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IMPURITY EFFECTS IN THE ADSORPTION AND DISSOCIATION OF CO_2 ON Rh

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The adsorption and dissociation of CO_2 on Rh(111) and Rh foil surfaces have been studied in UHV using Auger electron, electron energy loss (in the electronic range) and thermal desorption spectroscopy. CO_2 adsorbs weakly with a low sticking probability on clean Rh samples at 110 K. The adsorption is accompanied by the appearance of a loss feature at 14 eV. The adsorption of CO_2 took place in two stages, with $T_p = 244–233$ K (α) and 170 K (β). Adsorption of 180 L CO_2 at 3×10^{-7} Torr on clean Rh(111) at 300 K produced no observable changes in the LEEd, Auger electron, EEL or TD spectra and there was no indication of the dissociation of CO_2 either. Similar results were obtained for a clean Rh foil. However, boron impurity segregated on the surface of Rh exerted a dramatic influence on the adsorptive properties of this surface and caused the dissociation of CO_2 at 270–300 K. This was exhibited by the appearance of an intense loss in the EEL spectrum due to chemisorbed CO, by the buildup of surface oxygen and by the thermal desorption of CO at higher temperatures.

1. Introduction

Study of the adsorption and dissociation of CO_2 on Rh surfaces is of strong relevance to the better understanding of the mechanism of hydrogenation of CO_2, and hence to that of the hydrogenation of CO on Rh catalysts. Although the adsorption and dissociation of CO_2 appear to be simple processes, there is great controversy concerning these reactions in the literature, and the dispute between the various research groups on this topic does not seem to be abating. In the early studies, the adsorption of CO_2 was claimed to be weak and associative on Rh films [1], polycrystalline Rh [2] and alumina-supported Rh [3].

Somorjai et al., however, found that CO_2 does chemisorb and dissociate on Rh foil [4] and on several faces of Rh single-crystal surfaces [5–8] at 300 K, but this requires a higher CO_2 exposure. In the case of a supported Rh, Primet [9] inferred the dissociation of CO_2 at 300 K from the appearance of the weak CO bands at 2025 and 1860 cm^{-1} in the IR spectrum of Rh/Al_2O_3. In our more detailed IR spectroscopic investigations, including a study of the effect of the support [10–12], we observed a slight dissociation of CO_2 at 300 K. It was

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pointed out that this process is very sensitive to the mode of preparation of the catalyst, the dispersity of the Rh, and the nature of the support, and it is greatly facilitated by the presence of hydrogen [10]. Apart from an early misquotation of these results [13,14], Iizuka et al. confirmed our findings [15].

The recent calculations of Weinberg [16], based on the available thermodynamic and kinetic information on the interaction of CO_2 and Rh, suggested that the probability of dissociative chemisorption of CO_2 at low pressure (around 10^{-6} Torr) and at room temperature is of the order of 10^{-15}, i.e. some 14 orders of magnitude lower than reported previously [4–8]. However, Weinberg [16] pointed out that the rate of dissociation of CO_2 is significant above 300 K and a pressure of CO_2 of approximately one atmosphere.

Dubois and Somorjai [17] criticized the conclusions of Weinberg [16], stating that they were "based on oversimplified calculation using incorrect kinetic and thermodynamic parameters". They argue that the failure to observe the dissociation of CO_2 in the papers referred to [1–3,16] may simply be an artifact of the adsorption conditions or of the sample preparation.

It is quite clear that, in spite of the great efforts, the question of CO_2 dissociation has still not been resolved. We have to assume that all research workers performed their experiments very carefully and strived to avoid the generation of CO in the measuring cell or UHV chamber on the different filaments or the heating wires. If this is the case, the only way to explain the discrepancies is that there is some (so far undetected) property of the Rh surface which in certain circumstances becomes dominant and causes the dissociation of CO_2.

The primary aim of our present study is to investigate the adsorption of CO_2 on two different Rh surfaces, a polycrystalline Rh foil and the Rh(111) surface, to find out why it is easy to detect the dissociation in one case and not at all in the other. Special attention is focussed on the effects of pretreatment and of impurities in the Rh.

2. Experimental

The experiments were carried out in a Varian ion pumped UHV system which was equipped with a single-pass CMA (PHI), with a 3-grid retarding field analyzer (VG) and with a quadrupole mass analyzer. The base pressure was of 1.5×10^{-10} Torr.

For electron energy loss spectra the gun of CMA was used as a primary electron source with an energy of 70 eV and a beam current of 0.1–1.0 μA. The backscattered electrons were analyzed with CMA. A modulation voltage of 0.1 eV was found to be the optimum for the used system. The velocity of taking a spectrum was varied between 0.4–4 eV/s. The exact position of the peak maxima of energy losses were determerd by a Keithley electrometer. Electron energy loss spectra were taken in $\mathrm{d}N(E)/\mathrm{d}E$ form.

Two different Rh samples were used, a Rh(111) disk shape crystal (6 × 1 mm, Material Research Co., 99.99% purity) and a polycrystalline Rh foil (10 × 10 mm and 0.127 mm thick, Hicol Co., 99.9% purity). Initial cleaning procedures consisting of cycles of oxygen treatment at 300–1000 K, ion bombardment (typically 600 eV, 1×10^{-6} Torr Ar, 300 K, 3 μA for 10–30 min) and annealing at 1270 K for some seconds. As the Rh(111) sample has been used in a number of previous studies, its cleaning required no oxygen treatment in the present case. The purity of the Rh foil was lower than that of Rh(111). The major contaminants were B, P, S and C. The P, C and S were easily removed, but no complete elimination of boron was achieved even after several cleaning cycles. The final thermal treatment in this case was performed at 700 K. CO_2 was obtained from Messer-Griesheim. It was introduced into the chamber through a stainless steel capillary with a diameter of 0.8 mm.

3. Results and discussion

3.1. Clean Rh(111) surface

The Auger spectrum of a cleaned Rh(111) surface is shown in fig. 1. At the energy of boron Auger signal at around 178 eV, only a small break or shoulder can be observed.

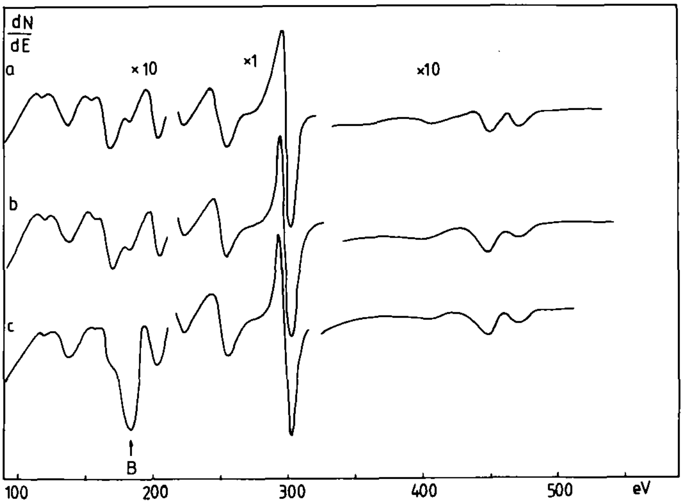

Fig. 1. Auger spectra of the Rh surfaces: (a) clean Rh(111) ($R_B \leq 0.003$); (b) clean Rh foil ($R_B \leq 0.003$); (c) Rh foil contaminated with boron $R_B \approx 0.040$.

3.1.1. Adsorption at 110 K

The adsorption of CO_2 on Rh(111) was first followed by EEL spectroscopy. This method has so far been used in our laboratory to study the adsorption of HNCO [18], HCOOH [19], CH_3OH [20], HCN [21] and C_2N_2 [22] on clean and oxgyen-dosed metal surfaces. It proved to be particularly sensitive for determination of the surface decomposition of these compounds by following the development of an intense loss at 13–13.5 eV due to chemisorbed CO.

The electron energy loss spectrum of a clean Rh(111) surface is shown in fig. 2. In harmony with our previous measurements, losses were observed at 2.6, 5.2, 6.6, 17.6–18.6 and 24.5 eV.

Adsorption of CO_2 on Rh(111) at 110 K slightly increased the intensities of the elastic peak and the loss at 5.2 eV. A relatively intense new loss appeared at 14 eV. Taking into account the UPS spectrum of adsorbed CO_2 on Pt [29], the 14 eV loss is tentatively assigned to $4\sigma_g$ (or $1\pi_u/3\sigma_u$)–$2\pi_u$ type electron transition. The intensity of this loss increased with increasing CO_2 exposure (fig. 2). Adsorption of CO under the same conditions yielded a strong loss at 13.0 eV and intensified the Rh loss at 5.2 eV. The 13.0 eV loss due to chemisorbed CO was observed on Cu [23], Pt [18,24], Pd [25], Ru [26], Ni [27,28] and Rh [19,20] surfaces, and was assigned to a $(1\pi/5\sigma)$–$2\pi^*$ type intramolecular electronic excitation.

The adsorption of CO on Cu(111) and Ni(110) surfaces also gave a loss feature at around 5–6 eV, where neither metal exhibits energy losses. This loss was assigned to a d–$2\pi^*$ type [27] or to 2π–$2\pi^*$ charge transfer excitation [24].

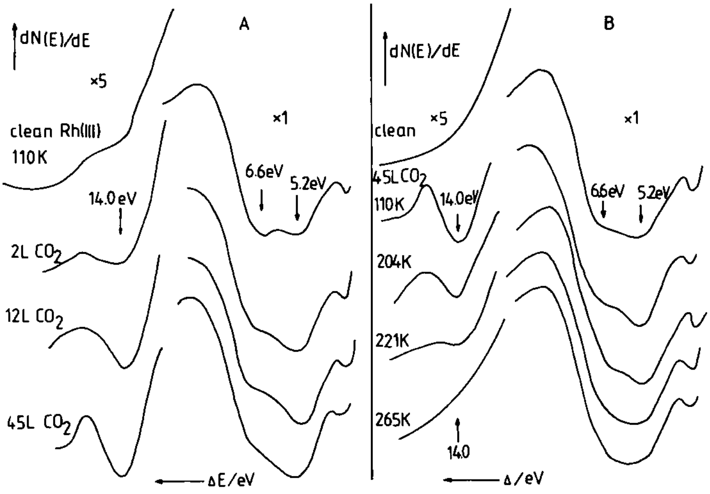

Fig. 2. (A) Electron energy loss spectra of Rh(111) as a function of CO_2 exposure at 110 K. (B) Electron energy loss spectra taken after heating the Rh(111) to different temperature. The surface was exposed to 45 L CO_2 at 110 K before heating.

On this basis it seems likely that the changes at 5.2 eV during the adsorption of CO and CO_2 are due to the development of a loss caused by adsorbed species, and not to an intensification of the Rh loss at this energy.

Although the position of the loss caused by CO_2 is very near the energy of the loss due to chemisorbed CO, its thermal behaviour allows us safely to exclude the possibility that the 14 eV loss is due to adsorbed CO formed in the dissociation of CO_2 on the Rh. As fig. 2 shows, the 14 eV loss could be completely eliminated by heating the sample to 265 K, without any new loss appearing in the EEL spectrum. In contrast, the 13.0 eV loss produced by CO adsorption remained unaltered in shape and intensity up to this temperature, and started to decrease only above 350–400 K, in accordance with the TD results for CO desorption [19,20].

The subsequent thermal desorption measurements are in harmony with the EELS results. We found a significant desorption of CO_2 after its adsorption at 110 K, but detected no desorption of CO. At lower CO_2 exposure the high-temperature peak (β) develops first; its T_p is shifted from 244 K to 235 K. With increasing coverage, from 6 L a low-temperature peak (α) is formed at $T_p = 170$ K, which is practically independent of the coverage. This is shown in fig. 3. In the fig. 4 the surface concentration of adsorbed CO_2 (calculated from peak area, MS sensitivity and pumping rate) is plotted against CO_2 exposure. For saturation coverage we obtained 1.3×10^{14} CO_2 molecules/cm^2. The sticking probability was estimated to be in order of 10^{-2}. Assuming a

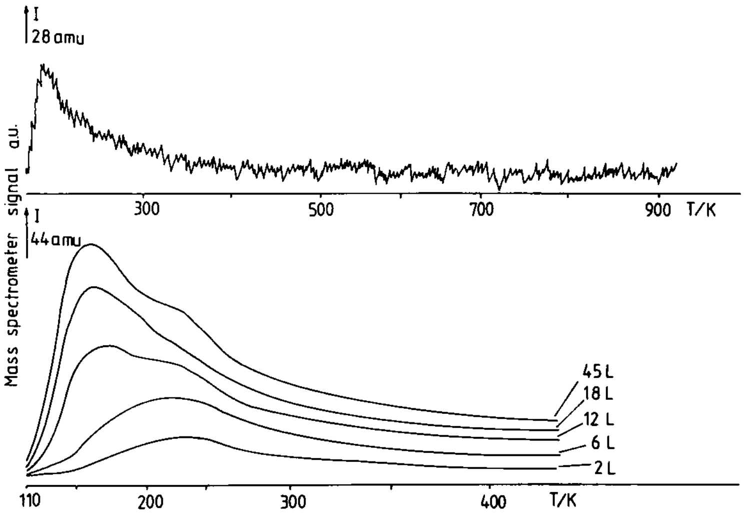

Fig. 3. Thermal desorption spectra following CO_2 adsorption on Rh(111) surface at 110 K.

preexponential factor of 10^{13}, we obtain activation energies of 42.7 kJ/mol for the desorption of α-CO_2, and 61.2 kJ/mol for the desorption of β-CO_2.

3.1.2. Adsorption of CO_2 at 300 K

Exposure of a clean Rh(111) surface to CO_2 up to 180 L at the pressure of 3×10^{-7} Torr CO_2 around the sample produced no observable change in the EEL spectrum of Rh. There was no indication of the development of losses due either to adsorbed CO_2 or to adsorbed CO. Assuming that CO may be formed at certain sites of the crystal, we scanned the Rh(111) plate very carefully from one area to others. Special attention was paid to the edges of the crystal, but without any positive result. No change was found in the LEED pattern of clean Rh(111), and the Auger spectrum of the sample was also unaltered. In agreement with this, no desorbing products were detected by subsequent thermal desorption measurements.

This is in contrast with the results of Dubois and Somorjai [7,8], who found an intense ^{13}CO peak at 480 K following 2 L $^{13}CO_2$ exposure at ~ 310 K. In addition, by vibration EEL spectroscopy they identified an intense loss at 2060 cm^{-1} due to chemisorbed CO at 5×10^{-7} Torr CO_2 background pressure and 300 K. From the observation that the adsorption of CO and CO_2 (the latter at higher exposure) led to identical LEED patterns [5–8], the surface concentration of CO formed in the surface dissociation of CO_2 was estimated to be at least ~ 4×10^{14} CO molecules/cm^2. This is a relatively high CO concentration,

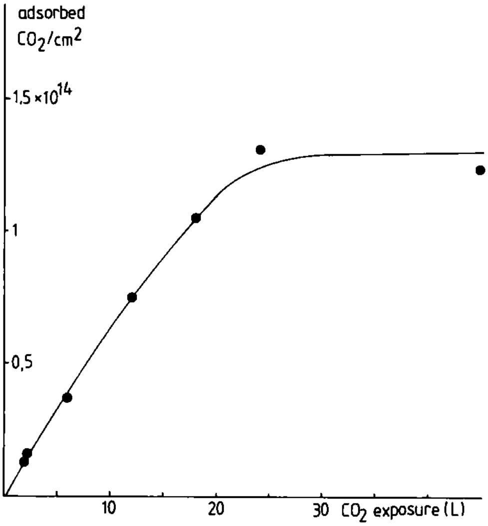

Fig. 4. Surface concentration of adsorbed CO_2 as a function of CO_2 exposure on a clean Rh(111) at 110 K determined from thermal desorption spectra.

which can easily be detected by EEL spectroscopy in the electronic range, not to mention thermal desorption measurements. Accordingly, we can exclude the possibility that the CO formed in the dissociative adsorption of CO_2 escaped detection by our techniques.

3.2. Rh foil

The experiments were repeated on Rh foil. As mentioned in section 2, the purity of this sample is lower than that of Rh(111). Even after the extensive cleaning procedure we obtained still an Auger signal at 178 eV (fig. 1). Its intensity relative to that of the main peak of Rh, B_{178}/Rh_{302}, was ~ 0.04. Experiments were begun with this surface.

3.2.1. Adsorption at 110 K

Similarly as in the case of Rh(111), the exposure of Rh foil to CO_2 at 110 K produced only one new loss, at 14 eV. Its intensity increased with rising CO_2 exposure. However, upon heating the CO_2-saturated surface to higher temperatures, we obtained basically different EEL spectra from those for the Rh(111) sample. In addition to a gradual decrease in intensity of the 14 eV loss, an apparent shift of the peak position from 14 eV to 13.0 eV occurred from 270 K (fig. 5).

With a higher resolution, i.e., an extended energy scale, a shoulder on the low-energy side of the 14 eV loss was detected at ~ 250 K. From 300 K the development of a very weak loss at 9.4 eV was observed: its intensity increased

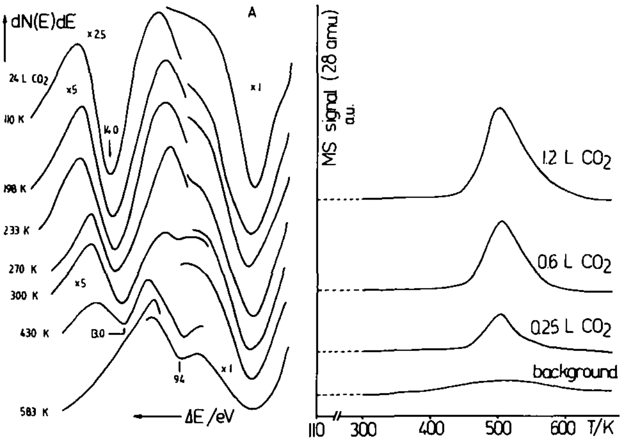

Fig. 5. (A) Electron energy loss spectra of Rh foil ($R_B \approx 0.04$) taken after heating the sample exposed to 24 L CO_2 at 110 K to different temperatures. (B) Thermal desorption spectra of CO following CO_2 adsorption on Rh foil ($R_B \approx 0.04$) at 110 K.

with rising temperature up to 640 K. It was eliminated only above 950 K. As discussed in more detail below, we have strong arguments indicating that the 9.4 eV loss is a result of the presence of chemisorbed oxygen on certain centers of the Rh surface.

We note here that the adsorption of CO from the background under similar conditions (cooling of the sample from 1200 K to 110 K in ~ 10 min), in the time when these experiments were conducted, resulted in a very weak CO loss, the intensity of which was 1/50 of the maximum value found after CO_2 adsorption.

All these findings suggest that the appearance of the 13.0 eV loss is a result of the dissociation of CO_2 to adsorbed CO and O

$$CO_{2(a)} \rightarrow CO_{(a)} + O_{(a)},$$

and is not due to the adsorption of CO from the background or to a simple shift of the 14 eV loss to lower energies. This is confirmed by subsequent TD measurements. In addition to the low temperature CO_2 desorption, a well detectable desorption of CO was established with peak maximum, $T_p \approx 500$ K (fig. 5B).

The surface concentration of CO formed was calculated by comparing the amount of CO desorbed following CO_2 adsorption with the value obtained after saturation of Rh with CO alone. The surface concentration of CO on Rh(111) at saturation is about 1.2×10^{15} molecules CO/cm^2 [30,31]. The corresponding value for Rh foil was given to be only 5×10^{14} molecules CO/cm^2 [2]. On the basis of the latter value we found that the maximum amount of CO formed upon heating Rh foil exposed to CO_2 at 110 K is ~ 8.0×10^{13} molecules/cm^2.

3.2.2. Adsorption of CO_2 at 300 K

CO_2 adsorption at this temperature produced an intense loss at 13.0 eV and a less intense one at 9.4 eV (fig. 6). The 13.0 eV loss appeared even at 3.6 L CO_2 exposure. It intensified with increasing CO_2 exposure. The intensity of the 9.4 eV loss increased only slightly with the CO_2 exposure. We further observed an enhancement of the intrinsic loss of Rh at 5.2 eV, at least relative to the 6.6 eV loss. Heating of the CO_2-exposed surface to higher temperatures led to the changes observed in fig. 6. The intensity of the 13.0 eV loss attenuated above 350 K, and was completely eliminated at 507 K. In contrast, the intensity of the 9.4 eV loss increases up to ~ 640 K and decreases only above this temperature.

For comparison, we determined the EEL spectrum of adsorbed CO on this Rh foil as a function of the CO exposure. The losses of the Rh underwent the same changes as in the case of CO_2 adsorption. A new loss appeared at 13.0 eV, even at very low CO exposure, 0.1 L, and enhancement of the 5.2 eV loss was also observed. *No loss feature appeared at 9.4 eV, however;* only an extremely slight shoulder could be detected at this energy, especially when the adsorbed layer was heated to 397 K.

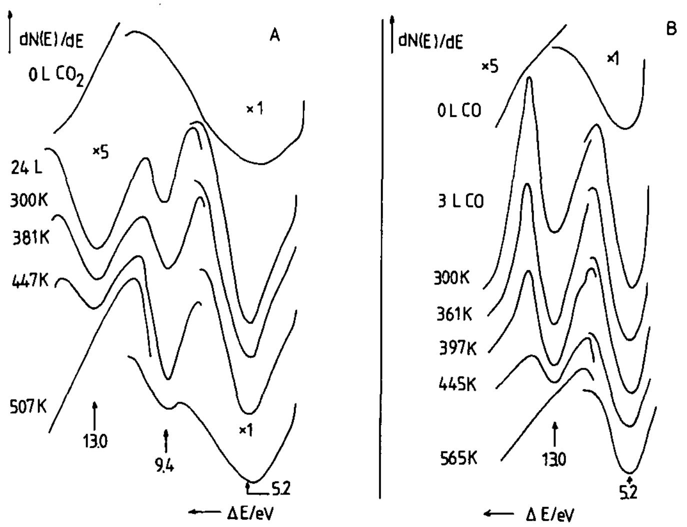

Fig. 6. Electron energy loss spectra taken after heating the Rh foil ($R_B \approx 0.04$) to different temperatures. The surface was exposed to 24 L CO_2 (A) or 3 L CO (B) at 300 K before heating.

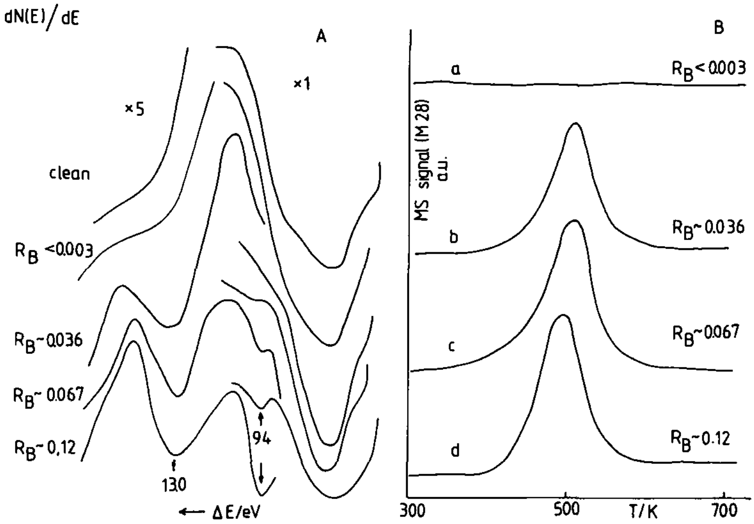

Fig. 7. (A) Electron energy loss spectra of Rh foils at different boron levels exposed to 24 L CO_2 at 300 K. (B) Thermal desorption spectra following 24 L CO_2 exposure on Rh foils at different boron levels at 300 K.

The thermal stability of the 13.0 eV loss (it is important to mention that this relates to the same intensities) was practically the same as after CO_2 adsorption (fig. 6).

Following the adsorption of CO_2 at 300 K, no desorption of CO_2 was demonstrated at any exposure. A significant desorption of CO was registered above 350–400 K (fig. 7B, curve b). It is an important observation that a weak oxygen signal was identified by AES after CO desorption.

All these results suggest, that in contrast to clean Rh(111), CO_2 does dissociate on Rh foil at 260–300 K. This is demonstrated by the thermal desorption measurements and by the appearance of an intense CO loss at 13 eV in the EEL spectrum.

One possible reason for the different behaviour of Rh(111) and polycrystalline Rh foil is that the surface of the latter contains several irregularities (kinks, steps and other defects) which may promote the dissociation of CO_2. While we can not exclude that these centres are preferential sites for this process, *we incline to think that the boron impurity of Rh foil plays a dominant role.*

A striking effect of boron impurity was already observed in the case of nitrogen desorption following the HNCO [18] and C_2N_2 adsorption [32] on the very same Rh foil. While the peak temperatures for the associative desorption of nitrogen were situated at 670 and 790 K in the case of clean Rh, no or only a very slight release of N_2 was found from boron contaminated Rh surfaces [18,32]. It appeared that atomic nitrogen forms a very stable species with boron (the dissociation energy of B–N is 389 kJ/mol) which scarcely releases nitrogen below 1200 K.

As oxygen also forms a very stable bond with boron (the dissociation energy of B–O is 787 kJ/mol), we may assume that the presence of boron in the surface of Rh foil promotes the dissociation of CO_2, i.e. the formation of B–O surface species is the driving force of this process.

The loss feature, observed at 9.4 eV in connection with the characteristic loss of CO formed in the CO_2 dissociation, is very probably due to the formation of B–O surface species. In the EEL spectrum of a clean Rh surface we never observed this loss after either CO or O_2 adsorption, although the O_2 dissociates easily on Rh at 300 K. However, we did observe the 9.4 eV loss when O_2 was adsorbed on a boron-contaminated Rh surface [33].

The preferential oxidation of impurity boron on Rh was recently demonstrated by Yates and coworkers [34]. The formation of a stable oxide-like species was detected using vibration EELS in the interaction of oxygen with low-level boron impurities on the surface of Rh(111). In contrast with the behaviour of chemisorbed oxygen on clean Rh, which begins desorbing at about 850 K, boron oxide at the surface is stable to heating above 1100 K in vacuum. Furthermore, Yates and coworkers [34] found that vibration EELS has a much higher sensitivity than AES in the detection of boron impurity, through its reaction with oxygen to form boron oxide with a high dynamic dipole. The present study may demonstrate that EELS in the electronic range is also sensitive in the identification of the boron impurity in the form of boron oxide.

3.2.3. *Variation of surface boron impurity concentration on Rh foil*

In order to see the effect of boron impurity more clearly in subsequent measurements the adsorption and dissociation of CO_2 were investigated at different boron impurity levels. An increase in the surface boron concentration was achieved by annealing the Rh foil at 850–1200 K. At the same time, a great effort was made to lower the boron concentration below the R_B value obtained for the sample used in the previous experiments.

After repeated extensive cleaning cycles, we succeeded in one exceptional case in lowering the B_{178}/Rh_{302} Auger intensity ratio to or below $R_B < 0.003$. The Auger spectrum of this sample is shown in fig. 1. On exposing this surface to 24 L CO_2 at 300 K, we found no indication of the loss characteristic of chemisorbed CO in the EEL spectrum.

The dissociation of CO_2 was observed first at $R_B = 0.029$–0.036, as indicated by the appearance of the loss at 13 eV. The 9.4 eV loss was detected at a somewhat higher level of boron impurity. Fig. 7 shows the EEL spectra of these Rh foils following 24 L CO_2 adsorption at 300 K.

The results of thermal desorption measurements were in agreement with the above picture. The amount of CO desorbed from the clean Rh foil ($R_B \leqslant 0.003$)

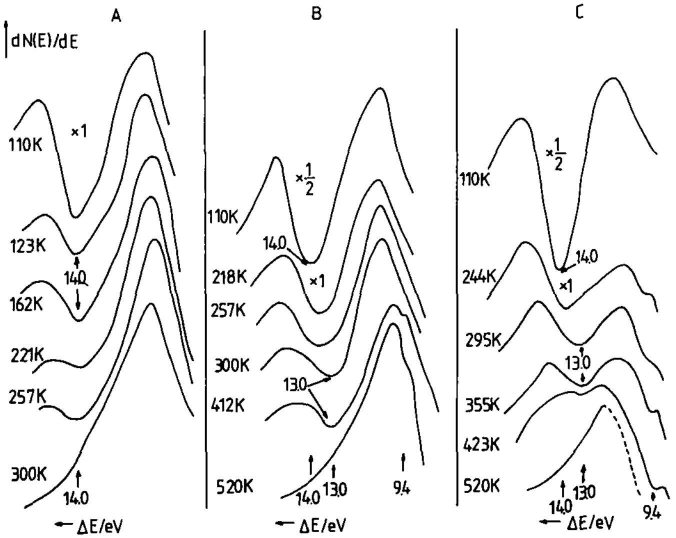

Fig. 8. Electron energy loss spectra of Rh foils taken after heating the samples exposed to 24 L CO_2 at 110 K to different temperatures: (A) $R_B \approx 0.003$; (B) $R_B \approx 0.029$; (C) $R_B \approx 0.1$.

was practically the same as obtained in blank experiments without CO_2 adsorption. With increase of the surface boron concentration, the amount of CO is slightly increased (fig. 7). The maximum amount of CO formed was 1.8×10^{14} molecules/cm^2.

Fig. 8 shows the EEL spectra of Rh foils at different boron concentration, following 24 L CO_2 exposure at 110 K, as a function of the sample temperature. While the spectra of a clean Rh foil ($R_B < 0.003$) displayed only the CO_2 loss at 14 eV, which disappeared above 260 K, in the EEL spectrum of Rh foil with higher boron concentration the development of the CO loss at around 13 eV can be clearly detected even at 244 K. The intensity of the CO loss, however, was less than that observed after CO_2 adsorption at 300 K. This is not surprising if we consider that the bulk of the adsorbed CO_2 desorbs before reaching the sufficiently high temperatures required for CO_2 dissociation.

In fig. 9 the results of more detailed TD measurements are presented for a sample with relatively high R_B value ($R_B \approx 0.08$).

3.3. Experiment on contaminated Rh(111)

The data presented in the previous section clearly show the basic difference between Rh(111) and Rh foil. In the latter case a variation in the pretreatment temperature resulted in a change in the extent of CO_2 dissociation.

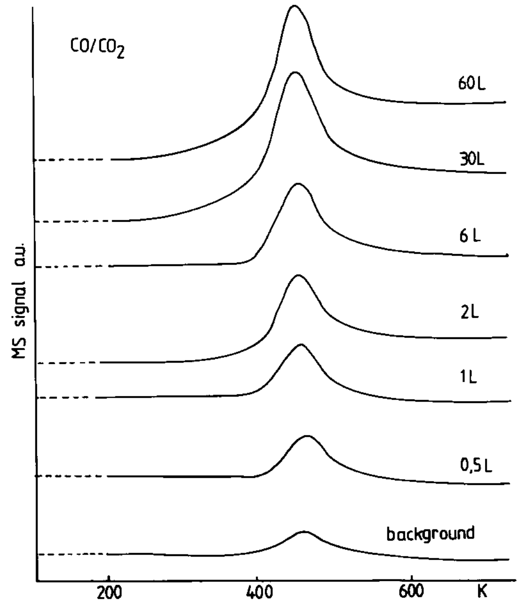

Fig. 9. Thermal desorption spectra following CO_2 adsorption at 110 K on Rh foil ($R_B \approx 0.08$).

As the density of various defects on the polycrystalline Rh foil is obviously much higher than on the Rh(111) face, one could argue that the higher reactivity of Rh foil can be ascribed to the higher density of surface defects, which may vary with the pretreatment of the sample. For this reason it seemed more than necessary to detect CO_2 dissociation on Rh(111) contaminated with boron.

Unfortunately, our Rh(111) sample has previously been used in a number of studies and the repeated extensive cleaning has led to boron depletion from the bulk, so that its segregation to the surface was limited.

After several unsuccessful attempts, a well-detectable Auger B signal was once obtained when the clean Rh(111) was kept at 1270 K for 2–3 min (fig. 10). The R_B value in this case was about 0.008. As can be seen in the Auger spectrum of this sample, this treatment of Rh(111) slightly increased the intensities of the Auger signals of other impurities, such as Si, P and C. Adsorption of 50 L CO_2 at background pressure of 3×10^{-7} on this sample at 300 K produced chemisorbed CO which desorbed at ~ 500 K (fig. 10). The amount of CO calculated was approximately 4.6×10^{13} molecules CO/cm^2. In this calculation the saturation CO value (1.2×10^{15} molecules/cm^2) given for Rh(111) was taken into account [30,31]. This result clearly demonstrates that CO_2 does dissociate on Rh(111) contaminated with boron.

3.4. Effects of hydrogen

In the study of CO_2 adsorption on supported Rh at 300–423 K, we observed only a very weak band at 2040 cm^{-1}, due to chemisorbed CO, indicative of the

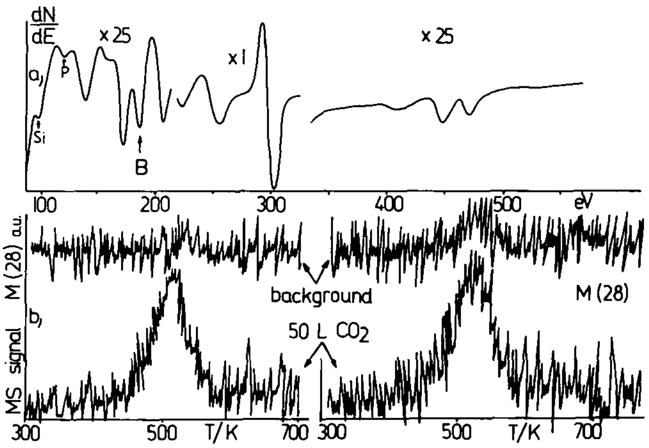

Fig. 10. Auger electron spectrum of the Rh(111) surface with some boron contamination (a), and thermal desorption spectra of CO following 50 L CO_2 adsorption on this sample at 300 K (b).

dissociation of CO_2 [10–12]. It appeared that the preparation of the catalyst, the dispersity of the Rh and the nature of the support all influence this process [10]. Our attempts to increase the intensities of the CO band for quantitative studies of these factors have remained unsuccessful so far. We found, however, that the presence of hydrogen greatly promoted the dissociation of CO_2 and an intense absorption band developed at 2030–2045 cm^{-1} [10–12]. At the same time, adsorbed formate ions also formed in the surface interaction, which was assumed to occur on the support.

As the results plotted in fig. 11 show, the presence of hydrogen promotes the dissociation of CO_2 on clean Rh(111) and on boron-contaminated Rh surfaces, too. This is exhibited by the larger quantity of CO desorbed at around 500 K, and by the enhanced intensity of the 13 eV loss due to adsorbed CO. This can be observed either following $H_2 + CO_2$ coadsorption at 200 K and heating of the co-adsorbed layer to higher temperatures, or after co-adsorption at 300 K. Interestingly, on boron-contaminated Rh the enhanced intensity of the CO loss at 13 eV was not accompanied by an increase in the loss at 9.4 eV. This indicates that the dissociation of CO_2 promoted by hydrogen occurs on the Rh, without any involvement of the impurity boron.

EELS studies of the surface gave no indication of the formation of formate species, which suggests that adsorbed CO and formate species are produced in two separate processes on supported Rh.

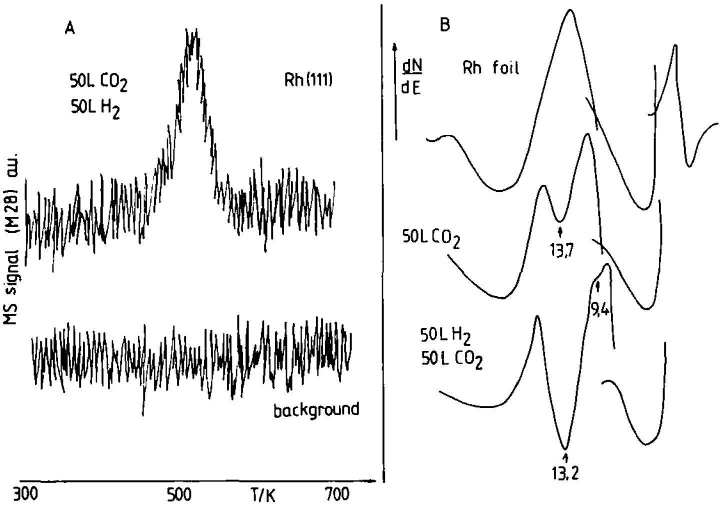

Fig. 11. Effects of hydrogen on the formation of CO from CO_2 on a clean Rh(111) and boron-contaminated Rh foil: (A) TD spetra on a clean Rh(111). (B) EEL spectra on Rh foil ($R_B \approx 0.08$). The adsorption of gases was performed at 300 K.

The results of this study illustrated the importance of surface contaminants in the determination of the reactivity of metal surfaces. Fortunately, AES provides us with a tool for the detection of surface impurity. However, there are a number of cases when impurity effects can go undetected by AES [34–38] or when AES does not have sufficient sensitivity. A good example of the phenomenon is the difficulty of detection of boron oxide on a Rh surface [34].

Furthermore, as we experienced in this study, the distribution of impurities segregated from the bulk metal is far from homogeneous on the surface; as a result, certain parts of the surface appear "clean", and others "contaminated".

4. Conclusions

(1) No dissociation of CO_2 was detected by EELS in the electronic range or by TD measurements on clean Rh(111) and Rh foil surfaces at 110–300 K up to 180 L CO_2 exposure and at a pressure of 3×10^{-7} Torr.

(2) The presence of boron impurity on the Rh surface, however, exerted a dramatic influence and caused the dissociation of CO_2 on both surfaces. Under the experimental conditions applied, we obtained 4.6×10^{13} molecules CO/cm^2 on the Rh(111), and $(0.5–1.8) \times 10^{14}$ molecules CO/cm^2 on the Rh foil, depending on the boron impurity level.

(3) The presence of hydrogen also facilitates the CO_2 dissociation.

(4) As regards the dispute concerning CO_2 dissociation on Rh, we do not claim that the results of the present study settle this question, as there are certainly factors which suppress and others which facilitate the dissociation of CO_2 on Rh. It appears that boron, a common impurity in Rh, greatly promotes this process.

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