

Review

The bonding, structure and reactions of CO₂ adsorbed on clean and promoted metal surfaces

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Abstract

The characteristics of the adsorption and reactions of CO₂ on Rh, Pd, Pt, Ni, Fe, Cu, Re, Al, Mg and Ag metals are discussed with particular emphasis on the activation of the CO₂ molecule. Strong spectroscopic evidence is presented for the formation of negatively charged CO₂⁻, which – depending on the nature of the metal – may dissociate into CO and O, or transform into CO₃ + CO. The presence of surface adatoms dramatically influences the adsorption and reactivity of CO₂. Alkali adatoms increase the binding energy of adsorbed CO₂, promote the dissociation and/or the transformation of CO₂ into CO₃ + O. In the presence of preadsorbed oxygen the formation of carbonate of different structures predominates.

Introduction

An increasing number of investigations have been concerned with homogeneous and heterogeneous catalytic transformations of CO₂ into more valuable compounds [1–3] such as carbon monoxide, methanol, formate, oxalate, organic acids, methane and hydrocarbons. An important observation in this field is that CO₂ is possibly the main source of carbon in the synthesis of methanol from H₂ + CO + CO₂ mixtures [4, 5]. Carbon dioxide can also be converted into useful forms of organic compounds by coupling with an organic substrate.

Any reaction of CO₂ requires its activation by a catalyst. The chemisorption and reactions of CO₂ on oxide surfaces are well-studied processes; the structure and bonding of adsorbed CO₂ and of the various carbonates formed have been established. Much less information is available on the interaction of CO₂ with metal surfaces. Several modern tools of surface science have recently been applied to the study of the adsorption of CO₂ on metal single crystals, and attention has also been paid to evaluation of the effects of surface adatoms or promoters in the activation of CO₂.

This article surveys the present state of knowledge concerning the bonding, structure and reactions of CO₂ adsorbed on clean and promoted metal surfaces.

Rhodium

Clean surface

The interaction of CO₂ and Rh metal has been the subject of a number of publications, because of the controversy concerning the nature of the interaction and particularly the dissociation of CO₂ on clean Rh surfaces under UHV conditions.

In the early studies, the adsorption of CO₂ was claimed to be weak and associative on Rh films [6], polycrystalline Rh [7] and alumina-supported Rh [8]. Somorjai *et al.* [9–13], however, found that CO₂ does chemisorb and dissociate on Rh foil and on several faces of Rh single crystals (Rh(111), (100) and (331)) at 300 K, but this requires a higher CO₂ exposure. They detected the CO formed by means of LEED, EELS (vibration) and thermal desorption measurements. The calculations of Weinberg [14], based on the available thermodynamic and kinetic information, showed that the probability of dissociative chemisorption of CO₂ at low pressure ($\sim 10^{-6}$ torr) and at room temperature is of order of 10^{-15} , *i.e.* some 14 orders of magnitude lower than reported previously [9–13]. The rate of dissociation could be significant only above 300 K and a CO₂ pressure of approximately 1 atm. The probability of the dissociation of CO₂ on Rh(111) was also calculated by Goodman *et al.* [15] from an analysis of the kinetic data obtained for the H₂ + CO₂ reaction, and a value of 10^{-11} was given for 300 K, which is consistent with the value of Weinberg. Dubois and Somorjai [16] criticized the conclusions of Weinberg, stating that they were “based on oversimplified calculation using incorrect kinetic and thermodynamic parameters”. They argued that the failure to observe the dissociation of CO₂ may simply be an artifact of the adsorption conditions or of sample preparation.

As the dissociation of CO₂ has been experimentally observed [10–13] several factors causing or preventing the dissociation can be considered, such as the presence of adsorbed oxygen (which may inhibit the dissociation), the presence of undetected impurities (which may promote the dissociation) and the surface irregularities (which could vary from sample to sample and could function as active sites for the CO₂ reaction).

Experiments carried out under carefully controlled conditions on polycrystalline Rh foil and Rh(111) single crystal surfaces did not provide evidence of a strong dissociative adsorption of CO₂ [17, 18]. The adsorption of CO₂ was found to be weak and nondissociative on both surfaces; the sticking coefficient was calculated to be as low as 0.01 at 100–110 K. At low CO₂ exposures, the desorption of CO₂ was characterized by a peak temperature of $T_p = 244$ K, which decreased to 177 K with increasing CO₂ exposure. An activation energy of 61.2 kJ mol⁻¹ was calculated for the desorption of CO₂. Following adsorption at lower temperature, 95 K, a well-resolved desorption peak also developed at 115 K; the activation energy for desorption was 28 kJ mol⁻¹ [19]. Subsequent TDS and EELS measurements revealed no indication of the formation of adsorbed CO, which is strongly bonded to Rh and can easily be detected by both methods. When the

adsorption of CO₂ (180 L) at 3×10^{-7} torr was performed at 300 K, no observable changes were found in the LEED, AES, EELS or TDS.

However, when boron impurity was allowed to segregate onto the Rh surface, strong evidence was obtained of the dissociation of CO₂ and the formation of adsorbed CO (see next section). As boron is a common impurity in Rh, and is not easy to detect by AES, it seemed highly probable that the dissociation of CO₂ observed in previous cases was due to the presence of boron impurity.

The interaction of CO₂ with a Rh tip has also been investigated by field emission microscopy (FEM) [20]. A value of 60 kJ mol⁻¹ was obtained for the activation energy of desorption of CO₂, which is in excellent agreement with the value determined on the Rh(111) face [17].

The FEM pattern indicated that CO₂ adsorption is markedly crystal face-specific. An analysis of the FEM pattern yielded no evidence of the dissociation of CO₂ on the (111), (100) surfaces. However, significant changes occurred above 210 K on the (100) surface with (111) steps, such as (533) and (711): these regions became dark, which was attributed to the dissociation of CO₂. The FEM picture resembled that given by a surface 50% covered with CO. No indication of the presence of adsorbed oxygen was obtained, however, which we consider to be an important point in further discussion. In the interpretation of the results, Hendrickx *et al.* [20] assumed that CO₂ is adsorbed in a monodentate structure on top of a Rh atom, on the (111) terrace of a stepped surface near a (111)-like step, which may facilitate the dissociation of CO₂.

These results point to the important role of the heterogeneity of the surface. The number of these sites, however, must be very limited, as Hendrickx *et al.* [20] failed to detect a product of the dissociation, *e.g.* CO, by TDS measurements. Since FEM is a very sensitive tool for the detection of a small amount of adsorption, we may speculate whether the changes observed in the FEM pattern were caused by the adsorption of CO from the background. This is not absolutely impossible, as the FEM pattern following CO₂ adsorption was the same as observed for adsorbed CO. This idea is apparently supported by FEM patterns which provided no indication of the presence of adsorbed oxygen either, which likewise can easily be detected by FEM. This feature was explained by oxygen diffusion into the bulk of the Rh. However, this interpretation is in disagreement with the recent findings and considerations of Fischer *et al.* [21], who discounted the diffusion of oxygen into Rh even at higher temperatures, and explained the phenomenon leading to this assumption in the former paper [22] in terms of the presence of near-surface carbon and CO and their reactions with oxygen.

Although it cannot be denied that surface heterogeneity may play an important role in the dissociation of adsorbed molecules on clean metal surfaces, the author of the present paper does not agree with the conclusion of Hendrickx *et al.* that this finding would explain the controversy concerning the dissociation of CO₂. The dissociation of CO₂ has been observed by the Berkeley group on polycrystalline Rh and on various perfect faces of Rh

single crystals [10–13], whereas both polycrystalline Rh and Rh(111) in a clean state were found to be inactive for this process in our measurements [17–19]. Further investigations on carefully cleaned stepped surfaces of Rh single crystals would be useful.

The weak interaction between CO₂ and clean Rh surfaces has recently been confirmed by photoelectron spectroscopy [23]. The adsorption of CO₂ on clean Rh(111) produced three new lines at 6.6, 10.7 and 12.1 eV in the UP spectrum. The first of these is due to the 1π g orbital, while the emissions at 10.7 and 12.1 eV correspond to unresolved 1π n/3 σ u and 4 σ g orbitals. The differences in binding energy 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 CO₂ [24], which supports the view that CO₂ adsorbs weakly and molecularly on Rh(111) at 90–100 K, without undergoing a strong distortion of its molecular electronic state. A similar conclusion was drawn from an analysis of the XPS spectrum of adsorbed CO₂. 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 CO₂, $\Delta E_g = 243.6$ eV.

When the adsorbed layer was heated to 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 adsorbed CO or O.

Effects of surface adatoms

The first detailed investigations on the effects of additives and impurities were performed on B-contaminated Rh foil [17, 18]. It was observed that B, a common impurity in Rh, can segregate to the surface, significantly changing the surface reactivity. Even if the surface was carefully cleaned and AES initially showed no impurity on the surface, B could accumulate on the surface during heating of the sample to ~650–700 K.

Following the adsorption of CO₂ on B-contaminated Rh foil, a clearly detectable amount of CO was produced, which was not the case for the B-free surface. At the same time, a new loss feature was observed at 9.4 eV in the ELS. This was a very stable loss and could be eliminated only above 950 K. This loss was never detected following oxygen adsorption on carefully cleaned B-free Rh surfaces. The 9.4 eV loss was attributed to the oxygen bonded to B impurity. This assignment was confirmed by a detailed study of oxygen adsorption on the B-containing surface, where an intense loss at 9.4 eV appeared even at 159 K and was eliminated again only above 950 K [25]. The maximum amount of CO formed on the Rh foil exposed to CO₂ at 110 K was 8.0×10^{13} molecules cm⁻².

The dissociation of CO₂ was also established on Rh(111) contaminated with B [17]. The maximum amount of CO formed was approximately 4.6×10^{13} molecules cm⁻².

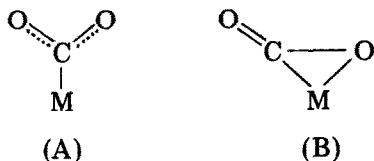
As concerns the *effect of alkali metal additives* on the bonding of CO₂, the first study was made on the Rh(111) [19] and Pd(100) [26] surfaces. Pre-adsorbed K exerted a dramatic influence on the adsorption and reactivity of CO₂ on Rh(111). It (i) increased the rate of adsorption of CO₂, (ii) induced

the formation of strongly bonded CO_2 species, and (iii) initiated the dissociation of CO_2 . At lower K coverages, new adsorption states were formed, which desorbed at temperatures between 343 and 500 K. At around monolayer K coverage, a very stable form of CO_2 was produced, with $T_p=724$ K. The amount of CO gradually increased with increasing K coverage and at the same time the desorption temperature of CO also increased. At monolayer coverage, CO desorbed with $T_p=704$ K.

An interesting feature of the interaction of CO_2 with K-dosed Rh(111) was that not only was the binding energy of CO_2 increased, but the K was also stabilized by adsorbed CO_2 . In the presence of adsorbed CO_2 the low-temperature desorption of K ceased and the desorption occurred in a narrow peak at the same temperature as that at which the highly stabilized CO and CO_2 desorbed.

The adsorption of CO_2 on a K-dosed surface resulted in an increase in the work function. This increase depended on θ_K ; it was 1.06 eV at $\theta_K=0.07$, when K exhibits mainly an ionic character, and it was 1.8 eV at monolayer K coverage, when the K is mainly metallic. CO_2 adsorption produced new losses at 15.0; 11.9 and 8.1 eV, which were stable up to 609 K (8.1 and 11.9 eV losses) and 690 K (15.6 eV loss), respectively.

The development of new losses in the EEL spectra and the work function changes suggested an electronic interaction between CO_2 and the K-dosed surface, a large negative charge on the chemisorbed CO_2 and the possible formation of a partially negatively charged species, $\text{CO}_2^{\delta-}$. These features were attributed to an enhanced back-donation of an electron from the K-dosed Rh into an empty π orbital of CO_2 . As a result of the enhanced electron donation, the binding energy of CO_2 to the surface is increased, as exhibited by the higher desorption temperature. The extended electron donation can cause a basic change in the bonding and structure of the adsorbed CO_2 . Whereas in the case of weak CO_2 adsorption it was assumed that CO_2 is bonded via an oxygen lone pair, with the molecular bond vertical, on K-promoted Rh the formation of a metal-carbon bond in the form of a monodentate (A) or bidentate (B) structure has been proposed:



In the latter form (B), an elongation of the interacting C—O bond is expected with respect to the non-coordinated bond, which may lead to an easier dissociation of CO_2 .

At higher K coverages, when K exhibits a metallic character, a direct interaction between CO_2 and K was assumed:

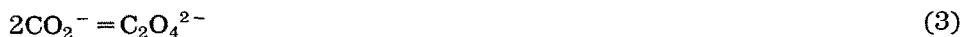


which also leads to formation of the CO_2^- anion radical.

Furthermore, it was assumed that CO_2^- is stabilized by forming a dimer with neutral CO_2 :



or dimerizes into oxalate



Both species can be transformed into carbonate-like species and $\text{CO}_{(a)}$ at higher temperature. The CO_2 evolution above 700 K ($T_p = 720$ K) and the coincident thermal desorption with K at that temperature were attributed to the decomposition of carbonate accelerated by contact with Rh. This route of transformation of CO_2^- is based on the findings of Kafafi *et al.* [27] in the study of the interaction of CO_2 with alkali metals.

The results of UPS and XPS studies confirmed the strong interaction between CO_2 and K-dosed Rh, and the formation of the CO_2^- species at and above 131 K [23]. Let us first consider the results obtained at higher K coverage, where the photo-emission peaks are more intense due to the higher CO_2 concentration. In this case, the He II UP spectrum exhibits three emissions, at 5.2, 8.7 and 10.9 eV. These peaks are distinctly different from those observed following CO_2 adsorption on a clean Rh surface, and agree well with those derived theoretically [28] and established experimentally for bent CO_2^- bonded to a clean Ni(110) surface [29]. As no signals due to adsorbed CO and O were detected in the photoemission spectra at this temperature, the above features were attributed to formation of the undissociated CO_2^- radical anion. The observed peaks were 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 at lower energies, in the XPS at 290.5 and 532.8 eV respectively, as compared to neutral CO_2 also indicates that the electron density in the CO_2 molecule is increased, which further supports this conclusion.

The orbitals of the bent CO_2^- were seen in the UPS and XPS up to 238 K, which signifies appreciable stability on this surface. CO_2^- species may exist even at higher temperatures: the detection is possibly hindered by the low intensities and by the development of other overlapping photoemission peaks.

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

Accordingly, it was concluded that the primary source of the formation of CO was not the dissociation of negatively charged CO_2^- . As the peaks of adsorbed CO and a carbonate-like species developed almost simultaneously, it seemed appropriate that they were formed in the same surface process. This could be the disproportionation of the CO_2^- radical anion:



An alternative pathway, via formation and decomposition of oxalate to carbonate and CO:



still awaits spectroscopic confirmation.

In the case of low K coverage, $\theta_{\text{K}}=0.1$, both UPS and XPS signals suggested that the activated CO_2 dissociates completely to CO and O even at 131–179 K:



as there was no spectral indication of the formation of any other species during heating of the coadsorbed layer to high temperature.

Palladium

Clean surface

The first observation concerning the nature of the adsorption of CO_2 on Pd under UHV conditions came from a study of the oxidation of CO on several Pd single crystal faces, which indicated that the adsorption of CO_2 is weak and non-dissociative [30, 31]. This feature was supported by the more detailed studies of Solymosi and Berkó [26, 32]. 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 AES 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, where a significant uptake of CO_2 was observed. However, this CO_2 desorbed at rather low temperature, $T_{\text{p}}=135$ K, with an activation energy of 34 kJ mol⁻¹.

A similar weak interaction was observed for the Pd(111) surface [33, 34].

Effect of surface adatoms

Potassium adatoms exerted a qualitatively similar influence on the adsorption of CO_2 as in the case of Rh(111), but a number of differences were exhibited in the details. The presence of K gradually 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 increased with increasing preadsorbed K. At $\theta_{\text{K}}=0.42$, it was larger by a factor of 50 as compared to the clean surface at the same exposure.

The formation of CO was first observed at $\theta_{\text{K}}=0.21$, with a peak temperature of 573 K. At $\theta_{\text{K}}=0.36$, another CO desorption state emerged at $T_{\text{p}}=663$ K.

The amount of CO formed increased considerably with the surface concentration of K, accompanied by a shift to higher peak temperatures.

Similarly to Rh(111), K is greatly stabilized in the adsorbed layer. This is exhibited above $\theta_K=0.3$, when the more stable state of CO_2 developed: desorption of K observed in the lower temperature range ceased and K desorbed in a narrow peak with $T_p=695$ K. This corresponds to a binding energy of 175 kJ mol^{-1} .

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 K significantly decreased the work function of Pd, *e.g.* by 3.38 eV at $\theta_K=0.32$. When CO_2 was adsorbed on a K-dosed surface, it led to a work function increase of 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. These changes indicate a substantial charge transfer from the K-dosed Pd to an empty π orbital of CO_2 .

The interaction of CO_2 with the K+Pd(111) surface has been described in a manner similar to the case of K-promoted Rh(111). The key process is the formation of the CO_2^- radical anion promoted by K.

It is interesting that a marked influence of K on the adsorption of CO_2 was not found by Matsushima [33] on the Pd(111) surface. Moreover, when the Pd(111) was fully covered by K, this surface interacted with CO_2 to a lesser extent than did K-free Pd. However, Matsushima detected considerable adsorption and stabilization of CO_2 after oxygen treatment of the K-dosed Pd surface. In this case, a single peak above 800 K ($T_p=800\text{--}920$ K) was found following CO_2 adsorption at 100 K. It was concluded that the high-temperature form of CO_2 arises from the decomposition of carbonate formed from CO_2 and K_2O . The scrambling of the oxygen isotope in this form supports this assignment, since the three oxygen atoms in the carbonate are in equivalent chemical environments.

The stabilizing effect of alkali metal adatoms on the adsorption of CO_2 on the Pd(100) surface was also observed by Egawa *et al.* [35], who deposited Na on the Pd surface. The Na adatoms significantly increased the binding energy of CO_2 , which desorbed in three peaks, with $T_p=380, 550$ and 650 K, at monolayer Na. In the case of a clean surface, CO_2 desorbed at 200 K. On an oxygen-covered surface, the peak at 550 K was missing: this site was probably already blocked by the pre-adsorbed oxygen. The oxygen isotope distribution in CO_2 desorbed at 650 K after C^{16}O_2 adsorption on the ^{18}O pre-adsorbed surface showed that random mixing occurred between adsorbed oxygen and $\text{CO}_{2(a)}$, which suggested that the highest peak is derived from the decomposition of sodium carbonate.

Qualitatively similar features for the effect of Na were observed on the Pd(111) surface [34]. At low Na precoverages ($\theta_{\text{Na}} \approx 0.25$) CO_2 adsorbed as linear, electronically undistorted or only slightly distorted molecules, with the molecular axis oriented parallel to the surface plane. The CO_2 molecules in this layer dissociated into CO and oxygen when the surface was heated from 85 K to 120 K. The CO molecules appeared to be bound to the Pd surface. From the angular dependence of the photoelectron spectra, the authors found no indication of an intrinsic dissociation precursor such as

CO_2^- on Pd(111). The possible reason is the narrow temperature range of existence of this species, as the dissociation of CO_2 certainly involves the activation of CO_2 and the transitory formation of the CO_2^- radical anion.

Completely different adsorption and reaction behavior was found at high Na precoverage ($\theta_{\text{Na}}=2.0$). Even at the lowest temperature accessible, *i.e.* $T=85$ K, CO_2 reacts with the surface to form a species identified as carbonate. Together with the carbonate, electronically undisturbed CO_2 physisorbs at low enough temperature. Upon heating of the surface, the amount of adsorbed carbonate increased and CO_2 was desorbed.

Whether this carbonate is formed via the disproportionation of CO_2 or possibly via the reaction of CO_2 with oxygen contamination was not established with certainty, but the fact that more CO_3 forms on increasing the temperature was considered an indication of the disproportionation reaction. The non-detection of adsorbed CO formed in the disproportionation of the CO_2^- anion was explained by the negligible adsorption of CO on the alkali metal layer.

Platinum

Clean surface

As concern the adsorption of CO_2 on clean Pt surface, Norton and Richards [36, 37] were able to measure the X-ray photoelectron spectrum of adsorbed CO_2 only at 77 K. They concluded that CO_2 is only physisorbed on a clean Pt film and the estimated heat of adsorption was 10 kcal mol^{-1} . In harmony with this conclusion, exposure of a clean Pt(111) surface to CO_2 up to 40 L at a pressure of 1×10^{-9} torr at 110–300 K produced no observable changes in AES and HREELS of Pt [38, 39].

Effect of surface adatoms

The interaction of CO_2 with a K-dosed Pt(111) surface has been studied by high-resolution electron energy loss (HREELS), and TD spectroscopy [38, 39]. Deposition of potassium on a clean Pt(111) surface produced only one loss at 190 cm^{-1} which was attributed to a K-substrate vibration. Adsorption of CO_2 on this surface at 112 K gave additional losses at 441, 820, 1340 and 1600 cm^{-1} .

An increase in the CO_2 exposure intensified all the losses, particularly at 1600 cm^{-1} , but their positions remained in the range of accuracy ($\pm 20 \text{ cm}^{-1}$) of the determination of peak positions. This coverage-independent behavior may be an indication of a direct interaction between CO_2 and K. The following losses were tentatively attributed to the asymmetric stretching ($1600 \pm 20 \text{ cm}^{-1}$), symmetric stretching ($1340 \pm 20 \text{ cm}^{-1}$) and the bending mode ($820 \pm 20 \text{ cm}^{-1}$) of a bent CO_2^- species formed by the direct interaction of metallic potassium and CO_2 which may be stabilized in the form of a dimer or oxalate (eqns. 2, 3).

At higher CO₂ exposures, loss features at 660 and 2350 cm⁻¹ were also observed, which were assigned to the bending and asymmetric stretching modes of weakly adsorbed and only slightly perturbed CO₂.

Upon heating the saturated layer, the first spectral changes occurred at 200 K. This consisted of (i) complete elimination of peaks assigned to weakly adsorbed CO₂ (660 and 2340–2350 cm⁻¹), (ii) significant attenuation of the loss at 1340 cm⁻¹, (iii) the formation of a new intense feature at 1440 cm⁻¹, and (iv) an intensification of the loss at 1600 cm⁻¹. The weak shoulder at 1340 cm⁻¹ vanished at slightly above 200 K, and the losses at 1440 and 1600 cm⁻¹ intensified further. It is important to point out that the intensities of 1440 and 1660 cm⁻¹ losses were ~30% higher than those at 1340 and 1600 cm⁻¹ measured at 150 K, which makes it very likely that both losses belong to new surface species. In addition, several very weak losses were resolved in the low-frequency region at 780, 870 and 1020 cm⁻¹. All these spectral changes was attributed to the occurrence of reaction (4). The loss at 1440 cm⁻¹ is assigned to carbonate and the feature at 1600 cm⁻¹ to the asymmetric stretch of CO perturbed by potassium.

The above description is supported by the high stability of these spectral features: between 200 and 650 K, HREEL spectra indicated very little alteration in the co-adsorbed layer. As one cannot expect such a high thermal stability from either CO₂⁻ or C₂O₄²⁻ anion, an alternative, carbonate, is required. Attenuation of the intense loss at 1600 cm⁻¹ starts above at 650 K, and it is completely eliminated around 710 and 870 cm⁻¹. In this temperature range the majority of potassium is also desorbed, generating free Pt sites on which CO may adsorb from the background. A significant attenuation of the loss at 1440 cm⁻¹ occurred between 680 and 750 K, and it was completely absent above 800 K. However, even after this temperature treatment, very weak losses remained at 190, 441 and 1000 cm⁻¹.

Supplementary TPD measurements revealed that CO ($T_p = 640$ K) and CO₂ ($T_p = 674$ and 790 K) desorbed in nearly equal amounts. The characteristic peak temperature ($T_p = 640$ K) agrees well with the peak temperatures of CO desorption from 1 monolayer of K on Pt(111) [40]. The evolution of CO₂ points to the decomposition of carbonate-like species.



Nickel

The most detailed picture concerning the nature of the adsorption of CO₂ and the structure of the adsorbed CO₂ is available for Ni surfaces. Angle-resolved photoemission, high-resolution electron spectroscopy and molecular beam and near edge X-ray adsorption fine structure (NEXAFS) and diffuse LEED methods were used [41–50].

The first observation regarding the nature of the adsorption on single crystal surface was made by Madix *et al.* [41, 42], who observed that CO₂

adsorbed dissociatively on the Ni(110) and Ni(100) surfaces. A 100 L exposure of CO_2 at 150 K resulted in 4×10^{13} molecule $\text{CO}_2 \text{ cm}^{-2}$ desorbed and 2.1×10^{14} molecule CO cm^{-2} desorbed. No CO_2 was observed to desorb from Ni(100) after 100 L exposure at 300 K, but CO was detected at 420 K.

The dynamics of the dissociative adsorption of CO_2 on Ni(100) was investigated by means of a supersonic molecular beam technique [43].

From a detailed analysis of the angle-resolved photoelectron spectra of adsorbed CO_2 on the Ni(100) surface, Bartos *et al.* [44] came to the conclusion that a bent CO_2 species is formed on this Ni surface at 140 K, this being the precursor of the dissociation. The bent CO_2^- anion is produced by the transfer of electronic charge from the metal to the CO_2 molecule. The additional electronic charge can be accommodated by the closed-shell CO_2 molecule only through the breaking of one of the two C–O double bonds and the formation of an additional oxygen lone pair. This bond-breaking process opens space on the carbon atom for the acceptance of the extra charge. The presence of charge transfer to the adsorbate is corroborated by the strong work function increase observed at 140 K, where much of the coadsorbed CO_2 was desorbed.

Possible coordination sites with mirror plane symmetry are shown in Fig. 1. While the sites on the left and right hand sides of Fig. 1 have C_{2v} symmetry, that shown in the middle has C_s symmetry. Analysis of photoelectron spectra suggested that the adsorbed CO_2 has C_{2v} symmetry. This interpretation and assignment were corroborated by subsequent EELS experiments [44]. When CO_2 was adsorbed at 140 K, dominant peaks were observed at 750/745 cm^{-1} . These values are compatible with the frequencies of the bending and the symmetric stretching modes of a bent CO_2 species. In the specular direction, no energy loss was observed between 1600 and 1700 cm^{-1} . In off-specular scattering geometry, however, a peak appears at 1620 cm^{-1} , which was assigned to an asymmetric stretching mode of a bent CO_2 species on the Ni(110) surface. The additional losses observed at 670, 1390 and 2350 cm^{-1} originate from the vibrational excitation of linear, undisturbed CO_2 . In agreement with the conclusions drawn from the photoemission results, this shows the coexistence of linear undisturbed CO_2 and a bent CO_2 species at a surface temperature of 140 K, similarly to that found for K-dosed Rh(111) and Pd(100) surfaces [19, 23, 32].

The absence of an asymmetric stretching loss in the specular direction, together with some symmetry considerations, led the authors to conclude

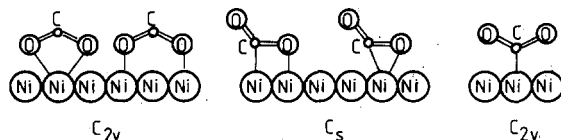


Fig. 1. Possible coordination sites of CO_2 together with the corresponding point group symmetries [44].

that the molecule is coordinated in a C_{2v} coordination site. For differentiation between the two possible C_{2v} coordination modes, the assignment of the 410 cm^{-1} loss to the Ni–O stretching vibration helped: this suggested that a C_{2v} coordination site with direct oxygen coordination is more likely than a carbon-coordinated site.

Many of these features were confirmed by the EELS study of Lindner *et al.* [47]. The bent species was found to be stable up to 220 K: at this temperature, dissociation into CO and O occurred.

Direct evidence as to the bonding geometry of CO_2 adsorbed on the Ni(110) face came from NEXAFS [48] and diffuse LEED studies [48, 49].

An assignment of the spectral features on NEXAFS was made by consideration of the M.O. scheme and by comparison with the EELS for free CO_2 . From the polarization dependence of the NEXAFS, which is in agreement with previous ARUPS and EELS measurements [44, 47], it was concluded that the molecular plane of the bent chemisorbed species is most probably oriented perpendicular to the surface plane, but there is no preferential orientation of molecular plane along the $\langle 110 \rangle$ or $\langle 100 \rangle$ surface azimuth. The latter observation is compatible with two different species oriented in each azimuth. In addition, there is a time dependence of the relative intensity of the resonance, which was interpreted as a preferential re-alignment along $\langle 110 \rangle$ under the influence of the X-ray beam. A high-resolution experiment at the carbon edge revealed that the width of the π resonance due to physisorbed CO_2 is much smaller than that of the chemisorbed species.

The polarization dependence of the physisorbed species suggests a lying-down configuration. Diffuse LEED structure analysis of adsorbed CO_2 supports the assumption that a bent CO_2^- species is adsorbed on top of the Ni rows in the (110) direction, which favors direct oxygen metal bonding over pure carbon coordination [49]. In a second study, no clear preferential azimuthal orientation was found [48]. R-factor analysis in diffuse LEED favored the coexistence of molecules aligned along each principal azimuth. Equal numbers of them on top sites appeared more likely than on hollow, long-bridge or short-bridge sites.

Although the chemisorbed CO_2 is now undoubtedly better characterized, the O–C–O angle is still unknown and it is not clear whether the molecule is bent upwards or downwards. By analogy with the surface formate species, the latter geometry is expected [48].

Effects of surface adatoms

The effects of pre-adsorbed oxygen on the adsorption and reactivity of CO_2 on Ni(110) have been investigated by photoelectron spectroscopy [44]. It was concluded that CO_2 at 85 K interacts at least weakly with adsorbed oxygen. Angle-resolved photoemission spectra suggested a molecular geometry similar to the geometry on the oxygen-free surface, and the CO_2 molecule is oriented parallel or almost ($\pm 20^\circ$) parallel to the Ni(111) surface.

EELS studies showed that adsorbed CO_2 is much more stable on oxygen-dosed surface than on the clean surface. It was an important observation

that a bent CO_2^- molecule was not detected on the oxygen-dosed surface and no indication of the presence of adsorbed CO was found either.

When the sample was heated to 170 K, a new species was formed on the surface, which was assumed to be bidentate carbonate.

The reaction between adsorbed O and CO_2 was investigated on Ni(100) by TDS and XPS, and the formation of surface carbonate was detected [50]. The C(1s) and binding energies for $\text{CO}_3/\text{Ni}(100)$ species were 283.0 and 531.2 eV, respectively, *i.e.* very close to those for bulk NiCO_3 . Furthermore, it was concluded that reaction occurs only between adsorbed CO_2 and an activated form of oxygen on the surface. It does not take place with the stable ordered $\text{O}_{(a)}$ or O_{ox} and nor by the direct impact of $\text{CO}_{2(g)}$. Tridentate bonding was proposed, with each O on the Ni surface in approximately equivalent positions.

Iron

Clean surface

A significant contribution to the understanding of the nature of the interaction of CO_2 with Fe surfaces was provided by Wedler *et al.* [51–54]. An interesting face specificity was observed by means of angle-integrated UP spectroscopy. At 77 K photoemission peaks characteristic of weakly held linear CO_2 molecules dominated the spectra. However, new photoemission signals attributed to formation of the CO_2^- anion were observed on Fe film even at 77 K. These signals were detected for the Fe(111) surface at ~ 100 K.

When identical experiments were carried out with Fe(110), no adsorption or decomposition of CO_2 occurred at all. There was only condensation of CO_2 at 77 K when the CO_2 pressure exceeded the saturation value. No interaction between CO_2 and Fe(110) was observed at 300 K either. (This was in contrast with an early observation that CO_2 dissociates on the Fe(110) surface at 300 K; a LEED pattern similar to that observed with CO adsorption was found [55]. As soon as regular steps were produced on the Fe(110) surface by means of ion bombardment, exposure to CO_2 led to results very similar to those described for Fe(111). The only difference was that the decomposition of CO_2 started at slightly elevated temperatures

It was concluded that the reactivity of Fe surfaces towards the adsorption of CO_2 is governed by their work function. Samples (Fe(110) and unannealed Fe film) with high work function (~ 4.4 eV) do not adsorb CO_2 , whereas the formation of both CO_2 (phys) and CO_2^- occurred on Fe surfaces (Fe(111) and annealed Fe film) of lower work function (~ 4.1 eV).

The results obtained for Fe(111) by low-resolution UP spectroscopy were verified in an angle-resolved photoemission study [54]. Linear CO_2 molecules desorbing at low temperature (below 140 K) and anionic CO_2^- species stable at 160–180 K were detected.

From a comparison of the angular dependence of the CO_2 -induced peaks with a similar data set for the $\text{CO}_2/\text{Ni}(110)$ system, it was concluded that

the CO_2 molecule is not oriented perpendicular to the surface, but the angle of inclination of the CO_2 molecular axis is likely to be larger than $\pm 20^\circ$ with respect to the surface plane.

The bent CO_2 species dissociates completely to adsorbed $\text{CO} + \text{O}$ at 300 K.

Copper

Renewed interest in the interaction of CO_2 with Cu was initiated by the recent discovery that CO_2 is the main source of 'carbon' in the synthesis of methanol from $\text{H}_2 + \text{CO} + \text{CO}_2$ mixtures [56–61]. The key step in the reaction scheme is the dissociation of CO_2 , *i.e.* the formation of $\text{O}_{(a)}$ and $\text{CO}_{(a)}$.

The early classical work of Collins and Trapnell [6] found no adsorption of CO_2 on evaporated Cu films at 195 and 273 K, which was attributed to the full d-bands precluding covalence. This feature was confirmed by a number of studies using tools of modern surface science [63–70].

At exposures up to 350 L, Rodriguez *et al.* [69] were unable to react any measurable amount of CO_2 with clean Cu(110) surface at 110 or 250 K, as evidenced by the complete absence of an oxygen signal in the XPS and AES after exposure. The same conclusion was reached by Bugyi *et al.* [70] for the Cu(111) surface from AES, TPD, UPS and XPS studies.

In stark contrast with these results, Wachs and Madix [71] reported that 99% of adsorbed CO_2 dissociated to form CO and a surface oxygen species. Although this observation was cited frequently by the ICI group [60], certain caution is required, as this statement was merely a side remark in a paper dealing with the adsorption and oxidation of several organic compounds on the Cu(100) surface. In addition, neither coverage nor temperature were given, which does not make this observation very useful.

The results obtained on polycrystalline Cu suggest an exceptionally high reactivity toward CO_2 [72]. When the Cu surface was exposed to 115 L of CO_2 at 80 K, the XPS spectrum in the C(1s) region exhibited two main features, one at 289 eV and the other at 291 eV. These peaks were assigned to the CO_2^- anion and physisorbed CO_2 , respectively. A weak signal at 293.4 eV was attributed to a CO_2 multilayer. At 93 K, the 289 eV peak dominated the spectrum, with a new peak at 285 eV ascribed to $\text{C}_{(a)}^0$. This assignment would mean that the complete dissociation of a CO_2 molecule could occur on the Cu sample at a temperature as low as 93 K (!), which clearly needs confirmation. Unfortunately, the oxygen region of the XPS spectrum was not shown and the behavior of these peaks above 93 K was not reported. The authors gave no concentration values, either for adsorbed CO_2 or for surface carbon.

The dissociation of CO_2 above 300 K was reported by the ICI group on Cu powder and on polycrystalline Cu foil [60, 61]. In this case, however, the pressure range was higher and the state of cleanness of the surface was not checked by electron spectroscopy.

Effect of surface adatoms

Wachs and Madix [71] reported that the presence of oxygen adatoms on the Cu(110) surface diminished the sticking probability of CO₂, and the total amount of CO₂ adsorbed decreased following initial exposure to oxygen. A similar observation was made by Bugyi *et al.* [70] for the Cu(111) surface.

A significant adsorption of CO₂ was observed by Copperthwaite *et al.* [72] on the pre-oxidized Cu(211) surface at 80 K. As regards the promoting or inhibiting effect of pre-adsorbed oxygen, no conclusion can be drawn, as no comparison with the clean Cu(211) surface was made. On heating of the adsorbed layer to 130 K, the CO₂ multilayers were desorbed and peaks ascribed to CO_{2(a)}⁻ and physisorbed CO₂ appeared in the XPS spectrum.

A much more drastic effect was observed in the presence of preadsorbed alkali metals [69, 70] which exerted an influence on the adsorption of CO₂ on Cu surface similar to the case of Pt metals.

It was found that the amount of adsorbed CO₂ and the probability of adsorption of CO₂ are enhanced as Cs is added to the Cu(110) surface. Several new adsorption states were produced, which desorbed in the intervals 110–170 K and 500–700 K. The low-temperature CO₂ was attributed to neutral CO₂ stabilized by Cs, and the high-temperature desorption to the thermal cracking of Cs·nCO_{3(a)} species. The stabilization of Cs in the adsorbed layer was also observed: Cs desorbed in a coincident peak with CO₂. The formation of adsorbed CO likewise occurred but, in contrast with the behavior observed for Pt metals, the CO formed was not stabilized by Cs; it was released below 250 K.

An interesting feature of this system is that carbonate formation, identified by XPS measurements, occurred at the adsorption temperature of 110 K. This is probably the reason why the authors found no spectral evidence for the existence of CO₂⁻ anion species. In the further description of the reactions of CO₂ on the K-dosed Cu surface, the same processes were taken into account as for Rh and Pd surfaces [19, 32].

Rhenium

The adsorption of CO₂ was studied on the Re(0001) surface [73]. Adsorption kinetics consistent with an extrinsic precursor state were observed at a crystal temperature of 80 K. A dissociation probability of 0.85 was found at coverages of less than $\theta = 0.1$ and was coverage-dependent, decreasing to 0.35 at saturation CO₂ coverage. The dissociation probability was crystal temperature-dependent, decreasing by a factor of 10 when the adsorption temperature was increased from 80 K to 310 K. This decrease was attributed to a reduction in the sticking probability of CO_{2(g)} at the surface, although a mechanism in which CO_{2(a)} desorption competes with the dissociation reaction was not ruled out. The CO_(a) and O_(a) fragments formed an ordered (2×2) structure.

More details on the CO₂-Re interaction were revealed by HREEL spectroscopy [74]. Following the adsorption of CO₂ (0.8 L) on Re(0001) at 83

K, the most intense loss feature was seen at 650 cm^{-1} with relatively weak modes at 1600 , 1935 and 2350 cm^{-1} . In the 10° off-specular direction, not only was the intensity at 1600 cm^{-1} enhanced relative to all other transitions, but a new vibrational mode at 1285 cm^{-1} was also distinctly observed. After a short annealing of the sample at 120 K , most of the 650 cm^{-1} peak and that at 2350 cm^{-1} disappeared. The vibrational mode at 1600 cm^{-1} persisted and was somewhat enhanced. Further heating of the sample to 135 K or above produced a new loss feature at 1970 cm^{-1} , indicative of a low coverage of CO on the Re(0001) surface. In the presence of adsorbed oxygen, the peak previously observed at 1600 cm^{-1} was shifted to 1650 cm^{-1} and a peak was clearly seen at 1290 cm^{-1} .

The HREELS peaks at 650 , 1290 and 2350 cm^{-1} were assigned to the vibrations of a linear molecular CO_2 lying parallel to the surface, while the observed extra modes at 1600 cm^{-1} (on a clean surface) and 1230 and 1650 cm^{-1} (on an oxygen-precovered surface) were considered to be indications of the presence of new surface species. These were attributed to a bent CO_2^- , which dissociates to $\text{CO}_{(a)}$ and $\text{O}_{(a)}$ above 130 K .

Aluminium

The interaction of CO_2 with clean Al foil was followed by XPS measurements at 80 – 295 K [75]. From an analysis of the O(1s) and C(1s) spectra, it was concluded that metastable surface carbonate is formed at 80 – 120 K . The formation of carbonate involves the dissociation of adsorbed CO_2 and the subsequent recombination of adsorbed O and CO_2 . The carbonate is thermally unstable and dissociates readily above 120 K to give carbon in two forms, carbide, $\text{C}_{(a)}^{\delta-}$, and graphitic $\text{C}_{(a)}^0$.

At 295 K and low CO_2 pressures (10^{-6} torr), there was no evidence of adsorption or reaction even at high exposures ($3 \times 10^3\text{ L}$). At high pressure (1 torr), the formation of both carbidic and graphitic-type species was established, suggesting that the metastable carbonate is a precursor state for dissociation.

Interestingly, no CO_2 adsorption was observed on the Al(100) surface at around 100 K . Surface atoms with low coordination numbers and significantly higher pressures were considered to be the main reasons for the high reactivity of a polycrystalline Al sample.

Effect of surface adatoms

A significant promotion of CO_2 adsorption was observed in the presence of Na adatoms [76]. The nature of the interaction and its explanation were practically the same as those proposed first for K-promoted Rh and Pd surfaces.

(i) The probability of CO_2 adsorption increases with alkali metal coverage.

(ii) Alkali metal promotion leads to CO_2 reduction, giving an anion radical, which is transformed into oxalate and carbonate at higher temperatures.

The HREEL spectra revealed two different states of CO₂ adsorption at 100 K and monolayer Na coverage: weakly bound molecular CO₂ and oxalate ions with low, possibly unidentate, coordination. The latter species was characterized by vibrational bands at 460, 1310 and 1480 cm⁻¹. Heating of the co-adsorbed layer to 330 K produced strong bands at 1050, 1350 and 1570 cm⁻¹, which were attributed to surface carbonate bound to the substrate via two oxygen atoms. The oxalate-carbonate transformation (as discussed previously) was accompanied by the release of CO at ~285 K.

Magnesium

Atomically clean Mg(0001) surface exhibited a high reactivity towards CO₂ [77]. Both XPS and EELS indicated the dissociation of CO₂ even around 100 K.

When the magnesium surface was exposed to carbon dioxide at room temperature, the resulting O(1s) spectra showed two peaks. The oxide peak at 530.7 ± 0.2 eV is close to its position at low temperature, but the O(1s) peak associated with the C(1s) feature at 292 eV now appears at a slightly higher binding energy of 534.0 ± 0.2 eV. The ratio of the intensities of the peaks at 292 eV and 534 eV indicates a stoichiometric ratio of C:O = $1:3.2 \pm 0.5$. This, together with the observation of similar peaks in the spectrum of bulk MgCO₃, constitutes strong evidence for a carbonate species. The data showed that the carbonate is confined to the topmost layer, while the oxide forms a thicker, uniform layer beneath.

The EELS spectra of the sample heated to 131 K exhibited losses at 850, 1090, 1390 and 1630 cm⁻¹, which were explained by the formation of bidentate carbonate, although the high intensity of 1390 cm⁻¹ (attributed to the asymmetric O-C-O stretch) is not in accord with this assignment.

Silver

Clean surface

The study of the interaction of CO₂ with silver metal has been the subject of several thorough works [78-94]. This interest was primarily motivated by the fact that silver is a catalyst industrially applied in the epoxidation of ethylene. The results unequivocally showed that the CO₂ adsorbs only very weakly on clean Ag surfaces.

The properties of CO₂ physisorbed on a Ag(111) surface at 40 K were studied by HREELS and LEED [78]. The observed loss energies at 83, 167 and 290 meV coincide with the vibrational energies of bending, symmetric stretching and asymmetric stretching modes of CO₂ in the gas phase within the accuracy of the measurements (± 3 meV). No diffraction spots of ordered structures of CO₂ layers were observed. Neither annealing to 70 K nor condensation at elevated substrate temperature (85 K) produced any change

in the LEED pattern. This agrees with the He diffraction experiment, in which no diffraction spots were registered [79]. It was concluded that layer-by-layer growth is not probable and that island formation occurs preferentially. It was assumed that at 40 K the deposited layer consists of three-dimensional microcrystals even at submonolayer coverages.

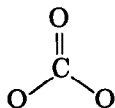
Effects of surface adatoms

The adsorption of CO_2 on an oxygen-dosed powdered silver specimen was studied first by Czanderna and Bregen [80–82] using a vacuum microbalance thermal desorption technique. They found that pre-adsorbed oxygen promoted the adsorption of CO_2 , which desorbed in a first order process with an activation energy of 84 to 102 kJ mol^{-1} and a pre-exponential factor in the range 10^{11} – 10^{13} s^{-1} .

Similar observations were made by Madix *et al.* [83–87] on Ag single crystal surfaces under UHV conditions. They have shown that an adsorbed carbonate species ($\text{CO}_{3(\text{a})}$) can be produced via the adsorption of CO_2 onto an Ag(110) surface pre-dosed with oxygen atoms [83]. The reaction of C^{16}O_2 with preadsorbed ^{18}O atoms showed that all oxygens in the $\text{CO}_{3(\text{a})}$ species are chemically equivalent. It was postulated that this equivalence was achieved by a facile interconversion of monodentate (MOCO_2) and bidentate (MO_2CO) species.

The thermal desorption spectrum following an exposure of 1.5×10^{15} molecules cm^{-2} of CO_2 at 100 K to the oxygen-covered Ag(110) surface showed two peaks at 130 and 480 K [85]. The high-temperature state is due to the decomposition of surface carbonate, $\text{CO}_{3(\text{a})}$, to yield $\text{CO}_{2(\text{g})}$ and $\text{O}_{(\text{a})}$. The low-temperature state is due to the desorption of molecular CO_2 . This form of CO_2 was thought to be induced by adsorbed carbonate, but its presence – which means a stabilization of physisorbed CO_2 – could be also due to chemisorbed oxygen.

EEL spectra following a CO_2 exposure of 1.5×10^{15} molecules cm^{-2} to the oxygen covered surface at 100 K confirmed the presence of molecularly adsorbed CO_2 and CO_3 species [85]. The losses observed were assigned as follows: 260 (AgO); 830 $\pi(\text{CO}_3)$; 1050 $\gamma(\text{CO})$; and 1360 cm^{-1} $\gamma_s(\text{OCO})$. The $\pi(\text{CO}_3)$ notation refers to the out-of-plane carbonate deformation, while $\gamma_s(\text{OCO})$ represents the symmetric OCO stretch. No loss was observed for the asymmetric stretch (expected to be around 1480 cm^{-1}). This indicates that the axis through the 'up' oxygens of the carbonate is parallel to the surface according to the dipole selection rule. The absence of a peak near 1600 cm^{-1} clearly rules out a structure of the form



Photoelectron spectroscopy of the CO_3 formed demonstrated little perturbation of the molecular orbitals or of electron distribution on the oxygen atoms due to bonding with the Ag(110) surface [86].

Suggestions for future work

As the surface chemistry of adsorbed CO_2 on metal single crystal surfaces has been rather neglected in the past, this subject is open for several studies using the tools of modern surface science. Without going into detail, we list some selected topics which need further consideration for the better understanding of the features summarized in the present review:

(1) Study of the effects of defects of transition metals on the adsorption and dissociation of CO_2 .

(2) Photochemical activation of CO_2 on metal surfaces with particular emphasis on the formation of CO_2^- radical anion.

(3) Determination of the structure and coordination mode of CO_2 in the presence of alkali promoters by NEXAFS, diffuse LEED and HREELS methods.

(4) Detection of the formation of alkali- CO_2 surface complex on transition metal surfaces by SIMS and/or by field desorption mass spectrometry.

(5) Further study of the nature of the interaction of CO_2 with different faces of a carefully cleaned Cu single crystal, as regards the formation of CO_2^- anion and the extent of dissociation.

(6) Study of the reactions of CO_2 , activated by alkali metals, with other gas molecules on different metal surfaces.

(7) Extension of the investigation of the adsorption of CO_2 to other metal surfaces.

Conclusions

It can be generally stated that CO_2 adsorbs weakly and molecularly on carefully cleaned Pt metals at 100–300 K under UHV conditions. It appears likely that the dissociation is also very limited on Cu surfaces, if it occurs at all. The adsorption of CO_2 is dissociative on Fe, Ni, Re, Al and Mg surfaces. The presence of oxygen adatoms promotes the bonding of CO_2 on metals in form of different carbonates and leads to its stabilisation.

The bonding, structure and reactivity of adsorbed CO_2 can be drastically influenced by alkali adatoms through the formation of surface CO_2^- radical anion. Depending on the state of alkali metals, CO_2^- may dissociate to CO and O, or transform into CO_3 and CO species. It is likely that a CO_2^- species plays a dominant role in the thermal and photocatalytic reactions of the CO_2 molecule.

References

- 1 R. P. A. Sneeden, in G. Wilkinson (ed.), *Comprehensive Organometallic Chemistry*, Pergamon, New York, 1982, Vol. 8.
- 2 D. J. Darensbourg, C. G. Bauch and C. Ovalles, *Rev. Inorg. Chem.*, 7 (1985) 315; D. J. Darensbourg and R. A. Kudarowski, *Adv. Organometall. Chem.*, 22 (1983) 129.
- 3 W. M. Ayers (ed.), *Catalytic Activation of CO_2* , ACS Symp. Ser., American Chemical Society, Washington D.C., 1988.

- 4 A. Ya. Rozovskii, G. Lim, L. B. Liberov, E. V. Slivinski, S. M. Loktev, Yu. B. Kagan and A. N. Bashkirov, *Kinet. Catal. (Engl. Transl.)*, 18 (1977) 691.
- 5 G. C. Chinchin, P. J. Denney, D. G. Parker, M. C. Spencer and D. Whan, *Appl. Catal.*, 30 (1987) 333.
- 6 A. C. Collins and B. M. W. Trapnell, *Trans. Faraday Soc.*, 53 (1957) 1436.
- 7 C. T. Campbell and J. M. White, *J. Catal.*, 54 (1978) 289.
- 8 A. C. Yang and C. W. Garland, *J. Phys. Chem.*, 61 (1957) 1504.
- 9 B. A. Sexton and G. A. Somorjai, *J. Catal.*, 46 (1977) 167.
- 10 D. G. Castner, B. A. Sexton and G. A. Somorjai, *Surf. Sci.*, 71 (1978) 519.
- 11 D. G. Castner and G. A. Somorjai, *Surf. Sci.*, 83 (1979) 60.
- 12 L. H. Dubois and G. A. Somorjai, *Surf. Sci.*, 88 (1979) L213.
- 13 L. H. Dubois and G. A. Somorjai, *Surf. Sci.*, 91 (1980) 514.
- 14 W. H. Weinberg, *Surf. Sci.*, 128 (1983) L224.
- 15 D. W. Goodman, D. E. Peables and J. M. White, *Surf. Sci.*, 140 (1984) L239.
- 16 L. H. Dubois and G. A. Somorjai, *Surf. Sci.*, 128 (1983) L231.
- 17 F. Solymosi and J. Kiss, *Surf. Sci.*, 17 (1985) 149.
- 18 F. Solymosi, J. Kiss, *Chem. Phys. Lett.*, 110 (1984) 639.
- 19 F. Solymosi and L. Bugyi, *J. Chem. Soc., Faraday Trans. 1*, 83 (1987) 2015.
- 20 H. A. C. M. Hendrickx, A. P. J. M. Jongenelis and B. E. Nieuwenhuys, *Surf. Sci.*, 154 (1985) 503.
- 21 G. B. Fischer, B. A. Sexton and J. L. Gland, *J. Vac. Sci. Technol.*, 17 (1980) 144.
- 22 P. A. Thiel, J. T. Yates and W. H. Weinberg, *Surf. Sci.*, 82 (1979) 22.
- 23 J. Kiss, K. Révész and F. Solymosi, *Surf. Sci.*, 207 (1988) 36.
- 24 D. W. Turner, H. D. Baker, C. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley, New York, 1970.
- 25 J. Kiss, K. Révész and F. Solymosi, *Appl. Surf. Sci.*, 37 (1989) 95.
- 26 A. Berkó and F. Solymosi, *Surf. Sci.*, 201 (1986), L489.
- 27 Z. H. Kafafi, R. H. Hauge, W. E. Billups and J. L. Margraven, *J. Am. Chem. Soc.*, 105 (1983) 3886.
- 28 H. J. Freund and R. P. Messmer, *Surf. Sci.*, 1 (1986) 172.
- 29 B. Bartos, H. J. Freund, H. Kuhlenbeck, M. Neumann, H. Linder and K. Müller, *Surf. Sci.*, 59 (1987) 179.
- 30 T. Engel and G. Ertl, *Adv. Catal.*, 1 (1979) 28.
- 31 T. Engel and G. Ertl, *J. Chem. Phys.*, 69 (1978) 1267.
- 32 F. Solymosi and A. Berkó, *J. Catal.*, 101 (1986) 458.
- 33 T. Matsushima, *J. Phys. Chem.*, 91 (1987) 6192.
- 34 J. Wambach, G. Odörfer, H. J. Freund, H. Kuhlenbeck and M. Neumann, *Surf. Sci.*, 209 (1989) 159; S. Wohlrab, D. Ehrlich, J. Wambach, H. Kuhlenbeck and H. J. Freund, *Surf. Sci.*, (1990) in press.
- 35 C. Egawa, I. Doi, S. Naito and K. Tamaru, *Surf. Sci.*, 176 (1986) 491.
- 36 P. R. Norton, *Surf. Sci.*, 44 (1974) 624.
- 37 P. R. Norton and P. J. Richards, *Surf. Sci.*, 49 (1975) 567.
- 38 Z. M. Lin, Y. Zhou, F. Solymosi and J. M. White, *J. Phys. Chem.*, 93 (1989) 4383.
- 39 Z. M. Lin, F. Solymosi and J. M. White, *Surf. Sci.*, in press.
- 40 C. M. Greenlief, P. L. Radloff, S. Akhter and J. M. White, *Surf. Sci.*, 186 (1987) 563; J. E. Crowell, E. L. Gerfunkel and G. A. Somorjai, *Surf. Sci.*, 121 (1982) 303.
- 41 I. McCarty, J. Falconer and R. J. Madix, *J. Catal.*, 30 (1973) 235.
- 42 J. B. Benzinger and R. J. Madix, *Surf. Sci.*, 79 (1979) 394.
- 43 M. P. D'Evelyn, A. V. Hamza, G. E. Gidowski and R. J. Madix, *Surf. Sci.*, 167 (1986) 451.
- 44 B. Bartos, H. J. Freund, H. Kuhlenbeck, M. Neumann, H. Lindner and K. Müller, *Surf. Sci.*, 59 (1987) 179.
- 45 H. J. Freund, H. Kossmann and V. Schmidt, *Chem. Phys. Lett.*, 123 (1986) 463.
- 46 H. J. Freund and R. P. Messmer, *Surf. Sci.*, 1 (1986) 172.
- 47 H. Lindner, D. Rupprecht, L. Hammer and K. Müller, *J. Electron Spectrosc. Relat. Phenom.*, 44 (1987) 141.

- 48 G. Illing, D. Heskett, E. W. Plummer, H.-J. Freund, J. Somers, Th. Lindner, A. M. Bradshaw, U. Buskotte, M. Neumann, U. Starke, K. Heinz, P. L. de Andres, D. Saldin and J. B. Pendry, *Surf. Sci.*, 206 (1988) 1.
- 49 K. Heinz, D. K. Saldin, J. B. Pendry, *Phys. Rev. Lett.*, 55 (1985) 231.
- 50 R. J. Behm and C. R. Brundle, *J. Vac. Sci. Technol.*, A1 (1983) 1223.
- 51 R. Dziembaj and G. Wedler, *Surf. Sci.*, 134 (1983) 283.
- 52 H. Behner, W. Spess, G. Wedler and D. Borgmann, *Surf. Sci.*, 175 (1986) 276.
- 53 R. Bauer, H. Behner, D. Borgmann, M. Pirner, W. Spess and G. Wedler, *J. Vac. Sci. Technol.*, (1987) 1110.
- 54 H. J. Freund, H. Behner, B. Bartos, G. Wedler, H. Kuhlenbeck and M. Neumann, *Surf. Sci.*, 180 (1987) 550.
- 55 R. Yoshida, G. Somorjai, *Surf. Sci.*, 75 (1978) 46.
- 56 A. Ya. Rozovskii, *Kinet. Katal.*, 21 (1980) 97.
- 57 Yu. B. Kagan, G. I. Lin, A. Ya. Rozovskii, S. M. Loktev, E. V. Slivinskii, A. N. Bashkirov, I. P. Naumov, I. K. Khludenev, S. A. Kudinov and Yu. I. Golovkin, *Kinet. Katal.*, 17 (1976) 440.
- 58 Yu. B. Kagan, A. Ya. Rozovskii, G. I. Lin, E. V. Slivinskii, S. M. Loktev, L. G. Liberov and A. N. Bashkirov, *Kinet. Katal.*, 16 (1975) 809.
- 59 A. Ya. Rozovskii, Yu. B. Kagan, G. I. Lin, E. V. Slivinskii, S. M. Loktev, L. G. Liberov, A. N. Bashkirov, *Kinet. Katal.*, 16 (1975) 810.
- 60 G. C. Chinchin, M. S. Spencer, K. C. Waugh, D. A. Whan, *J. Chem. Soc. Faraday Trans. 1*, 83 (1987) 2193.
- 61 G. C. Chinchin, P. J. Denny, D. G. Parker, M. S. Spencer and D. A. Whan, *Appl. Catal.*, 30 (1987) 333.
- 62 F. H. P. M. Habraken, E. Ph. Kieffer and G. A. Bootsma, *Surf. Sci.*, 83 (1979) 45.
- 63 P. R. Norton and R. L. Trapping, *Chem. Phys. Lett.*, 38 (1976) 207.
- 64 A. B. Anderson, *Surf. Sci.*, 62 (1977) 119.
- 65 N. K. Ray and A. B. Anderson, *Surf. Sci.*, 119 (1982) 35.
- 66 F. Solymosi and J. Kiss, *Surf. Sci.*, 108 (1981) 368.
- 67 F. Solymosi and J. Kiss, *Surf. Sci.*, 104 (1981) 181.
- 68 F. Solymosi and A. Berkó, *Surf. Sci.*, 122 (1982) 275.
- 69 J. A. Rodriguez, W. D. Clendinger and C. T. Campbell, *J. Phys. Chem.*, 93 (1989) 5238.
- 70 L. Bugyi, J. Kiss and F. Solymosi, *J. Catal.*, in press.
- 71 J. E. Wachs and R. J. Madix, *J. Catal.*, 53 (1978) 208.
- 72 R. G. Copperthwaite, P. R. Davies, M. A. Morris, M. W. Roberts and R. A. Ryder, *Catal. Lett.*, 1 (1988) 11.
- 73 H. Peled and M. Asscher, *Surf. Sci.*, 183 (1987) 201.
- 74 H. Asscher, C. T. Rao and G. A. Somorjai, *J. Phys. Chem.*, 92 (1988) 2711.
- 75 A. F. Carley, B. E. Gallagher and M. W. Roberts, *Surf. Sci.*, 183 (1987) L263; *idem*, *Spectrochim. Acta*, 43A (1987) 1447.
- 76 J. Paul and F. M. Hoffmann, *Catal. Lett.*, 1 (1988) 445.
- 77 S. Campbell, P. Hollins, E. McCash and M. W. Roberts, *J. Electron Spectrosc. Relat. Phenom.*, 39 (1986) 145.
- 78 M. Sukurai, T. Okano and Y. Tuzi, *J. Vac. Sci. Technol.*, (1987) 431.
- 79 T. H. Ellis, G. Scales, U. Valbusa, H. Johnson and J. H. Weare, *Surf. Sci.*, 155 (1985) 492.
- 80 A. W. Czanderna, *J. Colloid Interf. Sci.*, 22 (1966) 482.
- 81 A. W. Czanderna, *J. Phys. Chem.*, 70 (1966) 2120.
- 82 A. W. Czanderna and J. B. Bregen, *J. Vac. Sci. Technol.*, 8 (1971) 594.
- 83 M. Bowker, M. A. Barteau and R. J. Madix, *Surf. Sci.*, 92 (1980) 528.
- 84 M. A. Barteau and R. J. Madix, *Surf. Sci.*, 97 (1980) 101.
- 85 E. M. Stuve, R. J. Madix and B. A. Sexton, *Chem. Phys. Lett.*, 89 (1982) 48.
- 86 M. A. Barteau and R. J. Madix, *J. Chem. Phys.*, 74 (1981) 4144.
- 87 M. A. Barteau and R. J. Madix, *J. Electron Spectrosc. Relat. Phenom.*, 31 (1983) 101.
- 88 C. Backx, C. P. M. De Groot and P. Biloen, *Appl. Surf. Sci.*, 6 (1980) 256.

- 89 C. Baclcx, C. P. M. De Groot, P. Biloen and W. M. H. Sachtler, *Surf. Sci.*, 128 (1983) 81.
90 K. C. Prince and A. M. Bradshaw, *Surf. Sci.*, 126 (1983) 49.
91 C. T. Campbell and M. T. Paffett, *Surf. Sci.*, 143 (1984) 517.
92 J. Segner, C. T. Campbell, G. Doyen and G. Ertl, *Surf. Sci.*, 138 (1984) 505.
93 C. T. Campbell, G. Ertl, H. Kuipers and J. Segner, *Chem. Phys. Lett.*, 73 (1980) 5862.
94 C. T. Campbell, G. Ertl, H. Kuipers and J. Segner, *Surf. Sci.*, 107 (1981) 207, 220.