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Infrared spectroscopic investigation of CO adsorbed on Pd aggregates deposited on an alumina model support

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Abstract

We show that CO adsorption on Pd aggregates of varying size and order gives rise to several absorption bands in the range of CO stretching frequencies which we assign to different absorption sites. At low temperature (90 K) and saturation coverage we find the population of terminal as well as bridging sites. The CO molecules are preferentially terminally bound, but these exhibit the lower binding energies in agreement with earlier TDS studies. The CO-molecules on two-fold bridging sites are more tightly bound and the relative intensity of the corresponding absorption band increases with increasing size and order of the Pd aggregates. The observed bands may be assigned according to IR results on Pd(111) single crystals which is the orientation of the aggregate surfaces observed for the present deposits. The bands previously assigned to Pd(100), which gain intensity for the well-ordered aggregates with preferentially (111) oriented surfaces, we reassign to CO molecules bound to edges of the (111) facets. © 1998 Elsevier Science B.V.

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1. Introduction

Vibrational spectroscopy is considered to be one of the most powerful tools to investigate the interaction of small metal aggregates with molecules adsorbed from the gas phase. This method has been successfully applied to study colloidal systems in solution [1], clusters within zeolites [2–4], catalysts [5–8] as well as deposited metal aggregates on oxide surfaces [9–11].

In many cases, CO has been used as the test molecule in order to probe the structure and bonding abilities of the metal aggregates [10–12]. The correlation between the observed CO stretching frequencies and the binding site represents the

main method to deduce structural information [13]. However, this direct correlation which relies on the comparison with discrete carbonyl compound spectra where the structure is known from X-ray diffraction [14,15], has recently been questioned severely on the basis of photoelectron diffraction data [16,17]. The latter studies have clearly indicated that a direct correlation based only on the frequency analysis may lead to misinterpretations if used without caution. Along the same lines the comparison of IR data obtained on single crystal surfaces [18–23] has been used to assign and titrate the abundance of adsorbed species and facets on catalyst samples carrying small metal aggregates [6–11].

We show in the present paper that in the case of Pd–alumina model systems with carefully controlled morphology and structure of the aggregates

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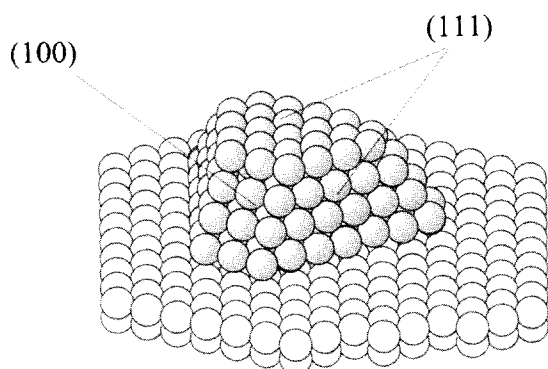


Fig. 1. Schematic view of the cubooctahedral symmetry of the ordered aggregates.

[24] the measured IR spectra are similar to previously published data [10,11], but their assignment is reconsidered. The larger Pd aggregates expose facets typical for shapes defined by a cubooctahedron shown in Fig. 1 [25]. These facets are mostly (111) and to a much lesser extent (100) oriented. In the present case, the IR spectra of adsorbed CO exhibit characteristics typical of CO adsorbed on defect rich Pd(111) single crystals at low coverage [18]. Adsorption on irregular sites at edges, corners or steps are identified at higher coverage. In addition, a terminally bound CO species is found which is typical for metal aggregates of all sizes studied within the present paper [24,25].

2. Experimental

The experiments have been carried out in an ultrahigh vacuum system with a base pressure of 3×10^{-10} Torr [26]. The system contains a preparation chamber where the order of the surface can be checked by LEED and its chemical constitution by Auger electron spectroscopy. The IR light is generated by a globar and after passing a Mattson-type (RS1) interferometer focused onto the sample. The interferometer is mounted in a homemade chamber which is evacuated to 10^{-3} Torr. The light passes through viton-O-ring sealed KBr-windows before and after reflection from the sample surface. It is detected with a liquid nitrogen-cooled MCT detector placed in a detector

chamber which is flushed with dry nitrogen. All spectra were recorded with a spectral resolution of 2 cm^{-1} accumulating 500 scans for each spectrum. At another sample position electron energy loss spectra may be recorded by a Leybold Heraeus ELS 22.

The aluminium oxide film was prepared by oxidation of a cleaned NiAl(110) single crystal alloy surface according to well-known recipes [27,28]. 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. From previous SPA-LEED and STM investigations the morphology of the deposited metal aggregates is known [24,25].

3. Results and discussion

Before we discuss the present findings we would like to briefly summarize the results of our published morphological studies [24,25].

On the well-ordered alumina film we find that the growth of particles strongly depends on the surface temperature during deposition and not strongly on annealing afterwards, as long as the temperature did not exceed 400 K. At 400 K the metal starts to diffuse into the film. This interdiffusion was not completed before 800 K [29]. A combined in situ SPA-LEED and STM study revealed that the aggregates at 300 K are three-dimensional and exhibit well-ordered (111) facets with extensions in the range of 40–60 Å, while those deposited at lower temperatures are considerably less ordered and of smaller size, i.e. 10–20 Å. Clearly defined facets and steps could not be detected by SPA-LEED as well as by STM for the low temperature deposits. Thermal desorption of CO has been studied and features characteristic of weakly chemisorbed CO ($T_{\text{max}} \approx 250 \text{ K}$) have been observed for small aggregates, while larger Pd aggregates exhibit TDS spectra with CO desorption maxima at temperatures in the range of those known for Pd single crystal surfaces, i.e. 400–550 K. If the TDS experiments were repeated after the weakly held species had been desorbed

by readsorbing CO and a second heating cycle, no dramatic changes were observed. In the present study we follow the fraction of molecules, not being desorbed but rather remaining on the metal aggregates.

The other starting point of our discussion is the existing literature on infrared spectroscopic investigations of single crystal surfaces [18–23,30]. This literature base is substantial and we would like to explicitly mention only a few recent results which are important for the subsequent discussion. We consider the Pd(111) and Pd(100) surfaces. For low CO coverages on a well-ordered Pd(111) surface ranging from below 0.1 to 0.5 several superstructures have been observed [30]; however, recent photoelectron diffraction studies have convincingly demonstrated that the adsorption site is always the three-fold hollow site [17] with stretching frequencies ranging from 1830 to 1920 cm^{-1} . For coverages of about $\theta = 0.6$ –0.7 CO is preferentially bridge bonded, i.e. the population of terminally bonded sites is near zero. The observed stretching frequencies are 1966 and 2092 cm^{-1} [20]. Upon increasing the coverage even further to $\theta = 0.75$ two intense bands are observed at 1894 and 2110 cm^{-1} with almost vanishing intensity in the range of 1940–1970 cm^{-1} , i.e. the bridge sites [30]. On Pd(100) the situation appears to be less complicated. The CO stretching frequency is 1895 cm^{-1} at very low coverages shifting continuously to higher frequencies with increasing coverage and finally reaches 1997 cm^{-1} at maximum coverage [19]. Ortega et al. [19] have studied CO adsorption on a roughened Pd(111) surface which was not completely annealed after an argon ion bombardment during the preparation of the surface. This defect rich surface was studied by Tushaus et al. [30]; however, his main effort was the investigation of the clean smooth Pd(111) surface. In the case of the roughened surface bands are formed at 1893, 1961, 1996, 2097 and 2110 cm^{-1} , with the bands at 1961 and 2097 cm^{-1} being the most intense ones. These bands are at least partially related to the presence of defects and their positions and in fact the coexistence is similar to our findings on the small particles which we discuss in the following.

We first discuss the IR-spectra for saturation

CO coverage as a function of average particle size as determined earlier via SPA-LEED and STM [24,25]. Fig. 2 contains corresponding data where on the left-hand side the Pd aggregates were grown at a substrate temperature near 90 K and on the right-hand side at a substrate temperature near 300 K. The aggregates deposited at 300 K are crystalline with (111) facets parallel to the substrate. Such a situation can be described by aggregates of cubooctahedral symmetry (Fig. 1) [24,25].

We note from Fig. 3 that the amount of adsorbed CO as judged by the integrated CO signal intensity is considerably larger for the low temperature Pd deposits than for the room temperature deposits for a given amount of deposited metal. This is due to the larger surface area exposed by the irregularly shaped aggregates deposited at low temperature. As a general observation from Figs. 2 and 3 we realize that the positions of the bands for deposits at both temperatures are comparable. Furthermore, the line widths observed in Fig. 2 are, perhaps not unexpectedly, larger for the low temperature deposits due to the inherent higher degree of microscopic heterogeneity of Pd positions in those aggregates. It is possible to assign three regimes of frequencies for both sets of deposits based on the spectra for saturation coverage shown in Fig. 2. Those regimes are 1930–1970, 1970–2000 and 2090–2120 cm^{-1} . On the basis of arguments presented below for the coverage dependent studies we assign these bands to bridge-bonded species on the terraces of the aggregates (1930–1970 cm^{-1}), to bridge-bonded species on the edges of the aggregates (1970–2000 cm^{-1}), and to terminally bonded CO (2090–2120 cm^{-1}), not necessarily situated on the terraces, of course. The bands that we assign to CO bridge bonded on the edges of the aggregates have previously been assigned to CO on Pd(100) sites [7,10,11]. The intensity of the absorption band in this region together with the results from earlier SPA-LEED and STM-studies [24,25] lead us to a different interpretation (see below).

For the low temperature deposits there is a clear trend if we compare the intensity in the region of bridge-bonded species with the intensity in the region of terminally bonded species as a function of aggregate size (Fig. 4, top). It is found that the

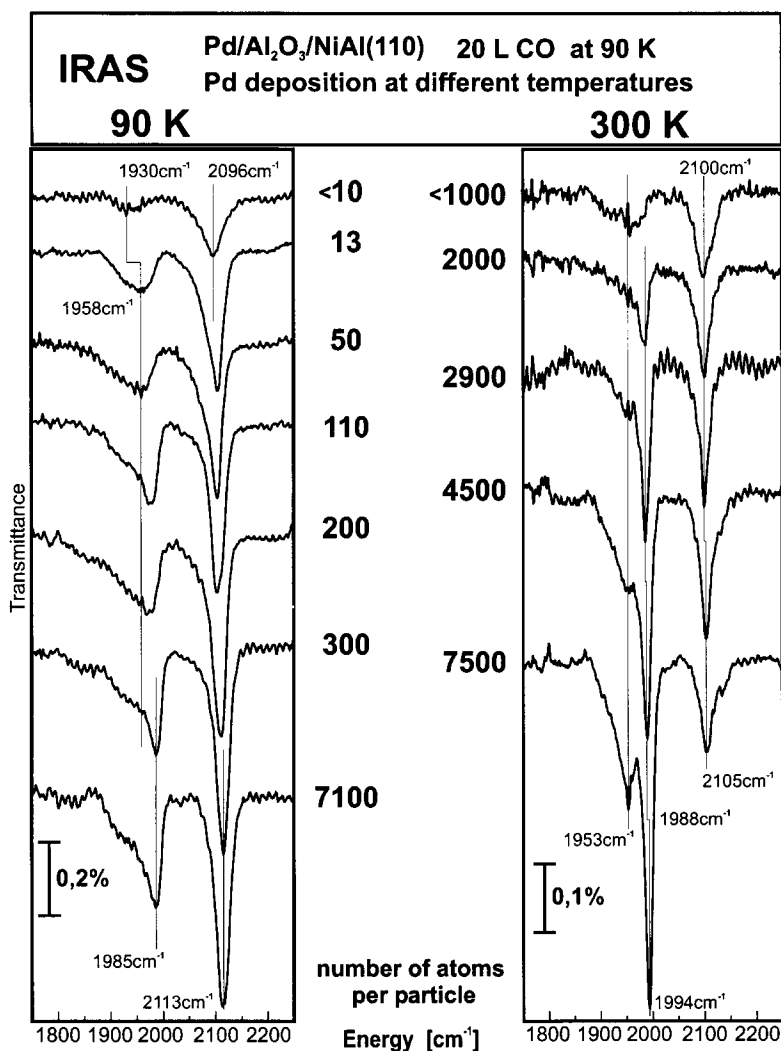


Fig. 2. Series of IR-spectra taken after deposition of different amounts of Pd at 90 K (left) and 300 K (right) and dosage of 20 L CO at 90 K. The average number of atoms per particle is given next to the spectra.

fraction of bridge-bonded species increases rapidly with the size of the aggregates until it reaches a saturation value. This is consistent with an increase of sites with two Pd atoms at the proper distance to be bridge bonded by CO molecules. If we compare this with the situation for the room temperature deposits also plotted in Fig. 4 (bottom), we realize the much slower increase starting from a higher level. Clearly, this is caused by the higher degree of order for the room temperature deposits already at the lowest metal coverage

where the particles expose small terraces with atomic arrangements allowing for a considerable number of bridge bonds to be formed. Once the aggregates have assumed their regular shape (Fig. 1), the relative ratio of bridge bonds to terminal bonds is only expected to change slowly [24,25]. On the other hand, Pd(111) terraces bind CO molecules in a terminal geometry only at very high CO coverages ($\theta > 0.7$) [30]. On Pd(111) the terminally bonded CO with an adsorption band at about 2100 cm^{-1} is always accompanied by an

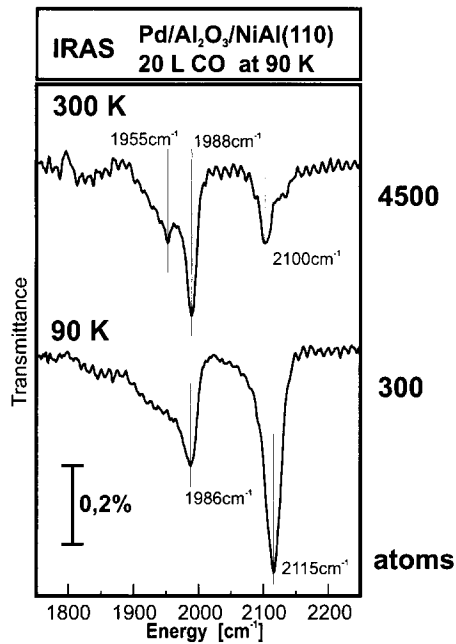


Fig. 3. Spectra for 4.4 Å Pd (average thickness) deposited at 300 and 90 K and a dosage of 20 L CO at 90 K.

intense band at about 1900 cm^{-1} which is assigned to a species adsorbed on three-fold hollow sites [20,22]. (The shift of this band from about 1830 cm^{-1} at very low CO coverages is caused by dipole coupling [17].) At this high coverage the population of bridge sites is extremely low on Pd(111) (see above). The peak at about 1900 cm^{-1} , characteristic for CO molecules bound in three-fold hollow sites at high coverages, is not found in our spectra with corresponding large intensity but, if at all, as a weak shoulder. On Pd(111) for coverages of about $\theta=0.6\text{--}0.7$ the amount of terminally bonded CO is nearly zero and the CO is predominantly bridge bonded (see above) [30]. Combining all arguments the spectra indicate on one hand that on the facets of the Pd clusters the saturation coverage is smaller than saturation coverage ($\theta=0.75$) on a Pd(111) single crystal, and the CO molecules are preferentially bridge bonded on the aggregates. On the other hand, the above reasoning also explains why the intensity in the region of terminally bonded CO is considerably lower for the room temperature deposits, which exhibit well-ordered facets, i.e.

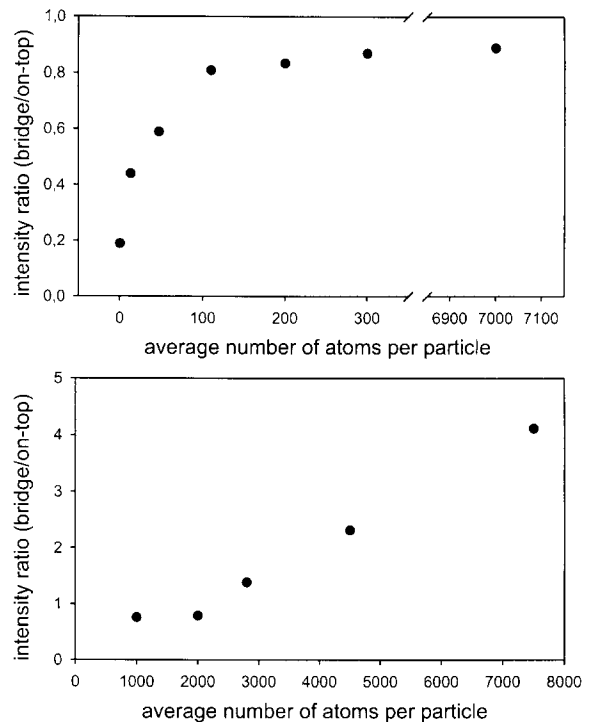


Fig. 4. Ratio of the integrated intensities of the absorption bands for bridge and on-top bonded CO for the 90 K (top) and the 300 K (bottom) deposits as a function of particle size.

because the coverage is below $\theta=0.75$. In the spectral region assigned to the bridge-bonded species there is a marked redistribution of intensity between the two sites, i.e. on the terraces and on the edges, favouring the edge bonded species for larger aggregates. This increase in intensity is too large to be understood on the basis of an increase in the number of sites [31] if we consider a cubooctahedron (Fig. 1). We suggest here that it 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 what is known from single crystal surfaces [32–34]. It is also consistent with the trend observed in Fig. 2 as the particle size increases. The larger the terraces grow and the more well ordered the adsorbed CO islands are, the more pronounced the intensity transfer in the IR spectra becomes. After all the intensity

transfer is a collective phenomenon depending on the size of the active domain [32–34].

As next step we investigate the CO coverage dependence of the spectra (Fig. 5). We do this by starting at saturation coverage and subsequently heat the sample to the given temperatures. The spectra are then recorded again at 90 K. It is, of course, important for a consistent interpretation to bear in mind that upon heating above certain values the morphology of the aggregates may change. Fig. 5 shows the coverage dependence for a smaller (i.e. 2.2 Å average thickness) and a larger

(i.e. 12 Å average thickness) Pd exposure created at a substrate temperature of 90 K. The spectra for the highest coverage (lowest temperature) are similar to those reported in Fig. 2 and represent saturation coverage. We note the stronger relative population of bridge sites for the larger deposits. Upon decrease of coverage the peak in the area of terminally bonded CO ($2090\text{--}2105\text{ cm}^{-1}$) loses intensity and decreases in width until above room temperature the signal has almost completely disappeared. When the sample was heated (before recording the spectra at 90 K) above 200 K the

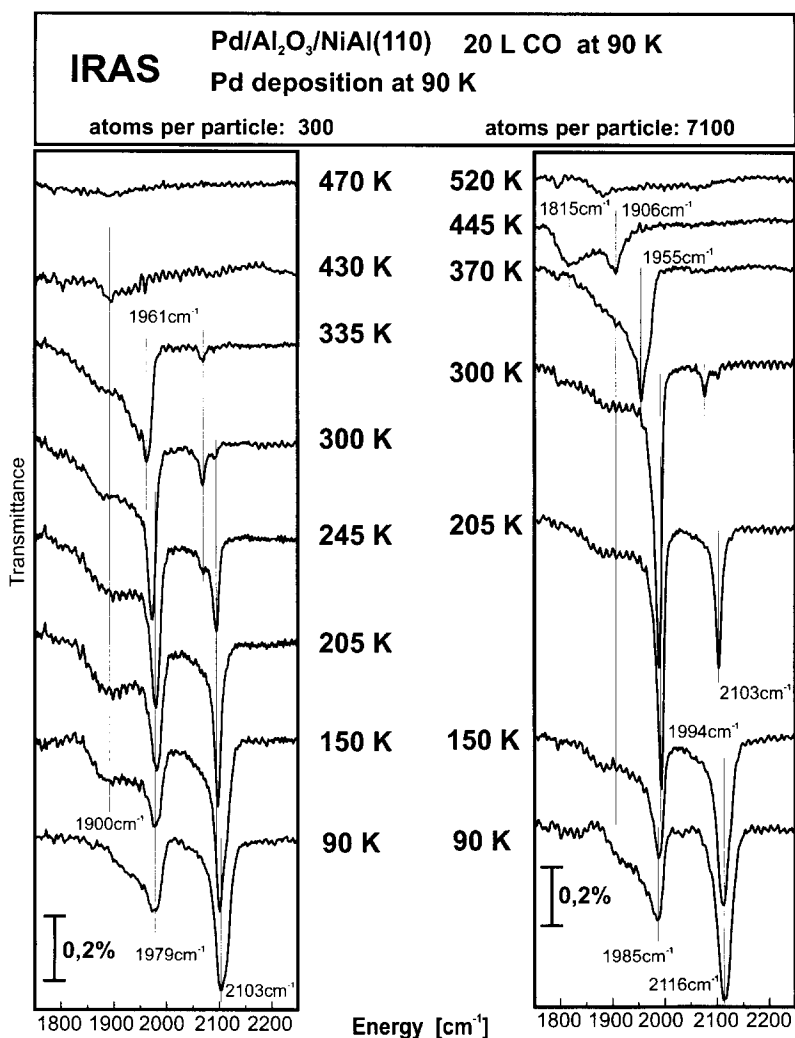


Fig. 5. IR-spectra for a lower (2.2 Å average thickness, left) and a higher (12 Å average thickness, right) Pd exposure at 90 K, dosage of 20 L CO and subsequent annealing the indicated temperatures.

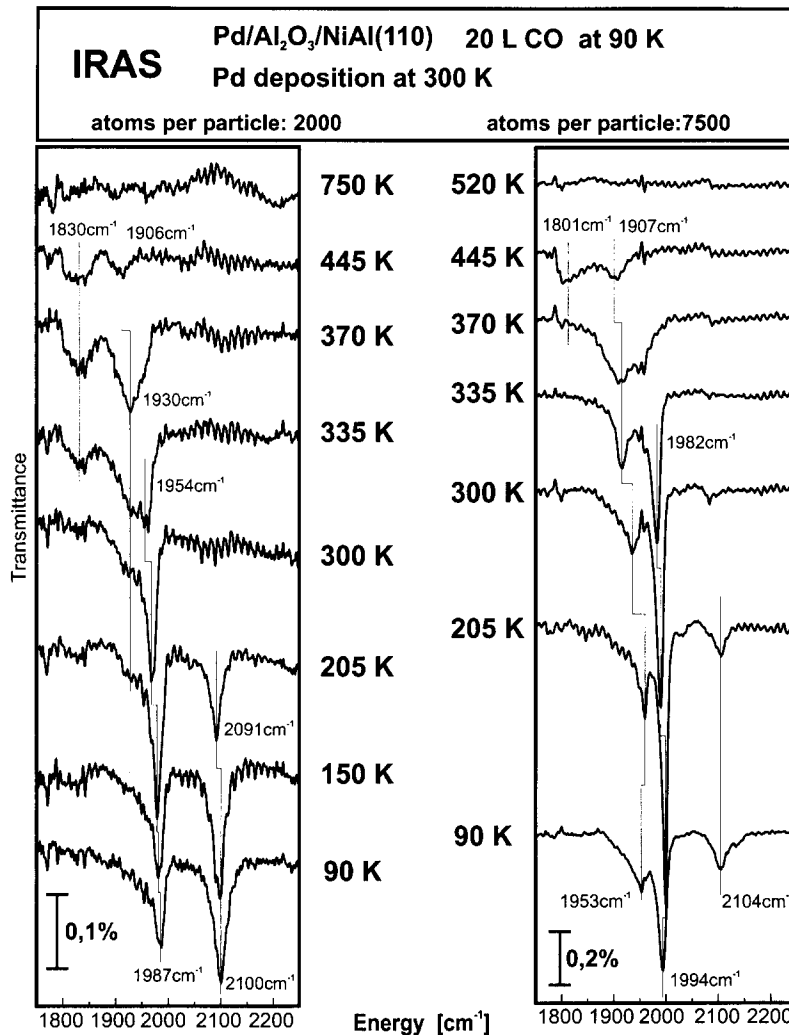


Fig. 6. Spectra of two different 300 K Pd deposits (average thickness: left, 1 Å; right, 12 Å), dosage of 20 L CO at 90 K and following annealing at the given temperatures.

band appeared to be split with a component located near 2070 cm⁻¹ growing in relative intensity. It is possible that this signal is due to isolated terminally bonded CO molecules [15,35]. As already discussed in connection with Fig. 2, the band due to bridge-bonded species on the edges gains intensity before it undergoes a substantial transformation for the larger deposits. This transformation of band shape is more pronounced compared with the bands observed for the smaller amount of deposited material where the changes are moderate.

To complement the discussion on the low temperature deposits again with corresponding data on the high temperature deposits, we show in Fig. 6 the coverage dependence for Pd deposited at 300 K. On the left, a small amount of Pd (i.e. 1 Å average thickness) and on the right, a larger amount of Pd (i.e. 12 Å average thickness) has been evaporated onto the aluminium oxide substrate. In comparison with Fig. 5 the observed band widths are generally somewhat smaller and the frequencies are shifted, but overall similar bands are found as discussed above. This is in

particular true if only small amounts of Pd are deposited. The relative population of bands due to bridge-bonded species is higher again but the coverage dependence up to an annealing temperature of 335 K is very similar to that observed for the low temperature Pd deposits. Above 335 K it is possible to completely desorb the bridging molecules on edges and to have only the bridging molecules on terraces as well as another species present. This extra species shows an absorption band near 1830 cm^{-1} and appears to be the most stable CO species on the aggregate. By comparison with data for low CO coverage on Pd(111) it must be assigned to adsorption in three-fold hollow sites, i.e. those sites which dominate adsorption on Pd(111) single crystal surfaces between small and half monolayer coverages [17].

For larger Pd deposits the situation at saturation coverage is different from the smaller Pd deposits. Due to the formation of more well-ordered facets and sufficiently low coverage (see above) the population of terminally bonded CO is very low. The bridge site region dominates the spectrum up to an annealing temperature of 370 K. Upon annealing to high temperature we also find a population of three-fold hollow sites, typical for the Pd(111) single crystal surfaces [17,22]. However, by comparing the present data with single crystal data of well-ordered surfaces it is obvious that there are very pronounced differences. The adsorption behaviour on the aggregates compares best with defect rich single crystal surfaces [30], i.e. spectra of a Pd(111) single crystal surface with a high density of defects also show an absorption band in the region of $1970\text{--}2000\text{ cm}^{-1}$ [30].

So far we have shown spectra recorded at low temperature. Fig. 7 shows a set of spectra recorded for a small Pd deposit at 300 K, comparable to Fig. 6, but recorded at room temperature. The on-top signal at 2064 cm^{-1} is, not surprisingly (see above), very low. The bands in the bridging region are broader than at 90 K and the change after subsequent heating cycles resembles the one found in Fig. 6. We believe that the larger widths of the lines are due to the fact that the molecules are rather dynamic on the aggregate, i.e. other sites become accessible at elevated temperatures. We show these spectra because they compare well with

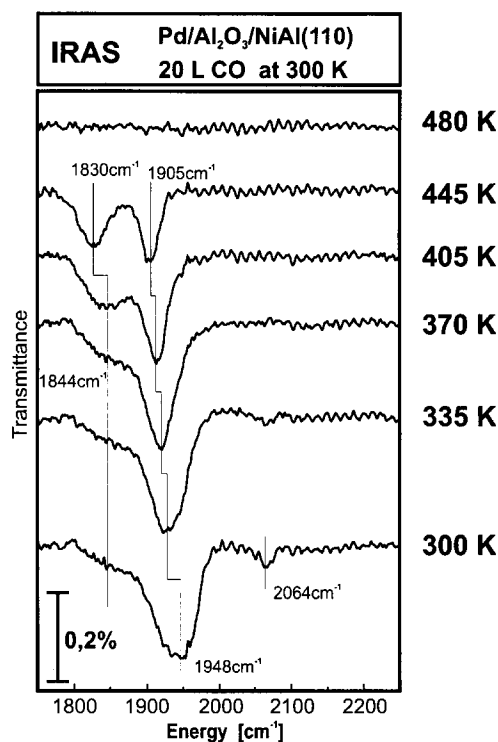


Fig. 7. Series of IR-spectra for deposition of 2.2 \AA Pd (average thickness) at 300 K, dosage of 20 L CO at 300 K and annealing at the given temperatures. The spectra were all recorded at 300 K.

those reported in the literature for small metal aggregates [9]. Those have also been assigned to bridge-bonded species. Henry et al. [9] published a similar spectrum for Pd deposited on MgO(100) where the aggregates also expose predominantly Pd(111) facets. However, Pd(111) and Pd(100) show similar spectra for saturation coverage at 300 K [18] so that a discrimination between the facets on the basis of the IRAS data recorded at 300 K is not really possible.

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 in comparison with data obtained on single crystal surfaces. It

transpires that it is not possible to interpret the spectra consistently for all investigated conditions by superimposing IR spectra of extended single crystal surfaces corresponding to the different facets present on the aggregates. In contrary, the spectra are dominated by those species typically bound near defects on single crystal surfaces, or on edges and corners. At saturation coverage a terminally bound CO species has been identified which is not found in higher abundance on single crystal surfaces. It is this species that gives rise to the low temperature signal in the CO thermal desorption spectra reported earlier [24]. The species bound to the aggregates at higher temperature are most probably bridge-bonded species. The three-fold hollow bound CO, typically found on single crystal Pd(111) surfaces is only identified for Pd deposits with well-ordered facets and there it is the most stable CO species. Infrared spectra recorded for different temperatures are consistent with considerable dynamical motion of CO within the adsorbate on the aggregate.

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