JOURNAL OF CATALYSIS **44**, 359–365 (1976)

The Thermal Desorption of Carbon Monoxide from Palladium and Palladium–Silver Films

J. J. STEPHAN, P. L. FRANKE, AND V. PONEC

Gorlaeus Laboratoria, Rijksuniversiteit, Leiden, The Netherlands

Received September 29, 1975

The extent of adsorption at 295 and 78 K and the thermal desorption of CO from Pd, Ag, and Pd–Ag alloy films have been measured in an ultrahigh vacuum system.

The adsorption data indicated that the surface of the alloys studied in this paper was enriched by Ag. Desorption spectra revealed several adsorption/desorption states, designed as γ_1, γ_2, α_1, α_2, and β. The nonspecific, most weakly bound γ_1-state was observed with all adsorbents. The γ_2-state, also weakly bound, was observed only on Pd. The α_1- and α_2-states were observed on Pd and Pd–Ag alloys; they were completely missing on Ag. The population of α-states decreased with increasing Ag content. This is explained by assuming that upon alloying of Pd with Ag the number of large ensembles necessary for strong adsorption decreases.

INTRODUCTION

Investigations of the surface of the Pt–Au and Ni–Cu alloy systems have already been described (*1*). Those alloys are formed from their components endothermically: the mutual perturbation of the alloy components is thus weak and no substantial changes in the local electronic structure of the metal atoms occur upon alloying. The main effect of alloying to be expected in catalytic and adsorption behavior is that of dilution of active sites; it leads to a variation in the distribution of the available ensembles (single atoms, doublets, triplets, etc.) and the mutual distance of these ensembles increases. Indeed, temperature-programmed desorption revealed a relative increase of weakly bound adsorption species (bound to small ensembles, according to the interpretation adopted) on alloys in comparison with the pure transition metal (*1*).

Pd–Ag alloys are formed exothermically (*2*) with a low heat of formation. Hence, we might expect that both components influence each other, but rather weakly. Nevertheless, this influence probably leads to a reorganization in the population of the Pd orbitals. The electronic structure changes (*3*) from $4d^{9.6}5s^{0.4}$ to $4d^{10}5s^{0}$. Apart from this, we expect that the distribution of Pd in alloys is more random (less clustering) than, for example, the distribution of Ni or Pt in a Ni–Cu or Pt–Au system. The interesting difference between Pt–Au, Ni–Cu on the one side, and Pd–Ag on the other side has led us, among others, to the choice of this last system for our present studies.

EXPERIMENTAL

Materials, apparatus, and data evaluation. The ultrahigh vacuum apparatus used was almost identical to that described previously (*1*). The films were prepared by simultaneous vapor deposition of Ag and Pd; Ag was evaporated from a tungsten filament and Pd was evaporated from a pure Pd filament as well as from a tungsten filament. The filaments were placed in the center of

TABLE 1

Adsorption Programs for Monolayer Coverage

Type	Temperature range adsorption (K)	t_a (min)	t_p (min)
a	295–78	30	10
b	295–78	10	10
c	295–78	2	10
d	295–78	10	2
e	78	—	10

a spherical vessel which was kept at 625 K during evaporation. After evaporation the films were equilibrated at 625 K for 20 hr. Amounts of adsorbed gas were measured by expanding the gases (L'Air Liquide, Brussels) from a known volume into the adsorption vessel, using a Pirani manometer to monitor the pressure. Desorption was performed in a pumped system (50 liters/sec Vac-ion pump, through a 1 liter/sec leak of the Granville–Phillips valve).

The necessary calibrations and the procedure of data evaluation have been described previously (*1*). The films were characterized by X-ray diffraction (Philips Goniometer P. W. 1050/25 and X-ray tube P. W. 1316). To this end a small Pyrex disk ($\Phi = 1.4$ cm) which was subject to the same treatment as the rest of the film was placed at the bottom of the cell.

Adsorption. In order to check the rate of adsorption, the interaction of various adsorption states[1] and the influence of of temperature, several adsorption–desorption programs were used as in ref. *1*. During all programs (besides e) adsorption was allowed, first, to proceed at 295 K during time t_a indicated in Table 1 (column 3) at a pressure of about 1×10^{-2} Torr. Then the film was cooled to 78 K which reduces the final pressure to about 2×10^{-3} Torr. Before desorption was started the gas phase was pumped off at 78 K during the time t_p indicated in Table 1. The amounts adsorbed, respectively, at 295 and 78 K at a pressure of 2×10^{-3} Torr are denoted by n (295 K) and n_b (78 K). The e-type adsorption distinguishes itself from the other types in adsorption temperature: adsorption was performed directly at 78 K. The amount adsorbed directly at 78 K and 2×10^{-3} Torr is denoted by n_e (78 K).

Desorption. Desorption was performed in a pumped system (Vac-ion pump). The temperature was raised from 78 to 575 K with a heating rate of about 0.5 K sec^{-1} (= 30 K min^{-1}). The temperature was measured with a chromel–alumel thermocouple which was in direct contact with the film inside the vessel. During desorption the pressure was measured by a mass spectrometer (AEI, MS 10) as an ion current in arbitrary units; these are the same for all desorption spectra.

RESULTS

Isothermal Adsorption

The adsorption is fast at 295 K as well as at 78 K. The extent of CO adsorption at 295 K and 2×10^{-3} Torr denoted by n (295 K) has been measured as a function of the alloy composition; the results are shown in Table 2 and Fig. 1. The amount adsorbed

TABLE 2

Properties of the Alloy Films

Film no.	Weight (mg)	Pd wt%	n(295 K) (10^{14} mol cm^{-2})[a]	n_b(78 K) (10^{14} mol cm^{-2})[a]
1	16.0	0	0	7.5
2	33.7	12	0.4	9.0
3	20.1	22	1.6	8.8
4	17.6	42	2.0	7.7
5	12.3	61	3.8	15
6	13.3	82	4.6	16
7	21.0	95	7.7	17
8	15.1	100	17.2	25
9	15.7	100	19.0	27
10	10.0	100	18.3	26

[a] All coverages are given in molecules per square-centimeter of geometric area.

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[1] More precisely, the states should be called desorption states, as the method used to detect these is thermal desorption.

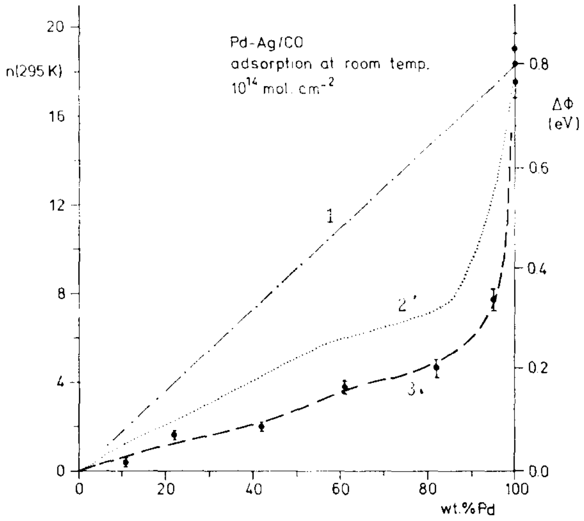

FIG. 1. Curve 1: Linear interpolation of the extent of adsorption on pure Ag and Pd. Curve 2: Increase in work function of Ag-Pd alloy films caused by CO adsorption as a function of alloy composition, as measured by Bouwman *et al.* (*9*). Curve 3: CO adsorption at 295 K and 2×10^{-3} Torr, n (295 K) as a function of alloy composition (this paper). Amounts adsorbed in molecules per square centimeter.

decreases gradually with decreasing Pd content of the alloys. Additional CO can be adsorbed after cooling the adsorption vessel from 295 to 78 K; the total amount adsorbed is then denoted by n_b (78 K) (see Table 2). With alloys, part of the CO is adsorbed by Ag at this low temperature. Although adsorption is fast at room temperature as well as at 78 K, a small part of the CO is adsorbed by an activated process. This is demonstrated by the fact that the extent of adsorption performed directly at 78 K, n_e (78 K), is lower than the n_b (78 K) value. On alloys n_e (78 K) is about 90% of n_b (78 K), and the difference tends to decrease with increasing Ag content. On pure Pd, n_e (78 K) is about 40% of n_b (78 K).

The percentage of n_b (78 K) that remains on the surface after pumping at 78 K for 10 min is about 95% for pure Pd, about 65% for the alloys, and about 40% for pure Ag.

By pumping at 575 K (at the end of the temperature program of desorption) CO cannot be removed completely; on the

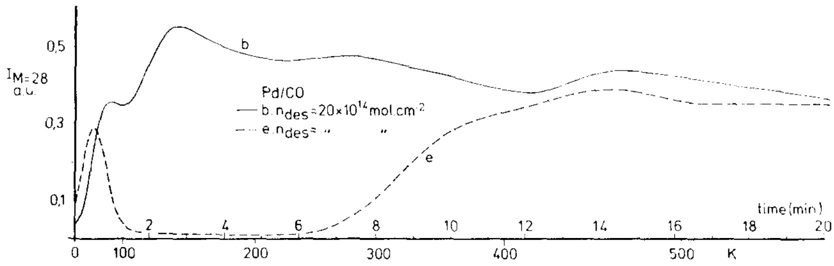

FIG. 2. Desorption spectrum of CO for pure Pd upon b- and e-type adsorption. Total amount desorbed indicated, in molecules per square centimeter.

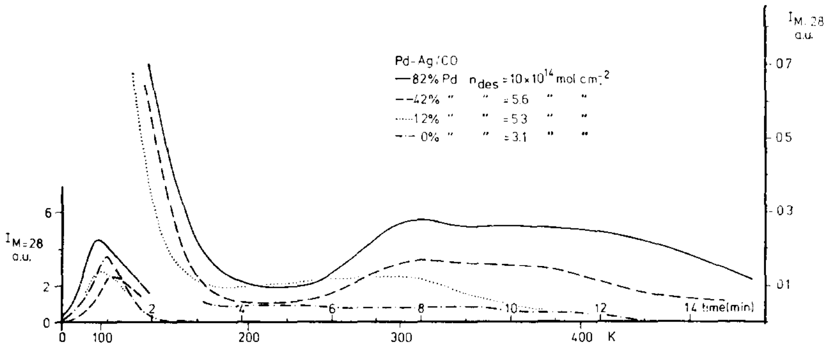

FIG. 3. Desorption spectrum of CO upon b-type adsorption for Pd–Ag alloys of various compositions. Alloy bulk composition and total amount desorbed indicated in molecules per square centimeter.

alloys about 20% and on pure Pd about 5% of n (295 K) remains on the surface, which part we call the β-state.

Thermal Desorption

The desorption profile of CO from pure Pd shows two low temperature peaks, denoted by γ_1 (100 K) and γ_2 (150 ± 30 K), and at high temperatures two broad maxima at 300 ± 30 K and 500 ± 30 K denoted by α_1 and α_2. A typical spectrum is shown in Fig. 2, curve b. Almost no influence of adsorption time on the desorption spectrum could be observed, with the precision of detection used here. Adsorption directly at 78 K, i.e., e-type adsorption, results in lower desorption peaks and a different desorption profile (one γ peak only) in comparison with b-type adsorption; see Fig. 2, curve e.

The desorption spectrum of the Pd–Ag alloys (Fig. 3) is totally different from pure Pd: the γ_2-state as a well-defined maximum is lacking and almost no α_2 desorption is observed. The amount desorbed in the α_1-state decreases gradually with increasing Ag content of the alloys. Although for pure Pd almost no influence of adsorption time is observed (one trivial reason could be the lower sensitivity in the higher pressure range reached here), for alloys the α_1 desorption peak increases slightly with increasing adsorption time (Fig. 4, curves a and c). On the alloys e-type adsorption

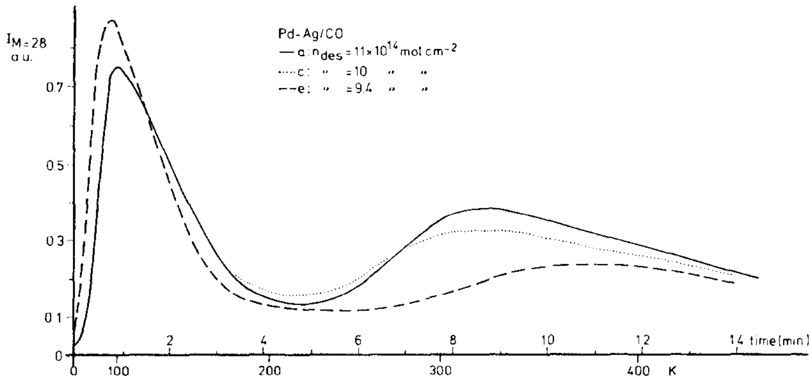

FIG. 4. Desorption spectrum of CO for Pd–Ag alloy (95 wt% Pd) upon a-, c-, and e-type adsorption (typical also for other alloys). Total amount desorbed indicated in molecules per square centimeter.

yields a lower α_1 desorption peak and a higher γ_1 desorption peak.

Short pumping time (d-type adsorption) results in a slightly higher γ_1 peak for the alloys and slightly higher γ_1 and γ_2 peaks for Pd; no influence on the α-states has been observed.

For several films the CO_2 desorption during a b-type CO desorption experiment has been checked; the extent of a possible CO_2 desorption appeared to be below the limits of detection for all alloys and for pure Pd it was detectable but almost negligible.

The phase composition was checked by X-ray diffraction measurements. It appeared that it was most difficult to obtain homogeneous films in the region 55–75% Pd[2]: actually the alloy of 61% Pd (Table 2; Fig. 1) revealed also two distinct lattice constants. Alloys with 0–55% and 75–100% Pd were less difficult to obtain in a form which gave only one X-ray diffraction maximum. However, the diffraction peaks of these films were still broad showing that there is a certain distribution of lattice constants.

We tried to determine the surface area of the films by Xe adsorption at 78 K by means of the BET method *(5)*. In some cases the Xe adsorption was unrealistically high. These high values were found in those cases where an "old" cell (cleaned with aqua regia several times) was used. The "old" Pyrex glass is porous and can adsorb more Xe *(6)*. This is only possible if a part of the glass wall was accessible for Xe. Indeed, it is known that Pd tends to agglomerate after heating *(7)*.

DISCUSSION

Let us concentrate the discussion on two main points: (i) the variety in adsorption/desorption states, as revealed by thermal desorption; (ii) the surface composition of the alloys studied.

Thermal Desorption

The γ_1-state is the most weakly bound and it has been observed not only on all Pd, Ag, and Pd–Ag films, but also on all other metals and alloys we have studied (Pt, Ni, Cu, Au) *(1)*. Hence, in this weak binding an interaction is involved which is nonspecific, like the Van der Waals forces.

The γ_2-state is a more specific adsorption. It was not observed on Ag and it could be eliminated by addition of Ag to Pd. We observed *(1)* that addition of 5% Ag already caused the γ_2-state to disappear as a well-defined peak. The γ_2-state was more easily formed upon b-type adsorption when the system is being cooled from 293 to 78 K in presence of CO than upon e-type adsorption (at 78 K).

The appearance of the γ_2-state is somehow related to the electronic structure of the metal; this state has been observed *(1)* with Pd, Ni, Cu, and Au, but not with Pt and Ag. However, the disappearance of this state upon alloying cannot be caused by the filling of the d-orbitals. For example, Cu has completely filled orbitals but reveals this state *(1)* and in the Ni–Cu system the number of d-holes on Ni does not vary with Cu content but the population of the γ_2-state does *(1)*. Because a rather small content of Ag in the film already reduces the γ_2 peak we conclude that several Pd atoms are necessary for binding a CO molecule in the γ_2-state.

The α-states are typical of transition metals (Pd, Ni, Pt); they are not observed with Ib metals (Cu, Ag, Au) *(1)*. The IR spectra of CO on Pd and on alloys with Ag show two bands *(8)* usually interpreted as two adsorption states of CO, namely, a multi- and a low-coordinated (here designed by M- and L-) molecule of CO. The easiest interpretation of the desorption spectra would be to relate the α_1- and α_2-states to these M- and L-adsorption complexes. However, caution is necessary for the following reasons.

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[2] More alloys have been prepared than shown in Table 2 and Fig. 1.

Ni and Ni–Cu alloys which reveal much similarity with Pd and Pd–Ag alloys also show two α-states, α_1 and α_2. However, with Ni–Cu the position of the α_2 peak (i.e., the chemisorption bond strength of particles bound in this state) shows a significant shift when Cu is added to Ni. In contrast to it, the shifts in the positions of the M- and L- ir-bands are negligible (*8*); it is mainly the population of the states which varies with Cu content, not the bond strength of the states. Therefore, it is not possible to identify in a straightforward manner the L-complex with the α_1-state and the M-complex with the α_2-state. Of course, there could be some relation. For example, the α_2-desorption state can be formed from the M-state during heating of the film upon thermal desorption. Due to these complications caution is necessary also in the interpretation of the desorption spectra on Pd and Pd–Ag alloys. In any case, it is a safe statement that the L-complex of CO desorbs as an α_1-state.

Surface Composition

When the surface composition of Pd–Ag alloys is equal to the bulk and the adsorption stoichiometry remains the same as on pure Pd, then the extent of CO adsorption as a function of alloy composition should follow curve 1 in Fig. 1. However, the experimental curve 3 strongly deviates from curve 1, showing a shape rather similar to curve 2, which is the change in work function upon CO adsorption as measured by Bouwman *et al.* (*9*).

Which reasons can be put forward to explain the low extent of adsorption on the alloys? First, let us consider the case that the surface composition is the same as the bulk composition. Then, the extent of the total adsorption (i.e., all forms together existing at 293 K) can be low because: (a) by dilution of Pd in Ag, adsorption modes which can only take place on large ensembles of Pd are completely eliminated and this leads to a drastic reduction in the total adsorption; (b) upon alloying, some of the Pd atoms become inactive in chemisorption because their electronic structure changes from $4d^{9.6}5s^{0.4}$ into $4d^{10}5s^0$. If neither of these possibilities can explain the decrease in the total adsorption of CO, we are left with a third possibility: (c) the alloy surface is enriched in Ag, and the Pd content of the surface is lower than that of the bulk.

Let us consider possibility (a) first. The infrared spectra of CO adsorbed on alloys do indeed show that the multiple-coordinated state is less populated on alloys than on Pd, but the same data do not bring any indication that the total adsorption (not only of one form of CO) is decreased drastically on alloys. They rather indicate that those Pd atoms which cannot be occupied by multiple-coordinated CO molecules are covered by single (low)-coordinated CO molecules. Thus, effect (a) alone cannot explain the data.

Let us consider possibility (b). The addition of 5% Ag causes some of the Pd atoms to convert their electronic structure from $4d^{9.6}$ to $4d^{10}$. According to the magnetic measurements, we would expect that at 5% Ag about 10% of Pd is converted into a form which might be completely inactive in chemisorption. Also this effect alone cannot explain the observed shape of curve 3 in Fig. 1. In this way we come to the conclusion that the surface of the alloys studied was, indeed, enriched in Ag to some extent.

It is still a question as to whether the enrichment found here is only because of thermodynamic reasons or whether slow diffusion (equilibration) kinetics did not allow equilibrium to be reached. Ag has a higher diffusion coefficient than Pd and it will always tend to cover the Pd-rich crystallites (regions) by a fast diffusion on their surface; this process will then be followed by mutual penetration of both components. The X-ray diffraction profiles of our alloy films were broad and a certain heterogeneity (a gradient of Pd concentration in the direction perpendicular to the surface) is not excluded. However, for further catalytic and adsorption work with these alloys it is most essential that the surface composition found (i.e., Ag enrichment) is a rather stable situation after sintering during a certain time period at a given temperature. It is also important that CO adsorption and the work function measurements (*9*) both indicate the same phenomenon. Moreover, the work by Bouwman and Sachtler (*4*) and by Franken (*10*) has shown that the surface layers of various alloys attain their equilibrium composition at a lower temperature and after much shorter sintering than the bulk of the film. Therefore, the surface composition of the films investigated in this paper was not necessarily very far from equilibrium.

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