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The Thermal Desorption of Carbon Monoxide from Platinum and Platinum–Gold Films

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The extent of CO adsorption at 295 K and at a pressure of 2×10^{-3} Torr has been measured on Pt and Pt–Au films. The amount adsorbed on Pt–Au alloys is low (17% of the value for pure Pt) and varies only marginally with alloy composition.

The thermal desorption of CO has been measured in the temperature region 78–575 K. The spectrum for Pt reveals three maxima which are identified with three states: γ (110 K), α_1 (310 K), and α_2 (410 K).

The desorption spectrum of CO from the alloys is dominated by a broad γ peak caused by desorption from Pt and by additional desorption from Au. Besides this peak a broad maximum in the range 300–400 K can be distinguished.

CO adsorption into a preadsorbed H_2 layer causes a weakening of the H–Pt bond.

INTRODUCTION

In our previous papers (*1*, *2*), the surfaces of platinum and platinum-gold films were investigated by hydrogen adsorption–desorption measurements. In those papers we related the number of hydrogen atoms adsorbed at room temperature to the number of Pt atoms in the surface. Hydrogen was thus used *to count* (titrate) the Pt atoms in the alloy surface. Hydrogen is a convenient gas, as the difference between Pt and Au in their affinity toward hydrogen is considerable: there is no measurable adsorption of hydrogen on Au while Pt adsorbs hydrogen readily. We have suggested on the grounds of adsorption–desorption measurements the following picture of the Pt–Au alloy surfaces. Hydrogen can be bound to ensembles (two-dimensional) of Pt atoms of various size; by alloying, the distribution (according to their size) of available ensembles varies. The presence of Pt ensembles even in alloys was connected with the formation of three-dimensional clusters of Pt atoms, because clustering can always by expected in endothermically formed alloys.

In order to gain more information on the Pt–Au alloy surfaces, we studied the adsorption and desorption of carbon monoxide. Carbon monoxide is adsorbed with higher heats of adsorption than hydrogen on most metals (*1*, *3*, *4*, *5*) and the same could be expected for the alloys. Probably CO can be adsorbed more easily than hydrogen by only one atom; e.g., one of the possible explanations of the existing infrared spectra (*6*, *7*) is that the so-called linear CO structures prevails. The possibility of checking an eventual role of the bond strength and adsorption geometry (one- or multiple-site adsorption complexes) by CO adsorption seemed to be attractive.

We also did some experiments on the mixed layers of hydrogen and CO in order to check the influence of preadsorbed hydrogen on CO adsorption.

EXPERIMENTAL

1. Materials, apparatus, data evaluation. The ultrahigh vacuum apparatus used was almost identical to that described previously (*1, 8*). The films were prepared by simultaneous evaporation of Pt and Au from two tungsten filaments placed in the center of a spherical adsorption vessel (kept at 625 K). After evaporation the films were equilibrated at 625 K for 5 hr. The amount adsorbed was measured by expanding the gases (L'Air Liquide, Bruxelles) from a known volume, using a Pirani manometer for measuring the pressure. During desorption the partial pressure of the gases was monitored by a mass spectrometer (AEI, MS 10) and the temperature was measured by a thermocouple which was in direct contact with the film. The necessary calibrations and the procedure of data evaluation were described previously (*1, 2*).

2. Adsorption of pure gases. Of the various adsorption–desorption programs described in our previous papers (*1, 2*), two were applied here. The b-type adsorption: An amount of gas was admitted to the film at 295 K such that a steady-state pressure of about 7×10^{-3} Torr (1 Torr = 133.33 N m^{-2}) was established. After a period of 10 min the adsorption vessel was cooled to 78 K, which reduced the final pressure to about 2×10^{-3} Torr. Before the thermal desorption was started the gas phase was pumped off by a Vac-ion pump (Varian, 50 liters/sec) for 10 min at 78 K. The amounts adsorbed at 295 and 78 K, respectively, and at a pressure of 2×10^{-3} Torr are denoted by n (295 K) and n_b (78 K).

The e-type adsorption: The gas was admitted to the film at 78 K directly and the amount adsorbed (denoted by n_e (78 K)) at a steady pressure of about 2×10^{-3} Torr was determined. Before the desorption was started the gas phase was pumped off for 10 min.

3. Composite layers. A "complete" hydrogen layer was preadsorbed as in the b-type experiments. After pumping off the gas phase hydrogen, CO was admitted in such an amount that a steady pressure of about 2×10^{-3} Torr was reached. Desorption was again started after a period of 10 min, pumping off the gas phase; during desorption the pressure of either CO or H_2 was monitored.

4. Desorption. Thermal desorption was followed in a system pumped by a Vac-ion pump; the heating rate was about 0.67 K sec^{-1} (40 K min^{-1}). The temperature rose almost linearly with time. After the maximum temperature, i.e., 575 K, was reached, the temperature was further kept constant for 5 min during additional pumping. The amount desorbed can be calculated from the area under the desorption curves and is denoted by n_{des}.

RESULTS

1. Isothermal adsorption-desorption experiments with CO. Adsorption of CO at 295 and 78 K is very fast and only a small part of the adsorption proceeds with a rate measurable at the given experimental conditions. However, the fact that the extent of adsorption when the film is cooled from 295 to 78 K in the presence of the gas is higher than the adsorption at 78 K directly shows that part of the film surface can be occupied only via an activated process.

The amounts adsorbed at 295 K and 2×10^{-3} Torr [n (295 K)] as a function of the alloy composition are shown in Fig. 1 and Table 1. It can be seen immediately that the amount adsorbed varies with alloy composition in rather narrow limits around the value of 1.5×10^{14} molec cm^{-2} (geometric surface area). This is 17% of the value found for pure Pt films. The amount adsorbed at 78 K and 2×10^{-3} Torr after adsorption at 295 K and cooling to 78 K (n_b (78 K)) is for pure Pt 12×10^{14} molec cm^{-2}, for pure Au 5.5×10^{14} molec cm^{-2} and alloys 8.9×10^{14} molec cm^{-2} (average of three films).

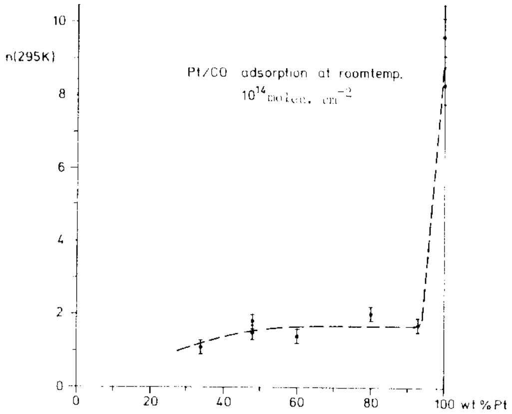

FIG. 1. Pt–Au Alloys. CO adsorption at 295 K and 2×10^{-3} Torr, n (295 K) as a function of alloy composition.

In contrast to hydrogen, CO is evidently adsorbed extensively also by Au. CO, also in contrast to hydrogen, reveals at a steady pressure of 2×10^{-3} Torr at 295 K a plateau (i.e., $dn_{\mathrm{CO}}(295)/dp(\mathrm{CO}) \approx 0$) on the isotherms.

By pumping at 575 K, CO cannot be removed from the surface completely. By comparing the amounts adsorbed at the first and repeated adsorptions (after pumping at 575 K), we found that about 10% of n (295 K) on Pt and about 30% of n (295 K) on alloys remains on the surface.

TABLE 1

Properties of the Alloy Films[a]

Film nr.	Wt% Pt	n_{CO} (295 K) (10^{+14} mol cm^{-2})	m
1	0	0.0	—
2	34	1.1	—
3	48	1.8	1.8
4	48	1.5	1.7
5	60	1.4	1.4
6	80	2.0	2.6
7	93	1.7	1.7
8	100	8.3	1.9
9	100	9.6	1.8

[a] All amounts are given in molecules per cm² geometric surface area. The surface roughness of alloys is abt. 1.4; of pure Pt-abt. 1.2.

Table 1 shows also the values of m which were determined as follows. Hydrogen was first adsorbed in a b-type adsorption process [n_{H_2} (295 K)], then completely desorbed and on the same surface the adsorption of CO [n_{CO} (295 K)] was determined. The parameter m is defined as the ratio $n_{\mathrm{CO}}(295)/n_{\mathrm{H}_2}(295)$. No relevant difference is found between the values of m for pure Pt and for alloys; the average of $m = 1.8$.

2. Temperature-programmed desorption of CO. The desorption spectrum of a b-type adsorption layer on pure Pt shows three

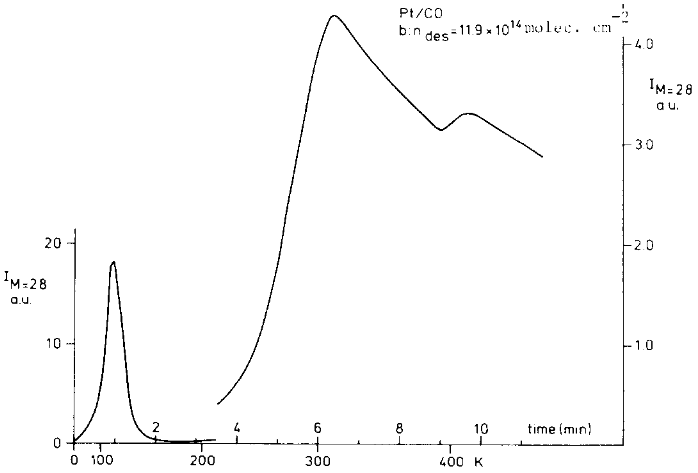

FIG. 2. Desorption spectrum of CO for pure Pt upon b-type adsorption. Total amount desorbed is indicated by n_{des}.

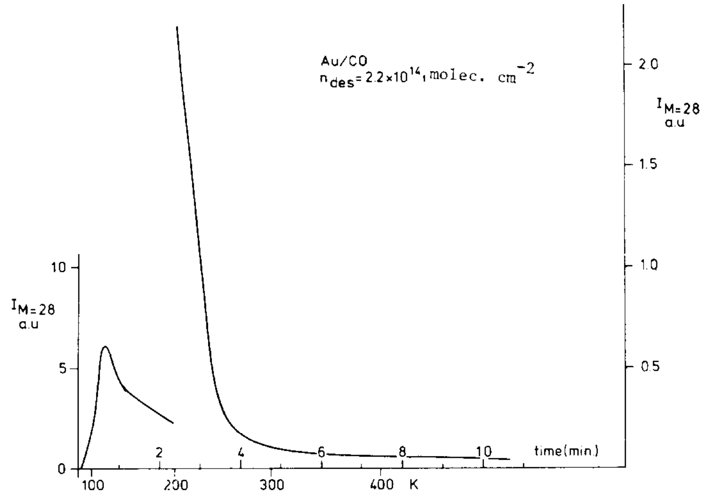

FIG. 3. Desorption spectrum of CO for pure Au upon b-type adsorption. Total amount desorbed is indicated by n_{des}.

peaks; a typical spectrum is shown in Fig. 2. We can distinguish three states, one clearly resolved at 110 K (γ state) and two states poorly resolved at 310 K (α_1) and 410 K (α_2). Part of the CO adsorbed does not desorb under these conditions.

The desorption spectrum of a pure Au film (see Fig. 3) shows one peak only, the γ state at 110 K. This peak has a broad shoulder, absent on Pt.

Alloys show a broad γ peak, similar to pure Au (see Fig. 4b). Although the spectrum is dominated by the high desorption from Au, a broad maximum in the region 300–400 K can be distinguished. With the precision of the experiments used here, no difference could be detected with different alloys.

The desorption in the α_1 state is lacking upon desorption from an e-type adsorption

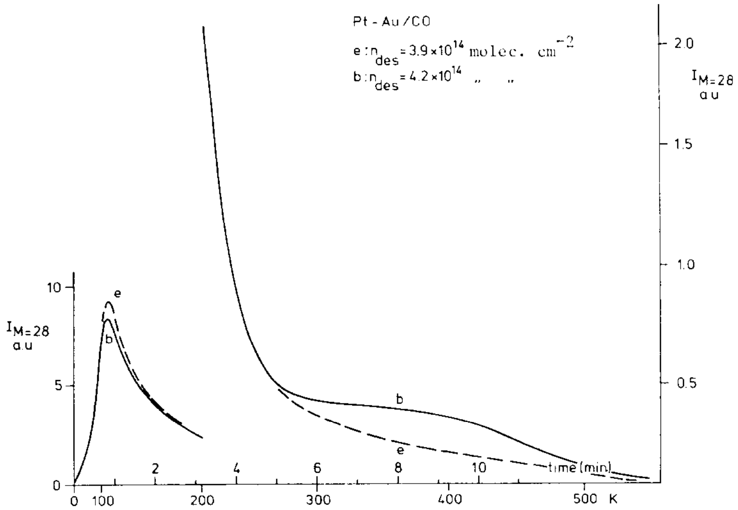

FIG. 4. Desorption spectrum of CO for a Pt–Au alloy (60 wt% Pt) upon adsorption programs b and e. Total amounts desorbed are indicated by b and e.

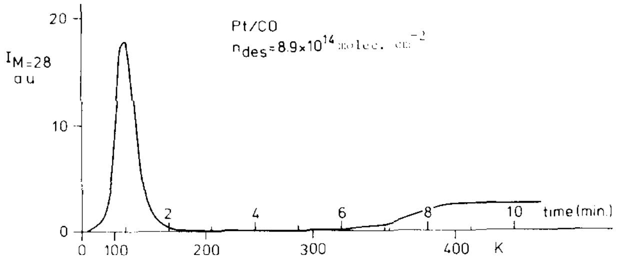

FIG. 5. Desorption spectrum of CO for pure Pt upon e-type adsorption. Total amount desorbed is indicated by n_{des}.

layer on Pt (Fig. 5), in contrast to a b-type adsorption. On the alloys the α_2 state is also lacking (Fig. 4e).

No influence was found in varying the duration of adsorption at 295 K or pumping at 78 K.

3. Composite layers. Considerable adsorption of CO (8.0×10^{14} molec cm^{-2}) is possible on a "complete" preadsorbed layer of H_2 at 78 K. The effect of CO on the preadsorbed hydrogen layer, shown in Fig. 6, is (a) a shift of the H_2 desorption peak to lower temperatures; (b) more hydrogen can be pumped off at 78 K. Curve 2 (Fig. 6) shows that in comparison with curve 1,[1] part of the "high-temperature" (330 K) β_2 state is desorbing at a slightly lower temperature, whereas the total amount of hydrogen desorbed from a composite layer (curve 2, $n_{des} = 8.6 \times 10^{14}$ molec cm^{-2}) is less than the amount desorbed in a pure H_2–Pt experiment (curve 1: $n_{des} = 9.2 \times 10^{14}$ molec cm^{-2}). Evidently, the adsorbed CO weakens the H–Pt bond.

As to which type of adsorbed CO changes the H–Pt bond, the desorption spectrum of CO from a composite layer (Fig. 7) shows a considerable γ desorption, but the α_1 desorption is lacking and only a "tail" of the α_2 state is observed. On alloys, the volume of hydrogen still adsorbed ($=n_{des}$ (H_2)) at the start of b-type desorption is lower with composite layers; it amounts to only 30% of the value for pure hydrogen layers.

DISCUSSION

The extent of CO adsorption as a function of alloy composition shows the same picture as has been found with hydrogen adsorption: The amount adsorbed on alloys is only marginally dependent on the alloy composition and it is substantially lower than the amount adsorbed by pure Pt. Such a behavior is a further support of the model suggested in the early work on Pt–Au (*2*, *9*): At the temperature at which the films were equilibrated, two Pt–Au alloy phases (17 and 97% Pt) are in equilibrium, the *surface of the alloys* (of compositions within the miscibility gap) is *formed by the Au-rich (17% Pt) phase.* CO proves to be a gas suitable for the determination of the contribution of Pt atoms to the total surface as it reveals an isotherm which flattens

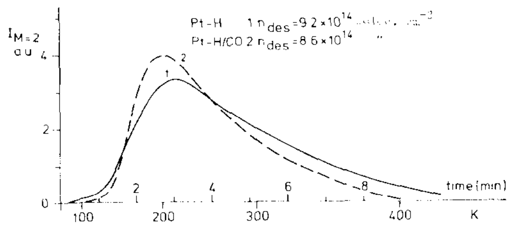

FIG. 6. Curve 1: Desorption spectrum of hydrogen from pure Pt upon b-type adsorption. Curve 2: Desorption spectrum of hydrogen from a *composite layer* on pure Pt. Total amounts are indicated by (1) and (2).

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[1] Because a b-type spectrum shown here was recorded with a low sensitivity of the mass-spectrometer, the γ and β_2 states described in the previous H_2–Pt work are not resolved.

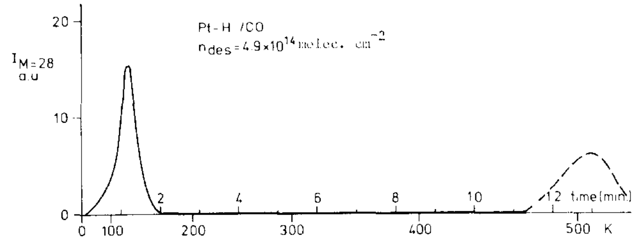

FIG. 7. Desorption spectrum of CO from a *composite layer* on pure Pt. Total amount desorbed is indicated by n_{des}.

sharply in the region of 10^{-3} Torr. However, it has been found to be less suitable, e.g., for determination by means of surface potentials because the change in work function of Pt upon CO adsorption is very low (*9*).

Another conclusion which can be made on the basis of the present data is that at 295 K and $2\cdot10^{-3}$ Torr the extent of CO adsorption determined on the same surface is 1.8 times higher than the extent of hydrogen $-n_{H_2}^-$ adsorption. This means that roughly one molecule of CO occupies one site for hydrogen adsorption. It should be mentioned that this ratio holds for pure Pt as well as for the Pt–Au alloys. We know from the literature that CO displaces hydrogen almost quantitatively from the surface of various metals such as Pt (*10*, *20*), Rh (*10*), Fe (*21*), or Ni (*17*, *20*, *23*) at 295 K. This means that the above-mentioned strong chemisorption of CO and H atoms takes place on the same sites.

Let us now discuss the information obtained from desorption spectra. We can discern the following types of adsorption states.

1. Weak adsorption of CO desorbing at 110 K. This type is present on Pt, on the alloys, and also on Au. In compliance with the literature we denote this type as the γ state. It should be noticed that the γ state is of a much higher extent than we would expect for a pure physical Van der Waals (liquid-like) adsorption,[2] for example, in the second adsorption layer. On Au (and on the alloys) two weakly bound states can actually be distinguished, namely, the γ peak (110 K) and a shoulder on this peak at about 170 K. On Ni and Pd these weakly bound states, which are denoted by γ_1 and γ_2, are clearly separated.

2. Medium-strong adsorption of CO. This type desorbs from Pt at 310 and 410 K, and from alloys in the region 300–400 K. Morgan and Somorjai (*11*, *12*) observed on Pt(100)- and (111)-planes adsorption states desorbing at 403 and 443 K. We shall use here the same notation as theirs and call these states α_1 (310 K) and α_2 (410 K).

3. Strong adsorption of CO. These molecules do not desorb from films at temperatures which could be used in this work. We denote this type as the β state.

Summarizing, we have three or four types of CO adsorption which have to be identified with adsorption either on various crystallographic sites or with various types of bonds on essentially the same sites in a geometric sense. Thermal desorption and adsorption measurements cannot, alone, lead to an unambiguous definite model of the adsorption layer. However, we shall make an attempt to suggest a model, using,

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[2] A rough estimate of the Van der Waals (liquid-like) adsorption can be performed as follows. At a very low relative pressure, the degree of occupation of the surface, Θ, is approximately $C_{BET}\cdot x$, where C is the constant from the BET equation and x is the relative pressure. It is a reasonable guess that $C_{BET}=10^2$. In our experiments the relative pressure is of the order of 10^{-5}, i.e., $\Theta\approx10^{-3}$. However, the γ adsorption which takes place on cooling from 295 to 78 K occupies about 30% of the surface.

in addition, some literature data on the CO adsorption.

The coverage of Pt by CO is high. Assuming an equal contribution of the two most dense crystallographic planes to the surface of Pt, the ratio CO/Pt (surface) at $2\cdot10^{-3}$ Torr and 293 K is about 0.7. To establish the CO/Pt (surface) ratio on the alloys, we first consider the following.

According to various experimental data (*1*, *2*, *9*, *25*), we assume that the Au-rich phase, known to be present according to the phase diagram (*26*), forms the surface of the alloy crystallites. Therefore, we expect at most 17% Pt atoms in the whole alloy surface. In reality, this figure might be lower because of an additional surface enrichment by the component with the lower heat of sublimation (Au). Nevertheless, the CO adsorption on alloys does not drop below 17% of the value of pure Pt, which means that also on alloys the CO/Pt ratio is 0.7 or higher. These facts have important consequences for the model to be suggested as an explanation of the adsorption and desorption phenomena. This model must allow coverages of the order of $\theta = 0.5$ to 1 on Pt as well as on the alloys.

If the only possible position for CO adsorption is on top of the Pt surface atoms, then the CO/Pt ratio on Pt as well as on Pt–Au can be easily near to 1 (eventually reaching 1 for sufficient high pressures). However, there are some reasons for not accepting this idea immediately.

According to quantum mechanical calculations (*14*, *15*), the *most favorable sites* for H_2 and CO adsorption are the *surface holes* among three [(111)-planes] or four [(100)-planes] atoms (Fig. 8b). Energetically less favorable are the sites between two atoms (Fig. 8c); still less binding are the positions on the top of metal atoms (Fig. 8a).

Let us consider the question of an adsorption site in more detail. Doyen and Ertl (*14*) showed that the above-mentioned difference in quality of the sites is least pronounced on (111)-planes and then on (100)-planes and it is quite high for planes of high index. Doyen and Ertl have also shown that the energetic difference of various positions is less pronounced for Pd than for Ni. It can be expected, according to various parameters characterizing the band structure of the metals in question, that Pt resembles Pd more than Ni. Further, we can expect that the surface of the crystallites is mainly formed by (111)- and (100)-planes. Keeping this in mind, we can proceed further.

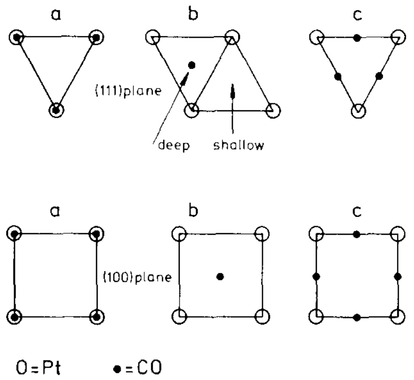

FIG. 8. Adsorption models of CO on a (111)- and a (100)-plane. CO molecules are situated *in* a level or *above* the level of the Pt atoms.

On pure Pt, it is possible to achieve a CO/Pt ratio close to 1 when CO is adsorbed in the valleys among three or four atoms: the number of surface atoms is almost equal to the number of surface holes. However, the condition is that the adsorbing plane is so large that edge effects can be neglected. The situation is totally different for an alloy surface with 17% Pt. We expect only small clusters which expose ensembles at the surface of about two to four atoms of Pt. If the only possible positions are again in the valleys among three or four surface atoms, we are unable to achieve such high CO/Pt ratios as found experimentally. Therefore, we have to consider one of the following possibilities.

(a) In spite of the quantum-mechanical predictions and against chemical "intuition," in both pure Pt and alloys the position of adsorbed CO (and we must assume for H atoms as well) is on top (Fig. 8a) of the Pt atoms, as has been mentioned at the beginning of this discussion.

(b) The most favorable position of CO on pure Pt is in the valley, but the difference between the valley and the top position is not very big. Therefore, if Pt is alloyed with Au, the position on the top of Pt atoms becomes more favorable than the positions in the valley among Pt and Au atoms.

(c) In the alloys there are small clusters of Pt present which are covered by adsorption in such a way that one Pt atom binds simultaneously more CO molecules, but the total ratio CO/Pt remains close to 1 (Figs. 8b and 8c). This is not possible on pure Pt because this way of adsorption would lead to a too-high coverage (CO/Pt ratio 2.0, in the case Fig. 8c, etc.).

At this point we would like to recall the results of the infrared absorption measurements (*6, 7, 22*) performed on Pt and some alloy systems. Spectra of CO on transition metals usually reveal two main peaks in a varying ratio: around 2050 and 1950 cm^{-1}. The first absorption band with lower back-donation is usually described as a form of binding to one metal site (single-site adsorption, or often called a linear adsorption complex), while the second can be interpreted as a form of binding to an ensemble of several sites (multiple-site complex, often called a bridge complex). On Pt, the 2050 cm^{-1} band usually prevails strongly or is even the only band found. If we accept the usual interpretation it would mean that on Pt the single-site adsorption prevails strongly (or is present exclusively) and we are back at the model (a) as discussed above. However, caution is necessary. If the difference between the back-donation to the adsorbed CO in the *valley* and *top* positions is very small with Pt (smaller than with Pd or Ni), there would be only one infrared band observable in any case. The metals, which have a more pronounced difference between the various positions, apparently show the following behavior. Alloying of Ni with Cu or Pd with Ag causes a disappearance of the 1950 cm^{-1} absorption band, while the 2050 cm^{-1} band stays as an intensive band up to a much lower concentration of Pd or Ni. The straightforward explanation is that in alloys there is a smaller chance of finding ensembles of several Pd (Ni) atoms necessary for a multisite adsorption (1950 cm^{-1} band). If we assume that Pt is similar to Ni or Pd in its behavior toward CO, we must assume that such changes occur in Pt–Au alloys as well, but that these are less visible in infrared because of the too-small difference in back-donation on various sites.

In this paper it has been found by TPD that the ratio of α_1 and α_2 adsorption states increases upon alloying. Therefore, it is tempting to relate the α_2 state to multisite adsorption (*bridge* complexes) and the α_1 state to the adsorption on a smaller adsorption site (*linear* complex). In other words, the strongly bound α_2- and β-species are presumably related to the adsorption complexes in the valley positions and the α_1 states are molecules bound to smaller ensembles, e.g., single sites. By alloying, which is actually diluting active sites in an inactive matrix, the chance decreases that a CO molecule will find an ensemble of several atoms. This leads to an α_2 adsorption of lower extent.

On the basis of the considerations above, we conclude that possibility (b) is the most reasonable model for the adsorption on Pt and Pt–Au alloys. Recent TPD data on the analogous systems Cu–Ni/CO and Pd–Ag/CO lead to the same conclusions concerning the possible sites for CO adsorption.

The above-mentioned models of CO adsorption and the previously described models for hydrogen adsorption (*2*) on Pt and Pt–Au alloys can also help us to understand the results of the thermal desorption of H_2 (Fig. 6) and CO (Fig. 7) from the composite layers. If CO is adsorbed at 78 K on the preadsorbed hydrogen layer, the CO molecules are adsorbed first on the sites for the γ adsorption (therefore, on Ni/H–CO (*17*) the same sign of dipole is observed as, e.g., for CO on Au or Cu), while H atoms still occupy the valleys. Upon heating, CO desorbs as the weakly bound γ state and almost no α_1 and little α_2 desorption is observed. When the system has gained sufficient energy, CO and H can interchange positions, as is witnessed by the fact that only weakly bound hydrogen desorbs (*21*) and at a higher temperature some desorption of CO is observed from places for medium-strong or strong CO adsorption (α_2).

In conclusion, we can say that CO appears to be a suitable gas for the *titration* of Pt in the alloy surface, but that it is somewhat less suitable for desorption measurements of the Pt–Au films in comparison to hydrogen. The results obtained support, or at least do not contradict, the conclusions made previously on the composition of Pt–Au (*1*, *2*, *9*) (or Ni–Cu) (*1*, *22*, *27*) alloy surfaces.

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