Coadsorption of Hydrogen and Carbon Monoxide on a Pd (110) Surface

H. CONRAD, G. ERTL, AND E. E. LATTA

Physikalisch-Chemisches Institut der Universität, München, Germany

The coadsorption of H_2 and CO on a Pd (110) single-crystal surface has been studied by means of LEED, flash desorption spectroscopy, and work function measurements. Carbon monoxide may displace preadsorbed hydrogen completely from the surface, whereas no displacement of adsorbed CO by hydrogen takes place. If the surface concentrations of adsorbed hydrogen and carbon monoxide are both equal to one-third of their maximum values, a mixed 1×3 structure is formed, where both species are in intimate contact. The mutual interaction must be rather weak since no variation of the desorption energy of H_2 was observed. The only desorbing particles were H_2 and CO without any detection of product formation. The contributions to the work function change from the individual components are additively superposed in the mixed adsorbate layers, indicating that the dipole moments are not mutually affected to any measurable extent.

1. INTRODUCTION

The interaction between H_2 and CO at metal surfaces may lead to very important catalytic reactions such as the Fischer-Tropsch synthesis (*1, 2*). Usually Fe, Co, or Ni serves as a catalyst, whereas among the noble metals only ruthenium has found some limited importance. Palladium appears to be without significant activity. On the other hand, it is a well-known fact that diffusion of hydrogen through Pd (whose rate is determined by surface processes) may be strongly influenced by the presence of adsorbed carbon monoxide (*3*). A mutual interaction of both adsorbed species is thus to be expected. Following previous studies on the adsorption of hydrogen (*4*) and carbon monoxide (*5*) on clean Pd single-crystal surfaces, we therefore studied the coadsorption of these gases at a Pd (110) surface.

2. EXPERIMENT

The experiments were performed with a UHV system (base pressure 10^{-10} Torr) equipped with facilities for low-energy electron diffraction (LEED), Auger electron spectroscopy, and contact potential measurements by means of the vibrating condenser method and a quadrupole mass spectrometer. Details on the sample preparation and cleaning processes, etc., may be found in foregoing papers (*4, 5*).

3. RESULTS

3.1 LEED

Hydrogen adsorbed on Pd (110) forms a "streaked" 1×2 structure (Fig. 1a) (*4*) and CO with increasing coverages $c2 \times 2$, 4×2, and 2×1 structures, respectively (*5*) (Figs. 1b–1d). It is therefore possible to use the LEED pattern as a "fingerprint" for the state of adsorption. All the following experiments were performed at room temperature.

If a hydrogen-covered Pd (110) surface is exposed to gaseous CO, the 1×2 structure was observed to transform after a dose of about 0.7 L (1 Langmuir (L) = 10^{-6} Torr sec) into a new 1×3 structure whose diffraction pattern is shown in Fig. 2. Since neither hydrogen nor CO *alone* produces
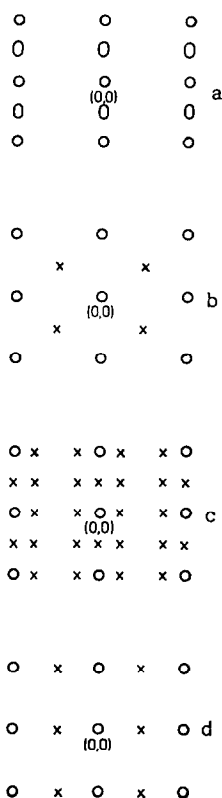
363

FIG. 1. Sketches of LEED patterns from adsorbate structures on a Pd (110) surface. (a) 1×2 structure after hydrogen adsorption; (b) $c2 \times 2$ structure after CO adsorption corresponding to $\theta_{CO} = \frac{1}{2}$; (c) "$4 \times 2$" CO-structure for $\theta_{CO} = \frac{3}{4}$; (d) 2×1 CO structure for $\theta_{CO} = 1$.

such a structure, it must be due to the formation of a mixed adsorbed phase ("cooperative" adsorption) whose unit cell contains adsorbed H and CO particles. In the case of domain formation (competitive adsorption) the diffraction pattern would consist of a superposition of spots from the already known single-component structures.

Such a domain formation is observed if the CO exposure is further increased beyond 0.7 L. Up to 0.9 L the diffraction pattern consists of "extra" spots from the CO 4×2 structure and from the 1×3 "mixed" structure, the intensity of the latter being continuously decreasing. After exposures > 1 L only the CO 4×2 structure is present. (Under the chosen conditions this is the stable final state of

CO adsorption since the 2×1 structure forms only at higher pressures.)

If the clean surface is exposed to about 0.7 L carbon monoxide, very diffuse spots of the $c2 \times 2$ structure are formed. This exposure leads to a coverage $\theta_{CO} \approx \frac{1}{3}$ (5). If hydrogen is then introduced into the vacuum system after a few Langmuirs again the formation of the 1×3 structure was observed. Unfortunately, no information on the absolute surface concentration of adsorbed H atoms is available, since the sticking coefficient is unknown and hydrogen is partially dissolved in the bulk (4). At higher concentrations of preadsorbed CO no further variation of the LEED pattern due to exposure to hydrogen could be observed. The 4×2 CO structure is completely stable in a hydrogen atmosphere.

The general conclusion to be drawn from the LEED experiments is that adsorbed CO and hydrogen, if present in the right proportions, may form an ordered mixed phase. Carbon monoxide may completely displace preadsorbed hydrogen, whereas this is not the case in the reverse sense.

3.2 Thermal Desorption

Thermal desorption experiments were performed by continuously increasing the temperature of the adsorbate-covered surface at a constant rate of 11°C/sec, and simultaneous monitoring of the partial pressure of the desorbing species by a "line-of-sight" mounted quadrupole mass spectrometer.

A hydrogen-covered Pd (110) surface exhibits an H_2 peak below 100°C, arising from the adsorbed species, and a second broad maximum at higher temperatures due to desorption of hydrogen which was originally dissolved in the bulk (4). With adsorbed CO a single peak around 220°C was observed (5).

Using a surface with a mixed adsorbate layer only desorption of H_2 and CO was observed, but never any possible reaction products like formaldehyde, methane, methanol, etc.

Flash desorption experiments with a Pd wire which was previously exposed to HCHO revealed also desorption of H_2 and

FIG. 2. LEED pattern of a 1 × 3 structure due to coadsorption of hydrogen and carbon monoxide.

CO, the stationary decomposition starting at temperatures around 50°C (6). So, even if this molecule were formed in the adsorbed state, it would decompose before desorbing.

The temperatures of the flash maxima found for CO and H_2 desorbing from the mixed adsorbate phase were nearly identical to that for the individual species if adsorbed alone, thus indicating that the binding energy of the hydrogen atoms to the surface is only very weakly influenced by the presence of coadsorbed CO molecules in intimate contact. Since H_2 is desorbing at lower temperatures than CO, no information about a possible variation of the CO adsorption energy is available.

The continuous displacement of pread-

sorbed hydrogen by CO also becomes evident from the thermal desorption spectra, a series of which is shown in Fig. 3. In every case the experiments were started with surfaces completely covered by hydrogen and subsequently exposed to various CO doses. The peak due to adsorbed hydrogen continuously decreases with increasing CO exposure and disappears completely around 1 L CO, whereas the second maximum arising from absorbed hydrogen is unaffected. The latter starts at temperatures where the CO molecules already desorbed; variations of its shape are due to different concentration profiles of dissolved H atoms (4).

If on the other hand, desorption spectra are taken for mass 28 (=CO), these are
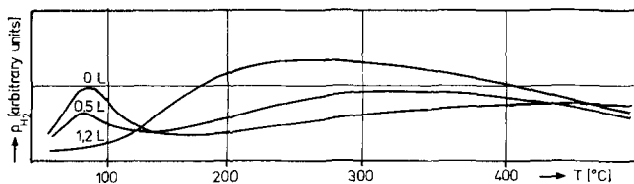

FIG. 3. Thermal desorption spectra for hydrogen under the influence of varying exposures to CO. The first peak due to adsorbed hydrogen decreases continuously with increasing CO exposure. The second broad maximum arises from hydrogen originally dissolved in the bulk, whose shape is determined by the concentration profile of hydrogen atoms below the surface.

not altered by exposing the surfaces to hydrogen, indicating that no displacement of adsorbed CO by hydrogen takes place as was already evident from the LEED experiments.

3.3 Contact Potential Measurements

Hydrogen causes on Pd (110) a maximum increase of the work function $\Delta\phi$ by 0.36 eV, whereby there is strong evidence that this quantity is, at least at not too high surface concentrations, directly proportional to the coverage (4). A much larger increase of the work function by more than 1 eV is associated with CO adsorption, where the proportionality between $\Delta\phi$ and the coverage θ was checked experimentally. The $c2 \times 2$ structure corresponding to $\theta = \frac{1}{2}$ is associated with a $\Delta\phi$ of 0.7 eV. If both gases were present together on the surface, all the obtained experimental results indicate that the total increase of the work function is composed additively from the contributions of both components. This somewhat surprising result is illustrated best by Fig. 4. In this series of experiments the surface was at first exposed to various amounts of CO leading to different values of $\Delta\phi_{CO}$ and then subsequently hydrogen was admitted (which we know is not able to displace adsorbed carbon monoxide) and the additional increase of the work function $\Delta\phi_H$ was recorded as a function of $\Delta\phi_{CO}$.

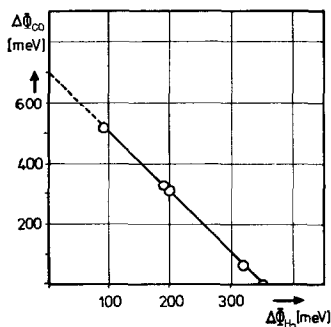The figure shows that for $\Delta\phi_{CO} \geqslant 0.7$ eV

FIG. 4. Variation of the work function $\Delta\phi_H$ due to hydrogen adsorption as a function of the work function change $\Delta\phi_{CO}$ caused by preadsorbed carbon monoxide.

no further hydrogen adsorption takes place ($\Delta\phi_H = 0$), which confirms the findings of the other methods. For $\Delta\phi_{CO} < 0.7$ eV, $\Delta\phi_{CO}$ and $\Delta\phi_H$ are correlated linearly. This fact may be formulated as

$$\Delta\phi_H = 0.36(1 - 2\theta_{CO}) \text{ [eV]} \qquad \text{for } \theta_{CO} < \tfrac{1}{2}$$

since we know that $\Delta\phi_{CO} = 0.7$ eV corresponds to $\theta_{CO} = \frac{1}{2}$ (5).

This linear correlation is somewhat surprising, since we know from the LEED pattern that at least the geometrical configuration of the CO molecules in the mixed adsorbed layer (1×3 structure) differs from that in the pure single-component structure ($c2 \times 2$ structure). On the other hand, the previous findings (5) demonstrated that the dipole moment of adsorbed CO is nearly unaffected by its arrangement on the surface.

4. DISCUSSION

The general result from all types of experiments is that CO displaces adsorbed hydrogen completely from the surface but H_2 does not displace adsorbed CO. The reason for this effect appears to be mainly an energetic one, since the adsorption energy for CO is about 15 kcal/mol larger than that for H_2 (4, 5). This result explains the findings from hydrogen penetration studies through Pd, whereafter this (surface controlled) process is inhibited by the presence of carbon monoxide (3). It is interesting to note that already at $\theta_{CO} = \frac{1}{2}$ no hydrogen adsorption takes place, whereas the surface is only saturated to 50% with respect to CO adsorption (5).

A serious problem which has to be discussed in this context is whether CO is indeed present on the surface in the form of adsorbed molecules. For CO interacting with a Ni (110) surface, for example, it was found that dissociation may occur at elevated temperatures or under the influence of an electron beam giving rise to alterations of the LEED patterns, of the flash desorption spectra, and of the $\Delta\phi$ data, and finally leading to the buildup of carbon layers (10). There is no indication for similar effects with the system CO/Pd (110), where adsorption was found to be completely re-

versible. Recently this system was further investigated by means of ultraviolet photoelectron spectroscopy (UPS) combined with LEED (11). Two peaks were detected at energies of 7.9 and 10.8 eV below the Fermi level, which are interpreted as being caused by electron emission from the 5σ and 2π orbitals of adsorbed CO molecules. These maxima were still present and not shifted in energy if hydrogen was coadsorbed leading to the 1×3 LEED pattern. There is therefore strong evidence that this structure is indeed caused by coadsorbed H atoms and CO molecules which mutually interact only rather weakly. [It should be mentioned in this context that a 1×3 structure is formed at Pd (110) also at small oxygen coverages (12). However this structure is thermally stable up to more than 500°C, whereas the mixed H–CO structure disappears below 200°C. Moreover, if adsorbed O atoms were present on the surface, these would react readily with H₂ already at room temperature and form water, which desorbs immediately (13).]

The arrangement of CO molecules at $\theta_{CO} = \frac{1}{2}$ (corresponding to completion of the $c2 \times 2$-structure) is drawn in Fig. 5a.
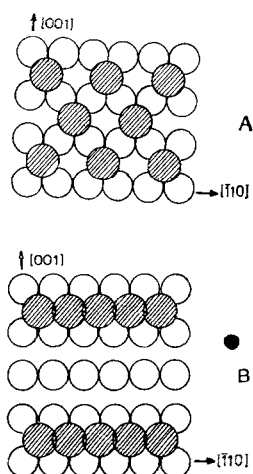

FIG. 5. (a) Structure model for CO molecules adsorbed alone on Pd (110) at $\theta = \frac{1}{2}$, leading to a $c2 \times 2$ structure (5). (b) Proposed arrangement of the CO molecules in the "mixed" layer with $\theta_{CO} = \frac{1}{3}$ corresponding to the 1×3 coadsorbate structure. The positions of the hydrogen atoms are unknown.

For $\theta_{CO} = \frac{1}{3}$ a mixed adsorbed layer with 1×3 structure is formed which must contain integral numbers of CO molecules and H atoms and may therefore be designed as a stoichiometric adsorbate complex. On Fe catalysts the existence of such complexes with a nominal composition H_2CO was concluded earlier by Kölbel et al. (7) from volumetric measurements. However, in contrast to iron, which catalyzes reactions between CO and H₂, the interaction energy between both components on Pd (110) appears to be rather weak; no product formation but only desorption of CO and H₂ was found, the adsorption energy of hydrogen being practically unaffected by the presence of adsorbed CO as indicated from the thermal desorption experiments. The observed linear superposition of the individual contributions to the work function change indicates that the dipole moments are not noticeably mutually affected, which supports this concept.

Flash desorption experiments with Pt (111) indicated that in this case larger variations of the binding energies take place, since, for example, a new H₂ desorption peak around 500°C was observed in the case of a mixed adsorbed layer (8). Recently Kraemer and Menzel (9) performed contact potential measurements with CO and H₂ coadsorbed on ruthenium and found very large deviations from a linear superposition of the individual contributions from which they concluded the existence of strong mutual interactions, in agreement with the known catalytic activity of this metal.

Since we know the absolute coverage for the CO/Pd (110) system and its correlation with $\Delta\phi$, exposure, etc., we are led to the conclusion that the mixed adsorbate layer with 1×3 structure corresponds to $\theta_{CO} = \frac{1}{3}$. This is in complete agreement with the size of the unit cell of this structure if it is assumed that it just contains one CO molecule. We thus arrive at a surface arrangement of the CO molecules in the 1×3 structure as shown in Fig. 5b. There are two remarkable points with this structure: There must be a long-range interaction between the CO mole-

cules in the [001] direction, leading to a length of periodicity of 11.64 Å which must be assisted by the presence of the hydrogen atoms. On the other hand, in the [$\bar{1}$10] direction the mutual distance between CO molecules is only 2.73 Å which is considerably smaller than the values >3.1 Å deduced for the pure CO structures on Pd (5). At present there is no satisfactory explanation for this effect.

For hydrogen adsorbed on Pd (110) we have no knowledge of the absolute surface concentration, and therefore we can only speculate on the number of H atoms contained in the unit cell of the 1 × 3 structure.

There is strong evidence that $\Delta\phi_H$ is proportional to θ_H (4), which may be assumed to be valid also in the case of coadsorption due to the observed linear superposition of $\Delta\phi_H$ and $\Delta\phi_{CO}$. The 1 × 3 structure is completed at $\Delta\phi_{CO} = 0.47$ eV ($\theta_{CO} = \frac{1}{3}$). According to Fig. 4 the corresponding $\Delta\phi_H$ is 0.12 eV, just $\frac{1}{3}$ of $\Delta\phi_{H,max} = 0.36$ eV. If we assume that the unit cell of the 1 × 3 structure contains just *one* H atom, then θ_H (1 × 3) $= \frac{1}{3}$ and with pure hydrogen adsorption $\theta_{H,max} = 1$. The latter case is characterized by a 1 × 2 structure, whose unit cell then would contain two hydrogen atoms, which was already suspected earlier (4). However, we cannot rule out the possibility that the unit cell of the 1 × 3 structure contains *two* hydrogen atoms (corresponding to a complex with nominal composition H_2CO); then $\theta_{H,max} = 2$ (i.e., 9.4×10^{14} molecules H_2/cm^2) and the unit cell of the 1 × 2 structure would contain four H atoms. This problem may only be resolved by a quantitative determination of the hydrogen surface concentration.

REFERENCES

1. ANDERSON, R. B., in "Catalysis" (P. H. Emmett, Ed.), Vol. 4, p. 1. Reinhold, New York, 1956.
2. BOND, G. C., "Catalysis by Metals," Academic Press, New York, 1962.
3. WICKE, E., AND MEYER, K., Z. Phys. Chem. N.F. 64, 225 (1969); HUBER, B., Diplomarbeit Münster, 1973.
4. CONRAD, H., ERTL, G., AND LATTA, E. E., Surface Sci. 41, 435 (1974).
5. CONRAD, H., ERTL, G., KOCH, J., AND LATTA, E. E., Surface Sci. 43, 462 (1974).
6. TORNAU, J., Thesis, Hannover, 1973.
7. KÖLBEL, H., PATZSCHKE, G., AND HAMMER, H., Z. Phys. Chem. N.F. 48, 145 (1966).
8. BALDWIN, V. H., AND HUDSON, J. B., J. Vac. Sci. Technol. 8, 49 (1971).
9. KRAEMER, K., AND MENZEL, D., Verh. Deut. Phys. Ges. (VI) 8, 441 (1973).
10. MADDEN, H. H., AND ERTL, G., Surface Sci. 35, 211 (1973).
11. KÜPPERS, J., CONRAD, H., ERTL, G., AND LATTA, E. E., Faraday Disc. 58 (1975), in press.
12. ERTL, G., AND RAU, P., Surface Sci. 15, 443 (1969).
13. CONRAD, H., ERTL, G., AND LATTA, E. E., unpublished results.