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PHOTOELECTRON SPECTROSCOPIC STUDIES OF THE ADSORPTION OF CO_2 ON POTASSIUM-PROMOTED Rh(111) SURFACE

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Adsorption of CO_2 has been studied on clean and potassium-dosed Rh(111) surfaces by means of UPS and XPS. CO_2 adsorbs molecularly at 90 K on clean Rh without a strong influence on the electronic structure of the adsorbed layer. Adsorption of CO_2 on potassium-dosed Rh(111) ($\theta_K = 0.33$) at 100 K and annealing the adsorbed layer at 131 K produced three peaks at 5.2, 8.7 and 10.9 eV in the HeII spectrum and 532.8 for O(1s) and 290.5 eV for C(1s) in XPS. These emissions were attributed to the formation of CO_2^- radical anions. At higher temperatures the CO_2^- radical is transformed into carbonate and CO. Carbonate species is characterized by the 3.5, 8.4 and 10.2 eV peaks in UPS, and by C(1s) at 289.0 eV and O(1s) at 531.8 eV levels in XPS. At lower potassium coverage ($\theta_K = 0.1$), carbonate formation was not observed, but the CO_2^- anion radical dissociated to CO and O at 131–179 K. This process was accompanied by the appearance of photoemission peaks at 8.2, 11.2 and 6.0 eV.

1. Introduction

The activation of the rather unreactive CO_2 is a difficult problem in its homogeneous and heterogeneous catalytic reactions [1,2]. In searches for an effective catalyst for the transformation of CO_2 into more valuable compounds, rhodium was found to be an excellent metal for the hydrogenation of CO_2 to hydrocarbons [3–8]. In further studies, we observed that potassium adatoms dramatically influenced the bonding and reactivity of CO_2 adsorbed on Rh(111) [9] and also on Pd(100) surfaces [10,11]. It increased the binding energy, induced the formation of new adsorption states and initiated the dissociation of CO_2 on both surfaces. Whereas the adsorption of CO_2 caused no measurable work function changes on clean Rh and Pd surfaces, it markedly increased the work function of K-dosed Rh and Pd, by about 1.07–2.2 eV. These features were explained by a charge transfer from the K-dosed metals to the CO_2 molecule and by the formation of the negatively

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charged CO_2^- species, the bonding and structure of which differed basically from those of weakly adsorbed CO_2 [9,11]. These studies presented the first experimental evidence for the formation of the CO_2^- anion radical on metal single-crystal surfaces, the existence of which has been assumed in the gas and solid phases [12–17]. In the further reactions of coadsorbed CO_2, the transformation of this CO_2^- anion radical played a key role. At higher temperatures it dissociated to CO(a) and O(a) and it was also converted (through various surface intermediates) to carbonate-like species [9,11].

In the present study, the interaction of CO_2 with K-dosed Rh(111) is investigated by means of UPS and XPS methods, with the aim of obtaining a deeper insight into the nature of this interaction and of substantiating the assumed surface complexes.

2. Experimental

The experiments were performed in an ultra-high vacuum system, with a background pressure in the low-to-middle 10^{-10} Torr range, produced by turbomolecular and titanium getter pumps. The system was equipped with a hemispherical analyzer (Leybold-Hereaus LHS-10) for UPS, XPS and AES, an Ar ion gun for cleaning and a quadrupole residual gas analyzer.

UPS was performed by using He I (21.22 eV) and He II (40.81 eV) radiation. The angles between the surface normal and the UV lamp and between the surface normal and the analyzer were 75 ° and 16 °, respectively. Spectra were taken in 5–10 min. Difference spectra are reported here for experiments with and without CO_2 adsorption at a given θ_K. Work function measurements were obtained from He I spectra, by using the energy difference between the photoelectron secondary onset and the Fermi edge (with the sample biased negatively). The photoelectrons were excited by Al Kα radiation (1486.7 eV) in the XPS regime. The energies of the XPS peaks were calibrated relative to the Fermi level of Rh. The peaks were measured by using a pass energy of 50 eV in order to get the optimum resolution by maintaining an acceptable signal-to-noise ratio at measuring times of 30–60 min.

The experimental data (UPS and XPS) were collected for further work-up with a multichannel analyzer (Tracor-Northem 1710) and a computer.

The cleaning procedure for the Rh(111) and crystal mount, previously described [9], allows resistive heating up to 1200 K and cooling down to < 100 K. The cleanness of the crystal was checked by AES. The upper limits of contaminants were below 1% of a monolayer.

A commercial SAES Getter alkali metal source was used to deposit K onto a Rh(111) surface situated 3 cm from the K source. The K coverage was determined by means of AES and TDS [9].

3. Results

3.1. Adsorption of CO_2 on clean Rh(111)

The adsorption of CO_2 on a clean Rh(111) surface at 90 K suppressed the intensity of the emission of the d-band of Rh, and three new lines appeared in the UPS spectrum, at 6.6, 10.7 and 12.1 eV with respect to the Fermi energy (fig. 1). Similar spectral features have been observed on Pt, Cu, [18], Au [19], Ni [20] and Fe [21,22]. The intensities of the peaks increased slightly with exposure and they reached a saturation value at around 60 L.

The positions of the peaks did not show any variation with the surface concentration of CO_2. When the adsorbed layer was heated to higher temperatures, no change was registered up to 130 K; and 165 K the intensities of the peaks slightly decreased and at 221 K all the CO_2 peaks disappeared. The spectrum of the clean surface was restored at this temperature, without any indication of the dissociation of CO_2 to adsorbed CO and O.

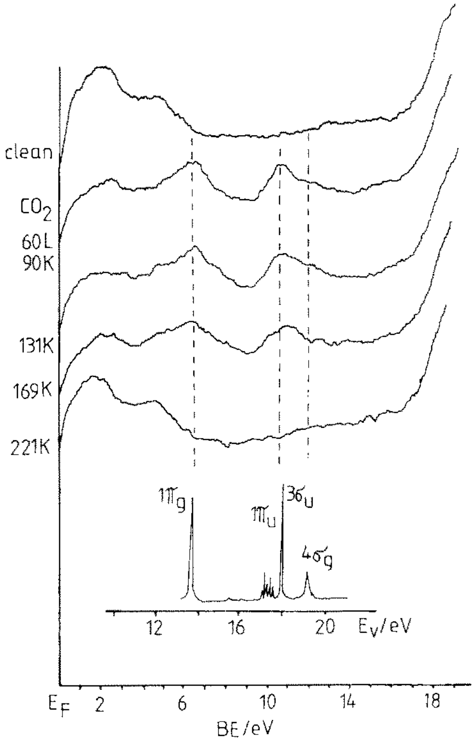


Fig. 1. HeII photoelectron spectra following CO_2 adsorption on clean Rh(111) at 90 K and after gradually heating the saturated layer to different temperatures. Spectrum of gaseous CO_2 is also shown.

Table 1
Binding energies (in eV) of adsorbates observed following CO_2 adsorption on Rh(111) and K/Rh(111)

	θ_K	UPS					XPS			
							O(1s)		C(1s)	
CO_2	0			6.6	10.7	12.1		534.7		292
	0.1			8.0	12.0	13.6		534.0		292
	0.33			8.8	13.0	14.5		534.0		292
CO_2	0									
	0.1							532.8		
	0.33			5.2	8.7	10.9		532.8		290.5
CO	0				(8.0)	(10.9)		(531.2)		(285.6)
	0.1	8.2	11.2		(8.4)	(11.5)	531.4	(531.4)	286.4	(286.1)
	0.33	9.4	11.7	(5.2)	(9.2)	(11.9)	531.4	(531.4)	285.6	(285.6)
CO_3^{2-}	0									
	0.1									
	0.33			3–4	8.4	10.2		531.7		289.0
O	0					(5.5–6)		(530.3)		
	0.1			6.0		(5.5–6)	530.4	(530.3)		
	0.33			5.5–6.0		(5.5–6)	530.4	(530.1)		

Values in brackets were obtained following CO and O_2 adsorption.

In the XPS, the the adsorption of CO_2 at 90 K produced only one peak for O(1s) and for C(1s), at 534.7 and 292.0 eV, respectively (table 1). The same binding energies were found on Pt, Cu [18] and Au [19] surfaces where the adsorption of CO_2 was also weak.

3.2. Adsorption of K on clean Rh(111)

It was shown in a previous paper [9] that the work function of Rh(111) decreased linearly with increasing coverage of K, and reached a minimum ($\Delta\phi = -3.5$ eV) at $\theta_K \approx 0.1$–0.17. Further K deposition led to a slight increase in the work function.

The adsorption of K on Rh(111) decreased and broadened the emission of the d-band of Rh. This effect increased with the K coverage (fig. 2). At $\theta_K \approx 0.1$, the K(3p) level was observed at 18.3 eV in the He II UPS spectrum. With increase of the K coverage, the 3p level was shifted to lower binding energy; at monolayer coverage ($\theta_K \approx 0.36$), the position of the peak was registered at 17.7 eV (fig. 2). Contributions from K(4s) electrons, which are expected near the Fermi level, could not be discerned. The non-detection of this level may be due to the low cross-section for this excitation at the photon energy used in this experiment ($h\nu = 40.81$ eV).

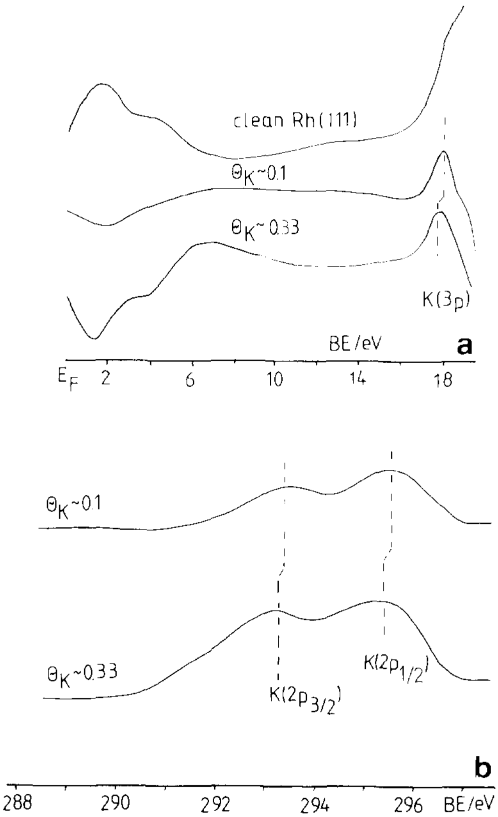


Fig. 2. (a) UPS difference spectra of K-covered Rh(111). (b) X-ray photoemission spectra of the K(2p) levels on K-covered Rh(111) surface at 300 K.

The K(2p) levels were detected by XPS (fig. 2). The clean Rh(111) XPS spectrum was subtracted from each of the K XPS spectra to give a linear background. The K(2p) peak is spin–orbit split into $2p_{3/2}$ and $2p_{1/2}$ components. The corresponding binding energies at monolayer K coverage are 293.3 and 295.4 eV. The values are shifted to lower binding energies compared to the 294.7 eV ($K(2p_{3/2})$) and 297.4 eV ($K(2p_{1/2})$) for K metal [23]. Both the work function changes [9] and the core level peak shifts support the notion of considerable charge transfer from K to Rh at small coverages, and a gradual neutralization at saturation [24].

3.3. Adsorption of CO_2 on K-dosed Rh(111)

The influence of K on the adsorption of CO_2 was investigated at two K coverages, $\theta_K \approx 0.1$, where the largest work function changes occurred, and $\theta_K \approx 0.36$, where monolayer K coverage was reached [9].

3.3.1. $\theta_K \approx 0.1$

Fig. 3 shows the He II photoelectron spectrum obtained after the adsorption of CO_2 at 90 K on a K-dosed surface at $\theta_K \approx 0.1$. The emission of the d-band decreased in response to CO_2 adsorption, and with the increase of the CO_2 exposure the K(3p) signal shifted to lower binding energy, 17.9 eV. Additionally, two strong and one weaker peak appeared in the spectrum, at 8.0, 12.0, and 13.6 eV. The intensities of the peaks increased with the CO_2 exposure up to 12 L, but the positions of the peaks did not change.

When the sample exposed to 18 L CO_2 was heated to 131 K, drastic decreases in the intensities of the peaks were observed. (Extensive CO_2 desorption was detected by TDS in this temperature range [9].) From 131 K the difference spectra show three very weak peaks, at around 6.0, 8.2 and 11.2 eV (fig. 4). The peak at 6.0 eV was seen even at 738 K, while the others were detected up to 474–595 K. The K(3p) level started to shift back to higher binding energy from 400 K, and disappeared above 738 K.

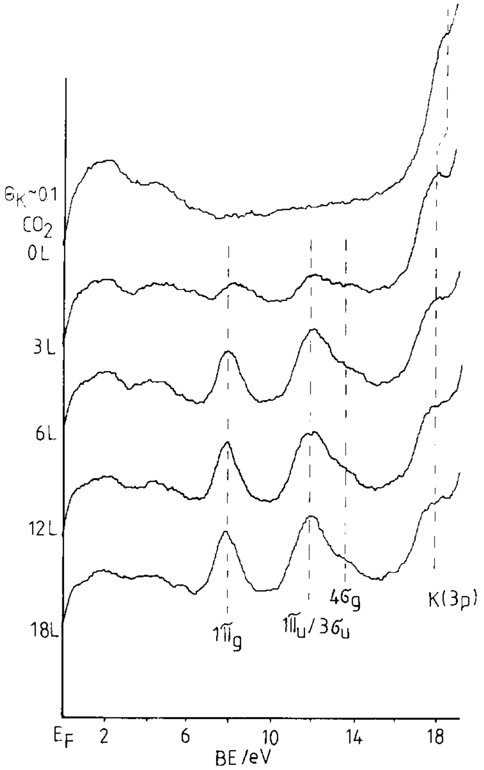


Fig. 3. He II photoelectron spectra of a K-covered Rh(111) ($\theta_K \approx 0.1$) as a function of CO_2 exposure at 90 K.

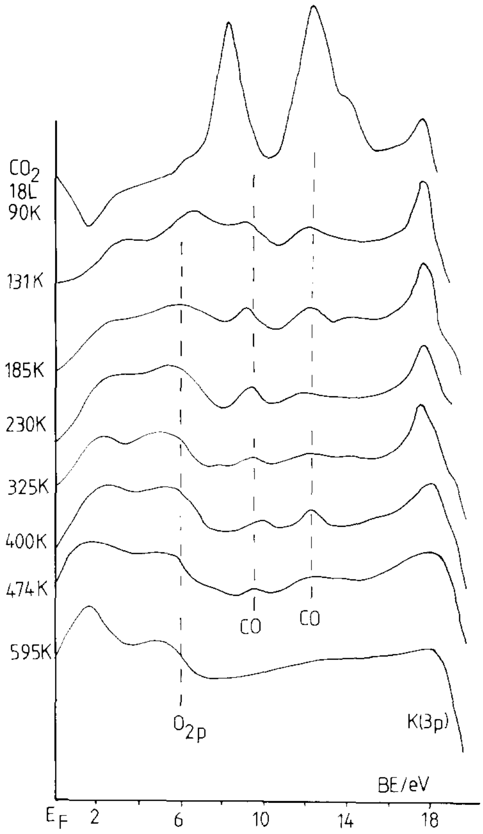


Fig. 4. Effects of heating on the HeII difference photoelectron spectra of adsorbed CO_2. CO_2 exposure = 18 L; $\theta_K = 0.1$; $T_a = 90$ K. The curve for 400 K is the result of other series of experiments.

For the assignment of the new peaks, the UP spectra of adsorbed CO and O_2 were determined on K-dosed Rh(111). Following the adsorption of CO at 90 K, two signals were found, at 8.4 and 11.5 eV. These emission peaks were eliminated only above 550 K. Oxygen exposure produced only one peak, at 5.5–6.0 eV, which was present up to about 800–900 K.

The adsorption of CO_2 on the K-dosed surface at 95 K produced two peaks in the XPS spectrum, at 534.0 for O(1s) and 292.0 eV for C(1s); their intensities were higher than in the case of clean Rh(111). These peaks decreased in intensity when the coadsorbed layer was heated to 131 K. A new very broad peak centred at 531.4 eV emerged in the O(1s) spectral region (fig. 5a). The 534.0 eV peak disappeared above 179 K, when a new emission developed at 530.4 eV. Both the 531.4 and 530.4 eV peaks decreased in

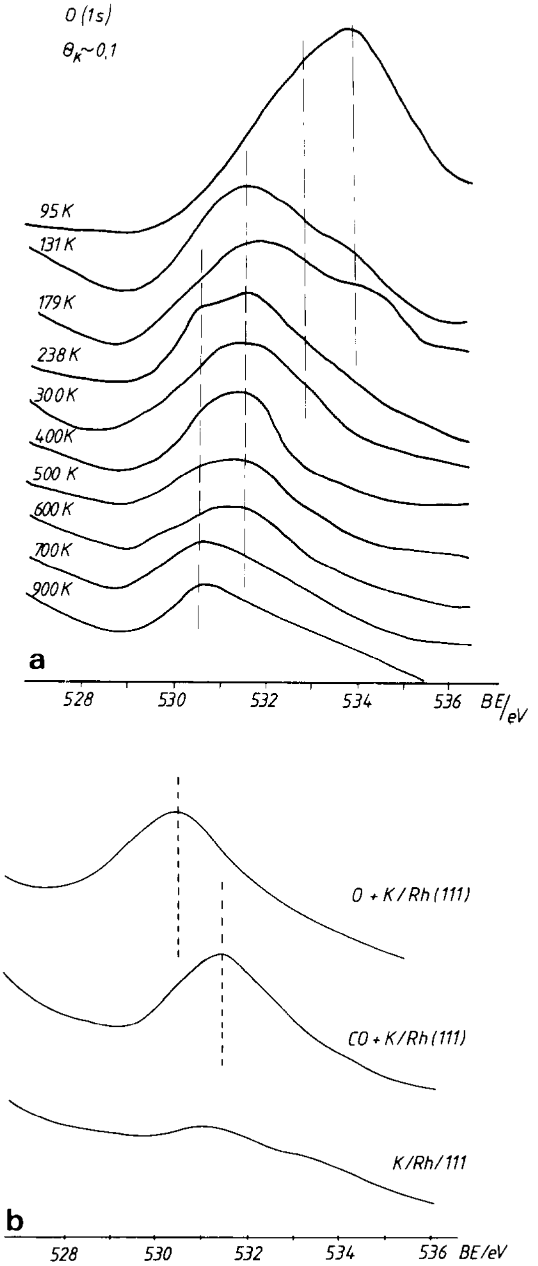


Fig. 5. (a) Effects of heating on the X-ray photoelectron spectra of the O(1s) level for CO_2 adsorption on K-covered Rh(111). $\theta_K \approx 0.1$, $T_a = 95$ K. (b) X-ray photoelectron spectra of O(1s) level for oxygen and CO adsorption on K-covered Rh(111) ($\theta_K \approx 0.1$, $T_a = 300$ K). The surface concentrations were $\sim 3 \times 10^{14}$ molecules/cm^2.

intensity above 300 K. The 531.4 eV peak disappeared between 600–700 K, while the emission at 530.4 eV was present even at 900 K. The broadening of the O(1s) peak and its asymmetric feature is very likely due to the readsorption of CO from the background gas during the long registration period.

As regards the changes in the C(1s) region the 292.0 eV peak disappeared at 131 K and a new peak appeared at 286.4 eV. It was detected up to 600 K.

In harmony with the literature data obtained for K-dosed Pt(111) [25], the adsorption of O_2 on this K-promoted Rh(111) surface produced a peak at 530.3 eV for O(1s). Following CO adsorption, the O(1s) peak appeared at 531.4 eV (fig. 5b). The corresponding C(1s) peak of adsorbed CO was detected at 286.1 eV. When the adlayer was heated, both peaks were present with unchanged binding energy up to 600–650 K.

3.3.2. $\theta_K \approx 0.33$ (monolayer K coverage)

The adsorption of CO_2 on the Rh(111) surface covered by monolayer K ($\theta_K \approx 0.33$) at 90 K caused a shift of the K(3p) signal from 17.7 eV to 17.2 eV,

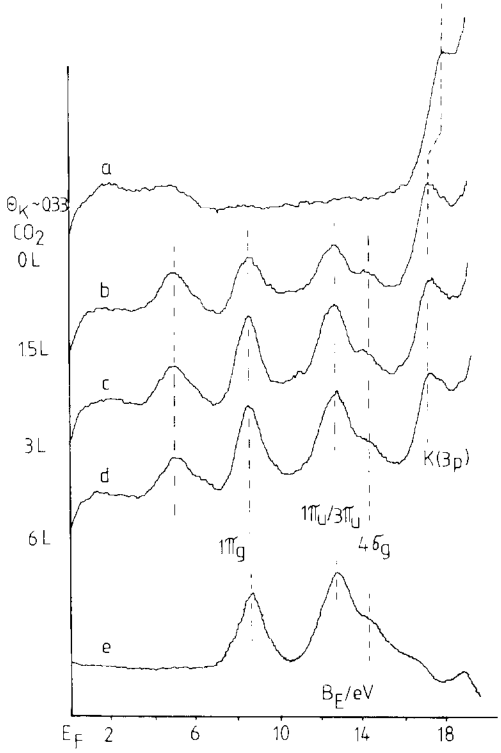


Fig. 6. HeII photoelectron spectra of a K-covered Rh(111) ($\theta_K \approx 0.33$) as a function of CO_2 exposure at 90 K (a–d). The difference spectrum between those taken at 90 K and 131 K is also shown (e).

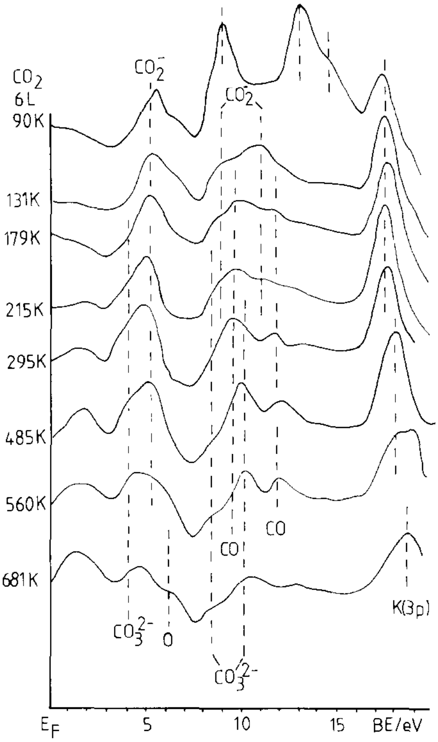


Fig. 7. Effects of heating on the He II difference photoelectron spectra of adsorbed CO_2. CO_2 exposure = 6 L, $\theta_K \approx 0.33$, $T_a = 90$ K.

and produced four new intense emissions in the He II UPS spectrum, at somewhat higher binding energies than at $\theta_K \approx 0.1$: 5.2, 8.8, 13.0 and 14.5 eV (fig. 6). The intensities of the peaks at 8.8, 13.0 and 14.5 eV increased with CO_2 exposure up to 6 L, while that of the signal at 5.2 eV did so only up to 1.5 L CO_2 exposure (fig. 6).

When the sample was heated to 131 K, the peak at 5.2 eV remained unchanged and two poorly resolved peaks emerged at 8.7 and 10.9 eV in the He II difference spectrum (fig. 7). These signals attenuated on further increase of the temperature, and were detectable as shoulders up to 295–325 K. At 179 K, two additional peaks developed, at 9.4 and 11.7 eV. Their intensities slightly increased up to 295 K. From 295 K, the peak originally centred at 9.4 eV shifted to 10.2 eV. The emission at 11.7 eV decreased in intensity above 560 K and was eliminated above 681 K. At 179–215 K, weak shoulders appeared at 3–4 and 8.4 eV. These features also disappeared above 681 K. In parallel with these changes, the intensity of the peak at 5.2 eV decreased from 386 K and broadened towards higher energies from 560 K.

The K(3p) orbital shifted back to higher energies from 386 K, and reached its original position with a reduced intensity at 681 K.

Following the adsorption of CO_2 on this K-dosed Rh at 95 K, significant changes were observed for the XPS, too. The O(1s) level was measured at 534 and 532.8 eV. For the C(1s) level, a peak was found at 292 eV. At 131 K, the intensity of the O(1s) level at 534 eV markedly dropped and that of the peak at 532.8 eV significantly increased (fig. 8a). The peak areas for O(1s) measured at 95 K and 131 K were identical, which suggests that the surface species formed at 95 K were transformed to new ones without significant desorption at this potassium coverage. With increase of the temperature from 131 K to 238 K, the O(1s) level centered at 532.8 eV continuously shifted to 531.7 eV. The peak remained unaltered up to 600 K; its intensity subsequently decreased. Above 700 K, a new peak developed at 530.4 eV. It disappeared only above 900 K.

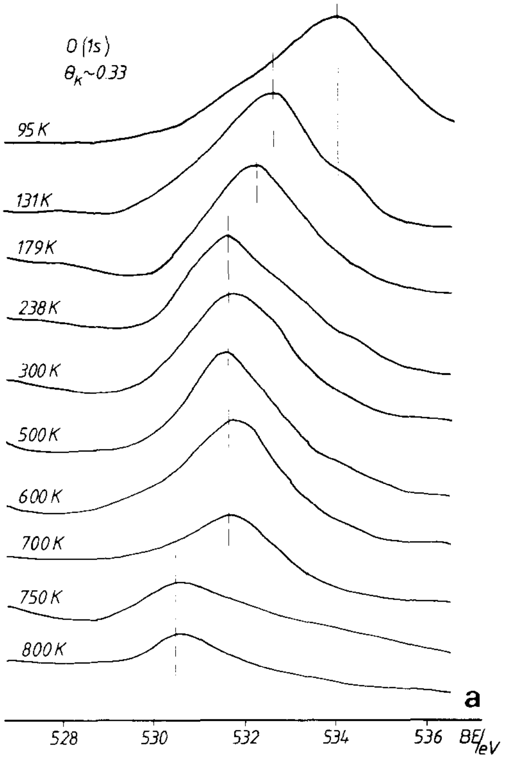


Fig. 8. Effects of heating on the X-ray photoelectron spectra of the O(1s) level (a) and C(1s) level (b) for CO_2 adsorption on K-covered Rh(111). $\theta_K \approx 0.33$, $T_a = 95$ K. The spectrum of the K-covered surface was subtracted in all cases.

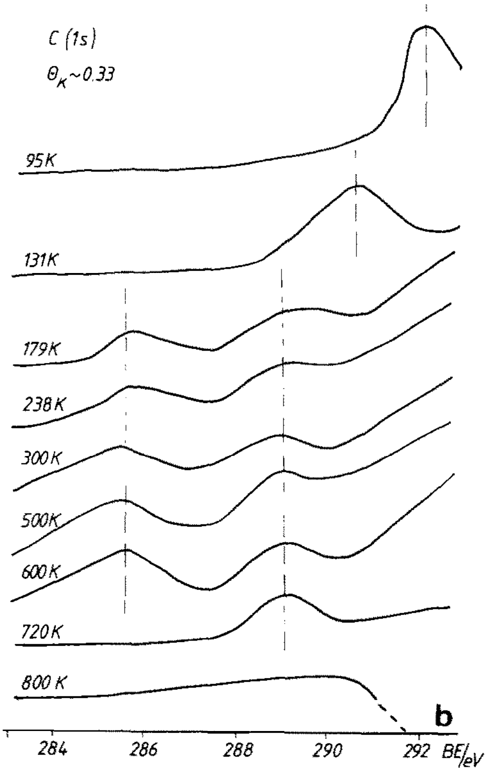


Fig. 8. Continued.

At 131 K, the peak due to the C(1s) level appeared at 290.5 eV (fig. 8b). Above this temperature, it was transformed into peaks at 285.6 and 289.0 eV. These peaks were stable up to 600 K. The level at 285.6 eV disappeared first at around 700 K, while the C(1s) orbital at 289.0 eV did so only above 720 K, indicating that these two peaks for C(1s) relate to different surface species.

4. Discussion

4.1. Adsorption of CO_2 on clean Rh(111)

Although the adsorption of CO_2 on Rh single-crystal surfaces has recently received great attention [26–31], no UPS and XPS measurements have so far been performed on this system. The adsorption of CO_2 on clean Rh(111) at 90 K produced three new lines in the UP spectrum, at 6.6, 10.7 and 12.1 eV, which agrees well with the spectral features established for other transition metals [18–22].

From a comparison of the observed spectrum with that of gaseous CO_2 [32] (fig. 1), it is evident that the signal at $E_B^F = 6.6$ eV is due to the $1\pi_g$ orbital, and the emissions at 10.7 and 12.1 eV correspond to unresolved $1\pi_u/3\sigma_u$ and $4\sigma_g$ orbitals. The differences in binding energies in the adsorbed layer on Rh(111), 4.1 and 5.5 eV, approximate well the values (3.8 and 5.6 eV) measured for gaseous CO_2 [32]. From this finding, we may conclude that CO_2 adsorbs weakly and molecularly on Rh(111) at 90 K, without undergoing a strong distortion of its molecular electronic structure.

A similar conclusion can be drawn from an analysis of the XP spectrum of adsorbed CO_2. The energy difference ($\Delta E = 242.7$ eV) between the O(1s) (534.7 eV) and C(1s) (292.0 eV) levels approximates well the value determined for undisturbed gaseous CO_2, $\Delta E_g = 243.6$ eV [33]. This finding is in harmony with the results of work function measurements: the adsorption of CO_2 caused no or only very small (~ 0.06 eV) work function changes [9], which was confirmed in the present study.

When the sample was heated up to about 220–250 K, all the photoemission peaks disappeared and the spectrum of the clean surface was restored. There was no sign of the development of new peaks due to CO(a) and O(a), which is in accord with our previous conclusion that CO_2 desorbs completely from the Rh surface without suffering any detectable dissociation [9,28–30].

4.2. Adsorption of CO_2 on K-dosed Rh(111)

4.2.1. General characteristics

Previous TDS, ELS (in the electronic range) and work function measurements revealed that preadsorbed K dramatically altered the behaviour of CO_2 adsorbed on the Rh(111) surface [9]. It increased the binding energy of CO_2: CO_2 desorbed in several peaks at 300–500 K (β) and 714–724 K (γ) (at $\theta_K \gtrsim 0.3$). Above $\theta_K = 0.3$, the K was also stabilized by CO_2 on the surface; K desorbed in a narrow peak with $T_p = 720$ K. The dissociation of CO_2 was observed even at low K coverage, $\theta_K = 0.03$. In contrast with the clean surface, the adsorption of CO_2 on K-dosed Rh led to a significant work function increase, 1.07 eV at $\theta_K = 0.07$. Similar characteristics have been observed for the interaction of CO_2 with the K-dosed Pd(100) surface [10,11]. These features were interpreted in terms of a substantial charge transfer from the K-dosed metal to an empty π-orbital of CO_2 and the formation of the negatively charged CO_2^- with different bonding and structural properties.

Although the formation of the anion radical CO_2^- had not been assumed to occur on metal crystal surfaces before the submission of our papers dealing with the interaction of CO_2 with K-dosed metals [9,10], there are several literature observations which demonstrate its existence under different conditions [12–17]. CO_2^- has been reported to form in the gas phase [12–14], under irradiation of sodium formate in an alkali metal halide matrix [15], under ultraviolet irradiation of CO_2 adsorbed on magnesia [16] and in the interactions of Li, Na and K with CO_2 at 77 K in an Ar and CO_2 matrix [17].

Recently, a very thorough theoretical work was devoted to the bonding and reactivity of CO_2 on clean metal surfaces and the formation of the CO_2^- anion in the interaction of CO_2 with Ni metal has also been postulated [34]. This postulation was confirmed experimentally on Ni(110) by subsequent angle-resolved photoemission studies [20]. The formation of CO_2^- has also been detected on a reactive Fe(111) surface [22].

The results of the present UPS and XPS studies confirmed the strong interaction between CO_2 and K-dosed Rh, and the formation of the CO_2^- species. Whereas the intense He II photoemission peaks observed following CO_2 adsorption at 90–95 K on the K-promoted surface indicated that the predominant species on the surface is the perturbed weakly bonded CO_2, when the sample was heated to *131 K* different spectral features were observed.

Let us first consider the results obtained at higher K coverage, where the photoemission peaks are more intense, due to the higher CO_2 concentration.

4.2.2. High K coverage, $\theta_K = 0.33$

In this case the He II UP spectrum exhibited three emissions, at 5.2, 8.7 and 10.9 eV (fig. 7). These peaks are distinctly different from those observed following CO_2 adsorption on a clean Rh surface, and agree well with those derived theoretically [34] and established experimentally for bent CO_2^- bonded to a clean Ni(110) surface [20]. As no signals due to adsorbed CO and O were detected in the photoemission spectra at this temperature, the above features can be attributed unambiguously to the formation of the undissociated CO_2^- radical anion. The observed peaks are assigned to the ($1a_2$, $4b_2$), ($5a_1$, $1b_1$, $3b_2$) and ($4a_1$) orbitals of CO_2^- respectively. The appearance of both the C(1s) and the O(1s) signals in the XPS at lower energies, 290.5 and 532.8 eV, respectively, compared to neutral CO_2, also indicates that the electron density in the CO_2 molecule is increased, which further supports the conclusion.

As the 5.2 eV photoemission peak appeared following CO_2 adsorption even at 90 K, we may infer that the CO_2^- radical anion is formed even at this low temperature, and its other spectral features are overshadowed by the peaks due to the large amount of weakly adsorbed CO_2. This is confirmed by the difference spectrum between those taken at 90 and 131 K (fig. 6), which clearly corresponds to weakly adsorbed neutral CO_2. The fact that the work function increases ($\Delta\phi = 0.2$ eV) further when the temperature is raised from 90 to 131 K suggests that the formation of CO_2^- was not complete at 90 K.

The orbitals of the bent CO_2^- can be detected via UPS and XPS up to 238 K, which signifies appreciable stability on this surface. We may count with its existence even at higher temperatures: the detection is possibly hindered by the low intensities and by the development of other, overlapping photoemission peaks.

There are several ways for the CO_2^- anion radical to be stabilized on the surface: (i) the formation of a dimer, $CO_2 \cdot CO_2^-$, with neutral CO_2, as was found in the gas phase [13,14], (ii) dimerization into the oxalate species, $C_2O_4^{2-}$ [17], and (iii) the formation of a surface compound "$K^+CO_2^-$". Although it is highly probable that the formation of $CO_2 \cdot CO_2^-$ dimer is responsible for the enhanced uptake of weakly adsorbed CO_2 on K-dosed Rh and Pd at 90–100 K [9,11] (the high ratio of weakly and strongly adsorbed CO_2 even suggests the formation of a cluster ion $(CO_2)_x^-$, as detected during the electron impact of gaseous CO_2 [13,14]), the photoemission spectra contain no signals due to neutral CO_2 at and above 131 K, and thus the stabilization of CO_2^- in this form above 131 K seems unlikely. We believe that the primary mode of stabilization of CO_2^- is its coupling with K^+. As K exhibits mainly metallic character at this coverage, we postulated that the CO_2^- anion radical is formed in a direct interaction with K [9]:

$$K(a) + CO_2(g) \rightleftharpoons K^+ \cdot CO_2^-(a). \qquad (1)$$

The species $K^+ \cdot CO_2^-$ may polymerize into a larger unit, forming an island.

When the adsorbed layer is heated, a portion of the CO_2 is released,

$$K^+ \cdot CO_2^-(a) \rightleftharpoons K(a) + CO_2(g), \qquad (2)$$

while another part is transformed into other surface species.

With regard to the He II photoemission spectra of adsorbed CO on K-dosed Rh (table 1), the 11.7 eV peak is attributed to adsorbed CO (4σ). This assignment means that the peak at 9.4 eV also contains the signal of CO (5σ/1π). The production of adsorbed CO is supported by the appearance of the C(1s) signal at 285.6 eV (fig. 8b). In control experiments when the same surface was exposed to CO we observed peaks at 285.6 eV for C(1s) and 531.4 eV for O(1s) (see table 1).

The development of these peaks occurred practically in parallel with the appearance of the UV photoemission peaks at 3–4, 8.4 and 10.2 eV, which were stable up to 700 K (fig. 7). We attribute these peaks to carbonate species and assign them to the (1e″, 4e′) doublet, the (3e′, 1a″) unresolved orbitals (8.4 eV) and the 4a′ orbital, respectively. The observed photoemission peaks conform well with those obtained for other carbonate species, including K_2CO_3 [35–37].

The formation of surface carbonate is reflected by the XP spectra (fig. 8): above 179–238 K, the O(1s) peak is located at 531.7 eV. Almost the same value, 532.0 eV, was observed when K_2CO_3 was deposited on an Fe surface [38], and a similar binding energy (531.5 eV) was obtained for $NiCO_3$ [39,40]. The corresponding C(1s) peak was found at 289.0 eV, which is also in accord with literature data for the C(1s) peak of carbonate [38,40]. The intensity of the C(1s) peak was lower than that of the O(1s) peak for three reasons: (i) the C(1s) cross section is lower than that of O(1s) in the XPS, (ii) the O : C ratio is high in carbonate, and (iii) the binding energy of the O(1s) of the adsorbed CO formed is situated in the same energy range (531.4 eV) as the O(1s) for carbonate.

As regards the formation of CO, it is very important to mention that there is no sign of a peak at 530.4 eV for O(1s) up to 550–600 K in the XPS spectra, or at around 5.5–6 eV (O(2p)) in the UPS, which are indicative of adsorbed oxygen.

Accordingly, we can conclude that the primary source of the formation of CO is not the dissociation of negatively charged CO_2^-:

$$CO_2^-(a) = CO(a) + O^-(a). \tag{3}$$

As the peaks of adsorbed CO and carbonate-like species developed almost simultaneously, it seems more probable that they are formed in the same surface process. This could be the disproportionation of the CO_2^- radical anion:

$$2\,CO_2^-(a) = CO(a) + CO_3^{2-}(a), \tag{4}$$

or the transformation of an oxalate species (if its existence is confirmed later):

$$C_2O_4^{2-}(a) = CO(a) + CO_3^{2-}(a), \tag{5}$$

which was considered as a possible form for the stabilization of CO_2^- species on the surface.

The peaks attributed to carbonate species were seen in the spectra up to 720 K. Above this temperature only the peaks for adsorbed oxygen (6 eV in the UPS, and 530.4 eV in the XPS) were detected which – taking into account the evolution of CO_2 around 720 K – points to the decomposition of potassium carbonate

$$K_2CO_3 = K_2O + CO_2(g). \tag{6}$$

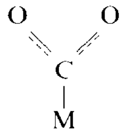
The observed behaviour is in harmony with the high stability of potassium carbonate (bulk K_2CO_3 decomposes only above 950 K [41]) and with the finding that metal surfaces can lower its thermal stability [38].

The above reaction scheme is supported by thermal desorption measurements performed under the same condition. The amount of CO formed in eqs. (4) or (5) (1.2×10^{14} CO molecules/cm^2, $T_p = 704$ K) agreed well with that of CO_2 (γ) produced by reaction (6) ($T_p = 720$ K).

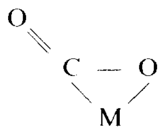
4.2.3. Low K coverage, $\theta_K = 0.1$

In this case, the He II UP spectrum of the chemisorbed layer ($T = 131$ K) showed three emissions, at 6.0, 8.2 and 11.2 eV. With increase of the temperature, only decreases in their intensities were registered, but neither the shifting of these peaks nor the formation of new peaks was observed. These peaks were also seen following oxygen adsorption (peak at 6.0 eV) and CO adsorption (peaks at 8.4 and 11.5 eV) on the same surface. As they also displayed the same thermal behaviour, we can conclude that the 6.0 eV peak relates to adsorbed oxygen and the 11.2 eV peaks to adsorbed CO. A similar comparison of the XPS spectra demonstrates that adsorbed oxygen and CO are formed on the surface above 131 K (table 1).

From these results we may infer that CO_2 completely dissociates on this surface at 131–179 K. We propose that the dissociation takes place through the transient formation of the CO_2^- anion radical. Due to the significantly lower concentration of the CO_2^- anion on this surface and also its lower thermal stability, its existence was not confirmed by spectroscopy. The broadening of the O(1s) spectrum (taken at 95 K) at 532–533 eV may suggest its presence. At this K coverage, the potassium adatoms are mainly ionic, due to charge transfer to the Rh surface, as concluded from the linear decrease in the work function up to this coverage. Accordingly, the CO_2^- radical anion may not be formed in the direct interaction between metallic potassium and CO_2, as was assumed at monolayer K coverage, but may be due to an enhanced back-donation of electrons from the potassium-dosed Rh into an empty π^* orbital of CO_2. The enhanced back-donation may increase the binding energy of CO_2 to the surface and cause basic changes in the bonding and the structure of the adsorbed CO_2, e.g. the formation of a metal–carbon bond in the form of a monodentate (A) or bidentate (B) structure [9]:



(A)



(B)

On analogy with the previous case (high potassium coverage), we may also count with the stabilization of the CO_2^- anion radical in the form of a dimer, $CO_2 \cdot CO_2^-$, or a cluster, $(CO_2)_2 \cdot CO_2^-$.

However, UPS and XPS results provided no experimental evidence of the existence of a neutral CO_2 molecule above 179 K; thus, if this complex does exist on the surface, its concentration is below the limit of its detection with these methods.

It appears that at this low potassium concentration the possibility of the transformation of the CO_2^- anion radical into other compounds (oxalate and carbonate-like species) is considerably less, as there was no spectral indication of the formation of any other species during heating of the coadsorbed layer to high temperature. In harmony with this, the high-temperature γ state ($T_p = 720$ K) of CO_2 in the TD spectrum did not develop on this surface [9]. We may conclude that, as a result of the extended back-donation of electrons from K-promoted Rh to CO_2, the metal–C bond is strengthened and the C–O bond is weakened to such a great extent that the dissociation occurs even around 131 K. It is likely that an elongation of the interacting C–O bond in the bidentate structure may also facilitate the dissociation of CO_2^-.

With regard to the stability of the CO_2^- anion radical, the reactivity of K-promoted Rh is similar to those of clean Ni(110) and Fe(111) surfaces, where CO_2^- was found to dissociate at 250 and 180 K, respectively [20,22].

The fact that CO_2 formation has been detected by thermal desorption measurements, at $T_p = 342$ and 500 K [9], suggests that the associative desorption of CO_2:

$$CO(a) + O(a) = CO_2(g),$$

also occurs from the coadsorbed layer before the desorption of CO ($T_p = 616$ K). This temperature of CO_2 formation is higher than that observed for the clean Rh surface [42], which can be attributed to the stabilizing influence of the potassium adatom. The study of the effect of potassium on the oxidation of CO by O forms the subject of another paper.

5. Conclusion

(1) UPS and XPS results revealed that preadsorbed potassium on Rh(111) drastically influences the adsorption and bonding of CO_2 and the reactive CO_2^- anion radical is produced.

(2) The formation of the CO_2^- anion has been described by a charge transfer from the K-dosed Rh to an empty π-orbital of CO_2 (at low K-coverage, when K exhibits mainly ionic character) and by a direct interaction between CO_2 and potassium metal (at high K coverage, when potassium exhibits metallic character).

(3) At low K coverage the CO_2^- anion radical dissociates to CO and O, whereas at high K coverage it is transformed into carbonate and CO.

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