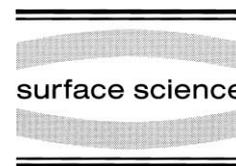




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Infrared study of CO adsorption on alumina supported palladium particles

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Abstract

We have studied the adsorption of CO on small palladium particles deposited on a well-ordered thin Al_2O_3 film on NiAl(110) using infrared reflection absorption spectroscopy (IRAS). Recent studies in our group with STM and SPA-LEED have shown that the deposited particles are predominantly terminated by (111)-type surfaces. The IR spectra exhibit several absorption bands, which are associated with linearly bound CO ($2090\text{--}2120\text{ cm}^{-1}$) and bridge bonded CO ($1930\text{--}1970\text{ cm}^{-1}$). On the larger, better ordered palladium aggregates another CO-induced band appears in the region of $1970\text{--}2000\text{ cm}^{-1}$, which we assign to CO molecules bound on the edges of the particles. Evaporation of Pd in presence of a CO atmosphere leads to the formation of a palladium carbonyl-like compound which is stable only at low temperatures. The IR spectra of this species show apparent similarities with the spectra of CO on the small particles. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium oxide; Carbon monoxide; Clusters; Infrared absorption spectroscopy; Palladium

1. Introduction

The interaction of small metal particles with molecules adsorbed from the gas phase has been the subject of various studies [1]. Among the different experimental investigation methods, vibrational spectroscopy provides a wide field of application in which the number and the frequencies of adsorbate vibrations can give information about the structure of the particles, as well as the bonding sites of the adsorbate molecules [2–4]. Infrared spectroscopy can be applied to colloidal systems in solution [5], disperse catalysts [6–8], clusters within zeolites [9–11] and deposited metal aggregates on oxide surfaces [3,4,12–14].

In this paper, we show IR spectra of CO on Pd

particles where the morphology and structure of the metal aggregates is well known from earlier SPA-LEED and STM studies [15,16]. The measured IR spectra are similar to previously published data [3,4], but information on the morphology and structure of the Pd particles allows us to reconsider the assignment of the infrared bands [13]. We followed the thermal behaviour of the particles with infrared spectroscopy for low- and high-temperature deposits [13]. Additionally, we compare these results with the behaviour of a Pd carbonyl surface compound which is prepared by Pd deposition in presence of a CO atmosphere [14].

2. Experimental

The infrared reflection absorption experiments have been carried out in an ultra-high vacuum

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system with a base pressure of 3×10^{-10} Torr [17]. The system contains a preparation chamber where the structure of the surface can be checked by LEED and its chemical constitution may be determined by Auger electron spectroscopy. All infrared spectra were recorded with a spectral resolution of 2 cm^{-1} accumulating 500 scans for each spectrum.

The aluminium oxide film has been prepared by oxidation of a cleaned NiAl(110) single crystal alloy surface according to well-known recipes [18,19]. The alumina film has a $\gamma\text{-Al}_2\text{O}_3(111)$ -like structure and a uniform thickness of 4–5 Å [18]. The reflectivity of the well-ordered thin oxide film is still very high due to the metal support. Pd has been evaporated from a rod via electron bombardment and the deposited amount has been controlled by a quartz balance.

3. Results and discussion

We discuss the temperature dependence of the IR spectra of three differently prepared Pd deposits. In each case, an amount of 2.2 Å Pd (average thickness) was deposited on the alumina surface which corresponds to 1.5×10^{15} atoms cm^{-2} . Fig. 1a contains a series of spectra of Pd aggregates deposited at a surface temperature near 90 K and consecutively saturated with CO at the same temperature. The average island size of the particles is about 20 Å [15,16]. Fig. 1b shows the IR spectra of the Pd aggregates grown at a substrate temperature near 300 K and saturated with CO at 90 K. The average island size of the Pd aggregates is 50 Å [15,16]. Generally, the positions of the bands for both deposits are comparable. It is possible to identify three regions of frequencies: 1930–1970 cm^{-1} ; 1970–2000 cm^{-1} ; and 2090–2120 cm^{-1} . The region around 2100 cm^{-1} is assigned to linearly bound CO molecules [20–24]. Upon annealing, this species turns out to be the most weakly bound species and desorbs first, in agreement with previously published thermal desorption data [16]. At 300 K, the linearly bound species has almost completely disappeared except for a small component near 2070 cm^{-1} , which is possibly due to isolated linearly bound CO mole-

cules [25]. The other two bands, which were not always well resolved, are assigned to bridge bonded species on the terraces of the aggregates (1930–1970 cm^{-1}) and to bridge bonded species on the edges of the aggregates (1970–2000 cm^{-1}). Previously, by analogy with spectra taken on Pd single crystal surfaces [21,24], the latter band has been assigned to CO on Pd(100) facets [3,4,8]. The intensity of the absorption band in this region in our spectra together with the results from earlier SPA-LEED and STM studies [15,16], however, lead us to a different interpretation [13]. It should be noted that spectra of a Pd(111) single crystal surface with a high density of defects also show an absorption band in the region of 1970–2000 cm^{-1} [26]. Our measurements show that the larger Pd aggregates grown at a substrate temperature near 300 K are crystalline and expose facets typical for shapes defined by a cubo-octahedron [16]. These facets are mostly (111) and to a much lesser extent (100) oriented with (111) facets oriented parallel to the substrate. For an ideal cubo-octahedron of size 50 Å – the average particle size of our 300 K deposits – the ratio of Pd(100):Pd(111) facets would be approximately 1:5 [27]. The smaller Pd aggregates grown at a substrate temperature near 90 K are less well ordered. SPA-LEED and STM studies showed that they do not exhibit ordered facets and are nearly amorphous [15,16]. The smaller aggregates deposited at 90 K expose a much larger surface area [27] and lead to a larger integrated absorbance (Fig. 2) in the region of the CO stretching frequency. Comparing the spectra measured after exposure to CO at 90 K of both low- and room-temperature deposits, the band due to bridge bonded species on the edges of the aggregates for the 300 K deposit is stronger relative to the absorption band of the bridge bonded species on the terraces. In addition, annealing the 90 K deposit leads to a strengthening of this band. The 300 K deposit exhibits this transformation of bandshape as well but the change is less pronounced. This can be understood by the ordering of the Pd aggregates, in the course of which the shape of the clusters becomes more defined. The intensity of the absorption band assigned to bridge bonded species on the edges of the aggregates is larger

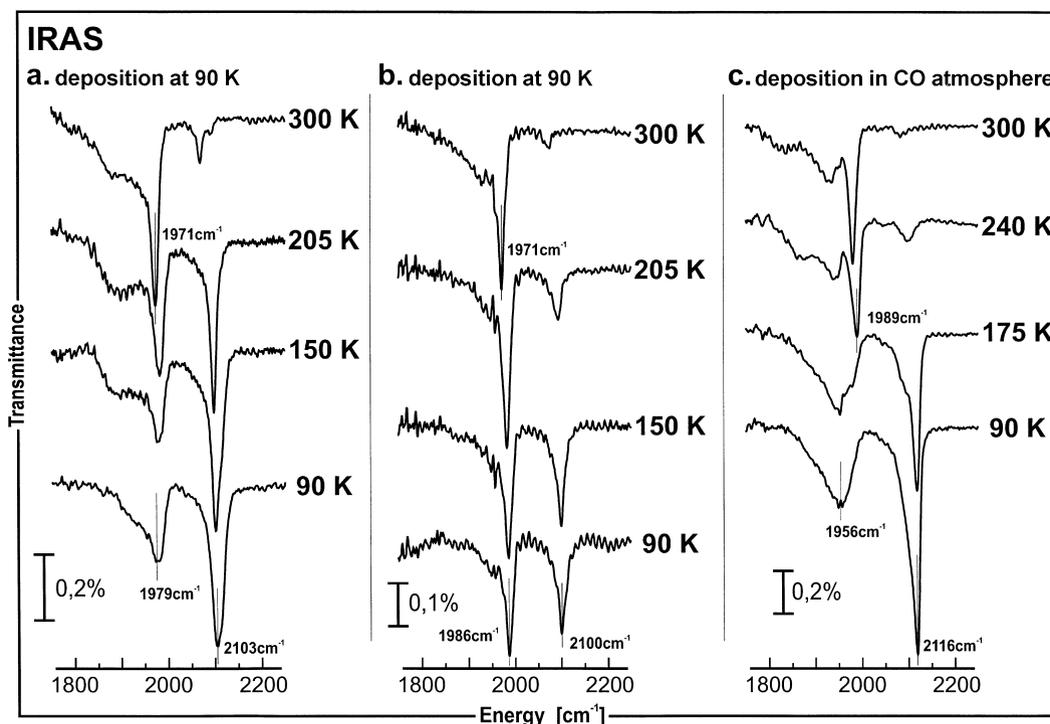


Fig. 1. Series of IR-spectra taken after deposition of 2.2 Pd (average thickness) at 90 K (a) and 300 K (b) and dosage of 20 L CO at 90 K and subsequent annealing to the indicated temperatures [the average particle diameter is (a) 20 Å and (b) 50 Å]. In (c), the deposition was taken out in the presence of a CO atmosphere of 3×10^{-6} mbar pressure. (The background spectrum was recorded after annealing the probe to 1000 K.)

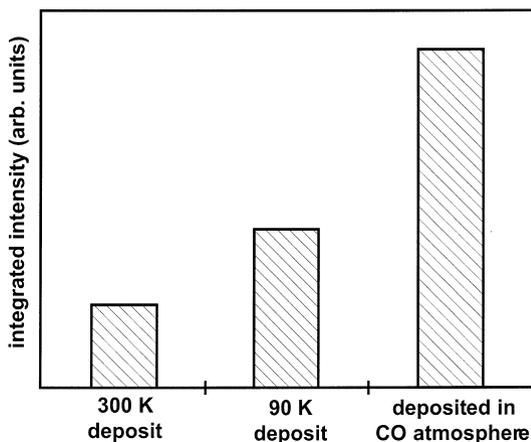


Fig. 2. Integrated intensities of the absorption bands of CO for the three different Pd deposits from Fig. 1.

than expected on the basis of the number of accessible absorption sites [27]. We suggest that this enhancement is due to dynamic intensity

transfer via dipole coupling between the terrace bridge species with stretching frequencies at lower frequency towards the edge bridging species at higher frequency. Such an intensity transfer through dipole coupling would be consistent with observations from single crystal surfaces [28].

It is now interesting to compare the IR spectra of Pd deposited in presence of a CO atmosphere with the results obtained on the UHV grown particles. The deposition of Pd in presence of a CO atmosphere leads to a Pd carbonyl surface compound [14]. Fig. 1c shows a set of spectra in the spectral region of the CO stretching frequency for 0.8 monolayers Pd deposited in an atmosphere of 3×10^{-6} mbar CO. The spectrum recorded at 90 K shows two absorption bands which can be assigned to linearly bound CO (2116 cm^{-1}) and bridge bonded CO (1956 cm^{-1}). The spectrum is rather similar to the one of the 90 K UHV deposit. However, the absence of the band for the CO

molecules bridge bonded on the edges of the aggregates indicates the complete absence of extended edges. The integrated absorption intensity on the other hand is much larger in this case as can be seen from Fig. 2. The reason for this is that the UHV grown particles only expose surface atoms to CO. In contrast to this, for the Pd carbonyl surface compound, the Pd:CO ratio has been estimated to about 1:2 (from XPS data) even for Pd coverages of several monolayers [29,30].

Upon annealing the compound, the spectrum is completely altered between 175 and 240 K. Accompanying the decomposition of the compound the linearly bound CO molecules are nearly completely desorbed. This is in full agreement with earlier TDS studies which showed the decomposition of the compound with a sharp intense mass peak of CO at 190 K [29,30]. In addition, in the infrared spectrum, a sharp peak appears at 1989 cm^{-1} , similar to the one found on the well-ordered UHV grown Pd aggregates. With respect to the assignment alluded to above this peak is due to bridge bonded CO molecules on the edges of Pd aggregates. This leads us to the conclusion that after decomposition of the Pd carbonyl surface compound large ordered CO covered Pd particles are formed on the substrate. Additionally, this decomposition is connected with a damping of the Fuchs–Kliwer phonon of the alumina film which has been reported elsewhere [14].

4. Conclusion

The present study has shown that CO adsorbed on Pd aggregates deposited onto a thin Al_2O_3 film exhibits IR spectra at low temperature (90 K) which are considerably different from data obtained on single crystal surfaces. The spectra are dominated by the bands of those species typically bound near defects on single crystal surfaces such as edges and corners. The formation of a Pd carbonyl surface compound has been followed by IR spectroscopy. Its decomposition to a situation similar to well ordered UHV grown aggregates was demonstrated by the change of the infrared spectra.

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