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Adsorption of CO_2 on Clean and Potassium-Covered Pd(100) Surfaces

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The adsorption of CO_2 on the clean and potassium-predosed Pd(100) surface is studied using Auger electron, electron energy loss (in the electronic range), and thermal desorption spectroscopies. Adsorption of CO_2 on a clean Pd(100) surface is weak and nondissociative. However, the preadsorbed potassium dramatically affected the adsorption behavior of CO_2 on Pd(100) and it caused significant changes in the electron energy loss spectrum of adsorbed CO_2. It increased (i) the amount of weakly adsorbed CO_2, (ii) the rate of CO_2 adsorption, and (iii) the binding energy of CO_2, and (iv) it induced the formation of new adsorption states and lowered the activation barrier for dissociation. The lowest potassium coverage where the dissociation of CO_2 was detected was $\theta_K = 0.21$. The peak temperatures for CO desorption were 624 and 693 K, which are significantly higher than those measured for the clean Pd(100) surface. The adsorption of CO_2 on potassium-dosed Pd leads to a work function increase of 2.20 eV at nearly monolayer of potassium. This indicates a substantial charge transfer from the potassium-dosed metal to an empty $CO_2\pi^*$ orbital; as a result the bonding and the structure of adsorbed CO_2 are basically changed. In the interpretation of the data a direct interaction between preadsorbed K and CO_2 leading to the formation of carbonate and CO is also considered.

INTRODUCTION

The finding of Rabó and co-workers (*1*) that palladium is one of the most active and selective catalysts for the synthesis of CH_3OH from an $H_2 + CO$ gas mixture at elevated pressure initiated great interest in this catalytic system. Palladium is also an effective catalyst in the hydrogenation of CO_2 into methanol, a reaction which is thermodynamically more favorable than the previous one (*2–5*). An attempt is being made in our laboratory to improve the performance of supported Pd catalyst by means of alkali metal additives. The method of activation has not yet been examined and utilized in this system. An important study in this direction was made on the Ni(100) surface (*6*). It was shown that preadsorbed K increases the rate of production of both CO and CH_4 in the hydrogenation of CO_2 at a total pressure of 97 Torr.

In the evaluation of the mechanism of the catalytic reaction of CO_2, it is necessary to establish the characteristics of the interaction of CO_2 with metal surfaces. In this respect, it is surprising that relatively little attention has so far been devoted to the adsorption of CO_2 on well-characterized clean metal surfaces. A notable exception is Rh, on which detailed studies have been performed (*7–18*).

However, the results of experiments and theoretical calculations are not in agreement. While Somorjai and co-workers (*9–13*) observed that CO_2 chemisorbs and dissociates on Rh(111) (and on other faces of Rh) at 300 K at low pressure (around 10^{-6} Torr), several other groups found no indication of the adsorption and dissociation of CO_2 on a carefully cleaned Rh(111) surface and on supported Rh surfaces at 300 K (*14–20*). Although the reasons for the different experimental results are not yet clear, we feel that the surface impurities played a decisive role. For instance, the presence of

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adsorbed oxygen may inhibit the chemisorption and dissociation of CO_2 (*13*). On the other hand, Solymosi and Kiss (*17, 18*) found that boron impurity in Rh exerts a dramatic influence on the adsorption properties of Rh and induces the dissociation of CO_2 at 270–300 K.

Recent work in our laboratory demonstrated that the presence of potassium on the Rh(111) surface also basically alters the adsorption and bonding characteristics of CO_2 (*21*).

We report in the present paper that CO_2 similarly adsorbs weakly and nondissociatively on the Pd(100) face, but the potassium adatoms exert a dramatic effect on these processes.

EXPERIMENTAL

The experiments were carried out in a stainless steel UHV chamber provided with a CMA (PHI) for AES and EELS, a quadrupole mass spectrometer (VG) for TDS, and a piezoelectronic-driven Kelvin probe for $\Delta\phi$ measurement. The ultrahigh vacuum was produced by ion getter and titanium sublimation pumps. The base pressure was 2×10^{-10} mbar. The experimental data for further workup were collected with a multichannel analyzer (Tracor-Northern 1710) and a computer.

The Pd(100) single crystal was mechanically polished with diamond paste (Diaplast, Winter) to 1 μm. The diameter of the (1 mm thick) disc sample was 11 mm. *In situ* cleaning was performed by argon ion bombardment at 1 kV and 5 $\mu A/cm^2$; then the sample was heated to 950 K in a 2×10^{-8} mbar oxygen atmosphere. This procedure was repeated until no sign of any contamination was indicated by AES.

The sample was heated directly by Ta filaments and cooled to 100 K by a Ta plate spotwelded onto the side of the sample. The Ta plate was in contact with a liquid nitrogen-cooled stainless steel tube. After flashing of the sample to 1200 K, a temperature of 100 K was reached within 6 min. The temperature was measured by a chromel–alumel thermocouple spotwelded onto the side of the sample.

CO_2 (Material Research Corp.) was introduced into the UHV system through a multicapillary doser 10 mm in diameter. During the CO_2 exposure, the distance between the sample and the doser was 10 mm.

Potassium was deposited onto the Pd(100) surface by heating a commercial SAES Getter source situated 3 cm from the sample. After several days of degassing at a 4-A flowing current, a clean evaporated K layer was obtained on the Pd single crystal, as checked by AES. At the beginning, 5.2 A was used to attain nearly half a monolayer of K on a 1-min exposure, but after extended use of the K source, the heating current had to be increased to reach the same coverage.

RESULTS

1. *Adsorption of K onto Pd(100)*

Detailed measurements have been performed on the characteristics of adsorption and desorption of potassium on the Pd(100) surface, as we found no data on this system in the literature. The results will be published elsewhere (*22*). The main characteristics of the interaction are as follows.

A monolayer of potassium on Pd(100) was found to correspond to a surface density of 6.2×10^{14} atoms/cm^2, or $\theta_K = 0.47$ potassium atom per surface palladium atom. Determination of the surface coverage of K was based on the relative Auger intensity of K, taking into account the contribution of surface Pd atoms to the Auger signal, as established by De Cooman *et al.* (*23*). The peak temperature for the desorption of K from Pd(100), T_p, is 950 K at $\theta_K = 0.05$, 460 K at monolayer coverage,[2] and 345 K for the multilayer. During heating of the K-covered surface, about 10–15% of the K monolayer diffused into the subsurface or into the bulk. A similar phenome-

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[2] $\theta_K = 0.47 \pm 5\%$.

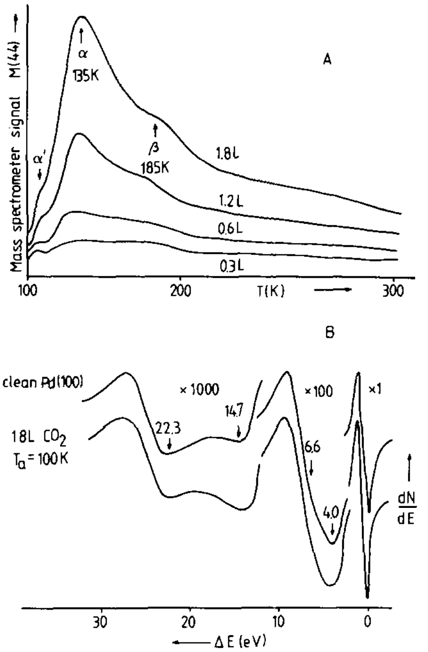

FIG. 1. (A) Thermal desorption of CO_2 following CO_2 adsorption on Pd(100) surface at 100 K. (B) Electron energy loss spectra of clean and CO_2-dosed Pd(100) surface at 100 K.

non was observed on Ni(100) by White and co-workers (*24*).

The deposition of K on Pd produced new losses in the electron energy loss spectrum (EELS) in the electronic range at 19.4, 18.3, and 3.5 eV. This is in good harmony with the results obtained for the K–Ni(100) system, where loss features were established at 19.9, 19.2 and 3.5 eV (*25*). The work function of Pd(100) decreases by 3.65 eV at the maximum ($\theta_K \approx 0.3$).

2. *Adsorption of CO_2 on Clean Pd(100) Surface*

Exposure of a clean Pd(100) surface to CO_2 up to 180 L at a pressure of 3×10^{-7} Torr CO_2 at around 300 K produced no observable changes in the Auger spectrum and EELS of Pd, and no desorbing products were detected in subsequent thermal desorption measurements.

The situation was different at an adsorption temperature of 100 K (T_a). At a lower CO_2 exposure, CO_2 desorbed in a broad peak. With the increase of the exposure, the main peak (denoted by α) appeared at $T_p = 135$ K (Fig. 1A). However, shoulders or breaks could be seen on both sides of the peak, at 110 K (α') and 185 K (β). Exact determination of the saturation was difficult, due to the contribution to the desorption from the specimen holder at higher exposures. Assuming a preexponential factor of 10^{13} s^{-1}, we obtain an activation energy of 34 kJ/mol for the desorption of CO_2 in the α state.

The adsorption of CO_2 was also followed by EELS. On the Rh(111) surface, the adsorption of CO_2 at 110 K produced a new loss at 14.0 eV (*17, 18*). The EELS of the clean Pd(100) surface is shown in Fig. 1B. Loss features were observed at 4.0, 6.6, 14.7, and 22.3 eV, in relatively good agreement with the results of Bader *et al.* (*26*) for Pd(100).

On CO_2 adsorption, the elastic peak increased by a factor of 1.3, but the positions and intensities of the Pd losses were practically unaltered. As Pd has a loss at 14.7 eV, it was not possible to resolve the loss due to adsorbed CO_2 at this energy. However, an increase in the intensity of the 14–14.7 eV loss can be established following CO_2 adsorption at 100 K (Fig. 1B). When the CO_2-covered surface was heated to a higher temperature, the original spectrum of Pd was attained even at ~180 K, without any new loss feature appearing, in accord with the expectation based on TD measurements.

3. *Adsorption of CO_2 on a K-Dosed Pd(100) Surface*

3.1 Thermal desorption measurements. The effect of the potassium coverage on the desorption of CO_2 following low-temperature adsorption is shown in Fig. 2. The presence of potassium greatly increased the energy of binding of CO_2 to the Pd surface and induced new adsorption states.

A striking effect was observed in the α state. The area of the CO_2 desorption peak in this weakly bonded state markedly in-

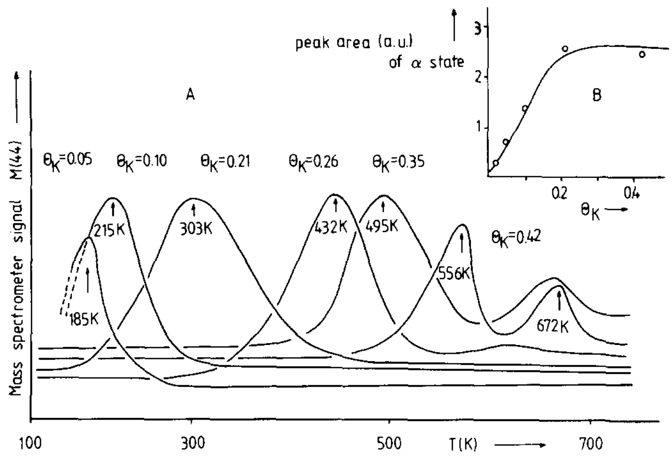

FIG. 2. (A) Effects of potassium coverage on the desorption of chemisorbed CO$_2$ from Pd(100). T_a = 100 K, CO$_2$ exposure = 0.1 L. (B) The amount of CO$_2$ desorbed in α peaks (not shown in (A)) as a function of K coverage.

creased with the rise of preadsorbed K. At θ_K = 0.42, it was larger by a factor of 50 as compared to the clean surface at the same exposure (Fig. 2B). With the increase in the CO$_2$ exposure, the peak temperature (α) shifted to a lower temperature at all K coverages, in general from 145 to 130 K. The peak became broad and slightly asymmetric on the high-temperature side. Saturation was attained at 0.1–3 L CO$_2$ exposure, depending on the K concentration.

At the lowest K coverage, θ_K = 0.05, a well-resolved peak appeared at 185 K (Fig. 2A), which was also observed as a break or shoulder in the absence of K (Fig. 1). At θ_K = 0.21, a new desorption state appeared at T_p = 303 K. The assumption that this is a new state is supported by the results of measurements to establish the effect of the CO$_2$ exposure (see below). The peak temperature of this state gradually shifted to a higher temperature with the increase of the K concentration. At nearly monolayer coverage of K, θ_K = 0.42, CO$_2$ desorbed in two high-temperature peaks, at T_p = 556 K and T_p = 672 K.

The development of these desorption states and their peak temperatures depended sensitively on the CO$_2$ exposure. This is demonstrated in Fig. 3. At θ_K = 0.05, CO$_2$ desorbed in one state (β_1), at T_p = 198 K. With the increase in the CO$_2$ exposure, this peak shifted to 184 K, when approximate saturation of the state was attained. The α state became apparent at 0.05 L CO$_2$ (Fig. 3A). The same situation was observed for θ_K = 0.1, but in this case the peak temperature for β was higher (Fig. 3B). However, the picture was basically different at θ_K = 0.21. In this case CO$_2$ desorbed at a low coverage at 359 K (β_2); this peak temperature was lowered to 272 K with the increase in the CO$_2$ exposure. The β_1 peak was detected at 0.1 L CO$_2$ exposure; its peak temperature varied in the range 243–204 K (Fig. 3C). At near monolayer coverage of K (θ_K = 0.42) and at low CO$_2$ exposures, two new high temperature desorption states appeared at 574 K (β_3) and 660 K (γ). Whereas the peak temperature of the γ state slightly increased with increasing CO$_2$ coverage, that of the β_3 state significantly decreased to 434 K. At the same time, the β_2 state with T_p = 354–325 K and the β_1 state with T_p = 255–243 K became dominant (Fig. 3D).

A new TD feature is that, in addition to CO$_2$, CO was desorbed from the K-dosed surfaces (Fig. 4). This appeared first at θ_K = 0.21, with a peak temperature of 573 K. At θ_K = 0.36, another CO desorption state (γ) emerged, at T_p = 663 K. The amount of CO

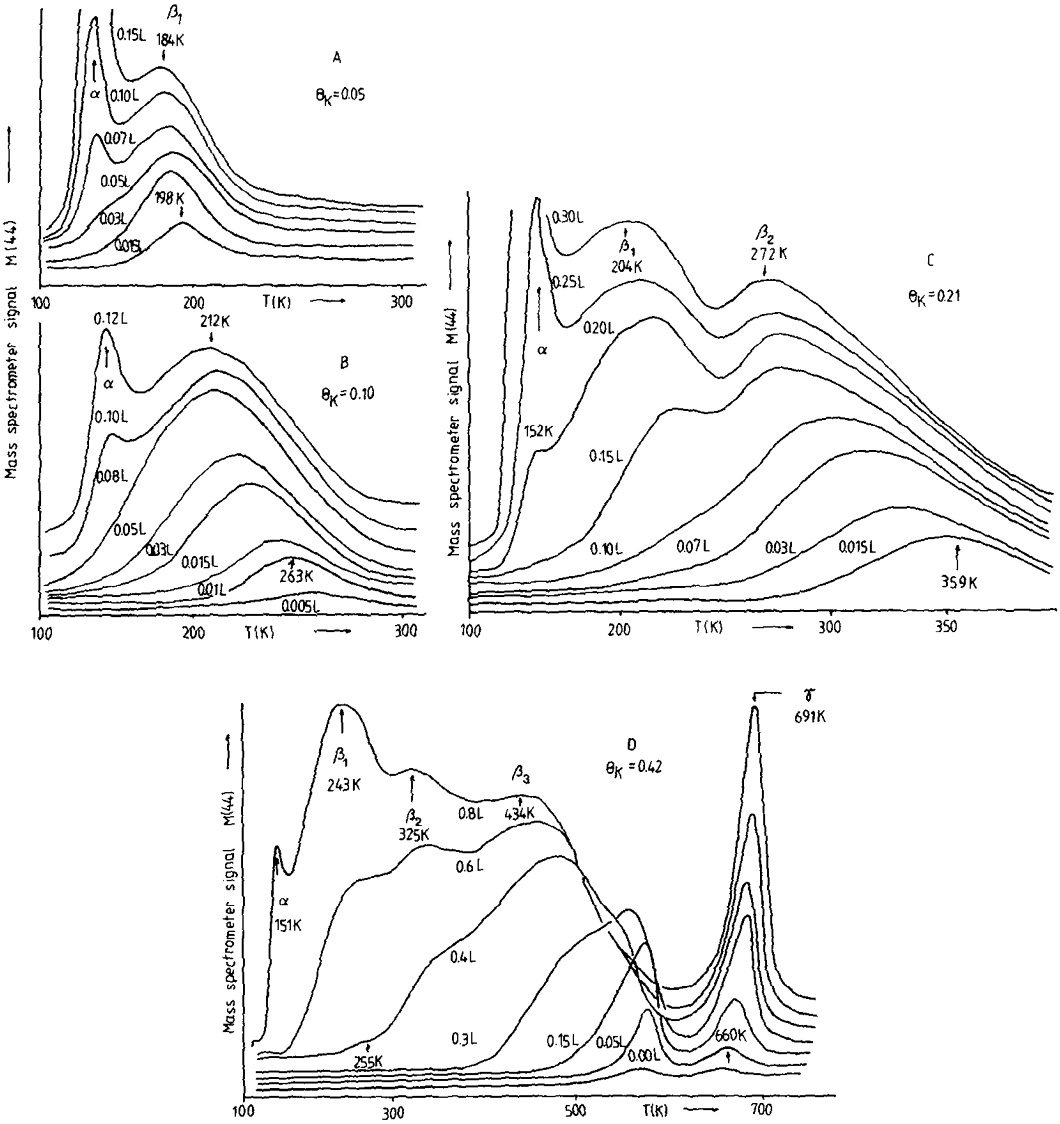

FIG. 3. Effects of CO_2 exposure on the desorption of CO_2 from Pd(100) at different K coverages. (A) θ_K = 0.05, (B) θ_K = 0.10, (C) θ_K = 0.21, (D) θ_K = 0.42; T_a = 100 K.

formed increased considerably with the surface concentration of K, to the accompaniment of a shift to higher peak temperatures.

Calculation of the amounts of CO_2 and CO desorbed was based on the determination of the amount of CO at saturation on the clean Pd surface (T_a = 350 K), taking into account the relative sensitivity of the mass spectrometer to CO and CO_2. The surface concentration of adsorbed CO on Pd(100) at saturation is 0.66 × 10^{15} CO molecules per cm^2 (27). In Fig. 5 some characteristic data for the desorption of CO_2 and CO are plotted against the K coverage and CO_2 exposure. It appears that the total amount of chemisorbed CO_2 increases with the K coverage (Fig. 5A). The same holds for the CO produced in the surface dissociation (Fig. 4). Data presented in Fig. 5B

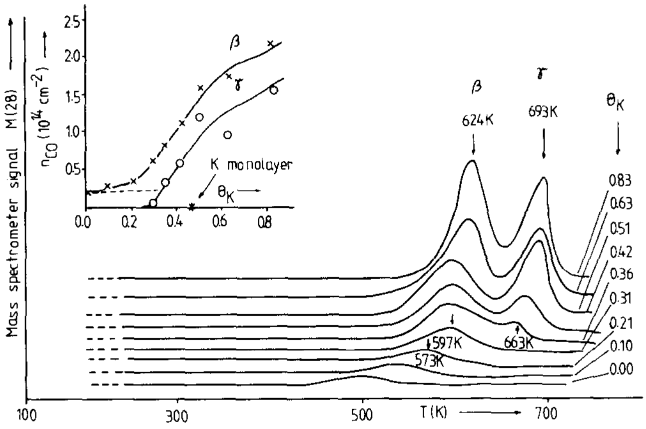

FIG. 4. Thermal desorption of CO produced in the dissociation of CO_2 at different K coverages. T_a = 100 K, CO_2 exposure = 1.2 L.

show that the amount of CO formed attains a constant value before the saturation coverage for adsorbed CO_2 is produced. The maximum amount of CO_2 adsorbed at monolayer K coverage, $\theta_K = 0.47$, is 3.1×10^{14} molecules CO_2/cm^2. (As CO is formed in the dissociation of CO_2, the amount of CO formed was added to the CO_2 value.) From this amount 1.9×10^{14} CO molecules/cm^2 is formed in the dissociation of CO_2.

From the data for the surface concentration the ratio of CO formed and the total amount of chemisorbed CO_2 was calculated. We obtain that this ratio increases with θ_K (Fig. 5A) and decreases with the increase in CO_2 exposure (Fig. 5C), suggesting that a greater proportion of the CO_2 undergoes dissociation at higher K and at lower CO_2 coverage.

The initial sticking coefficient (S_0) of CO_2 was calculated from TD measurements. It increased with the increase in K coverage

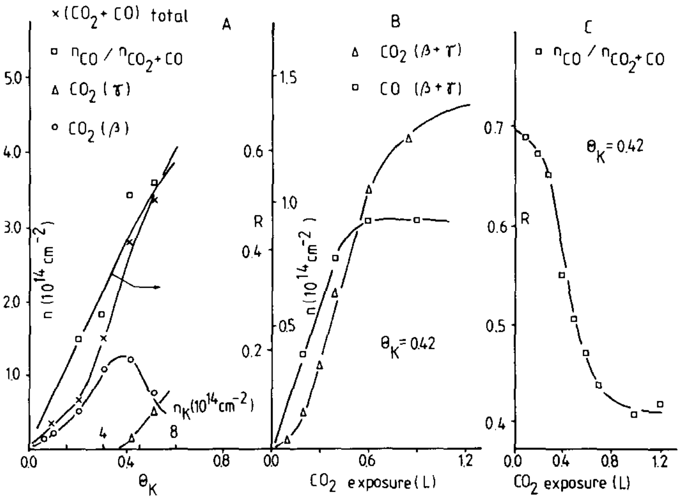

FIG. 5. Formation of CO and CO_2 and the relation of CO formed to the total amount of chemisorbed CO_2 as a function of K coverage and CO_2 exposure. In all experiments T_a was 100 K. CO_2 exposure was 1.2 L (A).

TABLE 1

Activation Energies for the Desorption of CO_2 and CO from Pd(100) at Different *K* Coverages

θ_K	T_p (K)	State	CO_2 (kJ/mol)	T_p (K)	State	CO (kJ/mol)
0.00	135	α	34 ± 0.5	500	β	126 ± 1
	185	β_1	47 ± 1			
0.05	142	α	36 ± 0.5		Not determined	
	184	β_1	46 ± 1			
0.10	143	α	36 ± 0.5	541	β	136 ± 1
	204	β_1	51 ± 1			
0.21	140	α	35 ± 0.5	573	β	144 ± 1
	204	β_1	51 ± 1			
	272	β_2	68 ± 1			
0.42	129	α	32 ± 0.5	595	β	150 ± 1
	243	β_1	61 ± 1	665	γ	167 ± 0.5
	325	β_2	82 ± 1			
	434	β_3	109 ± 1			
	691	γ	174 ± 0.5			

Note. Activation energies were calculated from the values of T_p at saturation with preexponential factor 10^{13} s^{-1}. The accuracy of the determination of the T_p values was ± 2 K for α, ± 5 K for β, and ± 2 K for γ states.

in the range $\theta_K = 0$–0.15 from 0.01 (clean surface) to near 1. At the higher coverage, $\theta_K = 0.42$, there is a drop in S_0 to 0.5.

Activation energies for desorption were calculated from the observed values of T_p with a preexponential factor of 10^{13} s^{-1}. The kinetic data are listed in Table 1.

3.2. EELS measurements at 110 K. Figure 6 shows EELS of K-dosed surfaces before and after CO_2 adsorption at two K coverages. The adsorption of CO_2 on K-dosed Pd ($\theta_K = 0.21$) intensified the 3.7 eV loss produced by K preadsorption, and changed the two well-separated losses of K at 18.7 and 20.1 eV into one loss at 19.3 eV. A new loss appeared at 15.3–15.6 eV. A significant increase in its intensity occurred at a higher CO_2 exposure, when another loss appeared at 11.9 eV (Fig. 6A). The same loss features and characteristics were observed at $\theta_K =$ 0.42 (Fig. 6B). In this case it was possible to detect another loss at 8.1 eV which was very sensitive to the electron beam.

Heating of the co-adsorbed layer ($\theta_K = 0.21$) to higher temperatures caused significant decreases in the intensities of the new losses. The 11.9-eV loss vanished at 120–130 K, while the 15.3-eV loss was eliminated by 425 K.

At higher K concentration ($\theta_K = 0.42$) the losses exhibited higher thermal stability. The 8.1-eV loss was detectable up to 158 K. The 15.3-eV loss exhibited more complex behavior; after a significant initial decay in its intensity, it gave a maximum at around 300 K, and was eliminated only above 650 K. A new feature of the EELS was the appearance of a weak loss at 12.5 eV, although we cannot exclude the possibility that the 11.9-eV loss was shifted to this energy. This loss was seen up to 450 K. These spectral changes are illustrated in Fig. 7.

3.3. Work function measurements. The interaction of CO_2 with a K-covered Pd surface was also investigated through work function measurements at two K concentrations. The exposure of a clean Pd(100) surface to potassium significantly decreased the work function of Pd, by 3.38 eV at $\theta_K = 0.42$ (Fig. 8). When CO_2 was adsorbed on a K-dosed surface, it led to a work function increase (Fig. 8). The maximum increases were about 0.79 eV at $\theta_K =$ 0.1, and 2.20 eV at $\theta_K = 0.42$. The final values attained were practically the same in the two cases.[3] When the CO_2-saturated surface was heated, an initial work function increase was experienced at 140–150 K in both cases, followed by a decrease to the value exhibited before CO_2 exposure. This state was attained at 700–750 K. Above this temperature, the work function increased as a result of the desorption of K to the value for the clean Pd surface.

3.4. Experiments at 300 K. When the adsorption of CO_2 was conducted at 300 K, the general features of the interaction remained the same. The desorption of CO_2 occurred immediately above 300 K and the

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[3] These changes indicate a substantial charge transfer from the K-dosed Pd to an empty CO_2 π orbital.

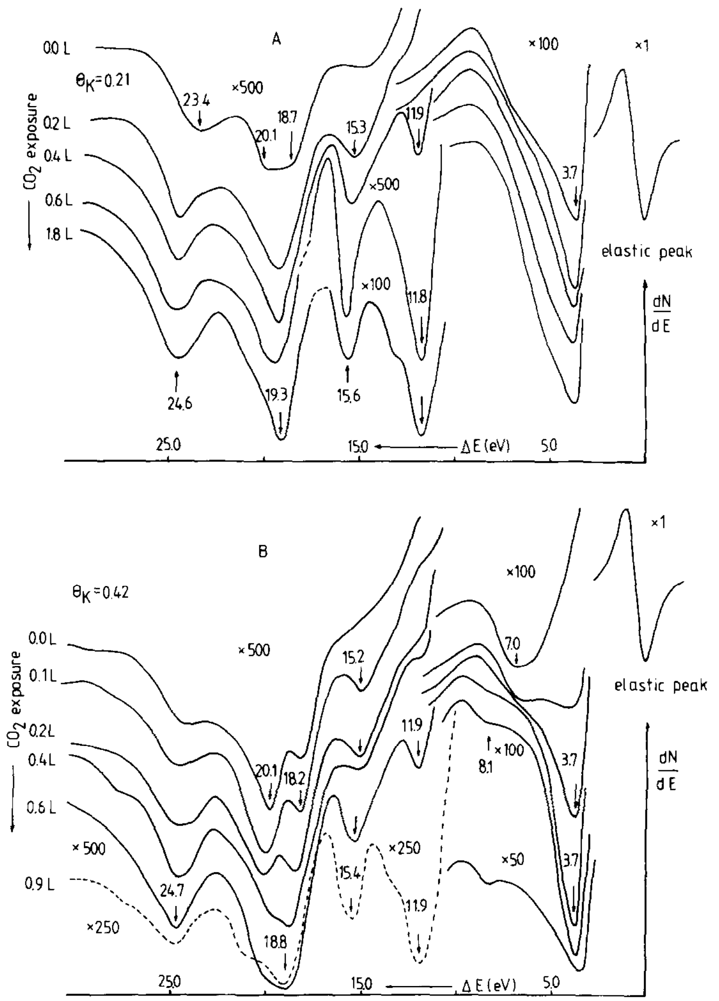

FIG. 6. Electron energy loss spectra of K-covered Pd(100) as a function of CO_2 exposure at 100 K; (A) θ_K = 0.21, (B) θ_K = 0.42. All spectra are the results of separate K and CO_2 exposures.

two high-temperature adsorption states developed from $\theta_K = 0.31$ (Fig. 9A). The formation of CO was observed first at $\theta_K = 0.20$, $T_p = 561$ K. With the further increase in the K coverage, this peak temperature shifted slightly to a higher temperature, at $\theta_K = 0.42$ to 614 K, and a new state (γ) started to develop from $\theta_K = 0.36$. At $\theta_K = 0.42$ its T_p was 661 K. The amount of CO relative to the total amount of adsorbed CO_2 was higher than in the case of $T_a = 100$ K for the same samples, and increased with the increase of K coverage. The work function changes were measured for Pd + K at $\theta_K = 0.42$. CO_2 adsorption led to an increase in the work function, with 1.37 eV at the maximum, which was less than that measured at $T_a = 100$ K. In the course of heating the adsorbed layer from 300 to 600 K, the work function gradually decreased to 0.16 eV below the value before CO_2 adsorption, and then increased to attain the value for the clean Pd(100) surface at 950 K.

In the EELS taken at 300 K, the new loss produced by CO_2 adsorption appeared at 15.0 eV (Fig. 9B). The 11.8-eV loss was totally missing and the 12.5 eV loss developed first at $\theta_K = 0.42$.

3.5. Desorption of potassium from the

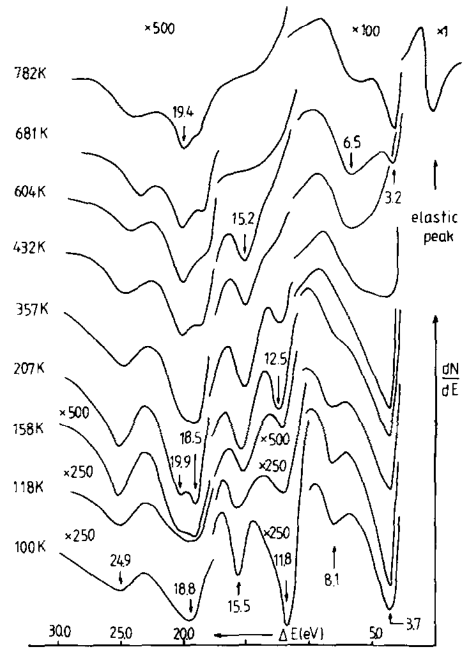

FIG. 7. Electron energy loss spectra taken after heating the K-covered (θ_K = 0.42) Pd(100) surface exposed to 1.2 L CO_2 to different temperatures. T_a = 100 K. All the spectra are the results of separate K and CO_2 exposures.

coadsorbed layer. Some experiments have been performed to establish the effect of adsorbed CO_2 on the desorption of potassium from the Pd surface. As the results presented in Fig. 10 show, potassium is greatly stabilized in the adsorbed layer. This is exhibited above θ_K = 0.3, when the γ state of CO_2 developed: the desorption observed in the lower temperature range ceased and potassium desorbed in a narrow peak with T_p = 695 K. This corresponds to a binding energy of 175 kJ/mol.

DISCUSSION

1. The Bonding and Dissociation of CO_2 on Clean Metals

Very little information is available concerning the bonding of CO_2 on clean metal surfaces. Two alternatives were considered, based on the coordination complexes of CO_2 (*28*): a monodentate structure with a C atom directed to the surface and with an OCO angle of 120°, and a bidentate structure bonding to the surface through carbon and oxygen. If CO_2 were bent on adsorption, this would result from the donation of an electron from the metal to an empty CO_2 π^* orbital (*29, 30*).

Photoemission studies of CO_2 adsorbed on Pt (*31*) and Cu (*32*) surfaces, however, indicated no energy level shifts, from which the formation of physisorbed CO_2 on these surfaces was inferred. Ray and Anderson (*30*) proposed a bonding via a lone pair of an O, with the molecular bond vertical. A

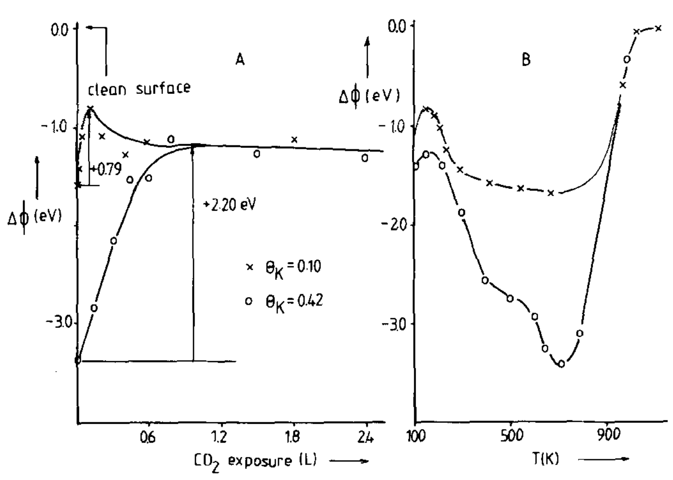

FIG. 8. Changes in the work function of K-covered Pd(100) as a function of CO_2 exposure at 100 K (A) and after heating the coadsorbed layer to different temperatures (B).

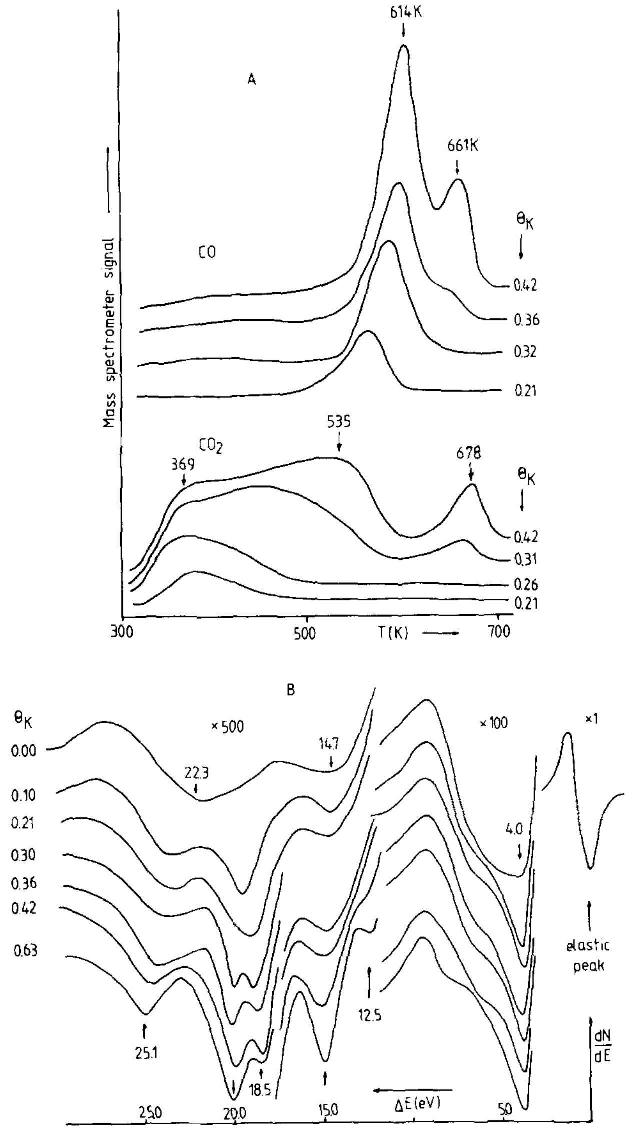

FIG. 9. Thermal desorption of CO_2 and CO (A) and electron energy loss spectra (B) of K-covered Pd(100) exposed to 1.2 L CO_2 at 300 K.

stronger interaction occurred on Fe(100) and (111) surfaces, and also on Fe film, involving the dissociation of CO_2 above 273 K (*33*). The majority of the new experimental data suggest that the adsorption of CO_2 is weak and nondissociative on Rh foil and Rh(111) surfaces (*15–18*). The binding energy for CO_2 on Rh, determined by two groups on Rh(111) (*18*, *21*) and Rh tip (*16*), showed excellent agreement (60 kJ/mol).

The behavior of clean Pd(100) resembles that of Rh; the adsorption of CO_2 is also weak and nondissociative. For the binding energy we obtained 34 kJ/mol.[4] The low binding energy of CO_2 on the clean Pd surface suggests that CO_2 bonds at the surface via a lone pair of O, with the molecular bond vertical, as proposed for Pt and Cu surfaces (*30*). The adsorption of CO_2 on

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[4] For the α state and 46.6 kJ/mol for the weak β state.

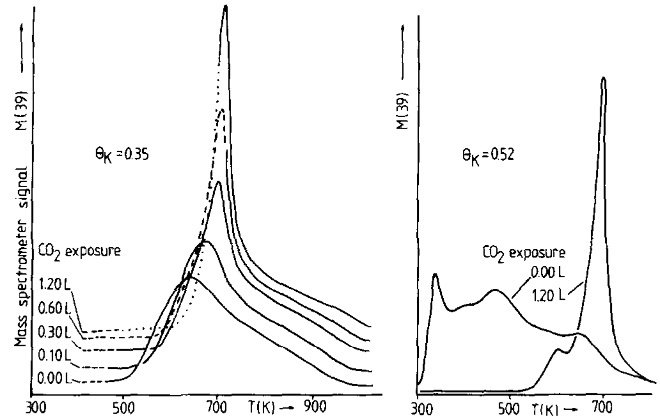


FIG. 10. Effects of adsorbed CO_2 on the desorption of potassium from Pd(100) surface. T_a = 100 K.

Pd(100) at 100 K produced the same loss feature at 14–14.5 eV in the EELS as observed for Rh(111). This loss was assigned to a $4\sigma_g$–$2\pi_u^*$ electron transition. When the CO_2-covered surface was heated, the intensity of this loss gradually decreased and it was eliminated by 180 K, in harmony with the TD results.

2. *Effects of Potassium*

2.1. General features on K-dosed Pd. Preadsorbed potassium dramatically influenced the chemisorption of CO_2 on the Pd(100) surface, as evidenced by changes in the work function, TD, and EELS. The most important features were as follows:

(i) While the adsorption of CO_2 on Pd(100) at 100–300 K is weak and nondissociative, the presence of K adatoms greatly increases the amount of weakly adsorbed CO_2 (α), the rate of CO_2 adsorption, and the binding energy of CO_2 chemisorbed to Pd.

(ii) From $\theta_K = 0.30$, K adatoms induce the formation of a new, very stable adsorption state (γ) with T_p = 660–691 K.

(iii) Preadsorbed potassium initiates the dissociation of CO_2 on Pd as well.

(iv) It also increases the binding energy of the CO formed.

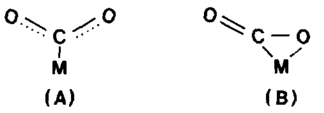
(v) The presence of CO_2 alters the desorption behavior of potassium by greatly increasing the potassium binding energy.

In many respects, similar features have been established concerning the effects of preadsorbed potassium on the adsorption and desorption of CO on transition metals (see, for example, Refs. (*34–40*) and references therein). As potassium lowers the work function of the metal surfaces, this leads to a larger electron donation from the metal into the back-bonding orbital of the adsorbed species, the effect of potassium has been attributed to the enhanced occupation of the $2\pi^*$ orbital of CO.

2.2. Physisorbed CO_2. The fact that the α state can readily be saturated on K-dosed surfaces is a strong indication that we are dealing with a physisorbed state and not with the condensation of CO_2. The surface concentration of adsorbed CO_2 in this state was about 2–3 times higher than that of chemisorbed CO_2 ($\beta + \gamma$) on the same surface. The desorption energy for this state was nearly the same as on clean Pd.

The enhanced adsorption of CO_2 in the weakly bonded α state may suggest that there is a weak interaction between CO_2 and potassium, and that CO_2 is probably adsorbed on top of the chemisorbed layer. The extended adsorption in the α state is reflected in the intensification of the 15.3-eV loss and in the appearance of new features in the EELS at 8.1 and 11.8 eV, which were not detected on either clean Pd(100) or Rh(111) surfaces (*18*). The possible reason for their appearance in the present case, compared to the clean surfaces, is that the amount of CO_2 in the α state is markedly higher (by a factor of 50 at $\theta_K = 0.42$) on the K-dosed Pd surface. Taking into account the UPS spectra of gaseous CO_2 and of adsorbed CO_2 on Pt (*32*), these losses can be assigned to $1\pi_g$–$2\pi_u^*$ and $1\pi_u$/$3\sigma_u$–$2\pi_u^*$ intramolecular electron transitions, respectively.

2.3. Stabilization and activation of chemisorbed CO_2. The presence of K adatoms leads to a great stabilization of CO_2 on a Pd surface. The work function changes for CO_2 on K-covered Pd indicate a large negative charge on the chemisorbed CO_2, which can be interpreted in terms of the enhanced back-donation of electrons into an empty π^* orbital of CO_2. This process is reflected in a slight shift in the position of the characteristic loss for CO_2 from 14 to 14.5 eV (clean surface) to 15.3–15.6 eV on the K-dosed surface, and also in the stabilization of this loss. It is very likely that this extended electronic interaction involves changes in the bonding and the structure of the adsorbed CO_2, i.e., the formation of a metal–carbon bond in the forms of a monodentate or bidentate structure:



As a result, the binding energy of CO_2 is greatly increased.

As shown by the TD spectra (Fig. 2), CO_2 desorbs in one peak at lower CO_2 exposures, but the peak temperature depends sensitively on the K coverage, and increases from 184 K to 556 K. In terms of binding energy, this corresponds to an increase from 46 to 140 kJ/mol. The single peak in the TD spectra (apart from the weakly bonded physisorbed state) suggests that at lower CO_2 coverage, up to about $\theta_K = 0.36$, all of the chemisorbed CO_2 is affected in a fairly uniform way by potassium.

As the CO_2 coverage is increased, the peak temperatures for CO_2 desorption decrease at all K coverages, and new adsorption states, desorbing at lower temperatures, are formed. In this case CO_2 desorbs continuously from 200 to 600 K, indicating the development of a large inhomogeneity in the degree of interaction, e.g., in the binding energy of CO_2.

From this behavior we may conclude that *local and nonlocal interactions* exist among the effects of K adatoms. A greater perturbation due to potassium is exhibited for the CO_2 bonded in its proximity, but the potassium can also affect (to a lesser extent) the CO_2 adsorbed at some distance from it. The occurrence of this long-range interaction in the adsorption states at 200–300 K is supported by the fact that no adsorption state of CO_2 exists on the clean Pd surface above 200 K, and it can therefore be excluded that these CO_2 molecules adsorb on the unperturbed clean Pd surface.

TD measurements indicated that *a release of CO* also occurred from the K-dosed surfaces, producing two peaks, at 624 K (β) and 693 K (γ) (Fig. 4). The lowest K coverage where the production of CO was clearly detected was $\theta_K = 0.21$.

The formation of CO could be also *a result of the electronic interaction between CO_2 and the Pd + K surface*, as previously discussed in detail; the strengthening of the Pd–CO_2 bond leads to the weakening and the rupturing of the C–O bond of the adsorbed CO_2. This obviously occurs more easily in the bent structure (B), which leads to a higher probability of the formation of a Pd–O bond with the adjacent Pd atoms. However, dissociation of the CO_2 does not occur at lower K coverage, below $\theta_K = 0.21$, or if it does, it is undetectably small. Taking into account the drastic effect of the K coverage on the binding energy of CO_2 and the interpretation of this, we may conclude that the dissociation of CO_2 on Pd + K requires a strong, more extended interaction in the adsorbed layer and probably the existence of adsorbed CO_2 at higher temperatures.

2.4. Direct interaction between preadsorbed K and CO_2. An alternative way of stabilization and activation of CO_2 is a direct interaction between K and CO_2 producing $K^+CO_2^-$ surface species. The formation of radical anion CO_2^- has been reported to occur in the interaction of Na, K, Li, and CO_2 at 77 K and a number of its properties has been determined (*43–49*). ESR and infrared spectroscopic studies in different matrices disclosed a surprisingly high stability of CO_2^- radical anion, which, depending on the matrix, can exist even up to 473 K (*47–49*). On the other hand, it was observed that under anhydrous conditions CO_2^- disproportionates

$$2CO_2^- = CO_3^{2-} + CO \qquad (1)$$

into carbonate anion and CO, or combines

$$2CO_2^- = C_2O_4^{2-} \qquad (2)$$

to give oxalate anion, which decomposes to carbonate and CO at higher temperatures. In the case of the Li–CO_2 system (which was studied in greater detail), the formation of $Li_2C_2O_4$ occurred above 100 K (*48*), while the transformation of oxalate into carbonate

$$C_2O_4^{2-} = CO_3^{2-} + CO \qquad (3)$$

proceeded in the temperature range 300–600 K without completion (*51, 52*).

As the formation of CO in the present case was detected above $\theta_K = 0.21$ we may conclude that the reactions following the direct interaction between preadsorbed K and CO_2 occurred to a detectable extent above this potassium coverage value. Note that the high temperature adsorption state (γ) for CO_2 was also produced above $\theta_K \approx 0.3$. On the basis of this consideration we propose that the occurrence of this γ state is strongly connected with the formation and decomposition of stable surface compounds, very probably carbonate-like species. We point out here that the adsorbed CO_2 has increased the binding energy of the potassium to the surface; potassium desorbed in a narrow peak at nearly the same temperature as the γ CO_2 and CO (Fig. 10). Although great care is needed to make a conclusion from the coincidence of the desorption peaks we believe that the same peak temperature and the mutual stabilization of adsorbed K and CO_2 is the result of a very strong surface interaction, probably of the formation of a surface compound.

Pure potassium carbonate is a very stable compound; its decomposition is endothermic and starts above 950 K (*50, 51*). However, we can expect that "K_2CO_3" surface species formed in the interaction of K and CO_2 on the Pd(100) face is not completely ordered and contains several defects, which lower its thermal stability. In addition, we can also assume that the transition metals catalyze the decomposition of surface carbonate. This is in harmony with the results of Bonzel *et al.* (*52*). XPS data showed that the decomposition of the K_2CO_3 deposited on the Fe foil occurs at 500–600 K and it is complete below 690 K (*52*).

2.5. Desorption of CO. Data in Fig. 4 illustrate that CO desorbs at a considerably higher temperature from the K-dosed surfaces than from the clean surface. While the binding energy of CO on the clean Pd surface varies between 118 and 126 kJ/mol, depending on the coverage (*41*), in the present case it amounts to 156 kJ/mol. This feature is in harmony with the stabilization of CO on alkali metal-dosed metal surfaces and was confirmed in a separate study for the Pd(100) + K surface also (*22*). Accordingly, the CO (β) formed either in the Pd + K induced dissociation of CO_2 or in the decomposition of surface oxalate remaining adsorbed on the surface.

An interesting feature of the desorption of CO from the Pd + K surface is that, on increase of the amount of CO released at different K coverages, the peak temperature for β CO is clearly shifted to a higher temperature (Fig. 4). This is apparently in contrast with the general behavior of CO desorption from metals, including Pd, where, due to the enhanced dipole–dipole coupling, T_p decreases from 500 K at low coverage to 470 K at saturation (*41, 42*). The reason for the different behavior in the present case is probably that the higher amount of CO formed is connected with *a stronger influence of potassium*. In other words, the greater effect of K at higher coverages may overcompensate the effect of dipole–dipole coupling between adsorbed CO molecules, leading to a relatively small increase in the peak temperature.

An important question arises at this stage, viz., the temperature of dissociation of CO_2. This question was not answered unambiguously even in the case of CO dissociation on K-covered metal surfaces. We may obtain information concerning this point from an analysis of the EELS (Figs. 6 and 7). For the sample with $\theta_K = 0.21$, there was no indication of the formation of any new loss features during heating of the sample to higher temperatures, but a well-detectable new loss was transitionally produced at 12.5 eV even below 300 K, at $\theta_K = 0.42$. As CO adsorbed on transition metals gives an intense loss feature near this energy, at 13–13.5 eV (18, 26, 53, 54), it is not totally impossible that this 12.5-eV loss is at least partly due to adsorbed CO. The fact that the CO on this Pd surface likewise gives a loss feature at 12.5 eV (*22*), and that the position of this loss is not altered in the presence of preadsorbed K (*22*), lends support to this conclusion. As the temperature of its formation agrees with that observed in the case of CO adsorption on Pd(100)–K surface (*22*), we conclude that its formation is a desorption rate-limited process.

A separate discussion is required for the existence of the γ state of adsorbed CO. It is important to point out that in the case of the desorption of CO from the K-covered Pd surface, this high-temperature state was missing even at higher potassium coverage (*22*). Accordingly, the surface layer formed during the interaction of CO_2 with the Pd–K surface (very probably during its heating) differs from that which exists following CO adsorption only. The amount of CO desorbed in this peak is only about one-third of the total amount of CO desorbed at $\theta_K = 0.3$–0.4.

As the decomposition of potassium carbonate produces no CO, we can assume that this CO is a result of the associative desorption of CO. Accordingly the CO formed in the dissociation of CO_2 can further dissociate due to the promoting effect of potassium. However, we had no evidence for the occurrence of this process on a Pd + K surface. At the moment, the most likely explanation is that this small amount of CO is formed either in the Pd + K induced dissociation of CO_2 released in the high-temperature decomposition of surface carbonate species, or in the decomposition of remaining surface oxalate species (step 3). The formation of CO in the γ state is very likely a reaction rate-limited process.

CONCLUSIONS

Preadsorbed potassium drastically increases the binding energy of CO_2 on the Pd surface, and it induces the dissociation of chemisorbed CO_2. Work function measurements indicate a large negative charge on the chemisorbed CO_2. Adsorbed CO_2 also leads to a great stabilization of potassium on a Pd surface and at $\theta_K > 0.3$ the desorption of potassium occurs simultaneously with that of CO_2. This feature indicates a strong interaction between K and CO_2, very probably a formation of carbonate-like species.

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