Electron-Stimulated and Thermal Desorption Studies on Palladium

II. Carbon Monoxide

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Chemisorption of CO on a Pd ribbon has been studied using a combination of electron-stimulated and thermal desorption methods. From the thermal desorption spectra the desorption energy was evaluated as a function of coverage. Electron bombardment of the Pd surface covered with CO produced an O^+ ion current whose intensity depended on the CO coverage. The observed changes in the adsorption energy and in the ion current with increase in coverage were interpreted on the basis of a lateral interaction and the Blyholder model for a chemisorption bond between CO and a transition metal.

INTRODUCTION

Adsorption of CO on palladium, which is an active catalyst for CO oxidation, has been studied by various methods. The data (*1–5*) on CO adsorption over polycrystalline and single-crystal samples show that desorption of CO is a first-order rate process with an initial desorption energy (determined by different authors) ranging from 32 to 40 kcal/mol. LEED studies (*2, 5*) have shown that at low coverages the CO molecules are adsorbed in a random-lattice gas configuration and do not form definite surface structures, whereas at coverages exceeding 0.5 monolayer close-packed layers tend to form. The study of CO adsorption on single crystals (*2, 5*) has shown that the different planes exhibit a quite similar behavior which is why polycrystalline samples are more or less uniform with respect to the adsorption sites for CO.

In the present paper electron-stimulated (ESD) and thermal desorption (TD) techniques have been combined to investigate the adsorption of CO on a palladium ribbon. The results obtained enable us to discuss the changes in the adsorption layer with change in coverage.

EXPERIMENTAL

Experimental details have been described in Part I (*6*). The adsorption experiments were carried out in the CO pressure range from 1×10^{-9} to 1×10^{-8} Torr.

RESULTS

Thermal Desorption

The experimentally obtained TD curves are shown in Fig. 1. They are broadened toward lower temperatures with increasing coverage. In the case of first-order desorption kinetics, this indicates dependence of the desorption energy, E_d, on the CO surface concentration.

To check whether the TD traces reflect the dependence of E_d on coverage, θ, isothermal desorption measurements were carried out. Figure 2 shows the experimentally obtained decrease in coverage with time during isothermal desorption at 400°K, compared to the calculated curve (dashed line) for E_d and ν independent of θ. The rate constant $k = \nu \exp(-E_d/RT)$ is chosen so as to yield the same coverage for both curves after 30 sec. The difference between the two curves shows that the experimen-
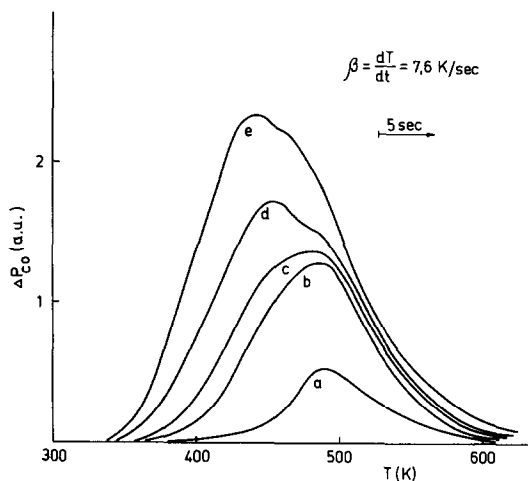
$$\beta = \frac{dT}{dt} = 7.6 \text{ K/sec}$$

⊢5 sec⊣

FIG. 1. TD spectra of CO from Pd with various CO exposures at 300°K: (a) 1.5×10^{-6}; (b) 4.5×10^{-6}; (c) 6×10^{-6}; (d) 9.0×10^{-6}; (e) 13.5×10^{-6} Torr/sec.

tally obtained TD traces could not be fitted for E_d and ν independent of coverage.

A complete analysis of the desorption curves was made by the method described by Bauer et al. (7, 8), using the kinetic Eq. (1) from Part I (6). Figure 3 shows the dependences E_d (θ) and ν (θ) which were obtained. It can be seen that for θ up to 0.25 of the saturated coverage, θ_{max} (we assumed $\theta_{max} = 1$), E_d decreases linearly with θ. At $\theta > 0.25$, E_d decreases more sharply and reaches almost a constant value at $\theta > 0.6$.
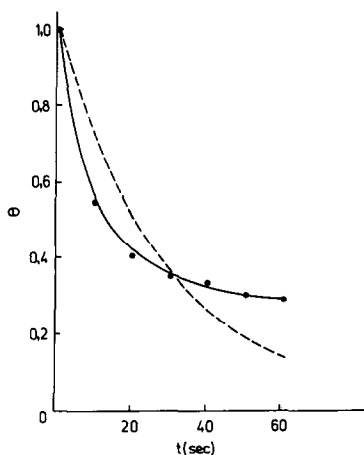
It should be noted that the E_d and ν values are derived neglecting the presence of a precursor state during desorption which, as King has shown (9), may affect the desorption kinetics.

Electron-Stimulated Desorption

The positive ion current, which consisted of O^+ ions only, was recorded on electron impact of the Pd surface covered with CO. Figure 4 shows the change in the intensity of the O^+ ion current, I_{O^+}, with increasing CO coverage. It is evident that at $\theta \sim 0.25$ the $I_{O^+}(\theta)$ curve passes through a maximum after which I_{O^+} decreases and reaches a constant value at θ close to θ_{max}.

Combined ESD and TD Experiments

In Fig. 5 the behavior of O^+ yields upon TD is shown. At coverages lower than 0.3 (Fig. 5a), the ion current I_{O^+} decreased within the temperature range of TD peak. For θ between 0.3 and 0.6 (Fig. 5b), I_{O^+} at first increased with temperature and then decreased down to zero. At θ near to θ_{max}, I_{O^+} continuously decreased during bombardment at 300°K and reached a lower value (Fig. 5c). This value did not change after additional adsorption.

FIG. 2. Coverage decrease with isothermal desorption at 400°K. Dashed curve is calibrated for E_d and ν independent of θ.
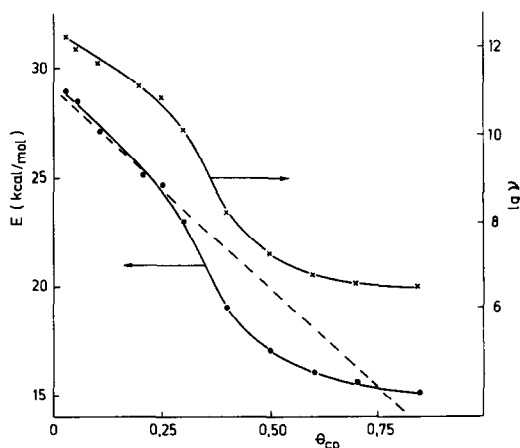

FIG. 3. Desorption energy E_d and frequency factor ν as a function of CO coverage. Dashed curve is the calibrated $E(\theta)$ for $w = 3$ kcal/mol.
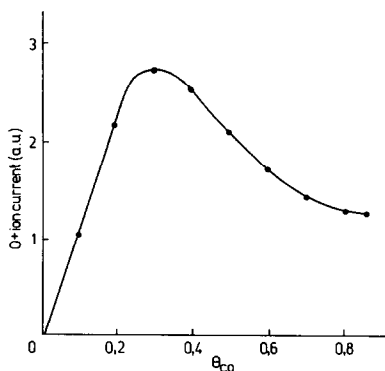
FIG. 4. ESD ion current, I_{O^+}, as a function of CO coverage, θ.

DISCUSSION

Assuming that the surface of the sample under consideration is uniform with respect to CO adsorption, the complex desorption curves obtained and the changes in E_d and ν with θ can be explained by the presence of repulsive lateral interactions between the adsorbed species. Using the model of lateral interactions between nearest neighbors for nondissociative adsorption (11, 12), E_d was calculated as a function of θ according to the equation:

$$E_d = E_{ad} = U_g - U_s$$
$$= (U_g - U_s)_{\theta=0} + zw\theta$$

where $(U_g - U_s)$ is the differential adsorption energy at a definite θ, $(U_g - U_s)_{\theta=0}$ is the initial differential adsorption energy at θ = O (in the case of nonactivated adsorption, E_{ad} is equal to E_d, z is the number of nearest-neighbor sites and w is the interaction energy between first neighbors. The number of adsorption sites, z = 6, was chosen on the basis of the LEED structures proposed by Tracy and Palmberg (2) and by Conrad et al. (5). The dependence $E_d(\theta)$ for w = 3 kcal/mol is in good agreement with the experimental results only for θ < 0.3 (see Fig. 3). When comparing the results for $E_d(\theta)$ in Fig. 3 with the dependence $I_{O^+}(\theta)$ in Fig. 4, one can see that the $I_{O^+}(\theta)$ curve has a maximum at a coverage at which the sharper decrease in E_d begins.

The interpretation of these results can be based on previous studies of CO adsorption on transition metals (2, 5, 13–24). Most authors are of the opinion that CO is adsorbed in both twofold bridge and on-top positions, adsorption in the "bridge" configuration being favored at θ < 0.5. In a recent paper by Scheffler (24) the observed shift of the ir spectra to higher frequencies with increasing coverage is attributed essentially to lateral interactions.

According to the Blyholder model (15, 16), a chemisorption bond is formed through the carbon atom when the occupied 5σ orbitals of CO donate electrons to the unoccupied d-metal orbitals and, in turn, d-electrons from the metal are back-donated into the antibonding $2\pi^*$ orbitals of CO. Blyholder showed that the wave function of the back donor–acceptor bond is bonding with respect to the C–M bond and antibonding with respect to the C–O bond. Thus the C–O bond in the chemisorbed molecule is weakened, which is confirmed by the shift of the ir spectra toward the lower frequencies in comparison with the spectra of CO in the gaseous phase.

As was shown above, desorption of O^+ ions alone was recorded on ESD of CO, the maxima of the energy distribution dependences being close to those for the gaseous phase. This also confirms the conception
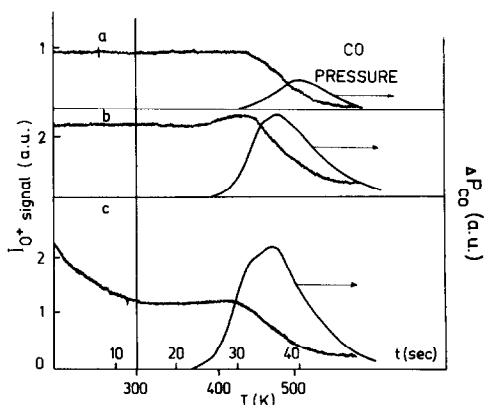

FIG. 5. TD spectra and I_{O^+} recorded following heating at three different CO coverages: (a) θ = 0.1; (b) θ = 0.4; (c) θ = 0.9.

that the M–CO bond is formed through the carbon atom.

The change of I_{O^+} and E_d with CO coverage observed in the present paper is in good agreement with the results of other authors (2, 5, 13–16, 20–24). The flux density of particles desorbed during ESD is described by the equation:

$$\dot{N} = QI^-\theta \qquad (25).$$

Here, Q is the desorption cross-section, $\dot{N}$ the density of the ion current, I^- the density of the electron current bombarding the surface, and θ is the CO coverage. It can be assumed that at low coverages Q has a constant value. Then the intensity of the ESD signal depends only on the concentration of adsorbed particles. In fact, when $\theta < 0.25$, I_{O^+} increases almost linearly with coverage (Fig. 4). At these low coverages, repulsive interactions between the nearest neighbors predominate, and since their number increases with coverage, E_d decreases linearly with θ (Fig. 3).

With further increase of coverage, the presence of an additional effect due to the overlapping of the partially occupied antibonding $2\pi^*$ orbitals of CO was assumed. Blyholder (15, 16) showed that when there is a repulsion between the $2\pi^*$ orbitals, the M–CO back donor–acceptor bond is weakened, which leads to strengthening of the C–O bond. According to theory (25, 26) ESD is a result of Franck–Condon transitions from the ground state to the repulsive neutral or ion state of the adsorbate system. The change in strength of the M–C–O bonds will probably lead to a change in the potential energy curves for the adsorbate energy levels relevant for ESD. These changes probably affect the values of the adsorption cross-section, Q. Thus, the observed decrease in density of the ion current at higher coverages (Fig. 4) can be attributed to the change in the energy levels at which the excited molecules exist after the Franck–Condon transition as a result of the electron impact, leading to a decrease in Q. This assumption satisfactorily explains the ob-

served initial increase in I_{O^+} during TD at higher CO coverage (Figs. 5b and c), which can be ascribed to the increase of Q as a result of partial CO desorption.

The overlapping of the $2\pi^*$ orbitals of CO and the possibility of long-range interactions between the adsorbed molecules satisfactorily explain the observed sharper change in E_d with θ higher than 0.25 (Fig. 3). For example, increase of the repulsive CO–CO interactions causes a considerable weakening of the Pd–CO bond, due mainly to the decrease in amount of the back-donating bonds from the d-metal orbitals to the $2\pi^*$ orbitals of CO. The electron bombardment effects observed in Fig. 5c are similar to those reported by Davis et al. (10) and suggest irreversible changes in the adsorption layer as a result of which a surface phase inactive toward ESD is formed. In order to elucidate the above effect, the normal TD curves (Fig. 6a) were compared with those obtained after the same exposure, with electron bombardment during adsorption (Fig. 6b). It was established that the TD curves obtained in the latter case (Fig. 6b) shift toward lower temperatures. Yates and King (27) proposed two explanations for an effect similar to that described above: (i) a decrease in E_d caused by residual carbon on the surface upon ESD; (ii) a decrease in E_d due to structural changes in the adsorption layer as a result of ESD. Since our further studies by Auger spectroscopy (28) have shown an increase of C on the surface following electron bom-
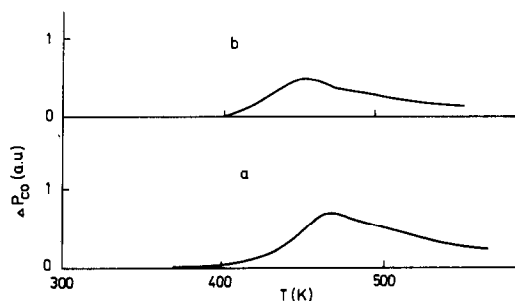

FIG. 6. TD curves: (a) without electron bombardment; (b) with electron bombardment.

bardment, the first explanation is more probable in our case, because the changes shown in Fig. 6 are observed at all coverages.

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