difference can be explained by the inter-particle distances on our planar systems being much smaller and the alumina film surface being smooth as compared to powdered catalysts. Both factors facilitate sintering.

However, metal migration into the support is usually not an issue for technical catalysts, whereas it is very important for the thin oxide films at higher temperatures. It appears that the thermal stability of the system metal/Al₂O₃/NiAl(110) is limited by the small thickness of the alumina film, which is about 5 Å [1,12]. Probably, the defect structure of the thin oxide layer provides some kind of "channels" for metal migration into the substrate, as was also observed for other thin film systems [17,18]. In the case of thicker films, migration into the support seems to be less important; here, sintering was reported to prevail [19–21].

In this context, it is worth noting that an oxygen treatment over deposited metals, which are able to dissociate oxygen, significantly increases the thickness of the alumina film grown on NiAl-(110) and does not affect the adsorption/desorption properties of the subsequently reduced metal (Pd, Rh) particles [22]. The thermal stability of these systems especially with respect to metal migration into the oxide is probably much higher. Corresponding studies are currently under way.

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