

## ADSORPTION OF CO ON Pd SINGLE CRYSTAL SURFACES

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Received 12 November 1973

Studies of CO adsorption on Pd(110), (210) and (311) surfaces as well as with a (111) plane with periodic step arrays were performed by means of LEED, contact potential and flash desorption measurements. Isothermic heats of adsorption were evaluated from adsorption isotherms. Earlier work with Pd(111) and Pd(100) surfaces is briefly reviewed, yielding the following general picture: The initial adsorption energies vary between 34 and 40 kcal/mole and close similarities exist for the dipole moments, the maximum densities of adsorbed particles and for the adsorption kinetics. At low and medium coverage the adsorbed particles are located at highly symmetrical adsorption sites, whereas saturation is characterized by the tendency for formation of close-packed layers.

### 1. Introduction

The chemisorption of carbon monoxide on transition metals has already been the subject of numerous investigations<sup>1)</sup>, mainly because this is the simplest molecule one can use to study with such problems. Whereas with some metals such as nickel<sup>2,3)</sup> the adsorbed CO molecule may thermally dissociate on the surface, with Pd only molecular adsorption is observed and is completely reversible. This system was therefore particularly chosen in order to obtain information about the "structural" factor of chemisorption, that is, the variation of the adsorption bond by the crystallographic orientation of the surfaces and by the configuration of the adsorbed particles with respect to the surface atoms. A series of results which were already available for the low index planes (111)<sup>4)</sup>, (100)<sup>5-7)</sup> and (110)<sup>8)</sup> are shortly reviewed and [in the case of Pd(110)], partly supplemented and revised. Furthermore measurements with (210) and (311) surface and a regularly stepped (111) plane are reported.

### 2. Experimental

The experiments were performed with a commercial UHV system with 4 grid LEED optics and an additional glancing angle electron gun for Auger electron spectroscopy. The apparatus was further equipped with a quadrupole

mass spectrometer for recording flash desorption spectra, and with a vibrating reference electrode for contact potential measurements by means of a self-compensating Kelvin method. A series of measurements was also performed by the diode method using the LEED gun as electron source. Details of the sample preparation and surface cleaning may be found in ref. 9.

### 3. Results

#### 3.1. Pd(111)

According to previous investigations<sup>4)</sup> CO adsorbs on Pd(111) with an initial isosteric adsorption energy of 34 kcal/mole. This value remains constant up to  $\frac{2}{3}$  of the saturation coverage, then it drops stepwise by 2 kcal/mole and decreases continuously with further increase of the coverage as can be seen from fig. 1. The LEED pattern already exhibits sharp "extra" spots of a  $\sqrt{3} \times \sqrt{3}/R$  30° structure at relatively low coverages indicating

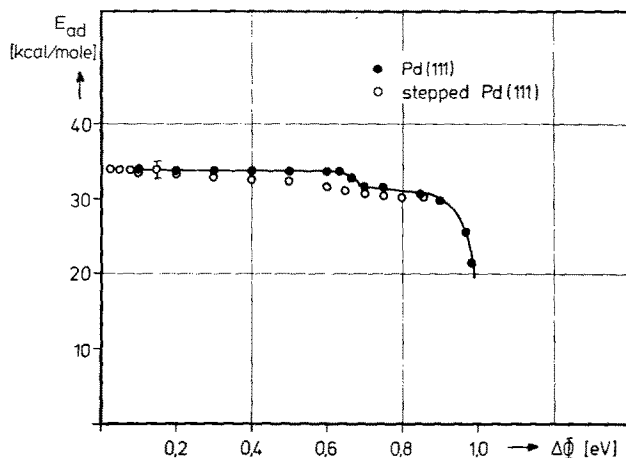


Fig. 1. Isosteric energy of adsorption on Pd(111) (full circles) and on a stepped Pd(111) surface (open circles) as a function of the work function increase  $\Delta\phi$ .

the formation of an island structure (i.e., relatively large patches of ordered arrangements of the adsorbed molecules separated by bare areas). This must be due to weak attractive interactions between the CO molecules and would also explain why  $E_{ad}$  is independent of coverage since increasing the coverage is equivalent to further growth of the islands. Such an effect was observed only with the (111) plane and is ascribed to indirect interactions via the metal electrons<sup>10)</sup>.

A possible model for the  $\sqrt{3} \times \sqrt{3}/R$   $30^\circ$  structure is drawn in fig. 2a. The arrangement of the CO molecules in "bridge" positions is of course ambiguous as long as no analysis of the LEED intensities is performed. However, the configuration of the adsorbed particles with respect to each other is a direct consequence of the positions of additional diffraction spots in the LEED pattern. In any case all CO molecules are equivalently coordinated to the surface atoms in the  $\sqrt{3} \times \sqrt{3}/R$   $30^\circ$  structure.

Upon increasing the CO exposure beyond the completion of this structure (corresponding to a coverage of  $\frac{1}{2}$ ) the unit cell is continuously compressed. The onset of this compression is accompanied by the observed small decrease of the adsorption energy by 2 kcal/mole, indicating that the surface is energetically rather homogeneous.

Saturation of the adsorbate layer may be characterized by the structure model in fig. 2b and corresponds to the formation of a densely packed layer with coverage  $\theta_{\max} = \frac{1}{2}$  and with a mutual distance between the adsorbed molecules of 3.6 Å. This value is in the same range as that determined for the "size" of gaseous CO<sup>11)</sup> and is also found with the other planes.

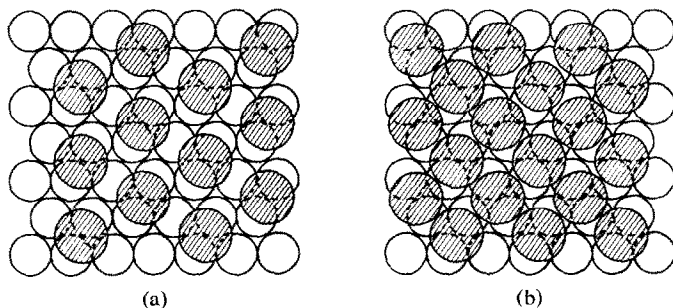


Fig. 2. Structure models for a CO adsorption on Pd(111)<sup>4)</sup>. (a)  $\sqrt{3} \times \sqrt{3}/R$   $30^\circ$  structure; (b) compressed structure at saturation.

### 3.2. Pd(100)

The first LEED observations with CO adsorbed on Pd(100) were made by Park and Madden<sup>5)</sup> who reported the formation of a  $4 \times 2/R$   $45^\circ$  structure for which they proposed a model as shown in fig. 3. In principle the same difficulty as for Pd(111) arises in the consideration of the configuration of CO molecules with respect to the surface atoms of Pd(100). However, the "bridge" positions as drawn in fig. 3 exhibit the only possibility for equal coordination of all adsorbed molecules. Therefore this model appears to be highly probable and is further confirmed by the results of theoretical evaluations of the energy profiles for CO adsorption on various Pd surfaces<sup>12)</sup>. More detailed studies were made by Tracy and Palmberg<sup>6)</sup> who found that

the ordered structure forms only at the corresponding coverage  $\theta = \frac{1}{2}$  [i.e. no island formation as in the case of Pd(111)], which must be due to repulsive interactions. This agrees with the observed continuous decrease of the adsorption energy with increasing coverage from the initial value of 36 kcal/mole.

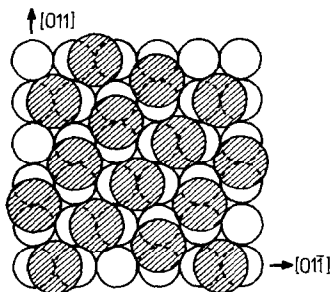


Fig. 3. Model for the  $4 \times 2/R 45^\circ$  structure of CO adsorbed on Pd(100) [after Park and Madden<sup>5</sup>].

The coverage may be increased beyond  $\theta = \frac{1}{2}$  (i.e. completion of the  $4 \times 2/R 45^\circ$  structure) which is again accompanied by a continuous compression of the unit cell<sup>6,7</sup>). At the onset of this compression the adsorption energy drops by about 7 kcal/mole<sup>6</sup>), indicating that the binding energy on this surface varies more strongly than on Pd(111). At room temperature and with CO pressures  $\leq 10^{-4}$  Torr a maximum coverage of about 0.65 is reached, which again means a distance between the adsorbed CO molecules of about 3.5 Å.

At still lower temperatures further compression down to  $\sim 3.1$  Å, characterized by a strongly decreasing adsorption energy was observed<sup>6</sup>).

### 3.3 Pd(110)

Some LEED observations with CO/Pd(110) performed a few years ago<sup>8</sup>) were essentially confirmed with the present extended re-investigation, although the previous interpretation has to be modified.

At an exposure of about 1 L CO at room temperature LEED spots of a  $c2 \times 2$  structure were observed (fig. 4a). This structure exists only in a rather limited range of exposure which is obviously the reason why it was not observed in our previous investigation. The "extra" spots were mostly rather diffuse, indicating the low stability of this structure which is completed after an exposure of 1.2 L. With higher successive exposures a rather stable structure appears, for which we propose the notation " $4 \times 2$ " (fig. 4b) (in contrast to ref. 8 where this structure was classified as " $5 \times 2$ "). It is highly probable that this structure represents a one-dimensional coincidence lattice as outlined below. In this case there are only minor differences between

" $4 \times 2$ " and " $5 \times 2$ " structures, e.g. coverages  $\theta = 0.75$  and  $0.80$ , respectively. Once the " $4 \times 2$ " structure is completed it is the stable final stage of CO chemisorption on Pd(110). However, a remarkable observation already made earlier<sup>8</sup>) was reconfirmed: If a clean Pd(110) surface is exposed to a sudden CO pressure exceeding  $\sim 10^{-6}$  Torr a  $2 \times 1$  structure is formed (fig. 4c). The diffraction spots ( $\pm \frac{1}{2}, 0$ ) may be much weaker than the other "extra" spots. At room temperature this structure is only stable at pressures  $> 10^{-6}$  Torr. With lower pressures it transformed irreversibly into the " $4 \times 2$ " structure.

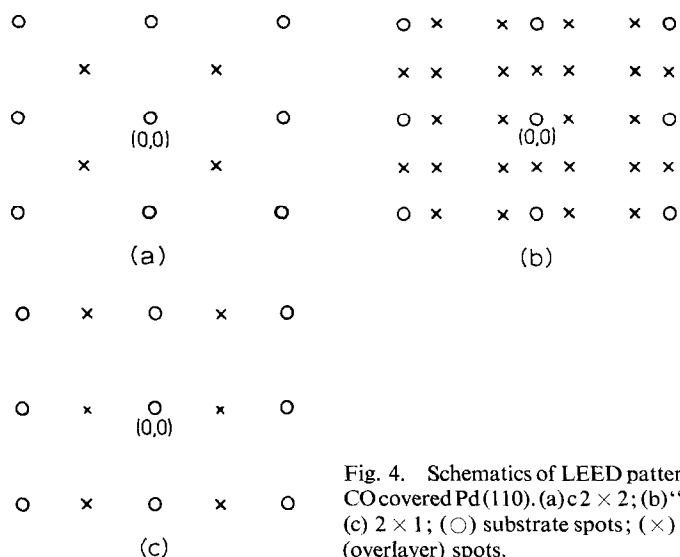


Fig. 4. Schematics of LEED patterns from CO-covered Pd(110). (a)  $c2 \times 2$ ; (b) " $4 \times 2$ "; (c)  $2 \times 1$ ; (O) substrate spots; (x) "extra" (overlayer) spots.

The  $c2 \times 2$  structure is associated with a work function increase  $\Delta\phi \approx 0.7$  eV (this value is not very accurate!). If the " $4 \times 2$ " structure is completed then  $\Delta\phi = 1.05$  eV, whereas a maximum increase of  $\Delta\phi = 1.25$  eV was measured in the case of the  $2 \times 1$  structure.

The variation of the work function was calibrated against the relative amount of adsorbed CO which was derived from the area below the flash desorption spectra. The result was that for all planes  $\Delta\phi$  is directly proportional to  $\theta$  at least up to about 80% of the saturation coverage. With CO/Pd(110) it appeared to be reasonable to measure adsorption isotherms  $\Delta\phi = f(P_{CO})$ ,  $T = \text{const.}$  only up to the completion of the  $c2 \times 2$  structure (i.e.  $\Delta\phi \approx 0.7$  eV) since at even higher coverages kinetic phenomena came into play, namely the competition for formation of the " $4 \times 2$ " structure or  $2 \times 1$  structure, depending on pressure and history. The isosteric heats

of adsorption as evaluated from the adsorption isotherms are shown in fig. 5. The initial heat of adsorption is 40 kcal/mole which remains constant up to about  $\Delta\phi = 0.25$  eV ( $\theta \approx 0.2$ ) and then decreases continuously, from which it is again concluded that repulsive interactions between the adsorbed CO molecules exist. This conclusion is also in agreement with the LEED observations, where the spots of the  $c2 \times 2$  structure only appear near the completion of this structure as was the case with the  $4 \times 2/R45^\circ$  structure on Pd(100).

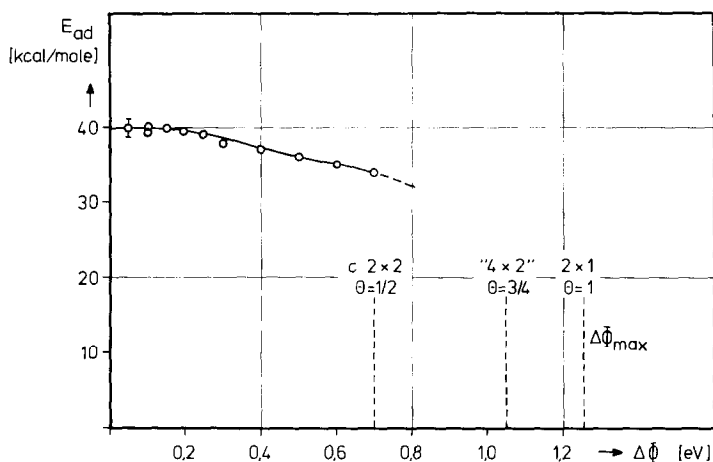


Fig. 5. Adsorption energy for Pd(110) as a function of the work function increase  $\Delta\phi$ .

The recorded flash desorption spectra are not reproduced here, since we believe that due to the high heating rate ( $22^\circ\text{C/sec}$ ) some temperature gradients across the sample existed and therefore the thermocouple reading did not represent the accurate surface temperature. Nevertheless the following information could be obtained from such measurements. After exposures  $< 1$  L only a single desorption peak emerged whose maximum shifted slightly towards lower temperatures with increasing coverage, in agreement with the continuous decrease of the adsorption energy. After exposures  $\geq 1.2$  L a second peak appeared in the flash desorption spectra corresponding to a state whose binding energy is  $\sim 5$  kcal/mole lower than that of the first state. From the LEED observations it followed that at 1.2 L the  $c2 \times 2$  structure is completed and starts to transform into the  $'4 \times 2'$  structure which is saturated at about 2 L.

If one compares the areas below the flash desorption curves (which are proportional to the surface concentrations) for the  $c2 \times 2$  and the  $'4 \times 2'$  structures a ratio of about  $\frac{2}{3}$  results. On the other hand from the structure mo-

del (see below) for the  $c2 \times 2$  structure a coverage  $\theta = \frac{1}{2}$  results, which means that the " $4 \times 2$ " structure corresponds to  $\theta = \frac{3}{4}$ . A quite similar result is obtained if the corresponding values for  $\Delta\phi$  (0.7 and 1.05 eV) are compared.

No flash desorption spectra were recorded for the  $2 \times 1$  structure since it becomes pumped-off slowly at room temperature. From earlier LEED observations a value of 27 kcal/mole for its binding energy was evaluated<sup>8)</sup>, which seems to give right order.

For the  $c2 \times 2$  structure a model with  $\theta = \frac{1}{2}$  is proposed as shown in fig. 6a. It is assumed that the adsorbed CO molecules are located between four Pd atoms of the surface layer which is also suggested by the theoretical results<sup>12)</sup>.

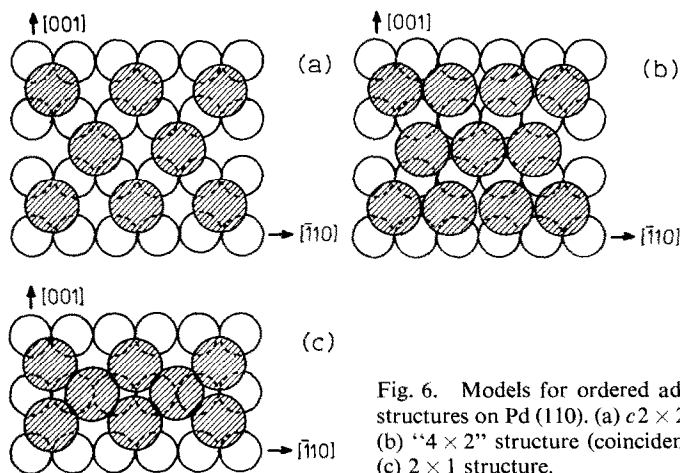


Fig. 6. Models for ordered adsorbed CO structures on Pd(110). (a)  $c2 \times 2$  structure; (b) " $4 \times 2$ " structure (coincidence lattice); (c)  $2 \times 1$  structure.

Since the adsorption energy varies only slightly up to this coverage it is concluded that at lower coverages the CO molecules are located on the same sites and are uniformly distributed over the surface. An analogous  $c2 \times 2$  structure (which was interpreted in the same manner) was found for CO adsorption on Ni(110), which, however, was less stable than in the present case and therefore only visible below room temperature<sup>13)</sup>.

Further agreement between Ni(110) and Pd(110) exists with the two other CO adsorption structures and their interpretations. Again that adsorption phase on Ni(110) which corresponds with the " $4 \times 2$ " structure on Pd(110) is less well ordered and was interpreted as being due to the formation of a one-dimensional incoherent structure<sup>14)</sup>. [Taylor and Estrup<sup>13)</sup> proposed a somewhat different model but with the same coverage.] Fig. 6b shows the model for the " $4 \times 2$ " structure on Pd(110), where the troughs on the surface are filled by CO molecules whose mutual distance is  $\frac{4}{3}a_0 = 3.64 \text{ \AA}$ .

The coverage of this structure is  $\theta = \frac{1}{2}$  which is in complete agreement with the flash desorption and work function data. A model for the  $2 \times 1$  structure ( $\theta = 1$ ) is shown in fig. 6c and again agrees with the findings for Ni(110)<sup>13,14</sup>. The CO-CO distance in this structure is 3.35 Å. However, in the latter case a continuous transformation of domains of the " $4 \times 2$ " structure into those of the  $2 \times 1$  structure takes place with increasing exposure, the adsorption energies in both phases differing by about 5 kcal/mole. With Pd(110) this energy difference is larger and is probably also the reason for the observed kinetic effect: the  $2 \times 1$  structure is only formed if the CO pressure (i.e. rate of impingement) exceeds a certain value. If the coverage is increased continuously by small CO doses the " $4 \times 2$ " structure, which is stable even under a subsequent pressure increase, is found. Further adsorption would be connected with place-exchange processes of the particles already present to less favourable sites which is obviously inhibited.

### 3.4 Pd(210)

The LEED pattern of the clean Pd(210) surface exhibits the expected substrate spots without any indication of faceting or reconstruction. All higher indexed surfaces [(210), (311) and the stepped surface] remained stable under the chosen experimental conditions.

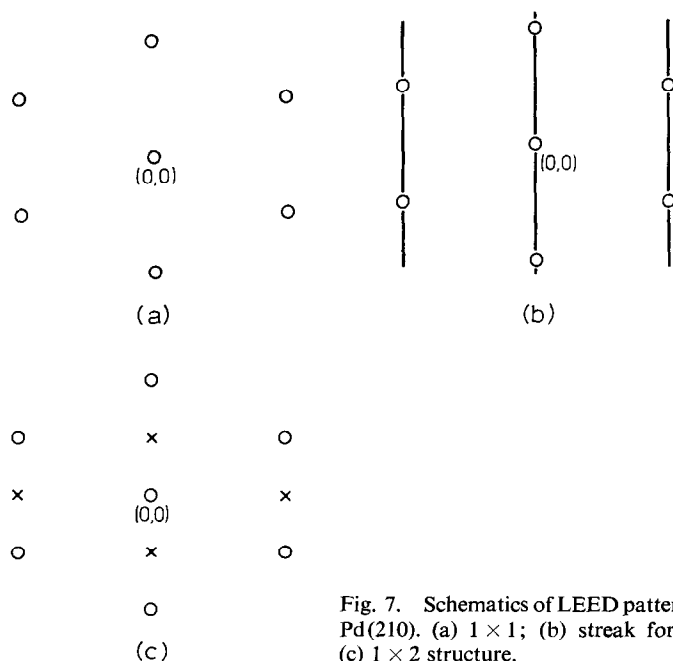


Fig. 7. Schematics of LEED patterns from Pd(210). (a)  $1 \times 1$ ; (b) streak formation; (c)  $1 \times 2$  structure.



Adsorption of CO leads at first to a (visual) variation of the intensities of the substrate spots without a noticeable increase of the background intensity, from which the formation of a  $1 \times 1$  structure may be concluded. However, no detailed intensity measurements were performed to further confirm this suggestion. Further exposure to CO then leads to the appearance of streaks in the diffraction pattern as drawn in fig. 7b which finally contract into spots of a  $1 \times 2$  diffraction pattern (fig. 7c).

The CO dose necessary for saturation is about 3 L, similar as with the other surfaces.

CO adsorption on Pd(210) caused a maximum increase of the work function by 1.07 eV. Again a comparison between  $\Delta\phi$  data and the areas below the flash desorption curves showed that  $\Delta\phi$  is proportional to the coverage at least up to about 80% of the maximum coverage. Fig. 8 shows a series of adsorption isotherms from which the isosteric heats of adsorption

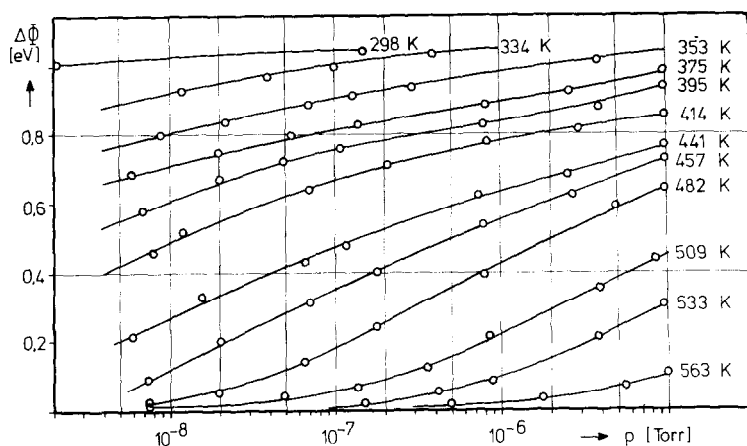


Fig. 8. Adsorption isotherms  $\Delta\phi$  versus  $P_{\text{CO}}$  for CO adsorption on Pd(210) at different temperatures.

were evaluated. From fig. 9 it can be seen that  $E_{\text{ad}}$  decreases continuously from its initial value of 35 kcal/mole. The flash desorption spectra exhibit only a single peak whose position on the temperature scale moves towards lower values with increasing coverage, which reflects the continuous variation of the adsorption energy. In contrast to all other planes which were studied the surface layer of Pd(210) does not contain atoms with their minimum distance  $a_0 = 2.73 \text{ \AA}$  (fig. 10). The distance in  $[001]$  direction is  $3.88 \text{ \AA}$  and in  $[1\bar{2}1]$  direction  $4.75 \text{ \AA}$ . If we assume a "diameter" of the adsorbed CO molecule of around  $3.5 \text{ \AA}$  then for geometrical reasons each lattice point on

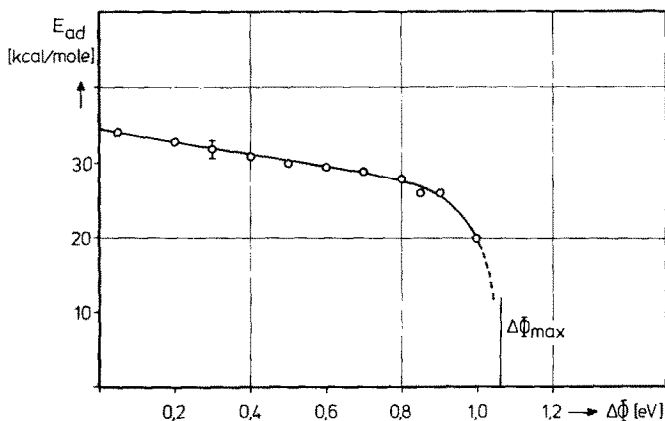


Fig. 9. Adsorption energy for Pd(210) as a function of the work function increase  $\Delta\phi$ .

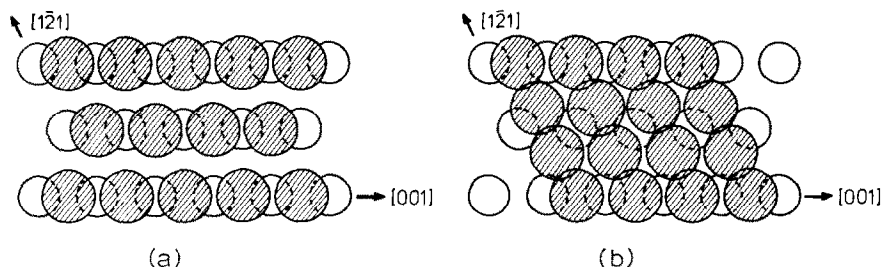


Fig. 10. Models for CO structures on Pd(210). (a)  $1 \times 1$  structure; (b)  $1 \times 2$  structure (coincidence lattice).

Pd(210) can be occupied, giving rise to the formation of a  $1 \times 1$  structure. The qualitatively observed variations of the intensities of the substrate spots support such a suggestion, although there is no unambiguous evidence, and therefore a configuration in the range of medium surface concentration as shown in fig. 10a is proposed. The location of the CO molecules is chosen at those sites for which the theoretical treatment<sup>12)</sup> proposes the occurrence of energy minima. The observed streakening in the diffraction pattern upon further increase of the coverage demonstrates that the distance of  $3.88 \text{ \AA}$  between the CO molecules in  $[001]$ -direction remains constant, whereas the periodicity in  $[1\bar{1}1]$  direction changes, becoming random initially until finally two-dimensional order with the  $1 \times 2$  structure is reached. The latter is certainly no simple structure with only one particle in the unit cell, which would imply a rather low maximum surface concentration in contrast to the high  $\Delta\phi$  value.

It is believed that the  $1 \times 2$  structure represents a coincidence lattice with a tendency for a close-packed arrangement of the CO molecules. A possible model is shown in fig. 10b, corresponding to a maximum surface concentration of  $8.5 \times 10^{14}$  CO molecules/cm<sup>2</sup> with a minimum distance of 3.16 Å between the adsorbed particles. Two equivalent domain orientations would be expected with this model, which however is certainly somewhat ambiguous, in particular since no further knowledge about the maximum coverage is available.

### 3.5. Pd(311)

The LEED pattern of the clean (311) surface again consisted of sharp substrate spots. In contrast to the other planes it was in this case, however, not possible to produce two-dimensionally ordered adsorbed phases. After small CO exposures the LEED pattern exhibited streaks as shown in fig. 11b, from which it is concluded that the adsorbed CO molecules are arranged with

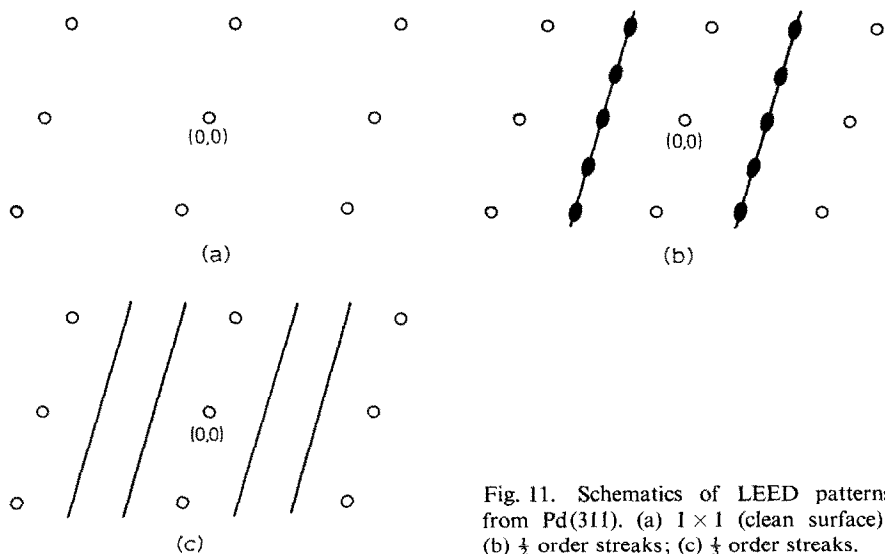


Fig. 11. Schematics of LEED patterns from Pd(311). (a)  $1 \times 1$  (clean surface); (b)  $\frac{1}{2}$  order streaks; (c)  $\frac{1}{3}$  order streaks.

a strict periodicity of  $2a_0$  in  $[01\bar{1}]$  direction, whereas no long-range order in the other crystallographic orientation exists. With careful admission of small CO doses under mild heat treatment it was sometimes possible to produce some intensity variations within the streaks, indicating the presence of small domains of a  $2 \times 1$  structure. If the CO exposure was further increased the background of the LEED pattern usually became considerably brighter, which must be due to disordered adsorption. However, in addition

streaks at  $h + \frac{1}{3}n$  ( $n = \text{integer}$ ) could be observed (fig. 11c), which demonstrated the existence of one-dimensionally ordered domains with a periodicity of  $3a_0$  in  $[01\bar{1}]$  direction. Saturation was again reached after an exposure of about 3 L.

In contrast to the LEED patterns the contact potential and flash desorption measurements were completely reproducible. This shows, that there is no noticeable influence of the degree of long-range order on the other adsorptive properties.

A maximum increase of the work function by 1.27 eV was found. The isosteric heats of adsorption as evaluated from the adsorption isotherms are reproduced in fig. 12.  $E_{\text{ad}}$  remains constant up to about  $\Delta\phi = 0.3$  eV and then decreases to a somewhat lower value which again remains constant over a

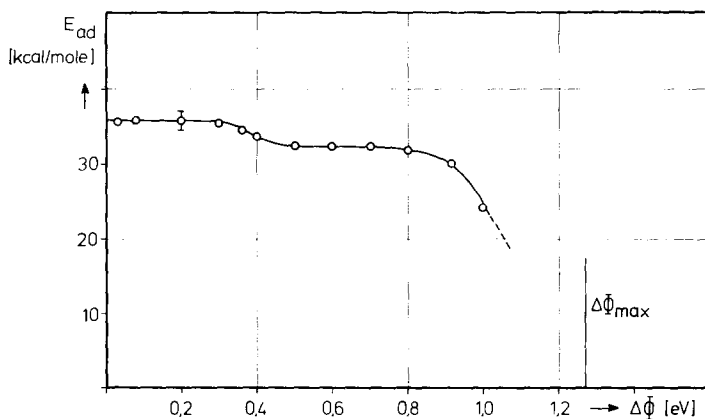


Fig. 12. Adsorption energy for Pd(311) as a function of the work function increase  $\Delta\phi$ .

larger portion of coverages. The flash desorption spectra indicate the existence of two states which are separated in energy by about 4 kcal/mole, in agreement with the isosteric heat data and also with the LEED observations.

The distance between surface atoms in  $[01\bar{1}]$  direction is  $a_0 = 2.73$  Å which implies that not every lattice site may be occupied, but suggests a twofold periodicity as observed in terms of the half-order streaks. For this state of adsorption a model is proposed as shown in fig. 13. The chosen adsorption sites are again those predicted theoretically to have minimum energy<sup>12)</sup>. It is obvious that two different domain orientations should exist. Since the lattice constant in  $[\bar{1}12]$  direction is rather large it can be assumed that the interactions between the adsorbed molecules in this direction are rather weak so that a random sequence of domain orientation results, leading to missing periodicity and streak formation in the LEED pattern. Sometimes

it seems to be possible to produce somewhat larger regions with uniform orientation which corresponds to the then observed  $2 \times 1$  structure.

Obviously CO molecules in the second adsorption state at higher coverages have an even lower tendency for the formation of long-range order. The  $\frac{1}{2}$  order streaks can be interpreted as being caused by a one-dimensional coincidence lattice, but it does not seem to be well justified to propose a plausible structure model.

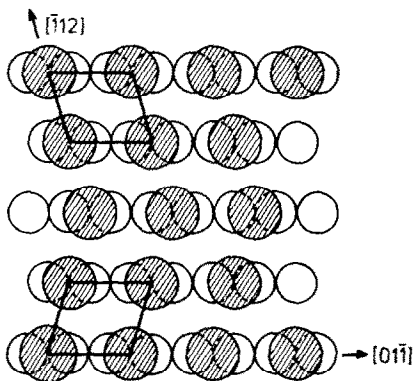


Fig. 13. Model for the double-spaced (one-dimensionally periodic) CO structure on Pd(311).

### 3.6. Pd(111) SURFACE WITH REGULAR STEP ARRAYS

A surface with periodic arrays of steps was prepared by cutting a (111) plane with a deviation of  $6.5 \pm 0.5^\circ$ . In Somorjai's nomenclature<sup>15</sup>) this surface is denoted as Pd(S)-[9(111)  $\times$  (111)], indicating terraces with (111) orientation, 9 atomic rows in width, separated by monoatomic steps also with (111) orientation. The LEED pattern showed the expected doublet spots, however, some portions of the surface exhibited other step orientations caused by the existence of domains. The same surface was previously used for the investigation of hydrogen adsorption in comparison with the normal (111) plane<sup>9</sup>). In this case a somewhat higher value for the work function increase was found with the stepped surface [0.23 eV as compared with 0.18 eV for Pd(111)], as well as a characteristic increase of adsorption energy with decreasing coverage, whereas  $E_{ad}$  remained constant with Pd(111). These effects were ascribed to the altered adsorptive properties of the step atoms.

In the present studies on CO adsorption only nearly negligible differences between both surfaces were found. The maximum increase of the work function is 1.02 eV as compared with 0.98 eV for Pd(111). A series of adsorption isotherms is reproduced in fig. 14, from which the isosteric heats of adsorption were evaluated. These values are shown in fig. 1 together

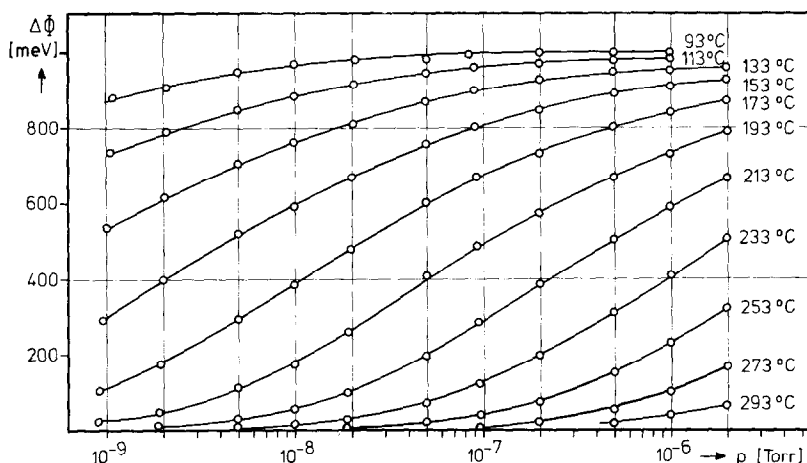


Fig. 14. Isotherms for CO adsorption on a stepped Pd(111) surface.

with the data for Pd(111) (which were taken about 3 years ago!). In both cases  $E_{ad} = 34$  kcal/mole is constant at low coverages. Minor variations between both planes probably exist in the range of medium coverages, but this effect is still within limits of error.

A similar LEED pattern after CO adsorption was observed as with Pd (111), but the additional spots were much more diffuse.

From this it can be concluded that on the individual terraces (with diameters of  $\sim 25$  Å) the arrangement of the adsorbed particles is the same as on the normal Pd(111) surface, but obviously no fixed scattering phase relations exist between the layers on different terraces. As can be seen from the structure model in fig. 2 three different domain orientations are possible. On the (111) surface large patches (i.e. with diameters which exceed the electron coherence width of  $\sim 50$  Å) with uniform orientations are formed, which is not possible with the stepped surfaces. A random sequence of different domain orientations will lead to enlarged diffraction spots.

### 3.7. ADSORPTION KINETICS

The relative sticking coefficient  $s' = s/s_0$  ( $s_0$  being the absolute sticking coefficient at zero coverage) and its variation with coverage may be evaluated from the change of the relative coverage (i.e.  $\Delta\phi$ ) with CO exposure.

All surfaces which were studied here showed a quite similar behaviour: At room temperature  $s'$  remains constant up to about half the saturation coverage and then decreases linearly. As an example fig. 15 shows the results for Pd(210); similar data for Pd(111) are reproduced in ref. 4b.

A simple model which explains such findings<sup>16)</sup> assumes that adsorption at first takes place into a physically adsorbed mobile precursor state which allows the molecule (even if it encounters an already occupied site) to move on the surface for a certain time and probably to find a free site. This mechanism may keep the sticking coefficient near the initial value  $s_0$  over an appreciable range of coverages. Some uncertainties exist in determining

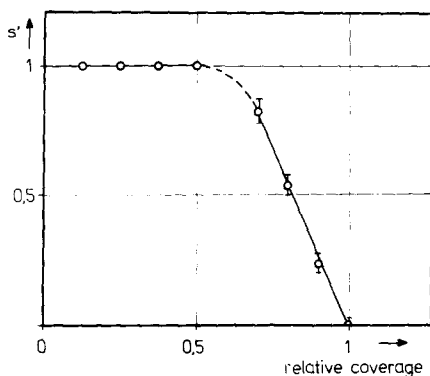


Fig. 15. Relative sticking coefficient  $s'$  as a function of coverage for CO/Pd(210).

$s_0$  with the present apparatus, for which in particular  $n_s$ , the number of adsorbed molecules per  $\text{cm}^2$ , is needed. In the case of the  $c2 \times 2$  structure on Pd(110) ( $\theta = \frac{1}{2}$ )  $n_s = 4.7 \times 10^{14} \text{ cm}^{-2}$  results from the structure model for which an exposure of 1.2 L CO is needed.

From these data for  $s_0$  a numerical value is derived which is very close to unity, however, the uncertainty is estimated to be at least 20%. With the other planes exposures in the range of 1 L are also sufficient to reach half the saturation coverage, so that similar values for  $s_0$  near unity would result.

## 4. Discussion

### 4.1. PREVIOUS RESULTS WITH POLYCRYSTALLINE SURFACES

A series of investigations on CO adsorption on polycrystalline Pd surfaces is reported in the literature, which was partly reviewed by Tracy and Palmberg<sup>6)</sup>. Using calorimetric measurements with evaporated films Brennan and Hayes<sup>17)</sup> found that with increasing coverage the heat of adsorption decreased continuously from 40 kcal/mole. This value is exactly the maximum adsorption energy as found in the single crystal studies with Pd(110). Agreement exists also with the data given by Kavtaradze and Sokolova<sup>18)</sup> which vary between 40 and 15 kcal/mole with increasing coverage.

Flash desorption experiments with a Pd wire (whose surface cleanliness was checked by Auger spectroscopy) revealed the existence of only a single adsorbed state with an additional shoulder at the low temperature side of the spectra at higher coverage<sup>19</sup>). The mean heat of adsorption was evaluated to be 32 kcal/mole which correlates with the data for Pd(111). The shapes of the flash desorption spectra were very similar to those found with the stepped Pd(111) surface.

Kawasaki et al.<sup>20</sup>) concluded from measurements of the variation of the electrical resistance of thin Pd films that CO is mainly adsorbed with "bridge" bonds, i.e. occupying two Pd atoms, a small amount however also being in the "linear" configuration. Similar conclusions were drawn from a series of infrared spectroscopic investigations<sup>21-26</sup>). The IR spectrum of CO on silica-supported Pd often shows two regions of absorption, near 4.8 and 5.2  $\mu\text{m}$ , assigned to the C-O stretching mode of "linear" and "bridged" species, the latter being enhanced by the presence of large crystallites. This correlation was established mainly by comparison with the absorption bands of carbonyl compounds. However, Blyholder<sup>27</sup>) demonstrated already in 1964 by means of a simple MO model, that this structural assignment is essentially meaningless since the shift of the infrared band is mainly governed by the effect of "back-donating" of metallic d-electrons into the antibonding  $2\pi^*$ -orbital of CO. This on the other hand also influences the strength of the chemisorption bond. The expected correlation between wavelength of the infrared band and adsorption energy was confirmed qualitatively in so far as the species with the 5.2  $\mu\text{m}$  absorption band was found to be more strongly bound than that absorbing at 4.8  $\mu\text{m}$ <sup>21, 25</sup>). The IR studies further gave strong evidence that CO adsorbs on Pd without dissociation and with bond formation through the C atom.

The first attempt to treat the adsorption energy quantum mechanically was performed by Grimley<sup>28</sup>). Extended calculations using a modified Anderson model were recently published<sup>12</sup>). In this paper also a detailed discussion of the mechanism of bond formation and a comparison with the present experimental results is given.

#### 4.2. ADSORPTION ON SINGLE CRYSTAL PLANES

The main results with Pd single crystal surfaces (except the structure models) are summarized in table 1. The general picture is, that differences between the various planes are only of minor relevance. The initial energies of adsorption vary between 34 and 40 kcal/mole and the maximum densities of adsorbed CO molecules (as derived from the structure models) between  $7.8$  and  $9.4 \times 10^{14} \text{ cm}^{-2}$ , although for example, the densities of surface atoms vary nearly by a factor of three, and the coordination of the surface



TABLE 1

	(111)	(100)	(110)	(311)	(210)
Surface orientation	(111)	(100)	(110)	(311)	(210)
Density of surface atoms $\times 10^{-15}$ (cm $^{-2}$ )	1.53	1.33	0.94	0.80	0.53
Numbers of nearest neighbours of the surface atoms	9	8	7	7	6
Initial energy of adsorption (kcal/mole)	34	36.5	40	35.5	35
Maximum increase of work function (eV)	0.98	> 0.75	1.26	1.27	1.06
Maximum density of adsorbed CO molecules (at room temperature, $P_{\text{CO}} \leq 10^{-4}$ Torr) $\times 10^{-15}$ (cm $^{-2}$ )	0.77	$\sim 0.80^*$	0.94	?	0.89
Dipole moment per adsorbed CO molecule at maximum coverage (Debye)	0.33	0.29	0.35		0.33
Maximum coverage (i.e. CO/Pd ratio)	0.5	$\sim 0.7$	1.0		1.5

\* This value increases at low temperatures up to about  $1 \times 10^{15}$ , which is connected with a strongly decreasing adsorption energy<sup>6</sup>).

atoms (i.e. their numbers of nearest neighbours) between 6 and 9. The defined introduction of structural defects (steps) is practically without any influence (in contrast to hydrogen adsorption on Pd<sup>9</sup>) and to the kinetic processes like carbon formation studied with Pt<sup>15</sup>). The latter effect is probably due to the fact that the "open" planes (210) and (311) show a quite similar behaviour as the most densely packed (111) plane.

The similar properties of the different planes are the reason why the polycrystalline samples appear to be more or less uniform without the appearance of many adsorption states. The few different states found (e.g. with the infrared experiments) have to be mainly ascribed to the transformation of the properties of the adsorbed layers on individual single crystal planes with increasing coverage and not so much to an a priori heterogeneity of the surfaces due to the existence of differently oriented surfaces. Obviously a concept whereafter a surface consists of certain adsorption sites, which are probably created by the spacial orientation of the "free valencies" of the surface atoms, is only of limited validity. The structure models suggest highly symmetrical coordination at low and medium coverages, maximum coverage is however not given by complete filling of these "sites" but by the tendency to find a compromise between the formation of a close packed adsorbate layer (which is determined by the "size" of the CO molecules) and with the periodicity of the surface.

The appearance of "compressed" structures associated with typical changes of the adsorption energy, for example, demonstrates that there may eventually exist only small energetic differences between different points on the surface, in agreement with the calculated energy profiles<sup>12)</sup>.

The tendency for the formation of close-packed adsorbate layers was so far observed mainly in cases of physical adsorption<sup>29)</sup> or of metallic adsorbates<sup>30)</sup>, whereas with the chemisorption of gases the operation of highly directed and localized surface valencies was frequently assumed<sup>31)</sup>, a model which predicts large differences between various single crystal planes. [The Pd(210) surface is of particular interest in this connection, since this is the only case where no surface atoms with the closest distance of  $a_0 = 2.73 \text{ \AA}$  exist. The minimum distance of  $3.88 \text{ \AA}$  would not allow the formation of the regular "bridge" bond<sup>18)</sup> in fact no anomaly was found with this plane.]

Since the maximum densities of adsorbed CO molecules per  $\text{cm}^2$  are quite similar, the maximum coverage, i.e. the ratio of the numbers of adsorbed CO molecules to the numbers of Pd surface atoms, varies considerably with surface orientation, as can be seen from the last line of table 1. These findings arise some doubt about the validity of attempts to "titrate" the numbers of exposed surface atoms of highly dispersed supported palladium catalysts by measuring the amount of adsorbed CO. In fact it was found with supported Pd-charcoal catalysts that the Pd : CO ratio may vary between 1 and 2, depending on the pretreatment, that means on the mean size of the crystallites and the types of exposed planes<sup>32)</sup>.

The overall result, that the "structural" factor is of minor importance, is not restricted to the system CO/Pd. Similar conclusions can be drawn from studies on CO adsorption on Ni<sup>3,14)</sup> and on Cu<sup>33,34)</sup>. In the latter case however the frequency of the infrared absorption band may be influenced sensitively by the surface orientation<sup>34)</sup>. However, it may not be assumed that this effect is of general validity in chemisorption. For example, the system  $\text{N}_2/\text{W}$  shows a quite pronounced plane specificity, where the work function variation may even change sign with surface orientation and large differences for the sticking coefficients were found, although on the other hand the binding energies again seem to be quite similar<sup>35)</sup>.

### Literature

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