

CO dissociation characteristics on size-distributed rhodium islands on alumina model substrates

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The dissociation of CO on size-distributed Rh particles supported on a thin alumina film has been studied with high resolution X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS). Adsorbed CO dissociates upon heating to temperatures above 300 K. The dissociation activity is dependent on the island size, exhibiting a maximum for islands with around 1000 atoms. We have identified size-dependent changes in the C 1s photoelectron spectra for these CO–Rh systems occurring at temperatures lower than the onset of both the dissociation and desorption processes. These changes are interpreted as being due to adsorbed CO shifting into more highly coordinated sites. The dissociation activity is directly correlated to the availability of these sites, where the observed dissociation is proposed to occur. These results can be interpreted primarily in terms of the size and shape of the deposited Rh particles. © 1998 American Institute of Physics. [S0021-9606(98)00607-2]

I. INTRODUCTION

Metal clusters, both in free form and deposited on surfaces, currently draw increasing attention. A general observation is that fundamental physical properties of the clusters can vary with size.¹ Of particular interest is the interaction between clusters and molecules, since it has been shown that the efficiency for different catalytic processes may vary with the particle size.^{2,3} As many applied catalysts consist of oxide-supported metal particles, such size-dependent variations could greatly affect the efficiency of the catalytic systems. Thus, detailed knowledge about size-dependent effects could be of great utility for the further development of catalysts.

A fundamental process in heterogeneous catalysis is the dissociation of CO. This step is crucial for, e.g., the Fischer–Tropsch processes (conversion of CO into hydrocarbons).⁴ This has motivated investigations of the fundamental properties of CO dissociation on different substrates using surface science techniques. Many of these studies were initially concentrated on single crystal surfaces of catalytically interesting metals, such as Pt and Rh. There were discussions on whether CO dissociates on Rh (See, for example, Refs. 5–7 and references therein). It has in any case been shown that CO dissociates on at least some more open surfaces such as Rh (210).⁸

Due to the technological importance of oxide-supported

metal particles, many studies on the interaction between CO and such systems have also been performed. Previous studies of the CO dissociation process includes adsorption on supported Rh particles, and attempts have been made in order to correlate the dissociation activity with particle size. However, Thermal Desorption Spectroscopy (TDS) studies have given seemingly contradictory results.^{9–11}

An alternative way to quantify the CO dissociation process is to directly monitor changes of the adsorbed CO and the formation of atomic carbon on the surface. This can be done with techniques such as X-ray Photoelectron Spectroscopy (XPS)^{8,12} and X-ray Absorption Spectroscopy (XAS) utilized in the electron yield mode. The atomic selectivity and the high surface sensitivity of these core level spectroscopies make them very suitable for the study of adsorbates and processes involving these. Industrially produced catalysts are, however, difficult to study with these techniques, due to the amorphous sample structure and because the insulation oxide can cause problems with charging when electron spectroscopic techniques are employed. To avoid these problems, different model systems, well suited for surface science studies, have been developed. For instance, a thin, well-characterized epitaxial Al₂O₃ film formed by oxidation of a NiAl(110) single crystal can be used as a support for the metal particles.¹³ Experiments on metal particles deposited on this type of substrate have

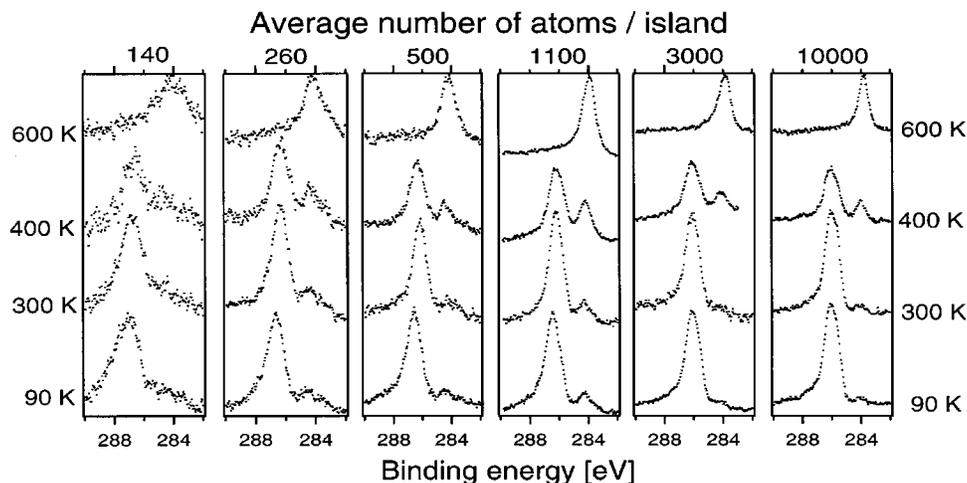


FIG. 1. C 1s photoelectron spectra for CO adsorbed on islands of the indicated average number of atoms. The spectra are recorded for the original 90 K adsorbates and after annealing the samples to 300, 400, and 600 K.

shown that it is a suitable support when studying, for example, island growth,^{14,15} size-dependent electronic structure¹⁶ and reactivity.^{12,17,18}

Recently, we presented a study of CO adsorption on Rh islands with an average diameter varying from 5 to 30 Å deposited on the thin Al₂O₃ film. A fraction of the adsorbed CO was found to dissociate upon heating, and the dissociation activity was found to increase with increasing island size.¹² However, a lower activity value reported for single crystal surfaces [10% dissociation efficiency⁸ for Rh(210)], indicated that there should exist one or more combinations of particle size, surface structure, and, perhaps, support that optimize the probability for dissociation of adsorbed CO.

We have now continued by investigating the CO dissociation behavior on Rh particles with sizes covering a much wider range. The results of these studies are presented in two steps: In Ref. 20 we discuss the structural properties of the system and establish that there is a pronounced maximum in the CO dissociation activity as a function of island size. In this paper we will proceed by elucidating important details of the dissociation process, in particular, the role played by heat-induced changes in the system observed at temperatures lower than the dissociation temperature. We find that two primary types of sites are occupied by the adsorbed CO. We propose that one of the sites is dissociative and that the other is desorptive. We surmise that the proportion of dissociative sites determines the size-dependent dissociation activity in the size range we have studied.

II. EXPERIMENT

The experiments were carried out at Beamline 22 at the Swedish synchrotron facility MAX-lab in Lund. The setup at the beamline consists of a modified Zeiss SX-700 monochromator in conjunction with a large hemispherical electron energy analyzer for photoemission and a multichannel plate with a retarding grid for x-ray absorption measurements by the detection of secondary electrons.¹⁹ XP spectra were recorded at a photon energy of 380 eV for C 1s (total resolution 0.4 eV). The XPS binding energies are referred to the

Fermi level of the NiAl(110) substrate. The XA spectra were measured in partial electron yield mode with a photon energy resolution of 0.2 eV at the C 1s edge. The absolute photon energies were determined using photoemission spectra excited by first- and second-order radiation. The preparation of the well-ordered Al₂O₃ film has been extensively described elsewhere.¹³

Rh (Heraeus, >99.9%) was deposited using a commercial evaporator (Focus EFM 3) based on electron bombardment, which allows evaporation from a rod. During evaporation the sample was put on a retarding potential to avoid effects due to ions produced in the evaporation source that are accelerated toward the sample. The evaporator had previously been calibrated using a quartz microbalance, which gives the nominal film thickness. During deposition the evaporation rate was controlled with the built-in flux monitor. During evaporation the substrate was held at room temperature and chamber pressure was in the range of 5×10^{-10} – 2×10^{-10} Torr. Initially the growth of two-dimensional Rh islands is observed, but as the size increases the islands start to grow three-dimensionally.¹⁵ All the islands studied in this work are expected to have three-dimensional character. In the present paper the average number of atoms per island, as estimated through STM measurements,²⁰ will be used to denote the different deposits. The average cluster sizes studied in this work range from 140 to more than 100 000 atoms per island.

The Rh islands were subsequently exposed to 40 L CO at a temperature of 90 K. This dose should be sufficient to saturate the islands with adsorbed CO.²¹ The samples were then quickly annealed to different temperatures and thereafter cooled to 90 K again before the spectra were recorded. The heating-induced changes were studied using XPS and XAS. The temperature of the sample was determined using a K-type thermocouple spot-welded to the crystal, and the heating was performed by passing a current through the tungsten wire holding the sample.

III. RESULTS AND DISCUSSION

A. Size-dependent dissociation activity upon heating

In this section we use core level photoemission spectra to demonstrate that the CO dissociation activity on the Rh particles is size dependent. This is done in a manner similar to that reported earlier,²⁰ but we focus on the changes undergone by the adsorbed CO. We will furthermore highlight some features in the spectra that will be of importance for the coming discussion.

Figure 1 shows the evolution of the C 1s XPS peaks for the different rhodium deposits as a function of sample heating. The lowest spectrum in each panel is obtained directly after CO adsorption at 90 K. The upper three spectra show the effect of annealing to successively higher temperatures, as described in Sec. II. The C 1s spectra are normalized with respect to the background level at a binding energy lower than the C 1s peak, so that the intensities after the different heating treatments of each cluster size can be directly compared.

The 90 K C 1s spectra all show a distinct peak at around 286–287 eV due to adsorbed CO. These binding energies are consistent with those found for CO adsorbed on Rh (111); 286.0 eV for CO adsorbed on top and 285.4 for CO in a three-fold hollow site.²² In most cases, a small peak at a binding energy of ~ 284 eV is also present. This peak appears already prior to CO dosage, and we identify it as atomic carbon. We have no direct explanation to the origin of this peak, but one possibility is that it is caused by dissociation of background CO during or directly after the Rh deposition.

The fact that the binding energies shift toward higher values for decreasing island size is a phenomenon generally observed both for clean metal clusters deposited on inert substrates^{23,24} and adsorbates upon these clusters.²⁵ The shift can be explained as a combination of several different effects, which are nontrivial to separate. There are initial state effects, such as rehybridizations due to changes in the interaction between the atoms within the cluster and between the cluster and the substrate. There are also final state effects, which in the case of photoemission are very much dependent on the screening properties of the system. In our case, there is a possibility that there is a charge left on the cluster due to inefficient screening from the substrate and there might also occur changes in the ability of the cluster to provide local screening.^{25,26} For the 10000-atom islands where the shift is expected to be very small the CO C 1s BE is almost identical to the values found for single crystal substrates.

When the samples are annealed to 300 K no significant changes in the integrated CO related C 1s intensities are seen. This is in line with previous (TDS) studies, which show that almost no CO will desorb at temperatures below 300 K.¹⁴ However, a shift toward lower binding energy can be observed for the CO peaks. This shift is small for the larger islands, but increases for the smaller islands. The line shape of the peaks also appears to change. These heating-induced changes will be discussed further in Sec. III B.

After heating to 400 K an intensity decrease is observed for the CO related C 1s peak. This is caused by desorption

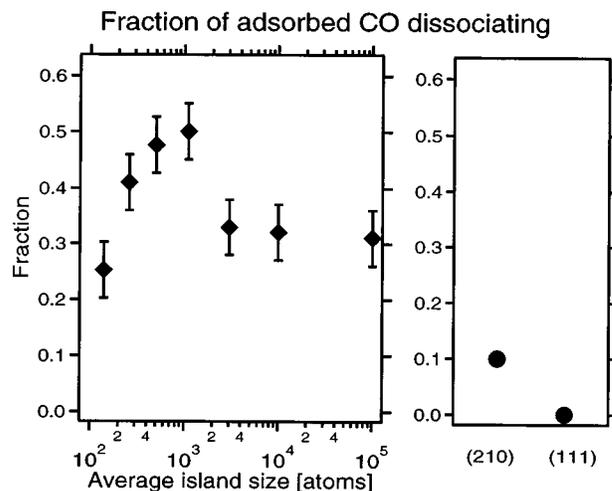


FIG. 2. The CO dissociation activity, as determined by comparing the original intensities of the CO peak and the final atomic C peak (corrected for initial 90 K C 1s intensity) for the different preparations. Efficiency values for Rh(210)⁸ and Rh(111)⁵ single crystal surfaces are presented in the graph to the right.

and dissociation of the originally adsorbed CO. The dissociation is evident from the pronounced enlargement of the atomic carbon C 1s peak at ~ 284 eV. After annealing to 600 K all the originally adsorbed CO has either desorbed or dissociated. In all cases a significant atomic carbon C 1s peak remains.

When comparing the areas of the C 1s peaks of the originally adsorbed CO and the final atomic carbon, it can be seen that different amounts of CO have dissociated in the different cases. To quantify these variations we determine the dissociation fraction as the area of the final atomic carbon peak (600 K), subtracting any 90 K atomic carbon contribution, divided by the area of the initial CO peak (90 K). The obtained values can be considered to be a measure of the heating-induced dissociation, and are presented in Fig. 2. This is a slightly different quantification of the dissociation than the one used in our other work,²⁰ but both methods give the same basic result.

Figure 2 shows that the fraction of CO that dissociates increases with increasing cluster size up to an average size of 1100 atoms. For islands larger than this the fraction drops again to values around 0.3, with a slight decrease with increasing size. The tendency for dissociation upon heating thus exhibits a strong size dependence, and a maximum fraction of $\sim 50\%$ is observed for the 1100-atom islands.

Single crystal studies have revealed that the fraction of adsorbed CO that dissociates on Rh(210) is around 0.1,⁸ whereas no dissociation is found on the more densely packed Rh(100)²⁷ and Rh(111)⁵ surfaces. These observations are consistent with the decreasing trend observed in Fig. 2, although the fraction observed for the clusters used in this investigation approaches a value much larger than what has been observed for single crystals. This is probably due to the fact that even the largest clusters in this study still exhibit a large number of steps, kinks, and other defects.^{15,20}

CO C 1s BE-shift as function of heating

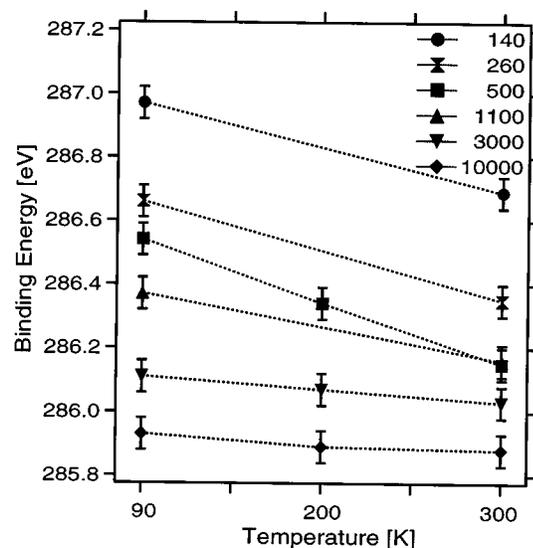


FIG. 3. The temperature-dependent CO C 1s binding energy shifts below the dissociation and desorption thresholds for the different island sizes.

B. Heating-induced changes

1. XPS and XAS results

As mentioned in Sec. III A, heating-induced changes can be seen in the C 1s XP spectra prior to dissociation. Upon heating from 90 to 300 K, the CO related C 1s peak shifts toward lower binding energy, as can be seen by comparing the two lowest spectra for each island size in Fig. 1. To present these results in a more accessible way, Fig. 3 shows the binding energies for the CO related C 1s peaks at 90 and 300 K for six samples obtained by curve fitting. For three of the samples (500, 3000, and 10000 atoms) spectra were also recorded after heating to an intermediate temperature (200 K). Figure 3 clearly shows that the magnitude of the shift depends on the cluster size: The CO peak shifts very little for the 3000- and 10000-atom islands, whereas there are significant shifts for the smaller clusters. The largest shift, almost 0.4 eV, is observed for the 500-atom islands.

If the line shape of the CO C 1s peak is studied in more detail, a shoulder is seen on the low BE side, indicating that the peak consists of two components. This additional feature was discernible for CO adsorbed on islands with an average of 500 atoms or more. Measurements with higher resolution, such as the spectrum presented in Fig. 4(a), show this even more clearly. Using curve fitting,²⁸ the spectra were decomposed into two different components, denoted A and B, respectively. This was done also for the 140- and 260-atom cases, although the two components could not be discerned in the raw data for these situations.

Figure 4(b) shows the fraction of total CO intensity attributed to component B for the different sizes at 90 K and after heating to 300 K. For the 90 K case, the ratio between the components is similar for all four situations. About 80% of the CO is associated with “species A” and the other 20% with “species B.” Upon heating, a redistribution of intensity from component A to component B is seen, and this change is noticeably larger for the medium-sized islands. For the

TABLE I. The determined binding energy separation between components A and B of the CO C 1s peak.

Average number of atoms	Observed separation (eV)
140	~0.44
260	~0.44
500	0.45
1100	0.46
3000	0.49
10000	0.56
Rh(111) (Ref. 22)	0.6

500-atom case the component B has increased to 46% and for the 1100-atom case the increase was to 52% of the total CO intensity. This clearly shows that the BE shift observed upon heating from 90 to 300 K is mainly due to a partial transformation of “species A” into “species B.” It is furthermore interesting to note that the binding energy separation between the components A and B increases with size, as presented in Table I.

The most remarkable point emerging from this analysis is seen when the 300 K curve from Fig. 4 is compared with

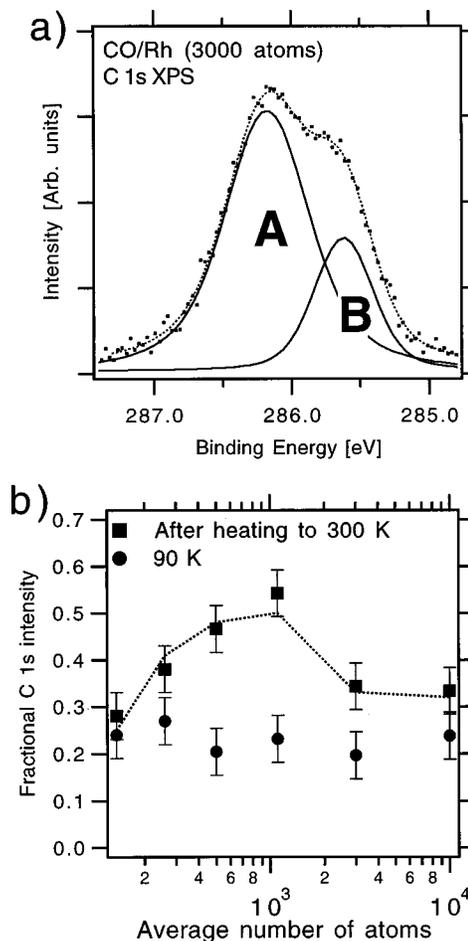


FIG. 4. (a) C 1s on 3000-atom Rh islands after CO adsorption at 90 K, with a total resolution of ~ 0.2 eV. The areas and shapes of the components A and B were determined through curve fitting.²⁸ (b) Fraction of CO in component B of the CO peak, at 90 K and after heating to 300 K. The dotted line shows the fraction of adsorbed CO ultimately dissociating when the given samples are heated to higher temperatures (see Fig. 2).

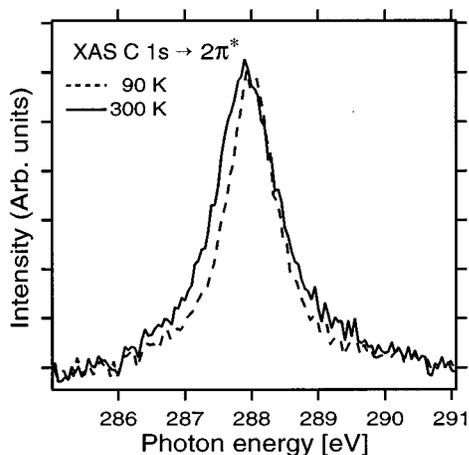


FIG. 5. The XA-resonance peak at 90 K and after heating to 300 K for islands with an average of 500 atoms. The intensities were normalized with respect to the resonance peak maximum.

the dissociation curve (Fig. 2), which is included in the figure as a dotted line. The two curves look very similar, indicating that there is a correlation between the occupancy of “species B” and the fraction of CO that dissociates. This correlation will be further discussed in Sec. III C.

Complementary information on the changes observed upon heating from 90 to 300 K were obtained by X-ray Absorption Spectroscopy (XAS). This technique allows us to probe the initially unoccupied molecular levels of the adsorbed CO and results in a neutral core-excited state. Figure 5 shows the C $1s \rightarrow 2\pi^*$ XA resonance peaks at 90 K and after heating to 300 K for islands with an average of 500 atoms. After heating, the resonance peak broadens, predominantly toward the low-photon-energy side of the peak. Similar changes were observed for all cases, and in Fig. 6 the widths of the CO C $1s \rightarrow 2\pi^*$ XA resonances for islands with an average number of atoms from 140 to 3000 are compared. Values are given both for the 90 K situation and after heating to 300 K.

For the 90 K case an increase of the $2\pi^*$ resonance width with island size can be seen. Though the shape of the

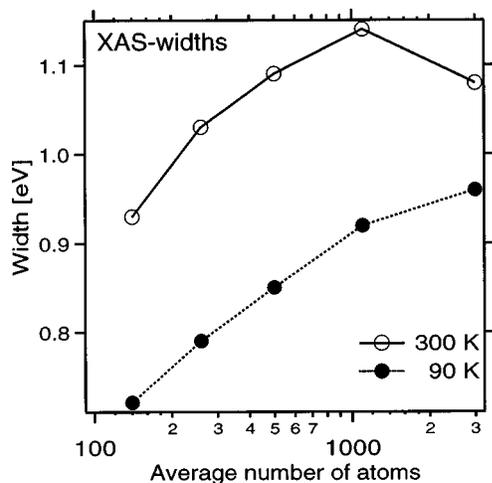


FIG. 6. The widths of the C $1s \rightarrow 2\pi^*$ XA-resonance peaks (see Fig. 5) as prepared at 90 K and after flashing to 300 K as a function of cluster size.

XA spectrum reflects the density of $2\pi^*$ states in the final state,^{29,30} it has been shown that the width of the C $1s \rightarrow 2\pi^*$ absorption resonance often is correlated to the bonding strength between the CO and the metal in the ground state, as measured by, for example, TDS.³¹ The observed broadening with increased size could then indicate that the bonding strength between the CO and the Rh island increases for larger clusters. However, the size-dependent changes of the resonance widths are rather small compared to what has previously been observed for Pd clusters,²⁵ which would indicate that the size-dependent changes in the interaction strength would be larger for Pd. This is also in accordance with TDS data, which shows that CO adsorbed on Pd clusters desorbs at considerably lower temperatures for smaller clusters as compared to large clusters and single crystal surfaces, whereas no such dramatic effect was seen for the Rh islands.¹⁴

Upon heating to 300 K the XA widths increase for all samples, and it is evident that the increase is size dependent. The change in width is largest for CO on the 1100-atom islands, where the $2\pi^*$ resonance peak is even broader than for the 3000-atom islands. As the broadening occurs mainly on the low-photon-energy side, the peak is also shifted slightly in this direction. This indicates that changes similar to those of the XPS peaks are also undergone by the XAS peak, i.e., intensity is shifted from one component at high photon energy to another, possibly broader, component at lower photon energy. However, due to the lack of features in the C $1s \rightarrow 2\pi^*$ XA-resonance peaks we are unable to conclusively identify any components.

2. Implications of XPS and XAS results: Predissociative changes

Based on the XPS and XAS results, we will now try to explain the existence of the two species and what causes the heating-induced effects seen for heating to 300 K. For this complex system there are a number of properties that may change upon heating, such as the size and geometrical structure of the Rh islands, the CO coverage, and the distribution of sites occupied by CO molecules. However, the island size distribution is expected to exhibit a single maximum, which should not give rise to two discrete C $1s$ peaks. The shift of the C $1s$ peak to lower BE upon heating could, in principle, be due to coalescence of the islands, but STM shows that this does not occur.²⁰ Such a shift would also be expected to be largest for small islands and decrease continuously with increasing size.

Local intra-island restructuring is more difficult to rule out. If we assume that we have the same CO species, i.e. the CO–Rh coordination is unaffected, the screening provided by the Rh atoms might change upon restructuring by, for instance, a change in the Rh–oxide interaction. However, the XAS data, which essentially monitor the properties of a neutral core-excited CO species, also show that the CO–Rh bonding properties have changed for some of the adsorbed CO. Desorption of some CO could, in principle, contribute to the observed shift, but as the CO C $1s$ intensity remains constant both desorption and binding energy shifts resulting from it should be negligible.

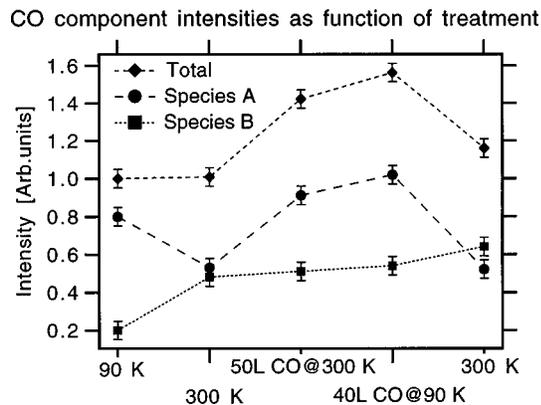


FIG. 7. The CO C 1s intensities for the total CO peak, "species A", and "species B" at different steps in the heating and readsorption process for islands with an average of 500 atoms.

A more reasonable explanation for the appearance of two species is the possibility for CO to occupy different sites. On Rh(111), the C 1s binding energies are 286.0 eV for CO in an on-top site and 285.4 eV for CO in a three-fold hollow site.²² This gives a binding energy separation of 0.6 eV, which is close to the separations found here (see Table I). Moreover, temperature-dependent changes have been observed for CO adsorbed on the Rh(111) surface,³² for which it was shown that heating caused the adsorbed CO to shift between sites of higher and lower coordination, in a direction dependent on the initial CO coverage. The situation on the (111) surface that most resembles the 90 K situation on the Rh islands is found at a CO coverage of 0.52 ML, where 20% of the CO occupies hollow sites (low-BE component) and the rest are in on-top sites (high-BE component). In this case, it is seen that the population in the low-BE hollow site increases upon heating, but unlike the changes observed on the clusters the changes on the (111) surface are reversible.³² It is noteworthy mentioning that NMR studies of CO adsorbed on Pd clusters have also shown temperature-dependent changes of the adsorption site.³³

The assignment of the two species as due to CO in different sites is consistent with the XAS observations. The photon energy positions of the absorption resonance peaks for different species are expected to shift in correlation with the core level XPS peaks.³⁴ An increase in the XPS component "B" at low BE would then be reflected as an increased intensity on the low-photon-energy side. A change to a more highly coordinated site is also expected to cause a broadening of the CO $2\pi^*$ resonance peak due to an increased CO $2\pi^*$ -substrate-metal d hybridization.^{31,34} In order to verify that this also applies for CO/Rh, we measured C 1s $\rightarrow 2\pi^*$ XAS spectra for CO/Rh(111)(4 \times 4), where CO only occupies on-top sites²² and for CO+K/Rh(111), where CO only occupies hollow sites.³⁵ The XA widths were found to be 1.1 eV for the on-top site and 1.7 eV for the three-fold hollow sites, supporting the arguments above. It was also found that the XA peak for CO adsorbed in the three-fold hollow site was at a photon energy ~ 0.35 eV lower than the peak for CO adsorbed on top.

The characteristic changes in the XPS and XAS spectra

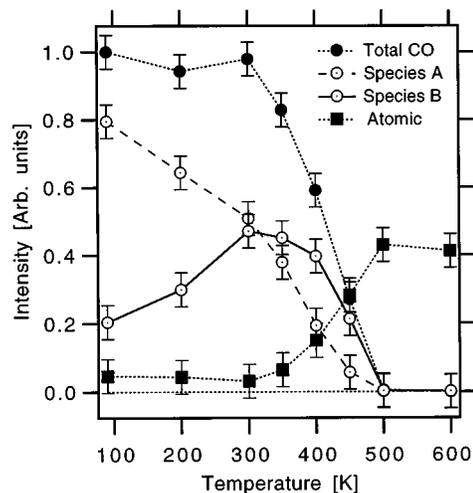


FIG. 8. The determined intensities for the atomic carbon C 1s peak, the CO C 1s peak, and its two components for the different heating steps. The islands consist of an average of 500 atoms.

observed upon heating can thus be interpreted as due to a change of some of the adsorbed CO from sites with lower coordination ("A") to more highly coordinated sites ("B"). This is confirmed by adsorption of additional CO after heating to 300 K, as presented in Fig. 7. Upon heating from 90 to 300 K a decrease of species "A" and a corresponding increase of species "B" is observed. When the system is exposed to additional CO, this adsorbs almost exclusively as species "A", and the amount adsorbed is comparable to the amount lost due to the transformation upon heating. This can be interpreted as a repopulation of "A" sites left open by CO moving to "B" sites. When the system once more is heated to 300 K, most of the additional CO desorbs, but some is transformed into species "B". Since the increase of species "B" is much smaller upon the second heating, we conclude that all available "B" sites are being occupied.

C. The dissociation process

In Sec. III B we have shown that the CO C 1s peak consists of two different components related to CO adsorbed in two different sites. Upon heating, some of the CO adsorbed in the less-coordinated sites shifts into more highly coordinated sites. To gain further information about this transformation and about the subsequent heating-induced dissociation process we now take a more detailed look at the intensity changes as a function of temperature. Figure 8 shows the intensities of the two CO components and the atomic carbon peak as a function of heating for islands with an average of 500 atoms. The total CO intensity is also included to show changes in the amount of adsorbed CO in the system. The general trends observed in this figure were also observed for other sizes.

Heating to 200 and 300 K yields a gradual transformation of species "A" into species "B", as discussed in Sec. III B. The total CO intensity remains the same, in agreement with the TDS results.^{14,36} Further heating leads to a decrease in the amount of CO adsorbed on the islands. This decrease is caused by the competing processes of desorption and dis-

sociation, as mentioned in Sec. III A. The amount of CO that dissociates is reflected by the increase in intensity of the atomic carbon C 1s peak.

At temperatures above 300 K, the CO intensities of both species "A" and species "B" decrease. The decrease is, however, more rapid for species "A". If the intensity changes for the two CO components are compared to the intensity changes of the atomic carbon peak, it is seen that the changes for species "B" and atomic carbon are inversely correlated. This strongly suggests that it is the CO adsorbed in sites of type "B" that dissociates, which is consistent with the trend presented in Sec. III B 1. This conclusion is corroborated by theoretical calculations for CO dissociation on Rh surfaces that suggest that CO is adsorbed in sites with high coordination prior to dissociation.³⁷ The intensity decrease of species "A" is well correlated with the CO desorption, as we show in more detail elsewhere.³⁸

Another result supporting the conclusion that it is the CO adsorbed in sites of type "B" that dissociates is found if the clusters are exposed to CO once more after dissociation. The new CO peak consists almost exclusively of species "A". The most plausible explanation for this is that the sites of species "B" are blocked by the atomic carbon produced by dissociation.

As concluded in Sec. III B, the adsorbed CO on the Rh islands consists of two species. We have now shown that upon heating above 300 K, these species exhibit very different behavior. Species "A" is mainly of desorptive character, whereas species "B" is dissociative.

D. The dissociative sites

The previous sections have shown that the size-dependent CO dissociation activity observed for Rh clusters is correlated to the availability of highly coordinated sites upon the clusters. These sites exhibit a relatively strong metal-CO bond, as was indicated by Fig. 8. However, factors other than the interaction strength between metal and adsorbate are affecting the probability for dissociation of adsorbed CO, as illustrated by the comparison with CO/Rh(111). The CO desorption temperature for this surface is similar to those observed for CO on the clusters. In addition, the XAS resonances for CO on the (111) surface are broader than for any CO species on the clusters, which also indicates a stronger CO-Rh bond.³¹ Nevertheless, no dissociation of CO is seen on the Rh(111) surface.⁵

Furthermore, the fact that the site changes observed on the clusters are irreversible is a clear indication that the more highly coordinated sites occupied by CO on the supported clusters are not comparable to the sites available on the (111) surface. This is supported by the smaller BE separation of the two components observed in the C 1s XP spectra for CO on the Rh particles, which suggests that the change in coordination between the two different sites is not as large on the islands as on single crystals. The trend of an increased splitting would then be explained by the clusters becoming more regular and ordered with increased size.^{15,20}

As previously mentioned, CO does not dissociate on close-packed crystal surfaces such as Rh(111)⁵ and Rh(100),²⁷ but does dissociate on at least some more open

and stepped surfaces, such as Rh(210).⁸ This indicates that steps play an important role in the dissociation process. Based on an atom-probe study of CO on Rh surfaces, Ren and Liu have suggested that the density of steps is crucial.^{39,40} The Rh clusters in this study are basically three-dimensional islands, and, in the initial stages of the growth, the number of steps on the island is expected to increase with island size. Beyond a certain size, however, the islands would be expected to develop more ordered surfaces, and the step density would begin to decrease. Thus, the number of steps on the islands is intuitively expected to change in a way similar to the dissociation activity we observe. It is therefore reasonable to assume that the reactive sites where CO dissociates are connected to the irregularities on the islands, which was proposed in our previous paper.²⁰

In the present study we demonstrate that only a fraction of the CO adsorbs in sites of type "B" at 90 K. Heating then causes more of the adsorbed CO to populate these sites. As Fig. 4 shows, a larger fraction of the available dissociative sites are initially occupied on both the smallest and the largest clusters in this study. This could be explained by changes in adsorbate mobility with varying island size. On the smaller and larger islands, which have a lower density of steps (and other defects), the adsorbed CO can diffuse to many of the available dissociative sites already at 90 K. For the medium-sized, more irregular, islands, the diffusion barriers for CO are larger, and a smaller fraction of the available dissociative sites are populated at 90 K. Upon heating to 300 K, the mobility of the adsorbed CO increases and more of the dissociative sites are populated. Consequently, since more such sites remains available for the clusters in the middle range, the heating-induced changes in the CO-site distribution will become larger for these.

In the size-range studied in this work the varying proportion of dissociative sites, as seen in Fig. 4(b), explains the size-dependent dissociation activity. For clusters smaller than those studied here, other factors would, however, be expected to affect the dissociation activity. As the islands get smaller and more two dimensional, the importance of the Rh-oxide interaction will increase drastically. It has also been shown that a certain minimum Rh area is required for dissociation to occur,^{41,37} so for very small clusters spatial constraints are expected to affect the dissociation activity. It remains to be seen what role these factors would play for ultrasmall Rh particles on the Al₂O₃ film.

To summarize this section we have shown that the observed dissociation maximum is caused mainly by the size-dependent variation of the availability of sites favorable for dissociation on the clusters.

IV. CONCLUSIONS

The heating-induced CO dissociation activity on Rh islands supported by a thin Al₂O₃ film shows a strong size dependence. The fraction of dissociating CO increases with size for islands up to ~1000 atoms, where a maximum is observed. After this point the dissociation probability exhibits a pronounced drop and then continues to decrease slowly with size.

Size-dependent changes in the C 1s XP spectra for these CO–Rh systems, which are strongly correlated with the dissociation efficiency, are observed prior to the onset for dissociation and desorption. These changes can be explained as a shift of adsorbed CO into more highly coordinated sites favorable for dissociation, and these sites are suggested to be connected to irregularities on the Rh surface. We propose that the size dependency of the dissociation activity is mainly caused by the proportion of sites favorable for dissociation on the islands.

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