Vibrational spectroscopy of imperfect CO/Pd(111) surfaces obtained by adsorption between 150 and 230 K

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Abstract
Sum frequency generation and IR absorption spectra of CO adsorbed on Pd(111) are reported. Adsorption of CO in the surface temperature range 150–230 K results in the appearance of extra peaks in the spectral range of the CO stretching vibration. The conditions of appearance of these peaks, and their stability, are investigated. The extra peaks are assigned to sites at antiphase domain boundaries, in which CO is less bonded than in the regular sites of the domains. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction
The adsorption of CO on transition metals is an important research area owing to its technolog-ical relevance in heterogeneous catalysis and for the reduction of car exhausts. Because of its large dynamic dipole, CO is also well adapted for being probed by the site sensitive IR absorption spectroscopy (IRAS) and it has been widely used to study site effects in adsorption and surface reactions [1]. The adsorption of well-ordered layers on most transition metal surfaces has been extensively studied with IRAS. CO on Pd(111) may adsorb on a variety of adsorption sites, depending on the surface coverage [1–6]. The saturation coverage itself depends on the surface temperature because the adsorption energy decreases with coverage, as a result of the repulsive CO–CO interactions. The order of stability for an isolated CO molecule on Pd(111) is threefold hollow > bridge > linear. Thus, threefold hollow sites are preferred at low coverage (θ ≤ 0.33 monolayer (ML)) (in this work, 1 ML is equal to the density of Pd atoms in the (111) plane, or 1.32 × 10^{15} cm^{-2}), with the well-defined structure \( \sqrt{3} \times \sqrt{3} \) \text{R} 30° at 0.33 ML. Above 0.33 ML, the relative stabilities of the three sites is no longer the dominant factor to determine the surface structure, which results from the combi-nation of the attractive Pd–CO and repulsive CO–CO interactions. Between 0.33 and 0.60 ML, CO molecules occupy bridge sites. Well defined structures occur at 0.5 ML (\( \sqrt{3} \times 2 \) or \( \sqrt{3} \times 2 \) rect) and 0.6 ML (\( \sqrt{3} \times 5 \) rect). Between 0.5

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and 0.6 ML, the structure consists of a mixture of phase and antiphase domains having the local density of 0.5 ML and the $\sqrt{3} \times 2$ rect structure, separated by regularly spaced domain walls where the local CO density is larger. The global surface structure is $\sqrt{3} \times \sqrt{3}$, with $a$ up to 35 at 0.514 ML. The compression of the CO layer between 0.5 and 0.6 ML is due to the decreasing separation between domain walls [6]. As a consequence of the repulsive CO-CO interaction, the adsorption energy of CO decreases with coverage from 1.5 eV on the clean surface to 0.8 eV at 0.5 ML and 0.4 eV at 0.6 ML [2,3,7]. Above 0.6 ML, the primitive cell of the adsorbate continues to decrease in size, while a combination of linear and bridge sites are occupied, with an adsorption energy of 0.26–0.52 eV, depending on the adsorption temperature [7]. Finally, above 0.66 ML, another structure is observed, with threefold hollow and linear sites, the ultimate saturation coverage (in the absence of gas phase CO) of 0.75 ML being obtained at $\approx 100$ K [8].

The knowledge of the structure of less ordered layers is far from being complete, although it is recognized that defects often mediate the nucleation and growth of adsorbed layers, and are essential for the reactivity of surfaces. Defects may be related to the substrate (adatoms, vacancies, step edges), but the adsorbed layer itself may not be perfectly ordered. In this paper, we report on such a disorder of the adsorbed layer on Pd(111), which appears by adsorption at “low” temperature. Our observations are related to two features which have already been reported and are still to be understood. One is a peak at 2158 cm$^{-1}$ when CO is adsorbed at 90 K followed by an anneal to 200 K [8,9]. This frequency is surprising because it is higher than that of gas phase CO, whereas chemisorption weakens the CO bond and thus is expected to reduce the CO stretch frequency. Such a high frequency CO peak has been encountered previously on SiO$_2$ [10], and on Pt(111) at large pressure and surface temperature ($\approx 50$ mbar CO, $\approx 130$ mbar O$_2$, $\approx 600$ K) [11]. The peak was assigned to a defect, and step edges were proposed [8]. The second feature is the variation of the desorption kinetics with adsorption temperature, a non-equilibrium effect which was attributed to the existence of domains [7]. The desorption energy is expected to vary between the domains and the boundaries. If the size and/or surface density of domains varies with adsorption temperature, the desorption kinetics will reflect this change, as observed. The nucleation of domains on the CO/Pd(111) surface at low coverage is supported by the observation of the $\sqrt{3} \times \sqrt{3}$ R 30° LEED pattern (corresponding to a nominal coverage of 1/3 ML) in a range of coverages that extends well below 1/3 ML [1].

In this work, we record IR spectra for different surface temperatures and CO pressures, with and without annealing of the CO adlayer. The stability of the observed extra sites is investigated. Our observations are consistent with the interpretation that the extra sites are at the frontiers between antiphase domains.

2. Experimental

Experiments were carried out under a base pressure of $2 \times 10^{-10}$ mbar. The UHV experimental set-up consists of two chambers. One chamber is dedicated to optical measurements. The sample can be transferred in UHV to the second chamber (described elsewhere [12]) where it can be characterized by LEED and Auger electron spectroscopy. The Pd single crystal is prepared by Ar$^+$ sputtering which appears by adsorption at ''low'' temperature. Our observations are related to two features which have already been reported and are still to be understood. One is a peak at 2158 cm$^{-1}$ when CO is adsorbed at 90 K followed by an anneal to 200 K [8,9]. This frequency is surprising because it is higher than that of gas phase CO, whereas chemisorption weakens the CO bond and thus is expected to reduce the CO stretch frequency. Such a high frequency CO peak has been encountered previously on SiO$_2$ [10], and on Pt(111) at large pressure and surface temperature ($\approx 50$ mbar CO, $\approx 130$ mbar O$_2$, $\approx 600$ K) [11]. The peak was assigned to a defect, and step edges were proposed [8]. The second feature is the variation of the desorption kinetics with adsorption temperature,
locked, pulsed YAG laser. The IR beam (\( \pm 10\,\text{ps}, 2\,\text{mJ cm}^{-2}, \pm 1500\,\text{pulses s}^{-1} \)) is scanned in the spectral region of the CO internal vibration. It is overlapped temporally and spatially on the Pd(111) single crystal with a frequency-doubled fraction of the pump laser (532 nm, \( \pm 10\,\text{ps}, 0.5\,\text{mJ cm}^{-2} \)). The SFG is detected on a photomultiplier tube after passing through a combination of filters and a monochromator used to reject the YAG and IR frequencies. The SFG signal from the sample is divided by a reference signal obtained by mixing a small fraction of the laser beams into a ZnSe crystal. This introduces a slope in the baseline because the response of ZnSe is not entirely frequency independent. The IR laser path to the chamber is not purged against atmospheric water, and this results in a considerable noise below 1900 cm\(^{-1}\), where the H\(_2\)O peaks are larger, despite the division by the signal from ZnSe. The thermal and photochemical laser-induced desorption was estimated in a separate study \[14\]. For the less bonded sites of CO on Pd(111), the photochemical desorption yield during a spectral scan from 2200 to 1800 cm\(^{-1}\) (which takes \( \pm 4\,\text{min} \)) was estimated to be \( \pm 3\% \), while the thermal desorption was estimated to be negligible.

The FTIR experiments are performed in the same UHV chamber at a resolution of 4 cm\(^{-1}\). 1000 scans are used for each spectrum. The apodization function is a triangle. The limitation of our signal to noise ratio in FTIR experiments arises from long term fluctuations of the H\(_2\)O concentration in the path between the spectrometer and the detector. The reference spectrum (Pd(111) without CO), which is collected before each adsorption, must be subtracted from the spectrum with some coefficient close to unity and chosen to eliminate the H\(_2\)O peaks. This procedure, however, affects the noise of the spectra. It also adds specific noise at the H\(_2\)O frequencies, probably because the noise on the H\(_2\)O line intensities is comparable with the CO peak intensities. The threefold hollow sites are strongly affected, and they are not quantitatively measured in this work, except when the absorption intensity is high (which occurs only when spectra are recorded with the surface in equilibrium with gas phase CO above \( 10^{-7}\,\text{mbar} \)). The low frequency side of the peak of the bridge sites is also affected, although to a much lesser extent. The other peaks are not directly affected, except through the noise added by subtracting the reference spectrum. The difference spectra presented in the figures are less affected because they correspond to spectra recorded at smaller intervals, and because they are directly subtracted from one another without using a reference spectrum.

3. Results

We obtain spectra which are very similar to those of the literature when the surface is cooled after adsorption at room temperature, or annealed to 300 ± 30 K under a CO pressure (Fig. 1a, Fig. 2, and Table 1). At CO pressures of \( \pm 10^{-7}\,\text{mbar} \) and below, the spectrum exhibits the two bands...
sites. The weaker band (2083 cm$^{-1}$, width 15 cm$^{-1}$ at 150 K) is assigned to linear sites. Its intensity is approximately 3 times smaller than that of the bridge sites: this ratio of 3 is equal to the ratio of the number of molecules occupying the two sites in the unit cell, showing that in this case the dynamic dipole is similar in the two sites (which is not always true). The widths of both lines increase with temperature.

At CO pressures above $10^{-6}$ mbar, the vibrational spectrum is modified (Fig. 2b and c and Table 1), due to the coexistence of the linear + bridge structure with a more closely packed linear + threefold hollow structure [1]. The presence of gas phase CO above 150 K allows a reversible conversion of a fraction of the CO adlayer by adsorption/desorption. As a result of the relative intensities and frequencies of the linear sites in the two structures (Table 1), the line of the linear site grows, shifts to higher frequencies, and narrows under an increased CO pressure. A peak in the spectral region of the threefold hollow sites appears at 1890 cm$^{-1}$. The peak intensity of the bridge sites decreases. The time dependence of the SFG signal at 2094 cm$^{-1}$ shows that the kinetics of interconversion is faster than the maximum time resolution (1 s) that can be achieved in the present experiment (Fig. 3). This finding is compatible with the adsorption/desorption mechanism of interconversion, because the latter becomes noticeable in the spectra only if the adsorption rate is at least comparable with the desorption rate. This occurs experimentally at $10^{-6}$ mbar, which corresponds to an adsorption rate of $1 \text{ML s}^{-1}$. A desorption rate of $1 \text{ML s}^{-1}$ cannot be followed with our time resolution.

![Fig. 2. Effect of a change of the CO pressure after the initial adsorption for a fully ordered CO layer on Pd(111) obtained by annealing to 380 K and cooling to 170 K under $10^{-7}$ mbar of CO. The spectra are recorded under a CO pressure of (a) $10^{-7}$ mbar, (b) $10^{-6}$ mbar and (c) $6 \times 10^{-6}$ mbar. The horizontal lines represent the zero of the spectra.](image)

Table 1
Properties of the various sites occupied by CO on Pd(111) in the temperature range 150–230 K.

<table>
<thead>
<tr>
<th>Type of site</th>
<th>Regular sites</th>
<th>Sites populated in presence of gas phase CO</th>
<th>Sites at antiphase domain boundaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (cm$^{-1}$)</td>
<td>Linear</td>
<td>Bridge</td>
<td>Linear</td>
</tr>
<tr>
<td>Linear</td>
<td>2083</td>
<td>1955</td>
<td>2103</td>
</tr>
</tbody>
</table>

* Observed only in equilibrium with gas phase CO above $10^{-6}$ mbar.
1 The assignment to domain boundaries is tentative.
2 Tentative.
3 Threefold hollow sites are observed only for an initial adsorption at a CO pressure higher than $10^{-6}$ mbar.
4 The frequencies depend on the actual surface temperature and CO pressure.
When CO is adsorbed below $\approx 270$ K, the spectra exhibit four extra peaks (Fig. 1b to d and Table 1) after cooling to $\approx 230$ K in equilibrium with gas phase CO, or by direct adsorption between 150 and $\approx 230$ K. The first peak at 2158 cm$^{-1}$ previously reported by Kuhn et al. [8] is the narrowest line of the whole spectrum (7 cm$^{-1}$) under all circumstances. This peak is also the only one to be totally insensitive to changes of the CO pressure once the surface has been saturated by CO (Fig. 1). However, its intensity increases by a factor of 2 as the CO pressure is increased from $10^{-7}$ to $5 \times 10^{-6}$ mbar during the initial adsorption (Fig. 4). The second extra peak is centred at $\approx 2093$ cm$^{-1}$. It overlaps the normal peak of the linear sites at $\approx 2083$ cm$^{-1}$, resulting in a broad peak, the shape of which depends on the frequencies and relative intensities of its two components (as the CO pressure during the adsorption increases, the component at 2083 cm$^{-1}$ shifts to lower frequencies like the peak of the bridge sites (Fig. 4)). A third extra peak is visible at 1940 cm$^{-1}$ as a shoulder of the peak of the bridge sites. A fourth extra peak appears at 1890 cm$^{-1}$ in the spectral region of the threefold hollow sites. Owing to the poor sensitivity in this region, it is not possible to ascertain whether it is populated or not upon adsorption at $10^{-7}$ mbar. The intensity of this peak increases with the CO pressure during the initial adsorption. The growth of the extra peaks is at the expense of the peak of the bridge sites. The decrease of the peak intensity is $\approx 30\%$ and $\approx 50\%$ for adsorption at $10^{-7}$ and $5 \times 10^{-6}$ mbar, respectively. The intensity integrated over all the peaks does not vary significantly with the adsorption conditions.

If the CO pressure is varied after surface saturation by CO at low temperature (Fig. 1b to d), the reversible interconversion to the linear + threefold hollow structure occurs as in the case of the well-ordered surface. It does not affect at all the peak at 2158 cm$^{-1}$. In this case, however, the overall integrated intensity does vary with the CO pressure. It decreases by a factor 0.83 as the CO pressure increases from $10^{-7}$ to $6 \times 10^{-6}$ mbar. This suggests that the difference in the dynamic dipole between the bridge and threefold hollow sites is larger than that between the linear + bridge sites and the extra sites.

The thermal stability of CO in the various sites is
illustrated in Fig. 5, which exhibits spectra of the surface recorded at a constant CO pressure of $10^{-7}$ mbar while the surface temperature is ramped up and down twice, the first time up to $\approx 230$ K (Fig. 5a–d), and the second time up to $\approx 330$ K (Fig. 5d–f). The extra sites are not so stable as the regular ones. CO desorbs at 200 K from the linear sites at 2093 cm$^{-1}$ and from the threefold hollow sites, and at $\approx 230$ K from the site at 2158 cm$^{-1}$ (the intensity at 2158 cm$^{-1}$ is only attenuated in Fig. 5c because the temperature is not kept constant during the recording of one single spectrum, and because the surface in this experiment is held in equilibrium with gas phase CO, allowing for readsorption). Although CO from the extra sites is desorbed at 230 K, the sites themselves are still present. They are repopulated after cooling (Fig. 5d). Some irreversible changes also occur, as evidenced in Fig. 5d and (d–c) by a slight frequency shift of the bridge sites. Only after annealing up to $\approx 300$ K does the surface reorder and the extra sites disappear, as shown by the final spectrum (Fig. 5f). In the set of spectra of Fig. 5, it appears clearly that the thermally less stable peak is that at 2093 cm$^{-1}$. Additional data concerning thermal desorption and photodesorption have been given elsewhere [14]. The extra sites are selectively photodesorbed at 532 nm with picosecond laser pulses, and at 308 nm with nanosecond pulses. In contrast, CO is not photodesorbed from the regular sites: the photoreactivity affects only the less stable sites in the case of CO on Pd(111).

4. Discussion

4.1. Nature of the site at 2158 cm$^{-1}$

The extra sites are well defined, because they give rise to narrow spectral features. The peak at 2158 cm$^{-1}$ has a narrow width (7 cm$^{-1}$). So does the peak at 2093 cm$^{-1}$, as can be judged from the difference spectra of Fig. 5 (b–a) and (c–b). The frequency value of 2093 cm$^{-1}$ suggests that linear sites are involved. By contrast, the frequency of 2158 cm$^{-1}$ is not normally observed for chemi-
are identical, the number of impurities should decrease when the adsorption pressure increases (because the time available for H$_2$O adsorption would decrease), in disagreement with the observations of Fig. 4. Also, the partial pressure of H$_2$O is permanently monitored during the experiments. The ratio between H$_2$O and CO pressures is always less than 10$^{-4}$ in our experiment, resulting in an H$_2$O coverage of at most 10$^{-5}$ ML. It is difficult to understand how such a small amount of water could produce changes of peak intensities corresponding to variations of the CO coverage in the bridge sites of a few tenths ML.

Other impurities leading to an extra site of CO could be oxygen, carbon, or nitrogen. In the absence of any leak, there is no source of nitrogen in our experiment. However, some oxygen and carbon might remain adsorbed if the cleaning procedure is not well done. It is dubious, however, that oxygen and carbon impurities are the source of the extra peaks, because these disappear at 300 K: oxygen desorbs between 700 and 900 K [16], while carbon cannot be removed from Pd(111) by heating [5].

A second possibility is that CO is physisorbed. Fig. 5. Thermal stability of CO in the extra sites: FTIR spectra of an unannealed CO layer on Pd(111) recorded under a CO pressure of 10$^{-7}$ mbar during two cycles of annealing and cooling. The temperature is raised to 230 K in the first cycle from (a) to (d) (allowing CO to desorb from the extra sites), and 330 K in the second cycle from (d) to (f) (also allowing the surface to reorder and the elimination of the extra sites which are not repopulated during cooling). The surface temperature varies during the recording of a spectrum (which lasts 4 min), so the values indicated are approximate. The initial adsorption was at 170 K and under 10$^{-7}$ mbar of CO.

sorbed CO, and it may originate from several causes.

One possibility is that CO would be coadsorbed with an impurity. H$_2$O does not adsorb on Pd(111) at room temperature [15], but it does in the temperature range where the extra peaks are observed. If H$_2$O coadsorption were responsible for their occurrence, the intensities of the extra peaks would be expected to increase under various experimental circumstances, such as an increase of the delay between cooling and CO adsorption; no such trend is observed. Also, if the other conditions are identical, the number of impurities should decrease when the adsorption pressure increases (because the time available for H$_2$O adsorption would decrease), in disagreement with the observations of Fig. 4. Also, the partial pressure of H$_2$O is permanently monitored during the experiments. The ratio between H$_2$O and CO pressures is always less than 10$^{-4}$ in our experiment, resulting in an H$_2$O coverage of at most 10$^{-5}$ ML. It is difficult to understand how such a small amount of water could produce changes of peak intensities corresponding to variations of the CO coverage in the bridge sites of a few tenths ML.

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A second possibility is that CO is physisorbed. It would be slightly raised above the plane of other CO molecules owing to the strong repulsive intermolecular forces which occur when the coverage is locally too large. In this case, a CO frequency close to the value in the gas phase (2143 cm$^{-1}$) is expected. A third possibility is that CO is chemisorbed and interacts strongly with the neighbouring molecules. The CO frequency would be greatly shifted by perturbation and would not be typical of the local chemical environment. From the data displayed in Fig. 5, it appears that the peak at 2158 cm$^{-1}$ is more stable than the peak at 2093 cm$^{-1}$ which is probably chemisorbed, suggesting (although not proving) that they are both “chemisorbed” sites. In the absence of additional experimental data (such as IRAS spectra of isotopically enriched CO) it seems reasonable to assume that the 2158 cm$^{-1}$ band corresponds to a chemisorbed, weakly bound state, the weak stability being due to a locally large coverage with repulsive interactions and strong perturbations. It follows that the relative intensity of the peak at 2158 cm$^{-1}$ with respect to the others may not
reflect the number of CO molecules occupying the different sites. In the next section, we propose an arrangement of antiphase domains that would result in such strongly interacting CO molecules in linear sites.

### 4.2 Surface structure

It is not straightforward to determine the surface structure accounting for the extra peaks. More data using other experimental techniques, e.g. STM at low temperature, would be necessary. However, the available information allows us to propose an explanation. Let us first summarize the results:

1. The nature of the extra sites is such that the normal peaks are also present, although they have a lower intensity. The thermal desorption of the CO layer above 230 K is normal, with desorption from the remaining linear sites first (\( \approx 300 \) K), then desorption of a fraction of the bridge sites until the remaining bridge are interconverted to threefold hollow (\( \approx 375 \) K), and then desorption of the remaining CO from the threefold hollow sites (\( \approx 500 \) K). The interconversion to the linear + threefold hollow sites structure by exposure to gas phase CO at a pressure higher than \( \approx 10^{-6} \) mbar is also unchanged on the less ordered surface with respect to the fully ordered one.

2. The surface structure is metastable. The presence of the extra peaks is a kinetic effect, which depends on the time scale of CO adsorption through the CO pressure. The shorter the time scale, the greater are the intensities of the extra peaks.

3. The presence of the extra sites results from a global arrangement of the CO adlayer. The sites exist until room temperature, although they are not populated above \( \approx 230 \) K, and they do not exist on the well-ordered surface.

All these results are compatible with the assumption that the type of defect is antiphase domains, the extra sites being located at domain boundaries. A possible arrangement of two antiphase domains with coverage 0.63 ML is depicted in Fig. 6. The unit cells of the two domains overlap at the frontier, showing that the density of CO at the domain boundary is higher than that in each domain. Therefore, the CO molecules at the frontier are subject to an increased repulsion from their neighbours. We assume that they occupy a site at a position intermediate between the two normal sites corresponding to each domain. With this assumption, half of the molecules at the domain boundary occupy distorted bridge sites, and half occupy distorted linear sites. Two linear sites are located on two next neighbour Pd atoms, an arrangement which is highly repulsive and which is not even found at the ultimate coverage of 0.75 ML. The actual positions of the CO may be slightly different from Fig. 6, and the next neighbours of the CO molecules at domain boundaries are probably also displaced, although to a lesser extent. Fig. 6 shows that the physical situation of CO interacting strongly in linear sites is reasonable, and that two kinds of linear sites (the one at the domain boundary and its next neighbour) may exist in addition to the normal linear site of the domains.

CO islands with local coverage of 0.33 ML and the \( \sqrt{3} \times \sqrt{3} \) \( R30^\circ \) structure are known to nucleate. When they merge at the global coverage of 0.33 ML, there is a finite probability that they are in antiphase with each other. There are certainly mechanisms allowing the islands to reorder by...
surface diffusion, but they take a finite time and require energy to overcome the potential energy barrier for diffusion. Lowering the surface temperature will eventually prevent the reordering, as observed. In addition, increasing the CO pressure will eventually not allow enough time for the reordering to take place entirely. This would explain why the intensity of the extra peaks increase with CO pressure. It is worth noting that this assignment of the extra peaks (which are observed above 0.60 ML) to sites at the antiphase domains boundaries (which form below 0.33 ML) implicitly assumes that the antiphase domains are not broken by continuing CO adsorption from 0.33 to 0.60 ML, although the surface structure and the unit cell change several times in this coverage range.

As stated in Section 1, Guo and Yates observed by thermal desorption that the desorption kinetics depend on the adsorption temperature between 87 K and room temperature [7]. The pre-exponential factor and the desorption energy exhibit variations with coverage which are related by the compensation effect. There is no doubt that Guo and Yates observed the same effect as we do using a different experimental technique. They have suggested that the formation of domains could provide a satisfactory explanation for their observations. They discussed their results in the light of a Monte Carlo simulation of the desorption of $N_2$ from Ru(001), which shows that for this system desorption occurs first from the domains and then from the boundaries [17]. However, it cannot be the case for CO/Pd(111) because we observe that the extra peaks desorb first, showing that desorption occurs first from the boundaries and then from the domains.

The occurrence of extra sites related to antiphase domains should probably be encountered in other systems. For instance, in the case of NO/Pt(111), an increase of the desorption yield by two orders of magnitude was observed when NO is adsorbed at low temperature [18]. Such a behaviour is very similar to that of CO/Pd(111), for which there is no photodesorption from the regular linear+ bridge structure of Fig. 1a, but there is a measurable desorption from the extra sites only.

5. Conclusion

New experimental data are presented concerning the conditions of appearance and the thermal stability of the extra peaks that are present in FTIR and SFG spectra of CO adsorbed on Pd(111) in the temperature range 150–230 K, by comparison with well-ordered CO overlayers. These observations are related to the thermal desorption spectroscopy results of Guo and Yates, that show large variations of the desorption kinetic parameters with adsorption temperature.

Although more theoretical and experimental work using complementary techniques will be necessary to understand fully the nature of the extra peaks, the available data suggest that the extra peaks are due to sites at antiphase domain boundaries. Our results show clearly that the sites at boundaries are less stable than the regular sites of the domains.

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References


