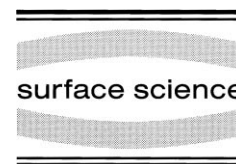




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Oxide-supported Rh particle structure probed with carbon monoxide

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Abstract

Rh deposits in a wide range of metal exposures have been grown on a thin, well-ordered alumina film under ultra-high vacuum conditions. Their morphologies range from individual Rh particles with sizes below ten atoms to closed metal films, as determined by scanning tunneling microscopy (STM). CO chemisorption on these deposits has been studied by infrared reflection absorption spectroscopy (IRAS) and X-ray photoelectron spectroscopy (XPS). At low metal coverages, the formation of isolated Rh carbonyl species associated with surface defects is observed. Changes in the infrared spectra of CO adsorbed on annealed Rh aggregates are attributed to a thermally induced ordering of the Rh particle surface on a local scale, leading to a reduction in the number of low coordinated metal atoms. This is accompanied by a marked decrease of the CO chemisorption capacity. Adsorbed CO reduces the extent of this ordering process, while the adlayer itself reorganizes. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum oxide; Carbon monoxide; Chemisorption; Clusters; Infrared absorption spectroscopy; Rhodium; Surface defects; Vibrations of adsorbed molecules

1. Introduction

The chemisorption properties of small metal particles on high-area oxide supports have been the subject of many studies in the past [1]. A prominent example is given by technical Rh/Al₂O₃ catalysts. Besides CO adsorption on the Rh particles in various sites, a disruption of small particles resulting in the formation of isolated Rh^I(CO)₂ species is observed [2,3]. Surface hydroxyl groups are believed to be responsible for the oxidation of the Rh [4].

Better control over the particle morphology and the nature of the oxide support can be obtained

by employing surface science techniques on flat, single-crystalline or thin-film oxide surfaces [5–8]. For example, it was found that rhodium gem-dicarbonyl species may also be formed on hydroxyl-free TiO₂(110) surfaces, presumably via stabilization of the dispersed Rh by oxygen vacancies [9,10].

In this work, we relate infrared and photoelectron spectroscopic data of CO adsorbed on alumina-supported Rh aggregates with information on their morphology obtained from STM. Focusing on thermally induced changes in these spectra, we shall see that CO constitutes a suitable probe molecule to detect changes in Rh–Rh coordination at the surface of the metal aggregates. Infrared data of CO adsorbed on Pd aggregates have been published elsewhere [11].

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2. Experimental

Experiments were performed in a multi-chamber ultra-high vacuum (UHV) system with a base pressure below 2×10^{-10} mbar. The NiAl(110) crystal was mounted on a sample carrier, which could be transferred between the various experimental stages. The crystal temperature was monitored by a NiCr/Ni thermocouple spot-welded to the sample.

STM images were taken with an Omicron variable-temperature STM operated at room temperature. Infrared spectra were acquired with a Bruker IFS 66v/S vacuum infrared spectrometer. A liquid-nitrogen-cooled MCT detector was used to detect the p-polarized light reflected from the sample surface at a grazing incidence of 84° . The instrumental resolution was set to 2 cm^{-1} (lowest Rh exposure: 4 cm^{-1}). Typically, 1024 scans were accumulated.

X-ray photoelectron spectra were recorded with a hemispherical electron energy analyser (Scienta) using non-monochromatized $\text{MgK}\alpha$ radiation. The XPS binding energies are referred to the Fermi level of the NiAl substrate.

The alumina film was prepared via oxidation of the NiAl(110) single crystal surface [12] and its quality checked by STM as well as via its phonon bands in the infrared spectrum.

Rh metal (ChemPur, >99.9%) was evaporated from a rod via electron bombardment. During evaporation, the sample was put on a retarding potential to avoid any effects due to Rh ions accelerated towards the sample. The metal flux, as calibrated with a quartz crystal microbalance, varied between 0.11 and 0.45 monolayers (ML) min^{-1} (1 ML Rh corresponds to 1.60×10^{15} atoms cm^{-2}). Each deposit and its adsorption properties were characterized by IRAS, XPS and STM.

3. Results and discussion

3.1. Particle morphology

A thin, well-ordered alumina film on a NiAl(110) single crystal [12] is used as a substrate for Rh deposits grown under UHV conditions at

a sample temperature of 90 K. Long-range ordered domains of the oxide film are separated from one another by a network of rotational and antiphase domain boundaries [13]. As shown in a previous study, these defects serve as nucleation sites for room-temperature Rh growth, whereas at 90 K, islands also nucleate within the domains [14].

In Fig. 1, STM images illustrating the growth process are presented. Clearly, a three-dimensional growth mode is found. At metal coverages below about 0.1 ML, nucleation of individual particles is observed (Fig. 1a). Upon further metal deposition, they grow in size (Fig. 1b) and finally coalesce until a corrugated metal film is formed (Fig. 1c). No indication of particles exposing extended close-packed facets has been found [14]. It must be taken into account that the observed STM image results from a convolution of the surface geometry with the tip shape [15]. Therefore, at sufficiently large metal coverages, small aggregates located close to larger aggregates are not imaged by the microscope. In this coverage regime (≥ 1 ML), we believe that SPA-LEED yields more reliable results [14], although the island density might be overestimated at the onset of coalescence. From the island density and the number of Rh atoms deposited, the average number of atoms per particle can be calculated. We find that the metal coverages employed in our study (≥ 0.024 ML) correspond to particle sizes from eight Rh atoms upwards. The island shapes, as observed by STM, appear to be unchanged by CO adsorption at room temperature [16].

It should be noted that the STM images shown in Fig. 1 were taken after the CO adsorption studies presented below and subsequent annealing to 600 K. In earlier STM and SPA-LEED investigations, however, we found a high thermal stability of the Rh particles in this temperature range [16,17]. Our observation of mean particle sizes of eight atoms (Fig. 1a) after this treatment confirms the stability of very small aggregates. Therefore, the average particle size at 90 K may be overestimated by this procedure only for the lowest Rh exposures.

3.2. Infrared studies

After metal deposition, CO was dosed at a sample temperature of 90 K until saturation was

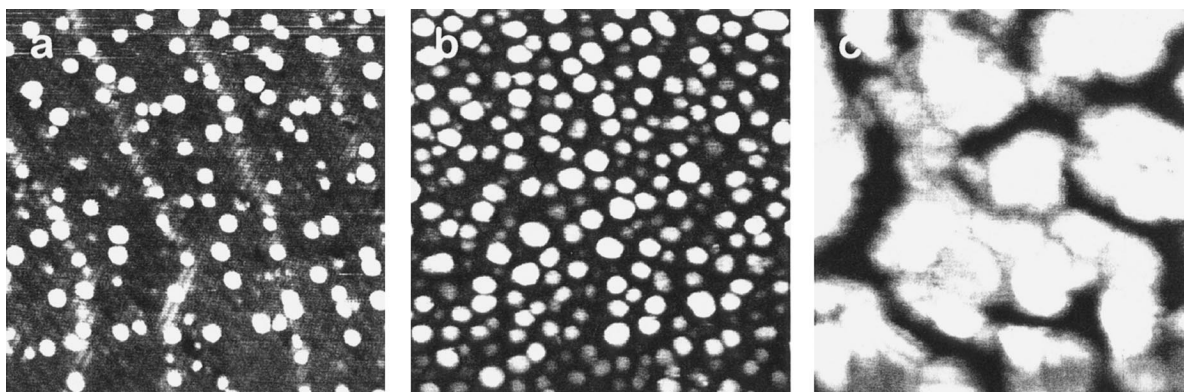


Fig. 1. STM images ($500 \times 500 \text{ \AA}^2$) of Rh deposits prepared at 90 K: (a) 0.024 ML, 8 atoms per particle, (b) 0.91 ML, 100 atoms per particle, (c) 18.2 ML, Rh film. The line protrusions in (a) are antiphase domain boundaries of the oxide film. The images are constant current topographies ($U_{\text{tip}} = 3.7\text{--}4.6 \text{ V}$, $I = 0.05\text{--}0.085 \text{ nA}$).

reached. In Fig. 2, a series of infrared spectra of the CO stretching region recorded at 90 K is displayed for a wide range of average Rh particle sizes. Most of the intensity is found in the frequency regime above approximately 1950 cm^{-1} ,

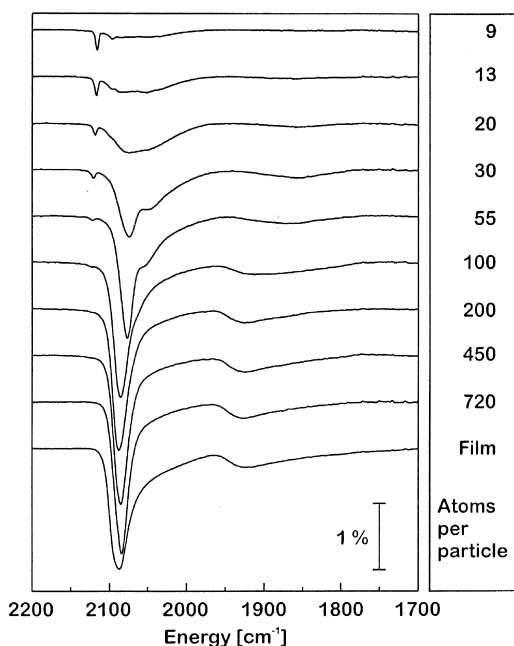


Fig. 2. Series of infrared spectra taken after deposition of different amounts of Rh and subsequent CO saturation at 90 K. The average number of Rh atoms per particle is given next to the spectra. The spectral resolution after apodization is 3.3 cm^{-1} in all cases.

which we assign to terminally bound CO molecules, whereas the broad signal between 1950 and 1770 cm^{-1} is assigned to CO in bridge or threefold-hollow sites. Here, we would like to focus on the on-top bands and their heating-induced changes.

Going from a thin Rh film to individual particles consisting of only nine atoms on average, the shape of the on-top absorption changes dramatically (Fig. 2). First, a narrow band centred at about 2080 cm^{-1} is observed. At particle sizes below 100 atoms, a low-frequency shoulder grows, whereas on the high-frequency side, a sharp band at about 2120 cm^{-1} gains intensity as the particle size decreases. Finally, the latter signal dominates the spectrum, accompanied by a broad, structured band due to terminally bound CO.

First, we focus on the signal at $\sim 2120 \text{ cm}^{-1}$. Its low halfwidth of less than 4 cm^{-1} and the absence of a frequency shift with increasing CO coverage (not shown here) point to the presence of uniform, isolated surface species. The observed frequency is similar to the frequency of the symmetric stretch of isolated rhodium gem-dicarbonyl species on technical Rh/ Al_2O_3 catalysts ($\sim 2100 \text{ cm}^{-1}$) [3,4] and on a $\text{TiO}_2(110)$ single crystal surface ($\sim 2110 \text{ cm}^{-1}$) [9,10]. A band at $\sim 2125 \text{ cm}^{-1}$ observed on oxidized Rh/ Al_2O_3 catalysts has been assigned to Rh^{2+}CO [18]. We note that the antisymmetric stretch of a gem-dicarbonyl species may not be observable on a thin oxide film on a metal support, since here the surface selection rule applies.

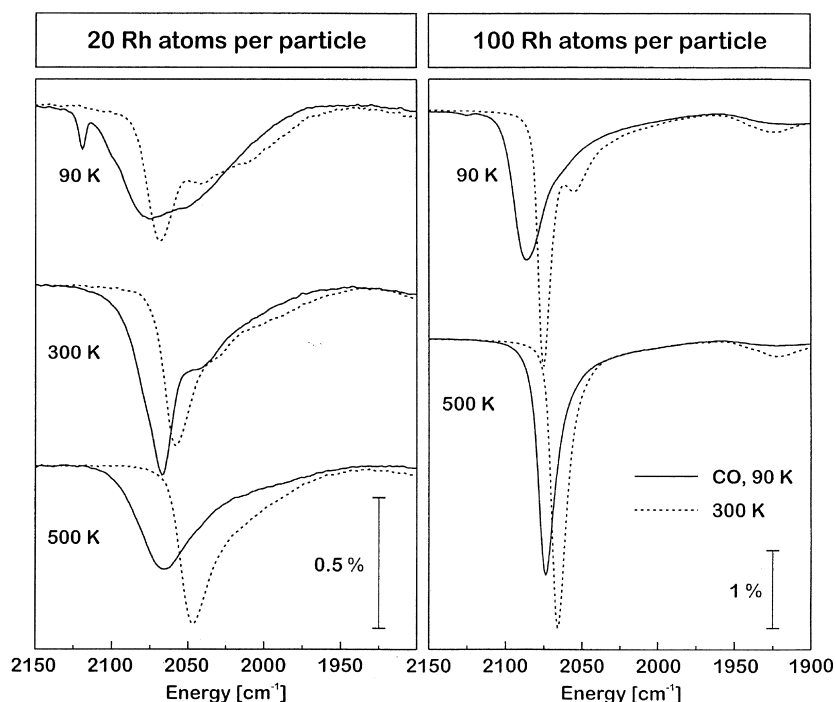


Fig. 3. Infrared spectra acquired at 90 K for two different particle sizes. Full lines: spectra taken after Rh growth at 90 K, annealing to the indicated temperatures and CO saturation at 90 K. Dashed lines: after subsequent heating to 300 K.

In order to reduce the diffusion coefficient of Rh adatoms during growth and thereby to decrease the average particle size further to less than five atoms, we have prepared a low-coverage (0.024 ML) metal deposit at a sample temperature of 55 K. In the complex infrared spectrum resulting from CO adsorption (not shown here), only a very weak band is observed at $\sim 2120\text{ cm}^{-1}$. This behaviour may be rationalized by assuming that this band arises from defect-bound Rh atoms saturated with CO, since at a sufficiently low temperature, the adatom diffusion length due to homogeneous nucleation becomes short, relative to the distances between oxide defects. This assignment is consistent with the decreasing signal intensity with increasing metal coverage in the Rh exposure range studied at 90 K (Fig. 2).

It is further supported by our observation of thermally induced changes in the infrared spectra (Fig. 3). Annealing the sample to 300 K either before or after CO dosage results in a complete suppression of the feature at $\sim 2120\text{ cm}^{-1}$.

Therefore, the band is likely to stem from particles weakly bound to oxide defects, which start diffusing between 90 and 300 K. Consequently, we propose that the infrared band near 2120 cm^{-1} is due to isolated rhodium mono- or dicarbonyl species located at oxide defects.

Photoelectron spectra of the C 1s region taken after CO saturation of freshly deposited and annealed metal aggregates at 90 K are shown in Fig. 4. A single signal at a binding energy typical for molecularly adsorbed CO can be observed. The higher binding energy in the case of the smaller Rh particles can be attributed to the positive charge left on the particles in the photoemission final state [8,19]. Heating a deposit of 20 atoms per particle to 300 K results in a shift of the C 1s emission to a lower binding energy and in a reduction of its halfwidth. Similar observations are made in the Rh 3d spectra, indicating a reordering or some loss of small islands via coalescence. More importantly, for both deposits, a markedly lower C 1s intensity, and hence a decrease in CO

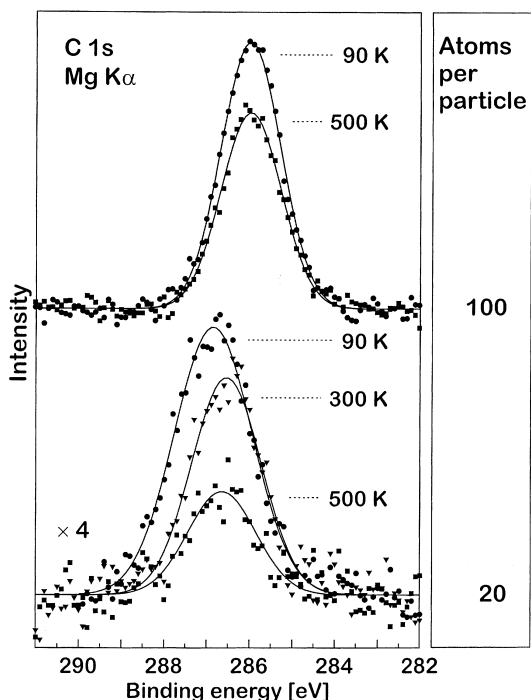


Fig. 4. C 1s photoelectron spectra taken at 90 K after Rh growth at 90 K, annealing to the indicated temperatures and CO saturation at 90 K for two different particle sizes. Measuring times were ~ 15 min (20 atoms) and ~ 8 min (100 atoms). A Shirley background was subtracted from the spectra.

chemisorption capacity, is observed after annealing.

In conjunction with this reduction in the number of CO adsorption sites, we find that (except for the 20-atom deposit annealed to 500 K) the intensity of the low-frequency shoulder of the main infrared band is reduced by the thermal treatment (Fig. 3, full lines). We attribute this to the loss of low coordinated metal atoms at the surface or edge of the Rh particles due to local ordering. This assignment is consistent with the observation that, for CO molecules bound to such defect sites on transition metals, an increased occupation of the antibonding CO 2π orbital leads to a reduction in vibrational stretching frequency as compared to terrace molecules [20]. The fractional intensity assigned to defect-bound molecules may be much smaller than the true population of such sites due to intensity borrowing caused by dipole coupling [20].

Upon annealing of the CO-saturated particles to 300 K, both the main band at ~ 2070 cm^{-1} and the features at a lower wavenumber become narrower, accompanied by a downshift in frequency (Fig. 3, dashed lines). This points to a reorganization of the adlayer, leading to reduced dipole interactions, although in the case of the smallest Rh aggregates some CO desorption taking place already at room temperature cannot be excluded [17]. A similar restructuring has been observed by high-resolution photoemission [21,22]. The IR spectra of annealed CO adsorbates also reflect the ordering of the Rh as discussed above. Here, even the 20-atom deposits indicate a further reduction of defect sites in going from 300 to 500 K, whereas the unexpected broad absorption of the latter deposit saturated with CO at 90 K is presently not understood. Judging from the shoulder intensities after annealing the CO-saturated particles, we find a much smaller defect density on the aggregates preannealed to 300 K than on the non-annealed particles. Thus, the adlayer reduces the extent of thermally induced local ordering of the metal particles.

4. Summary and conclusion

We have demonstrated the usefulness of a combination of chemical probes such as infrared spectroscopy and photoemission with structural tools like scanning tunneling microscopy for the characterization of complex model catalytic systems.

In particular, we have shown that CO constitutes a suitable molecule to probe the structure of alumina-supported Rh aggregates. An infrared band near 2120 cm^{-1} observed in the case of low metal exposures is due to a defect-bound Rh carbonyl surface species. By infrared spectroscopy, we have monitored a thermally induced ordering of the Rh particle surface on a local scale, leading to a reduction of the number of highly coordinatively unsaturated metal atoms. Concomitantly, the capacity of the Rh particles for CO chemisorption decreases. A CO adlayer present during annealing reduces the extent of the ordering process. A

restructuring of the adsorbed CO below 300 K has been observed.

Acknowledgements

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