CO$_2$ chemisorption at Mg and MgO surfaces: a study with MIES and UPS(He I)

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Abstract

The interaction of CO$_2$ with Mg and MgO films (on Si substrates) is studied with MIES in conjunction with UPS(He I) at room temperature On Mg surfaces the presence of a carbonate (CO$_3^{2-}$) species is detected on top of an oxide layer On MgO surfaces chemisorption does not take place at regular sites, but presumably at low-coordinated O^{2-} ions as found at step sites Again a CO$_3^{2-}$ species can be identified with MIES Coadsorbed alkali atoms (Li) increase the rate of carbonate formation on MgO by about a factor of three at room temperature © 1998 Elsevier Science B V

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1. Introduction

The interest in the surface chemistry of CO$_2$ on Mg surfaces stems from several sources [1,2]: (i) CO$_2$ is of interest as a reactant in hydrocarbon synthesis. (ii) CO$_2$ is to a large extent responsible for the green house effect and therefore contributes to global warming; the catalytic reduction of CO$_2$ or, alternatively, its conversion into more valuable chemicals, such as hydrocarbons, methanol and others, is therefore of considerable interest. (iii) The activation of CO$_2$ at biological surfaces involves metal complexes. In photosynthesis, Mg ions, with oxygen directly coordinated to them, are the active centres in CO$_2$ fixation.

Studies of the CO$_2$ interaction with Mg and MgO surfaces are rather scarce. For MgO this

may be related to the fact that the application of most surface analytical techniques is restricted to conducting substrates although the charge-up problem on insulators can be eliminated by preparing highly ordered ultrathin oxide films on conducting substrates [3].

AES and UPS(He II) were applied to the study of the interaction of CO and CO$_2$ with polycrystalline clean and oxidized Mg surfaces [4]; considerable attention was paid to the chemisorption of CO$_2$ in the form of a carbonate which takes place above about 123 K

The reaction of CO$_2$ with a clean and preoxidized Mg(0001) surface was studied with XPS and EELS [5]. A mechanism for the carbonate formation observed above about 100 K was put forward: dissociative adsorption of oxygen takes place, followed by the chemisorption of CO$_2$ at oxygen sites.

The interaction of CO$_2$, among other oxygen containing molecules, with MgO single crystal

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surfaces was studied applying XPS, UPS(He II) and LEED [6]. Carbonate formation was detected on faceted MgO(111).

The physi- and chemisorption of CO_2 at regular and defective sites on MgO(100) was the subject of ab initio cluster calculations [7,8]. Chemisorption in the form of CO_3^{2-} takes place at defective sites with low-coordinated oxygen ions. The mechanism can be visualized as charge flow from the HOMO ($2p_z$) of O^{2-} to the LUMO ($2\pi_u^*$) of CO_2.

This paper is dedicated to the purpose of finding out whether metastable impact electron spectroscopy (MIES), in conjunction with UPS(He I), may serve as a tool for the detection and characterisation of CO_2 chemisorbed at surfaces of metals and, in particular, their oxides. We have chosen Mg and MgO surfaces because of (1) their interest for application (see above); (2) the availability of XPS and HREELS results for the interaction of CO_2 with Mg surfaces [5]; (3) the availability of numerical results for the chemisorption of CO_2, i.e. carbonate formation at MgO surfaces [7,8], and (4) our previous experience with these surfaces applying MIES/UPS [9].

The strategy pursued in the paper is as follows: firstly, we focus on the confirmation of the results obtained in Ref. [5] for the interaction of CO_2 with Mg surfaces using a combination of MIES and UPS(He I) (instead of XPS and HREELS as in Ref. [5]). Subsequently, we will test the predictions made in Refs. [7,8] concerning the interaction of CO_2 with MgO surfaces Since it is well known that the presence of alkali atoms at *metal* surfaces often greatly enhances the adsorption rate [1], we have finally studied the influence of alkali (Li) adsorption at the oxide surface on the reactivity against CO_2.

2. Experimental details

The apparatus has been described in detail previously [9–11]. Briefly, it is equipped with a cold-cathode gas discharge source for the production of metastable He*($2^3S/2^1S$) ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energies and He I photons ($E^* = 21.2$ eV) as a source for UPS. The

triplet to singlet ratio has been measured by He*–Ar impact as 7.1. Metastable and photon contributions within the beam are separated by means of a time-of-flight technique combined with a double counter system allowing to measure MIES and UPS quasi-simultaneously. The angle of incidence of the probe beams onto the surface is 45°; electrons emitted in the direction normal to the surface are analyzed. The simultaneous collection of a MIES and UPS spectrum requires about two minutes MIES and UPS measurements are performed using a hemispherical analyzer (VSW HA100) with an energy resolution of 250 meV for MIES/UPS. The experiments were performed biasing the target by 50 eV; this has been shown to have no influence on the spectral features. All spectra are displayed as a function of the binding energy E_B with respect to the Fermi level E_F Thus, zero binding energy corresponds to electrons emitted from the Fermi level of the substrate. The low-energy onset of the electron spectra reflects directly the surface work function; therefore, its variation with exposure gives directly the exposure dependence of the work function. The apparatus is furthermore equipped with LEED, XPS and AES.

Mg layers are produced by evaporating Mg from a commercial Knudsen cell on Si(100) substrates. The substrate was prepared as described in our previous work on alkali adsorption on Si(100) [12]. The evaporation is done at a cell temperature of 570 K thus producing about one half of a monolayer of Mg per minute. The electronic properties of this film display the same features as polycrystalline magnesium as judged from MIES and UPS(He I) spectra [9]. No LEED spots were obtained from the Mg layer.

Magnesia films were produced by oxygen exposure of magnesium films at room temperature followed by annealing to 800 K in an oxygen atmosphere; details can be found in Ref. [9]. Oxygen is offered through an UHV valve; the oxygen partial pressure is measured with a quadrupole mass spectrometer. The resulting MgO surface produces the same valence band emission in the MIES and UPS spectra as MgO(100) single crystals (see Ref. [9] and Section 3 2). In particular, the spectra show no indication for occupied point defect states in the lower part of the bandgap

(below the Fermi level). No LEED spots were obtained from the oxide film. The thickness of the MgO layer on Si(100) is estimated as 10 nm on the basis of the ratio of $Si(2p)$ and $Mg(2p)$ XPS peaks. This ratio decreases exponentially as a function of layer thickness.

The base pressure of the apparatus amounts to 7×10^{-11} Torr; during the evaporation of Mg the pressure rises to 3×10^{-10} Torr All measurements are performed at room temperature. The results are presented as a function of the CO_2 exposure.

3. Results

3 1 CO_2 interaction with Mg

Figs. 1 and 2 show the MIES and UPS(He I) results obtained during the CO_2 exposure of a Mg film on Si(100). We will not discuss the spectra from the metallic Mg film in detail (see Ref [9]). Briefly, the MIES spectrum obtained from the clean Mg film (bottom spectrum in Fig. 1) is mostly due to the Auger capture process, involving two electrons from the metallic Mg film (see Refs. [13,14] for introductions into MIES). Only for binding energies between zero and about 1 eV can a weak contribution from Auger deexcitation of the metastable probe atom, involving only one electron from the Mg film, can be seen. With increasing CO_2 exposure the contribution to the spectra originating from metallic parts of the film (between 0 and 5.5 eV) gradually disappears. The development of a region with very little emission in this energy range is characteristic for the formation of an insulating film having a bandgap of about 5.5 eV width below the Fermi level. In the exposure range above 600 L the MIES spectra are practically due to the Auger deexcitation process only.

The CO_2-induced peaks at $E_B = 7$ 6 and 12.2 eV (labelled CO_3^{2-}) can be identified as due to carbonate (CO_3^{2-}) formation by comparison with literature data (see Refs. [4,6,15] and references given therein); they must be assigned to the MO's ($1a_2'$; $1e''$; $4e'$) (7.6 eV) and ($3e'$; $1a_2''$) (12 2 eV). There is no indication of the third peak expected from the ionization of the $4a'$ MO [15]. In MIES this peak will be difficult to detect because it would be
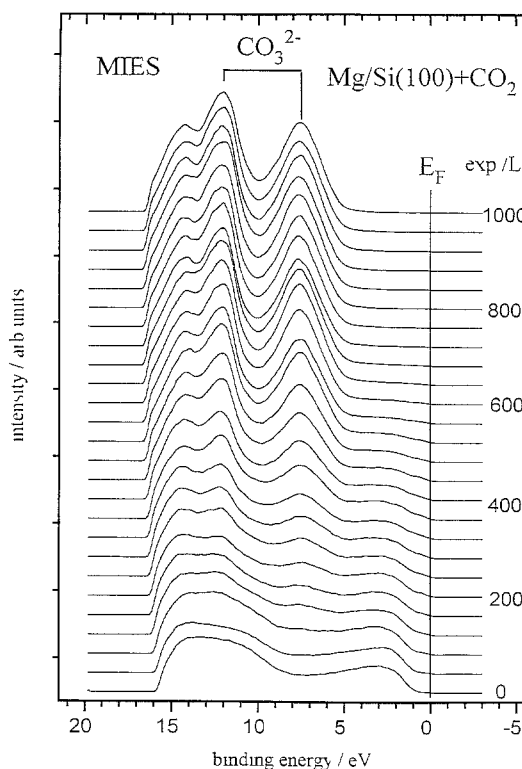
located close to the low energy cutoff of the spectra which is affected by secondary electron emission. The CO_2-induced features are also seen with UPS where they are superimposed on oxygen-induced features (see below). The spectra are rather different from those obtained when the Mg film is exposed to O_2 (or N_2O [16]), in these cases the spectrum displayed in Fig. 3a (see below) is obtained.

The identification of the structure labelled $O(2p)$ (extending from about 5 to 10 eV below E_F), seen prominently in the UPS(He I) spectra of Fig. 2, follows from our studies on MgO: the same structure was seen for MgO(100) single crystals and oxidized Mg films [9]. In these cases it is due to emission from MgO valence band states having predominantly $O(2p)$ character. Thus, in the present case the structure must also arise from the
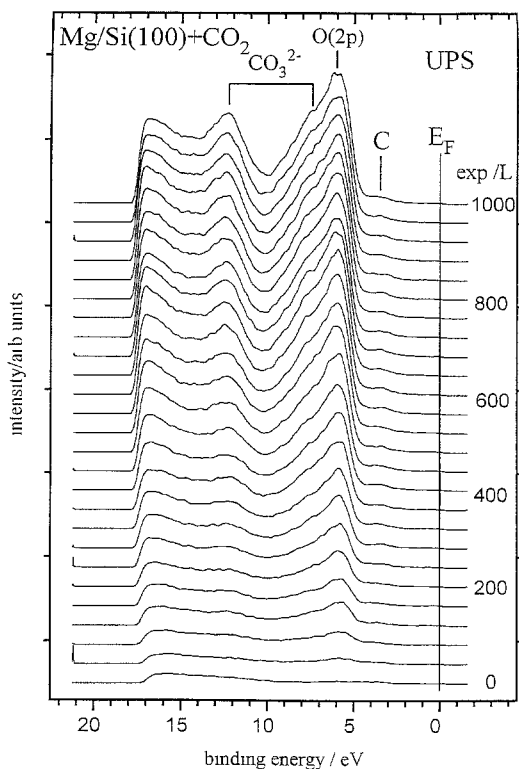

Fig 1 MIES spectra from Mg film on Si(100) (thickness about 10 nm) as a function of CO_2 exposure. The bottom spectrum is for the clean Mg film The CO_2 exposure increases by 40 L between each two spectra

Fig 2 UPS spectra from Mg film on Si(100) (about 10 nm) as a function of CO_2 exposure The bottom spectrum is for the clean Mg film The CO_2 exposure increases by 40 L between two spectra

Fig 3 MIES spectra from MgO film on Si(100) (about 10 nm) (a) "As prepared" MgO film and (b) difference spectrum after 360 L CO_2 exposure

formation of (Mg–O) bonds. Interestingly, O(2p) is not seen with MIES. The features ($E_B = 7.6$ and 12 2 eV), attributed to carbonate (CO_3^{2-}) formation, are also seen; they are comparatively weak, in particular the peak at 7.6 eV. UPS, but not MIES, shows additional intensity at $E_B = 3$ eV (labelled C in Fig. 2).

3.2. CO_2 interaction with MgO

Fig 3 shows MIES results for MgO films on Si(100). The oxide film thickness is of the order of 10 nm [9]. The spectrum of the oxide film (a) shows the O(2p) valence band structure (see also Fig. 2); a detailed discussion of results obtained for clean MgO surfaces, together with a comparison of the results obtained for MgO(100) bulk crystals, can be found in Ref. [9].
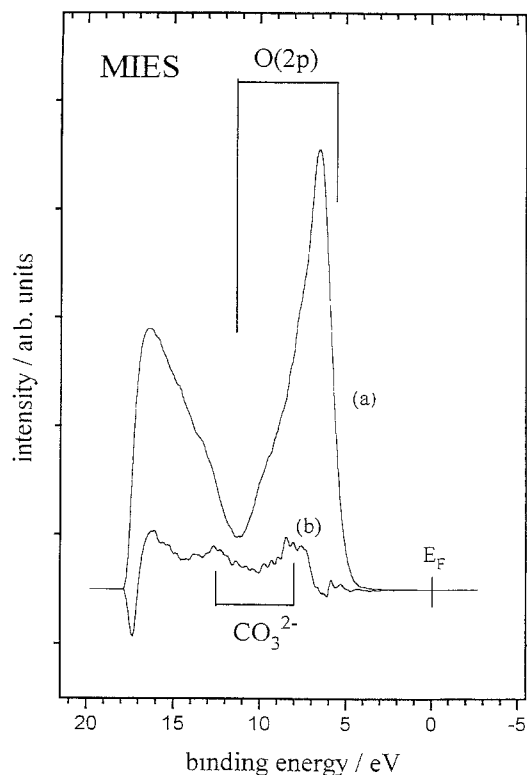
Upon CO_2 exposure the same features as discussed in Section 3 1 appear, now at $E_B = 7$ 8 and 12.6 eV. They are seen more clearly in the difference between the spectra for 360 L exposure and the "as prepared" MgO surface shown in Fig. 3b. As in Section 3.1, we attribute the CO_2-induced emission to the formation of a carbonate species. The intensity of the features is of the order of one percent of that obtained during the exposure of a Mg film to CO_2. Moreover, the valence band emission (denoted by O(2p)) is at most weakened by ten percent during the CO_2 exposure. This indicates that the CO_3^{2-} species does not cover the entire surface, i.e does not chemisorb at regular surface sites No other additional features appear upon CO_2 exposure; in particular no signature can be seen of an O_2^{2-} species Such a species could originate from CO_2 dissociation, followed by the

interaction of the oxygen fragment with surface oxygen. Spectral features from the ionization of O_2^{2-} at MgO surfaces should appear as split-off states close to both the bottom and the top of the valence band emission [17].

We do not show any UPS results here because they are identical with those from MgO bulk surfaces [9]. No changes occur in the studied range of exposures, i.e. below 360 L; in particular, no carbonate features appear.

3.3. CO_2 coadsorbed with Li atoms on MgO

We have also made some exploratory studies dealing with the influence of Li atoms to the rate of CO_2 chemisorption (Fig. 4). Fig. 4a shows again the MIES spectrum of the MgO film; also shown are the difference spectra for the Li dosed oxide film (saturation Li dose at room temperature after 360 L CO_2 exposure) (Fig. 4b); after exposing the surface of (b) simultaneously to CO_2 and Li (Fig. 4c); and after the end of the Li supply and additional CO_2 exposure (200 L) (Fig. 4d).

A peak at zero binding energy is present after Li dosing (see (Fig. 4b)); a similar peak was also seen for adsorption of Cs atoms on metal oxides, including MgO [18]. It was attributed to the formation of Cs clusters at the oxide surface. Therefore, in accordance with Ref. [18], we attribute the zero energy feature to the interaction of the He metastable atoms with metallic Li areas on the film As for exposure to Cs [18] it is not possible at room temperature to attenuate the MgO valence band emission by more than about 20% by the exposure to Li. This suggests that no uniform Li overlayer can be formed under these conditions.

The extra features attributed to carbonate formation (seen now at $E_B = 7.8$ and 12.6 eV) are about a factor of three stronger than without Li coadsorption at the same CO_2 exposure.

4. Discussion

4.1. CO_2 interaction with Mg

From the combined information obtained with MIES and UPS and taking into account that
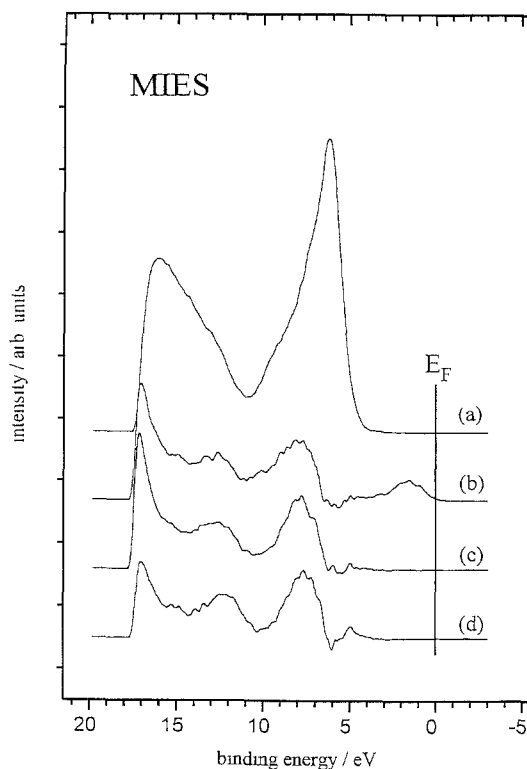

Fig 4 MIES spectra for a MgO film subjected to CO_2 exposure (a) "As prepared" MgO film, (b) difference spectrum after 360 L CO_2 exposure and Li dosing (saturation coverage at room temperature), (c) difference spectrum after coadsorption of Li atoms and CO_2 on the surface prepared in step (b), and (d) difference spectrum after stopping the Li supply and supplying additional 200 L CO_2

MIES cannot "see" below the top layer, we conclude that the outermost layer consists of a carbonate species while an oxide layer is underneath. It is well known that CO_2 adsorption is dissociative on a number of metals [1]. In these cases the presence of oxygen adatoms at the surface promotes the bonding of CO_2 in the form of carbonates. Thus, we feel that the carbonate formation on Mg occurs in two steps: at first, the CO_2 dissociates on the surface and (Mg–O) bonds are formed. In the second step, impinging CO_2 molecules chemisorb at sites which are oxygen terminated (Mg–O bonds) This leads to the formation of CO_3^{2-}. MIES, being sensitive to the outermost edge of the surface, sees only the carbonate ter-

mination of the surface, but cannot eject electrons from the oxide. Campbell et al. arrived at the same adsorption scenario on the basis of their EELS and XPS results [5]

Further support for dissociative adsorption as the first step in carbonate formation comes from results for the interaction of N_2O with Mg [16]: the valence band spectra obtained with MIES and UPS(He I) are simply those of MgO films. In contrast to CO_2 the oxygen-modified film does not possess further reactivity against N_2O

The structure labelled C in Fig. 2 could be due to the formation of carbide below the surface (possibly resulting from a partial decomposition of the carbonate species at room temperature). A similar feature was seen in the UPS(He II) spectra obtained after CO interaction with clean Mg surfaces [4] However, it appears also possible that further interaction of CO_2 with the oxygen-modified film produces a species resembling O_2^{2-} [17].

4.2 CO_2 interaction with MgO

The comparison of the UPS and MIES results clearly demonstrates the superior sensitivity of MIES for the detection of surface adsorbed CO_3^{2-} species at MgO surfaces. The signature of the carbonate species is the same as for the Mg film exposed to CO_2. It is predicted that on MgO chemisorption (as CO_3^{2-}) takes place at surface defects only, namely at four-coordinated O^{2-} species as found at step sites [7,8]. Our results support this prediction. MIES appears to exclude occupied point defects as possible alternative chemisorption sites, and the formation of CO_3^{2-} (and not CO_2^{8-}) indicates that these defect sites are low-coordinated oxygen O^{2-} (and not Mg^{2+}) ions. The numerical results predict furthermore that the chemisorption produces a monodentate carbonate species. This suggests that the two CO_2-induced features (at $E_B = 7.8$ and 12.6 eV) are the signature of a monodentate CO_3^{2-} species.

It was suggested in Ref. [9] that O_2^{2-} complexes may be formed during the oxygenation of Mg surfaces, here during the MgO film preparation. The numerical results of Ref. [17] also do not exclude that such complexes may be present at MgO surfaces We have exposed the oxide film to

CO. Given the presence of O_2^{2-} complexes at the surface, we would expect that CO_3^{2-} formation occurs also via the reaction $O_2^{2-} + CO \rightarrow CO_3^{2-}$. We find (see Ref. [16]) that the exposure to CO does not lead to carbonate formation. This confirms the results of Ref. [5], but disagrees with Ref [6]. At present it appears that O_2^{2-} complexes (if at all present at the surface of MgO films) are not important for the formation of carbonate species.

The numerical results of Refs [7,8] provide evidence (see above) that a monodentate CO_3^{2-} species is present at the MgO surface. On the Mg film, as discussed in Section 4.1, the CO_2 molecules bond also to atomic oxygen (coordinated to Mg) which results from CO_2 dissociation Therefore a monodentate carbonate species should be present in both cases This statement is supported by our finding that the spectral features from the ionization of the carbonate species at the MgO film and at the Mg surface subjected to CO_2 are very similar both in their energetic position and relative intensities. On the other hand, the EELS spectra of Ref. [5] seemed to favour a bidentate carbonate species (see however the criticism formulated in Ref. [1]). Apparently, additional information is required to elucidate this point further.

4.3. CO_2 coadsorbed with Li atoms on MgO

The promotion of carbonate formation by coadsorbed Li may be of considerable interest because Li doped MgO is known to act as catalyzer for the conversion of methane to ethane [19]. However, the interpretation of the results is hampered by the fact that we have no information on the Li adsorption site. Therefore, at present, we can only speculate on reasons for the enhancement of the rate for CO_2 chemisorption in the presence of the Li species:

(1) It was shown that the bonding of CO_2 on MgO can be viewed as a HOMO–LUMO interaction, i.e as a flow of charge from the O 2p orbital to the lowest unoccupied $2\pi_u^*$ MO of CO_2 [7,8]. This leads to an O–C–O surface complex which is considerably distorted from the linear structure of the isolated CO_2 molecule; in particular, the O–C–O angle is reduced to about $130°$ At the clean MgO surface the

carbonate complex is unstable against dissociation into CO_2^- and (O–Mg), except at sites with low-coordinated oxygen atoms [7,8]. Possibly, the presence of alkali atoms facilitates the charge flow into the $2\pi_u^*$ MO and leads to the stabilisation of the carbonate complex. The strong influence of alkali atoms onto the adsorption of CO_2 on *metals* is well established [1].

(2) The second possibility to explain the Li influence could be the transfer of the Li 2s electron into an oxygen vacancy (V_a centre) at the surface leading to the formation of a surface colour centre (F^+). The formation of ($Li–F^+$) complexes could modify the Madelung potential at the sites of nearby O^{2-} anions in a way that carbonate formation becomes feasible at such sites.

(3) At the present stage of our knowledge, we like to exclude Li^0 centres, i.e. ($Li^+–O^-$) complexes [20], as the possible origin for the enhanced CO_2 chemisorption as CO_3^{2-}: the CO_3^{2-} formation requires an O^{2-} site rather than the O^- surface site of the Li^0 centre

5. Summary

We have been able to demonstrate that MIES in conjunction with UPS(He I) is a sensitive tool for the detection and characterisation of carbonate species formed at Mg and MgO surfaces. The following results were obtained: (i) For CO_2 interacting with Mg surfaces, here a Mg film on a silicon surface, we have verified the results of Roberts and coworkers [5], namely that the interaction of CO_2 with a Mg surface leads to a carbonate layer on top of an oxide layer. (ii) When CO_2 interacts with MgO at room temperature, a fraction of the order of 10^{-2} of a full CO_3^{2-} monolayer is formed. Our results support the prediction of Pacchioni et al. [7,8] that chemisorption (connected with CO_3^{2-} formation) takes place only at surface sites with low-coordinated O^{2-} ions (as found at step sites). (iii) The coadsorption of alkali atoms (Li) increases the yield for CO_3^{2-} formation by about a factor of three. (iv) Our results are compatible with the assumption that, both at the MgO and the Mg surface exposed to CO_2, the carbonate is present as a monodentate species.

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