THE ACTIVATION OF CARBON DIOXIDE AT A MAGNESIUM (100) SURFACE THE ROLE OF OXYGEN TRANSIENTS

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Abstract

X-ray photoelectron and high resolution electron energy loss spectroscopic (XPS-HREELS) studies have shown that the adsorption of carbon dioxide at Mg(100) surfaces at 80K is followed by a dissociative reaction leading to the formation of a metastable surface carbonate above 80K. The formation of a carbonate species is proposed to proceed through oxidation of $CO_2(g)$ by an active oxygen surface transient $O^-_{(s)}$ formed by dissociation of dioxygen or dissociative chemisorption of carbon dioxide. The O(ls) data establish that oxidation and carbonate formation occur simultaneously suggesting that dissociative chemisorption involves the formation of an oxygen adatom which can either form oxide or react with CO_2 to form carbonate.

Introduction

Recently there has been an increasing number of investigations concerning the catalytic transformation of $CO_2(g)$ into more valuable compounds such as methanol, organic acids and other hydrocarbons [1-2]. The discovery that $CO_2(g)$ is the main source of carbon for the production of methanol from $H_2/CO_2/CO$ mixtures [3] has increased interest in the catalytic activation of $CO_2(g)$ [4].

The activation of $CO_2(g)$ by a clean Al surface has already been studied [5]. X-ray photoelectron spectroscopy was used to show that in the temperature range 80-120K, $CO_2(g)$ adsorbs at the surface and then dissociates to produce a metastable carbonate species. On warming, this carbonate is deoxygenated to produce two forms of carbon, one carbidic, $C^\delta_{(a)}$, and the other, graphite, $C^0_{(a)}$.

An atomically clean Mg(0001) surface exhibited a high reactivity towards $CO_2(g)$ [6]. Both XPS and HREELS showed the adsorption to be molecular at 85K while above 95K dissociation and subsequent recombination to form carbonate occurs. It has also been shown recently [7] that surface transients present during the dissociative adsorption of dioxygen may react directly with a coadsorbed species. In the Mg(0001)-ammonia-dioxygen system [8], an oxygen surface transient, designated $O^\delta_{(s)}$ and with an estimated surface lifetime of ca. 10^{-8} seconds at 295K, was shown by XPS to be the reactive species, whereas the thermodynamically stable $O^{2-}_{(a)}$ species was, by comparison, unreactive. We have thus extended our studies to the coadsorption of $CO_2(g)$ and $O_2(g)$ at an atomically clean Mg(100) surface with the aim of obtaining XPS and HREELS data to investigate the role of oxygen transients in the chemistry of dioxygen at clean Mg surfaces.
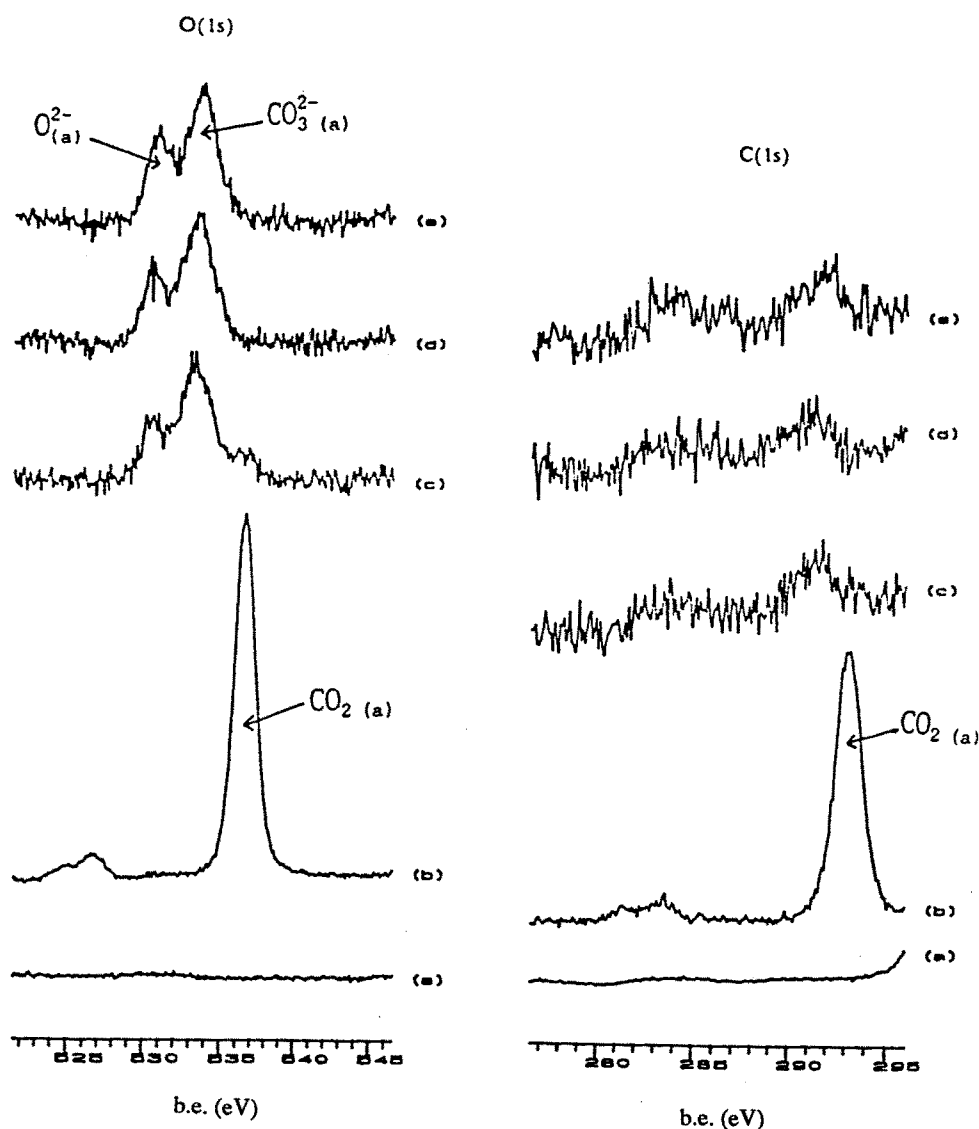
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Figure 1. O(ls) and C(ls) spectra observed after exposing a clean Mg(100) surface to a CO_2/O_2 (approx. 1% O_2) mixture. (a) is the clean surface, (b) shows the effect of a 300L exposure at 80K, (c), (d) and (e) show the effect of warming the surface to 98K, 173K and 243K in a continuous flow of oxygen.

Experimental Section

The apparatus used in this investigation combines both photoelectron and vibrational spectroscopies, with facilities also for low energy electron diffraction. V.G. Scientific provided the X-ray photoelectron spectroscopy facility while Vacuum Science workshops (Manchester) supplied the electron-energy loss spectrometer. The data from the spectrometers were collected using a commercial acquisition package (SPECTRA), and analysed using software developed in Cardiff university [9].

A 99.9% pure Mg(100) crystal was purchased from Metal and Oxides Ltd. (Cambridge). It was mechanically polished on successively finer grades of diamond paste down to 1μ diameter. Cleaning was carried out by repeated cycles of argon ion bombardment (5KV; 20μA cm^{-2}) at room temperature, and annealing to 220°C. The high purity CO_2 was supplied in 1 litre bulbs (99.9%, P.J. Mason Ltd.). This was further purified with several freeze-pump-thaw cycles. The frozen gas was then allowed to warm slowly and the first evaporate captured in the separately pumped, stainless-steel gas handling line, thus leaving any less volatile impurities (such as water) behind in the bulb. Fur-
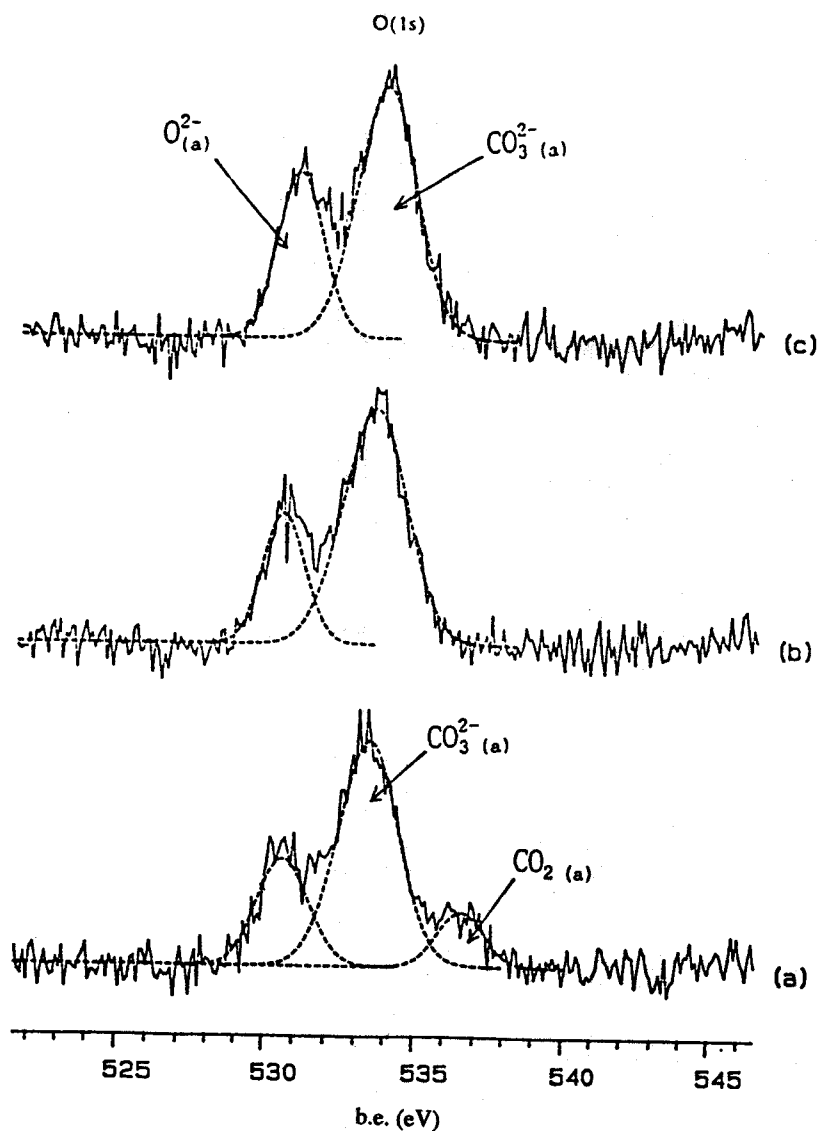
Figure 2. Curve-fitted O(1s) spectra observed after exposing a clean Mg(100) surface to a CO_2/O_2 (approx. 1% O_2) mixture at 80K, and then warmed to (a) 98K (b) 173K and (c) 243K in a continuous flow of oxygen.

ther purification of triply distilled water was performed by several freeze-pump-thaw cycles. Gases were admitted to the chamber via all-metal leak valves, and their purity and mixture composition checked using a Multiquad quadrupole mass spectrometer (Ledamass Ltd.).

Results

(a) Coadsorption of CO_2/O_2

Figure 1 shows the O(1s) and C(1s) spectra observed when an atomically clean Mg(100) surface is exposed to a mixture of $CO_2(g)$ and $O_2(g)$ (approx. 1%

O_2) at 80K, and then warmed to 98K, 173K and finally 243K in a continuous flow of oxygen. After exposure of 300L (1L= 10^{-6} Torr for 1 second) of the mixture the O(1s) and C(1s) spectra exhibit single peaks with binding energies of 536.6 eV and 293.2 eV respectively. These can both be assigned to physisorbed CO_2, they have characteristic binding energies [6,10] and the calculated surface coverages produce a stoichiometric ratio C:O of 1:2.

Warming the sample in a continuous flow of oxygen (10^{-6} mbar) results in drastic changes in both the O(1s) and the C(1s) spectra. The intensity of both features corresponding to $CO_2(a)$ has decreased at 98K
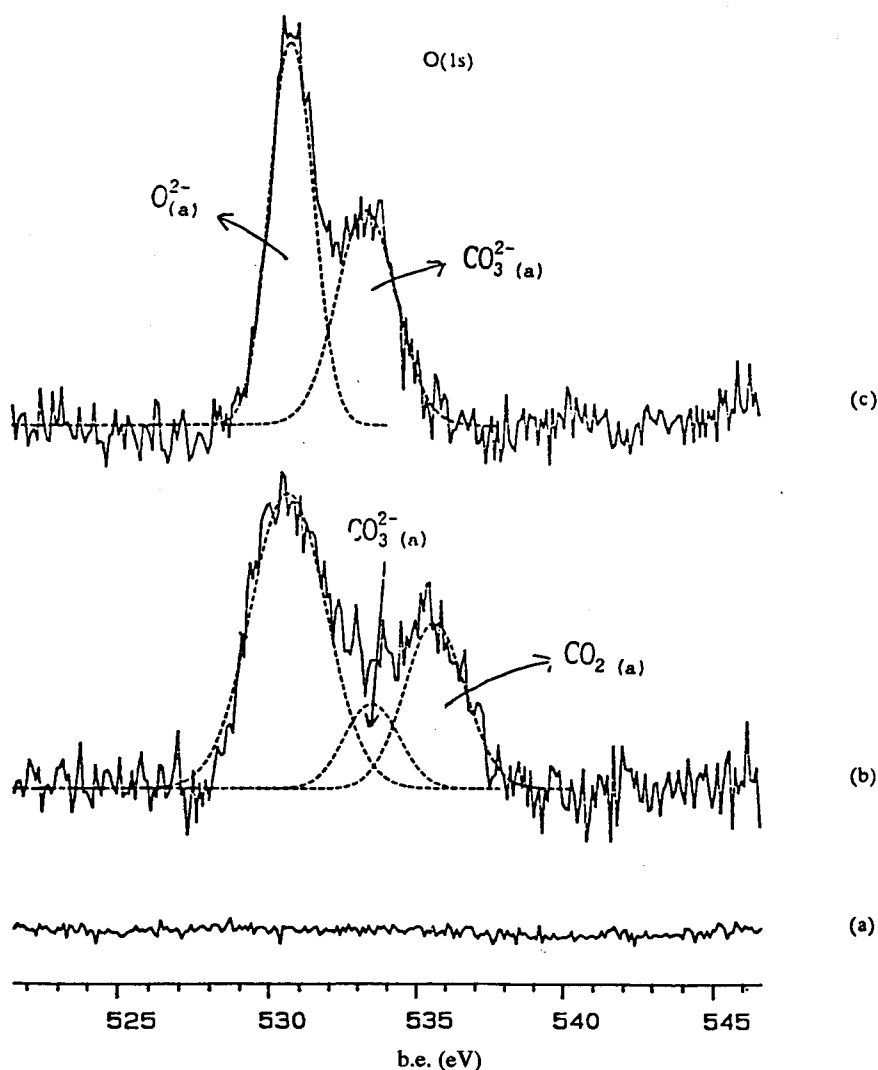
Figure 3. O(ls) spectra observed after exposing a clean Mg(100) surface to a CO_2/O_2 (approx. 10% O_2) mixture. Spectra show (a) the clean surface, (b) the effect of a 300L exposure of the mixture at 80K and (c) the effect of warming to room temperature. The dotted lines represent the curve-fitted data.

and is not detectable at 173K. Concomitant with this we observe the development of new components with lower binding energy in both the O(ls) and C(ls) regions. The O(ls) peaks at 98K have been curve fitted using Gaussian peak shapes (Fig. 2), showing the presence of two or three components. The O(ls) peak at 536.6 eV due to physisorbed CO_2 is still visible at 98K, two new peaks at 533.4 eV and 530.5 eV are assigned to carbonate and oxide respectively. This is consistent with the work on Al [5] and Mg(0001) [6]. The spectra observed above 173K show the CO_2(a) to be totally desorbed, leaving oxide and carbonate.

The photoelectron spectrum of the Mg(100) surface exposed to 300L of a CO_2: O_2 mixture (10% O_2)

at 80K and then warmed to room temperature, is shown in Figure 3. The O(ls) spectra have again been fitted using Gaussian shaped peaks. Three components are observed after a 300L exposure at binding energies of 535.7 eV, 533.5 eV and 530.7 eV. The assignments are the same as for the 100:1 mixture; the change in binding energy for the physisorbed CO_2 is due to the reduced amount at the surface. When multilayers are present, the outer layers experience less influence from the surface, and have a reduced extra relaxation shift due to increased distance from the surface. This effect has also been seen on an Au surface by Brundle and Roberts [11]. On warming to room temperature, the physisorbed CO_2 has completely desorbed while
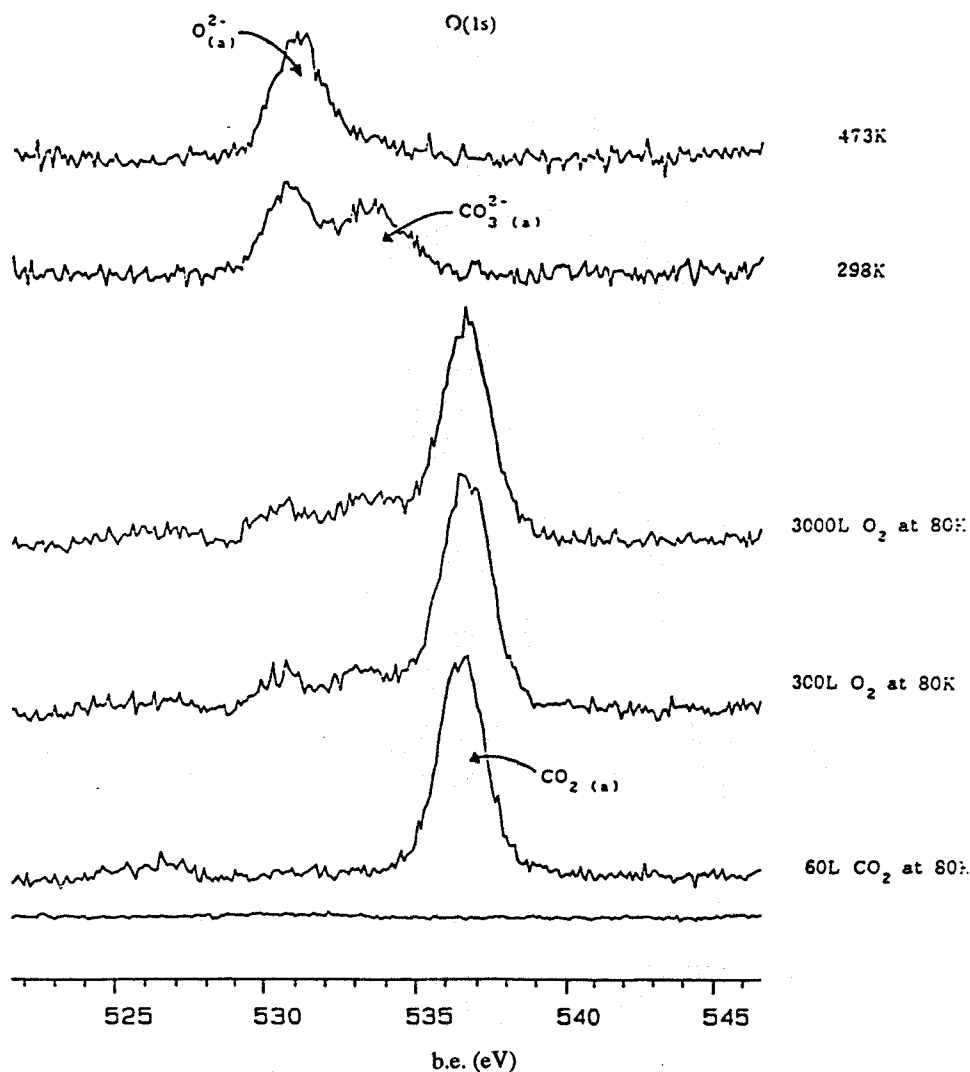
Figure 4. O(ls) spectra observed after sequential adsorption of CO_2 and O_2 (a) the clean surface, (b) the effect of a 60L exposure of CO_2 at 80K, (c) and (d) the effect of exposing the physisorbed CO_2 to 300L and 3000L of O_2 at 80K, and (e) and (f) the effect of warming the surface to 298K and 473K.

the carbonate coverage has increased from 3.9×10^{14} to 1.2×10^{15} atoms cm^{-2}. The oxide coverage has decreased by 3×10^{14} atoms cm^{-2} due to the effect of warming; this could be due to diffusion of surface oxygen into the subsurface.

(b) Sequential Adsorption of CO_2 and O_2

Figure 4 shows the spectra observed when an Mg(100) surface is exposed to 60L of $CO_2(g)$ and then 300L and 3000L of $O_2(g)$ at 80K, followed by warming to 298K and 473K. A single peak is produced by 60L of $CO_2(g)$ in the O(ls) region at 536.6 eV due to

physisorbed CO_2 (Fig. 4). Exposure of this overlayer to 300L and then 3000L of O_2 (g) at 80K (Figs. 4b, 4c) produces carbonate and oxide with binding energies of 533.5 eV and 530.5 eV, consistent with the coadsorption work. On warming the sample to room temperature, the feature due to physisorbed CO_2 is not detectable (Fig. 4e) but there is a large increase in the intensity of the features due to oxide and carbonate. Further warming of the sample (Fig. 4e) results in decomposition of the carbonate to oxide, as can be seen clearly in the O(ls) spectra.
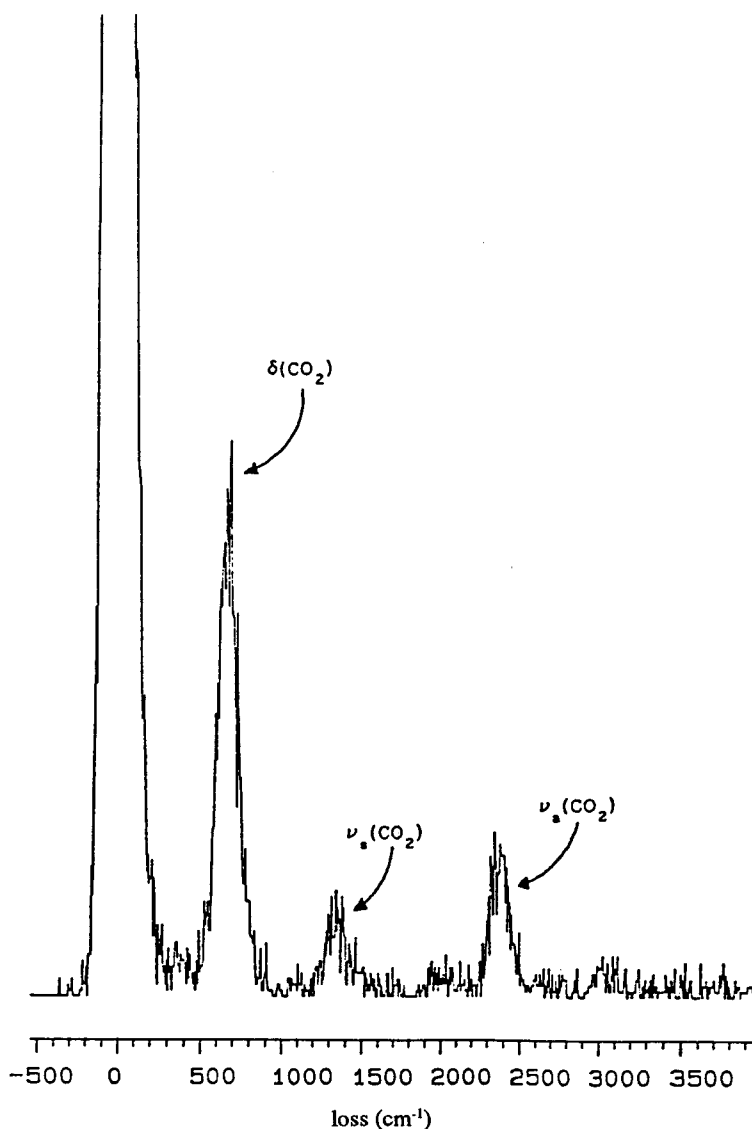
Figure 5. HREELs spectrum observed after an atomically clean Mg(100) surface was exposed to 60L of $CO_2(g)$ at 80K.

(c) HREELS Spectra

Figure 5 shows the HREEL spectrum observed after a clean Mg(100) surface was exposed to 60L of $CO_2(g)$ at 80K, the loss peaks were observed at 690 cm^{-1}, 1350 cm^{-1}, and 2380 cm^{-1}. On the introduction of 300L of $O_2(g)$ at 80K (Fig. 6), the loss peak at 690 cm^{-1} shifted to 660 cm^{-1}. The HREELS spectra suggest the presence of molecular adsorption of CO_2, since $C_{(a)}$ and $O_{(a)}$ can not produce the observed vibrational bands. For molecular adsorption of CO_2, the expected bands are the molecule-substrate stretch, the C-O stretch and the bending mode of the adsorbed CO_2

molecule. By comparison with the literature [12, 13], the vibrational mode at 690 cm^{-1} is assigned to bending mode of CO_2, the 1350 cm^{-1} loss peak is attributed to symmetric stretching vibration of CO_2 and the loss peak at 2380 cm^{-1} is assigned to asymmetric stretching vibration mode of CO_2. The intense feature at 660 cm^{-1} is identified as the Mg-O stretching vibration [13]. The presence of molecular CO_2 at this temperature is also justified by our XPS data (see Fig. 1). Warming the sample to room temperature results in complete desorption of CO_2 from the surface and the generation of oxide and carbonate surface species as
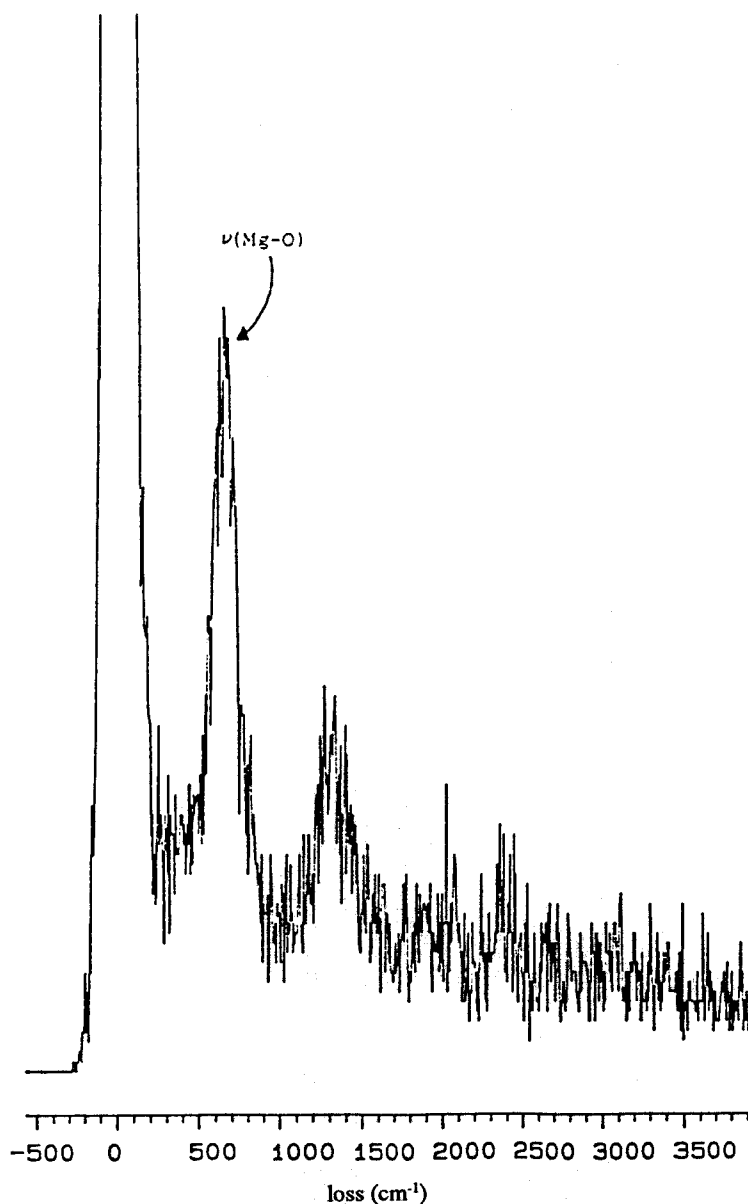
Figure 6. HREELs spectrum recorded after a clean Mg(100) surface was exposed to 60L of CO_2 at 80K, then to 300L of O_2 at 80K.

clearly illustrated by XPS (Fig. 4). Unfortunately, the metal-oxide stretch and its overtones completely dominate the spectrum thus making losses due to carbonate unobservable. Campbell *et al.* [6] and Evans and Whatley [14] quote carbonate on Mg to produce loss peaks at 850 cm^{-1}, 1090 cm^{-1}, 1390 cm^{-1} and 1630 cm^{-1} although these are different to the losses reported for bulk $MgCO_3$ [15] and for the species formed following adsorption of CO_2 on MgO at room temperature [16]. We are unable to quote any HREELS data for the coadsorption experiments be-

cause of this "oxide domination."

Discussion

We consider first the changes in the O(ls) and C(ls) regions of the photoelectron spectrum of an initially clean Mg(100) surface which was exposed to 300L of a mixture of $CO_2(g)$ and $O_2(g)$ at 80K. At the very lowest temperatures, the O(ls) spectrum is dominated by a peak at a binding energy of 536.6 eV which is attributed to physisorbed CO_2 [6, 10]. Warming the sample in a continuous flow of oxygen (10 mbar) to

98K leads to desorption and reaction, producing a fall in intensity of physisorbed CO_2, while new components with lower binding energy develop at 533.4 eV and 530.5 eV. The C(ls) region of the spectrum evolves similarly during this stage, an initial peak at 293.2 eV losing intensity. Further warming causes the feature associated with molecular CO_2 to fall further, and by 173K loss of this species is almost complete. The feature at binding energy of 530.5 eV appears at 98 K and grows in intensity as the temperature rises. This peak is identical to the main peak observed during oxidation of clean magnesium by dioxygen [17]. The feature at binding energy of 533.4 eV is assigned to carbonate [6, 18]. We note that Mg(100) surface did not show any measureable reactivity toward carbon monoxide [19].

XPS results indicate that the adsorption of carbon dioxide is dissociative resulting in both surface oxide and carbonate. The O(ls) data show that oxidation and carbonate formation occur simultaneously suggesting that dissociative adsorption involves the formation of an oxygen adatom which can either form oxide or react with CO_2 to form carbonate.

One of the conclusions from studies of oxygen species present during the formation of an oxide overlayer at a metal surface at low temperatures is the formation of a metastable oxide overlayer $O^-_{(s)}$ [20] which is a highly reactive species, whereas the thermodynamically stable O^{-2} (ads) species is by comparison unreactive [7]. We note that $O^-(s)$ is only present at low temperatures. This is illustrated in the following reaction scheme:

CO_2 (g) → CO_2(s)

CO_2 (s) → CO(g) + O^-(s)

O^-(s) + CO_2(s) → CO_3^{2-}(a)

O^-(s) → O^{2-}(a)
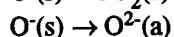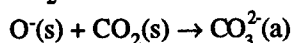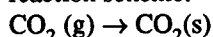
The symbol (s) represents the transient or short-lived nature of a species.

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