

## Chapter 5

### CO<sub>2</sub> Adsorption on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}2$ ) Surfaces

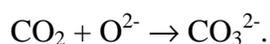
#### 5.1 Introduction

CO<sub>2</sub> is used often as an acidic probe molecule for characterizing the basicity of oxide surfaces [1-6]. CO<sub>2</sub> is traditionally viewed as a weak Lewis acid, which probes strong basic sites because of the electropositive nature of the carbon atom [7]. The nature of acidic and basic sites on oxide surfaces can be described in both Lewis and Brønsted terms. For clean metal oxide surfaces (no surface protons), the properties are principally described in terms of Lewis acidity and basicity. On metal oxides, coordinately unsaturated metal cations are generally thought of as Lewis acid sites, while the oxygen anions are thought of as Lewis base sites [8,9]. The electron-deficient metal cations exhibit acidic, electron-acceptor character, while the electron-rich oxygen anions exhibit basic, electron-donor character [8,9].

A molecular view of the relationship between the acidity and basicity of metal oxide surfaces has proven useful in studying the chemistry of well-defined oxide systems. Vohs and Barteau have shown that cation/anion accessibility is required for the dissociation of Brønsted acids on single crystal ZnO surfaces [10]. The (0001)-Zn surface exposes oxygen anions and zinc cations that provide the acid/base site pair necessary to dissociatively adsorb many Brønsted acids. The (0001)-O surface is terminated by oxygen anions that sterically block the zinc cations. This anion-terminated

surface is inert with respect to dissociation of Brønsted acids because there are no accessible cations to form the acid/base site pairs [10-16].

The electrophilic properties of CO<sub>2</sub> lead to an expectation of charge transfer from the surface to the molecule to form an anion. One consequence of the degenerate ground state electronic structure of CO<sub>2</sub> is that anion formation gives rise to changes in molecular geometry which tend to give “bent” chemisorbed species [17]. Stabilization of the anion occurs by distorting the molecular geometry to a lower, non-linear symmetry to split the degeneracy of the CO<sub>2</sub> 2π<sub>u</sub> LUMO, an effect readily illustrated by a Walsh diagram [17]. On oxide surfaces, the adsorption of CO<sub>2</sub> can be viewed simplistically as an acid/base reaction involving the addition of a basic oxide ion to acidic CO<sub>2</sub> to form carbonate:



However, many forms of adsorbed CO<sub>2</sub> have been reported on oxide surfaces, including bent CO<sub>2</sub><sup>δ-</sup> anions at metal centers, linear unperturbed physisorbates, and monodentate and bidentate carbonate species [18-20].

In an early study using NEXAFS, Freund and coworkers made a preliminary assignment of bidentate carbonate following CO<sub>2</sub> adsorption on Cr<sub>2</sub>O<sub>3</sub> (0001) thin film surfaces, epitaxially grown over Cr (110) [3]. On the basis of infrared data, it was later reported that bidentate carbonates were not formed, and the strongly adsorbed CO<sub>2</sub> was attributed to a surface carboxylate, described as a bent CO<sub>2</sub><sup>δ-</sup> species adsorbed at chromium ions on (0001) surface [19]. These results are in contrast to the infrared observations of bidentate carbonates over α-Cr<sub>2</sub>O<sub>3</sub> microcrystal powders [2]. Freund and coworkers attribute the difference to the fact that α-Cr<sub>2</sub>O<sub>3</sub> microcrystal powders do not expose faces with the (0001) termination as the primary surface [21]. The predominant

surface on chromia powders is the  $(10\bar{1}2)$  surface, which is the one that is under study in this investigation [21].

The  $\text{CO}_2\text{-Cr}_2\text{O}_3$  interaction has been well documented over chromia powders [2]. Zecchina *et al.* used infrared spectroscopy to study  $\text{CO}_2$  adsorption over unsupported  $\text{Cr}_2\text{O}_3$  microcrystalline powders where the predominant surface is the  $(10\bar{1}2)$  and showed  $\text{CO}_2$  bonding in a bidentate arrangement where the main active sites are the coordinately unsaturated  $\text{Cr}^{3+}$  and  $\text{O}^{2-}$  couples [2,19,21]. Such site pairs are also available on the ordered, stoichiometric  $\text{Cr}_2\text{O}_3$   $(10\bar{1}2)$  surface prepared by ion bombardment and annealing in UHV, where the presence of surface OH, H, and excess O can be eliminated [22].

In this study,  $\text{CO}_2$  adsorption on the well-defined  $\text{Cr}_2\text{O}_3$   $(10\bar{1}2)$  single crystal surface was used to understand the details of the adsorption process.  $\text{Cr}_2\text{O}_3$   $(10\bar{1}2)$  is an useful model surface for studying the properties and reactivity of surface oxygen anions because of the flexibility it allows in exposing coordinately-inequivalent forms of lattice oxygen by the formation of stoichiometric and oxygen-terminated surfaces. [22]. The interaction of  $\text{CO}_2$  has been studied on surfaces exposing cation/anion site pairs and oxygen-terminated surfaces exposing terminal chromyl oxygen species.

## 5.2 Experimental

For TDS experiments, all surfaces were exposed to  $\text{CO}_2$  at 190 K and heated to 700 K using a linear temperature ramp of 2 K/sec. During TDS experiments, the background pressure was less than  $2 \times 10^{-10}$  Torr between doses.

XPS spectra were collected at 125 K from  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surfaces. Uniform steady-state charging occurs due to the insulating nature of  $\text{Cr}_2\text{O}_3$  [22]. To reference the binding energy scale, short XPS runs were made at a sample temperature of 900 K where the conductivity of the material is sufficient to prevent charging. The Cr  $2p_{3/2}$  binding energies at 900 K fall at  $576.9 \pm 0.2$  eV for a nearly-stoichiometric surface. This value is within the range typically attributed to  $\text{Cr}^{3+}$  in  $\text{Cr}_2\text{O}_3$  [23-25]. The binding energy scale of all XPS spectra has been shifted to align the Cr  $2p_{3/2}$  peak to 576.9 eV to compensate for the steady-state charging. XPS experiments were run at pass energies of 60 eV, which gives a FWHM of 1.06 eV for Ag  $3d_{5/2}$ .

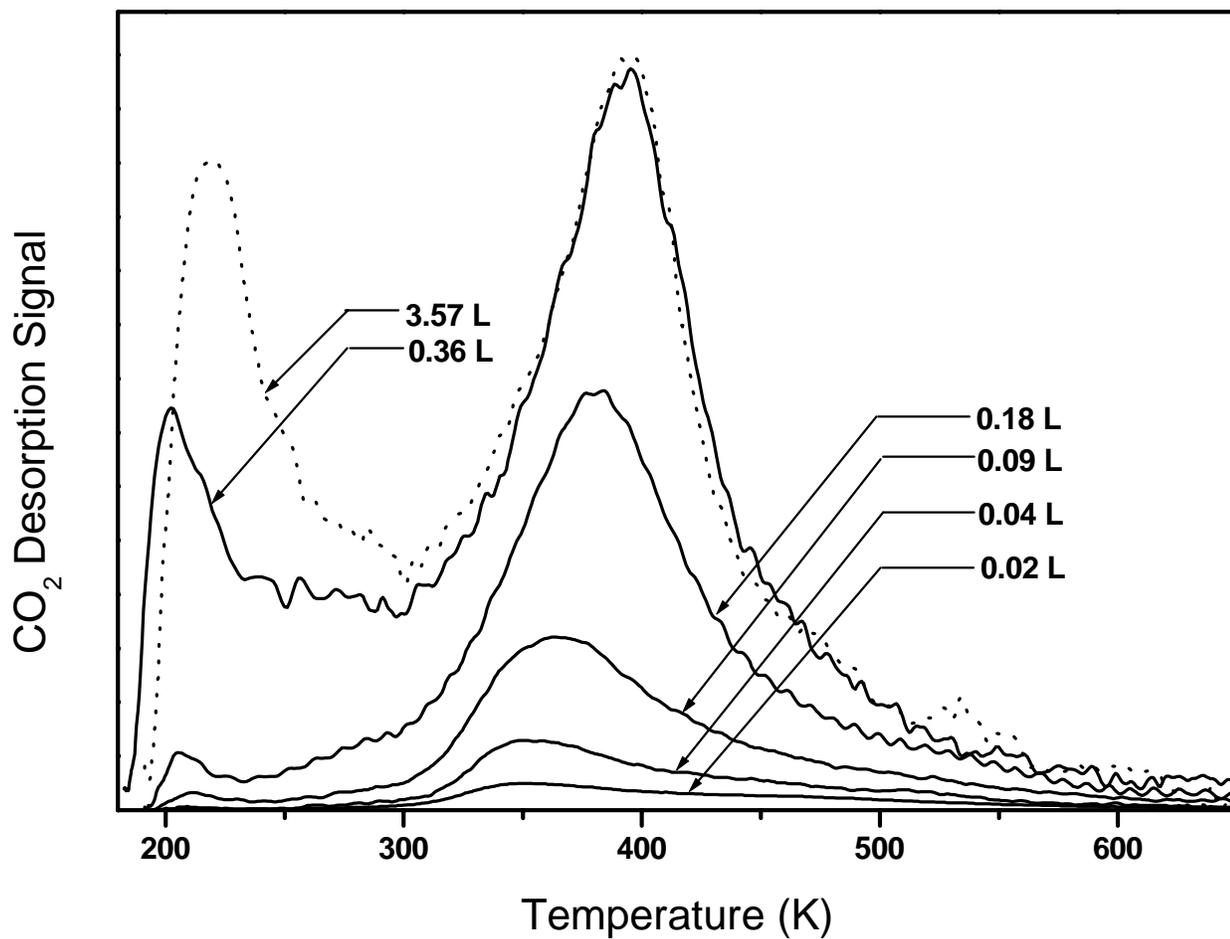
## 5.3 Results

### 5.3.1 Thermal Desorption Spectroscopy

Variations in  $\text{CO}_2$  adsorption were examined by TDS for all the surface preparations described above. All desorption features are thought to be first-order and originate from a molecular  $\text{CO}_2$  adsorbate. Only  $\text{CO}_2$  was observed in TDS following  $\text{CO}_2$  adsorption. Desorption of CO was checked for but not observed, hence no reduction of  $\text{CO}_2$  to CO was seen. The lack of reaction products suggests no dissociation of  $\text{CO}_2$ .

#### 5.3.1.1 Nearly-Stoichiometric Surface

The coverage dependence of the  $\text{CO}_2$  desorption traces from a clean, nearly-stoichiometric surface following adsorption at 190 K is shown in Figure 5.1. At the lowest dose investigated, 0.02 L ( $1\text{L}=10^{-6}$  Torr-sec), one  $\text{CO}_2$  desorption peak is observed with a peak maximum at 350 K. This feature shifts up in temperature to 395 K with

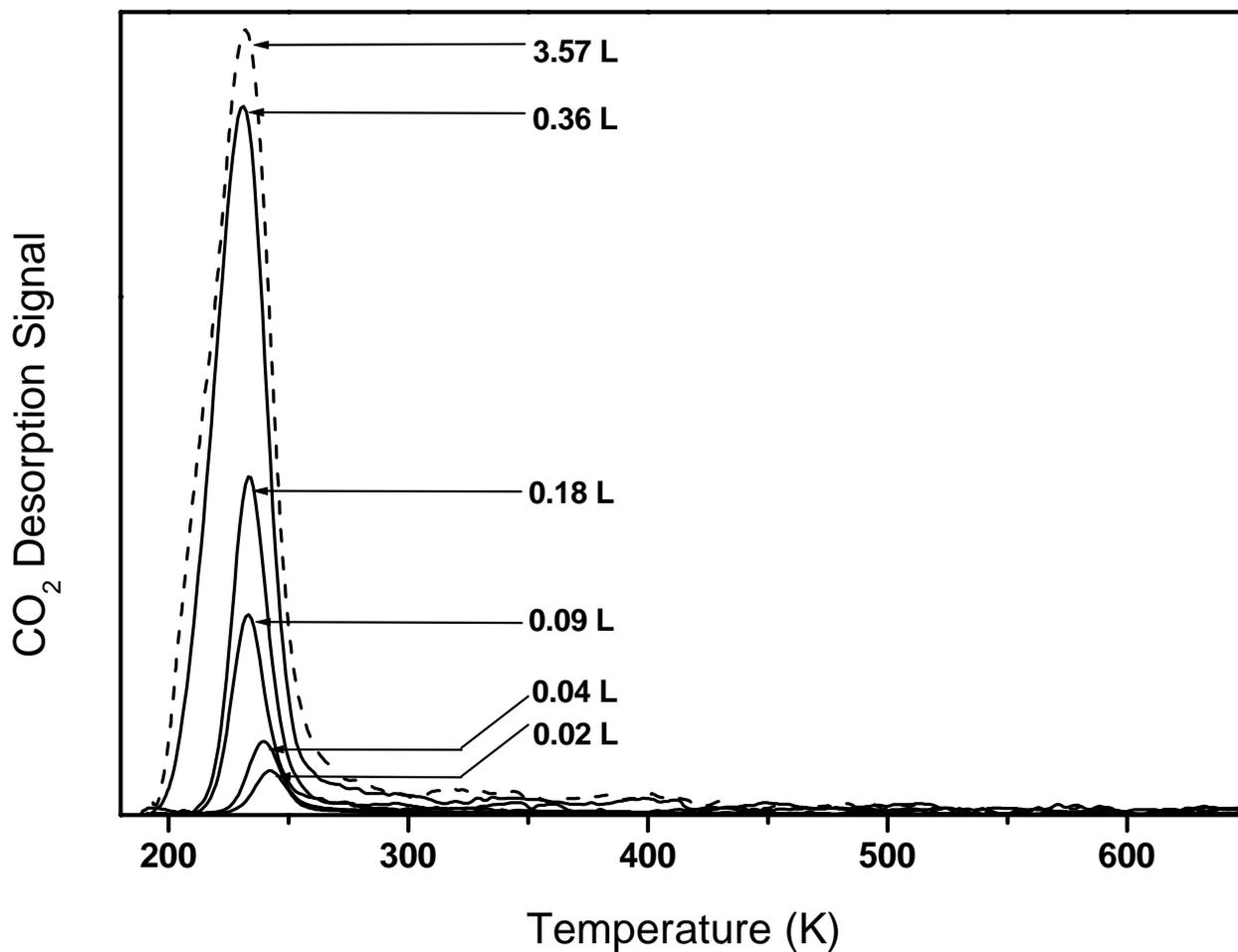


**Figure 5.1 TDS spectra showing desorption intensity versus temperature for 0.02-3.57 L exposures of CO<sub>2</sub> adsorbed on a nearly-stoichiometric Cr<sub>2</sub>O<sub>3</sub> surface.**

increasing coverage and saturates before a CO<sub>2</sub> exposure of 0.36 L. Also noticeable in the spectrum shown in Figure 5.1 is a broad, low-temperature feature near 220 K, which grows in at higher surface coverages. For this low-temperature feature, CO<sub>2</sub> desorption is seen immediately upon heating the surface. The observation suggests that an adsorption temperature of 190 K is not low enough to accommodate a fully-populated low temperature adsorption state. Hence, it is expected that a higher CO<sub>2</sub> coverage could be obtained with a lower adsorption temperature. (Note: On Cr<sub>2</sub>O<sub>3</sub> (0001) films, 180 K and 120 K desorption features are observed following adsorption at 90 K [19].) Assuming a normal first-order pre-exponential of 10<sup>13</sup> s<sup>-1</sup>, a range of 21.9-24.8 kcal/mol is found for the first-order activation energy for desorption of the higher-temperature (350-395 K) feature using the Redhead equation [26]. No attempt was made to independently determine the pre-exponential via the method of heating rate variation. The 220 K and 350 K CO<sub>2</sub> desorption temperatures on the nearly-stoichiometric surface are similar to the reported CO<sub>2</sub> desorption temperatures of 180 K and 330 K seen on Cr<sub>2</sub>O<sub>3</sub> (0001) films [19].

### ***5.3.1.2 Oxygen-Terminated Surface***

The coverage dependence of the CO<sub>2</sub> desorption traces from an oxygen-terminated surface following adsorption at 190 K is illustrated in Figure 5.2. At the lowest dose investigated, 0.02 L (1L=10<sup>-6</sup> Torr-sec), one CO<sub>2</sub> desorption peak is observed with a peak maximum at 240 K which falls between the desorption temperatures of the two features seen on the nearly-stoichiometric surface. This feature shifts down in temperature to 230 K with increasing coverage and approaches saturation near a CO<sub>2</sub>



**Figure 5.2 TDS spectra showing desorption intensity versus temperature for 0.02-3.57 L exposures of CO<sub>2</sub> adsorbed on an oxygen-terminated Cr<sub>2</sub>O<sub>3</sub> surface.**

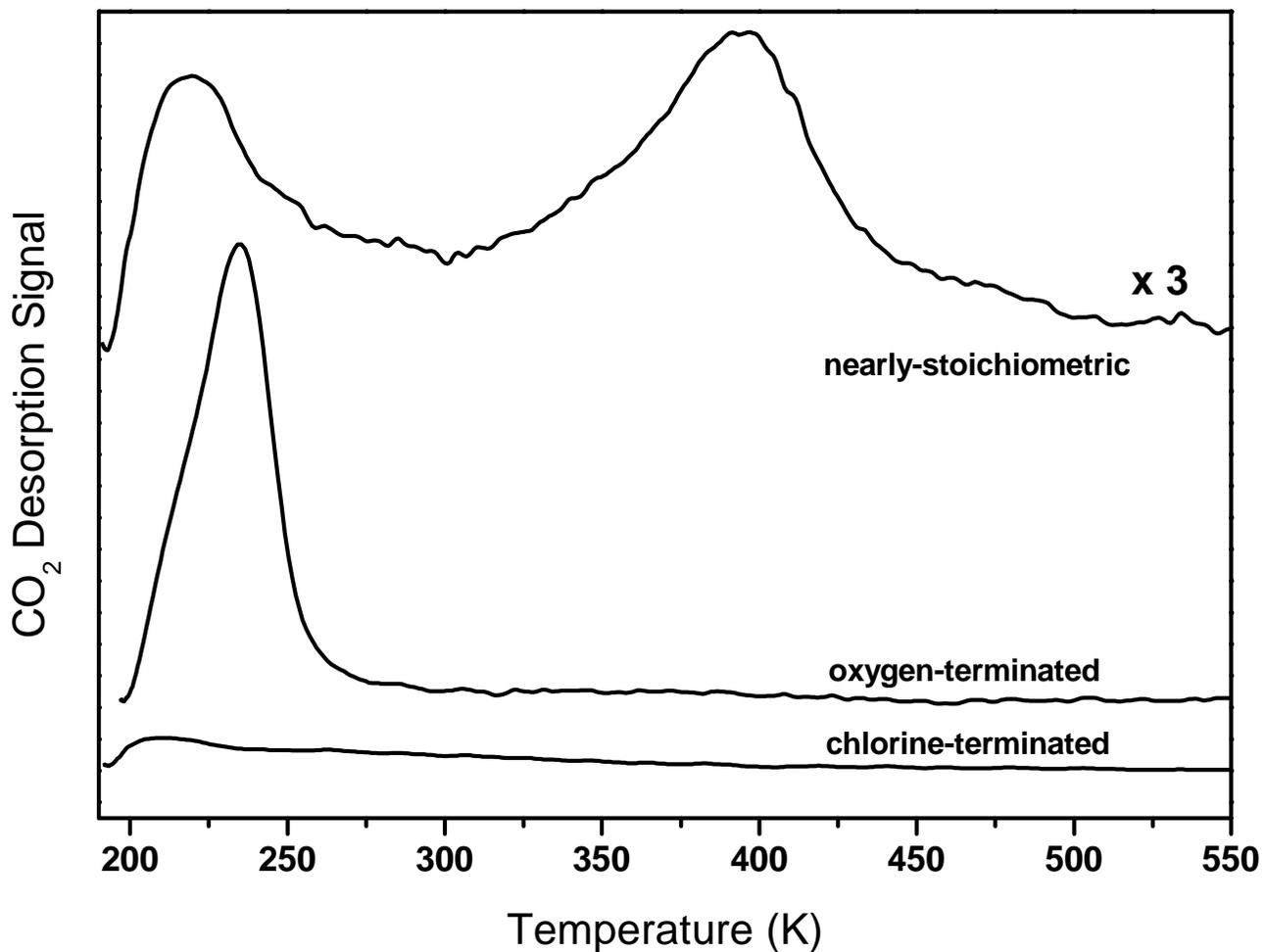
exposure of 0.36 L. Again, CO<sub>2</sub> desorption is seen immediately upon heating the surface, which suggests that the adsorption temperature of 190 K is not low enough to fully populate this low-temperature (230 K) feature. Assuming a normal first-order pre-exponential of 10<sup>13</sup> s<sup>-1</sup>, a first-order activation energy for desorption of about 14.6 kcal/mol can be estimated from the Redhead equation [26]. The 230 K CO<sub>2</sub> desorption temperature on the oxygen-terminated surface falls between the two desorption features from the nearly-stoichiometric surface.

### ***5.3.1.3 Chlorine-Terminated Surface***

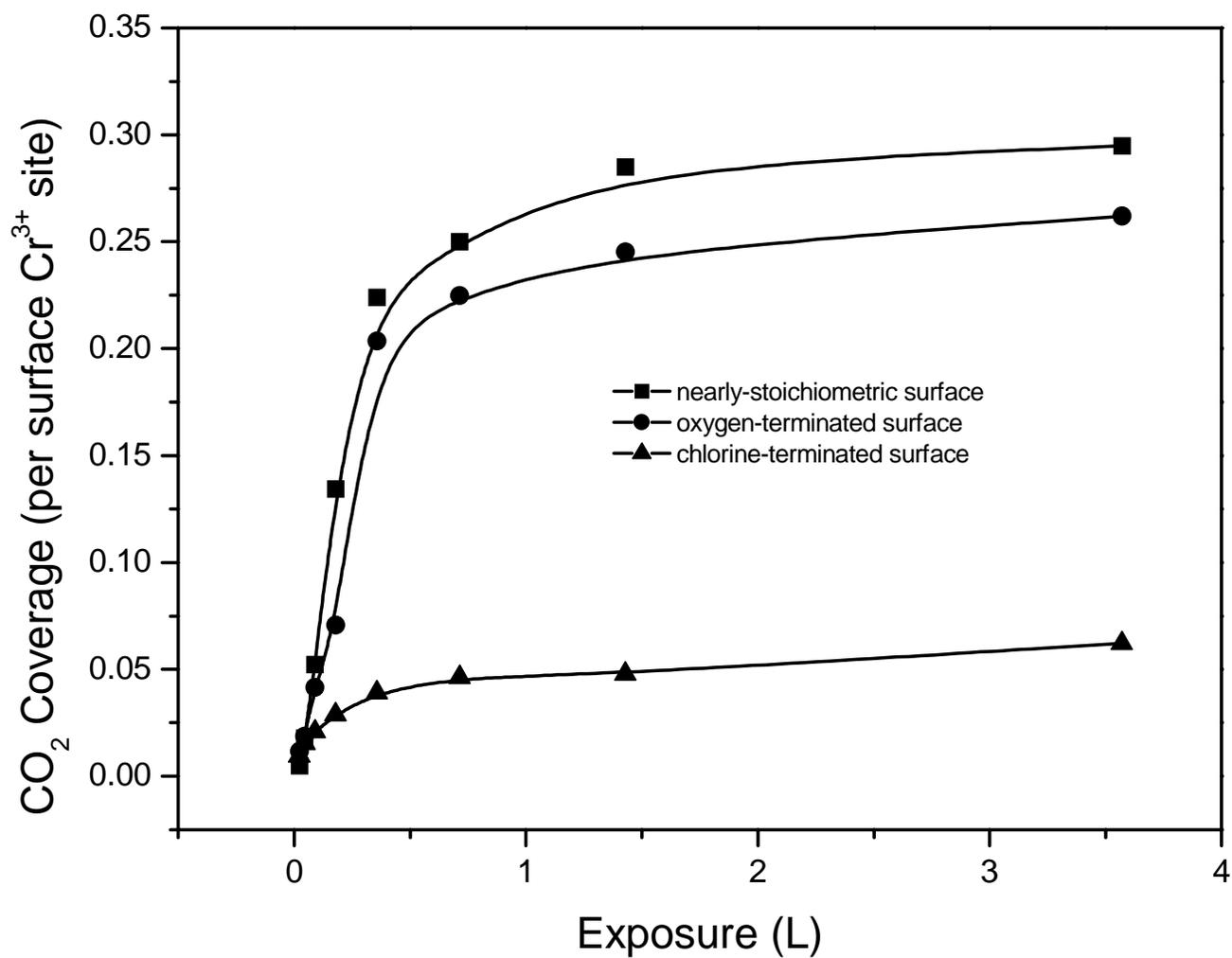
Very little CO<sub>2</sub> uptake was detected on the chlorine-terminated surface. The small desorption features that were observed can be attributed to desorption from the sample holder hardware. A comparison of TDS traces following 5 L CO<sub>2</sub> exposures on the three surfaces is shown in Figure 5.3 and demonstrates that CO<sub>2</sub> uptake on the chlorine-terminated surface is greatly suppressed.

### ***5.3.2 Coverage Estimates***

An upper limit estimate of the coverage of CO<sub>2</sub> as a function of dose at 190 K is shown in Figure 5.4 for the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated surfaces. To estimate the coverage of CO<sub>2</sub> molecules, an initial sticking coefficient of unity was assumed, along with a density of Cr<sup>3+</sup> sites estimated from the Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) unit cell parameters [17]. The nearly-stoichiometric surface is estimated to expose 4.86×10<sup>14</sup> five-coordinate Cr<sup>3+</sup> sites/cm<sup>2</sup> [22]. In Figure 5.4, monolayer coverage is defined as one CO<sub>2</sub> molecule per surface cation (1 ML = 4.86×10<sup>14</sup> CO<sub>2</sub>



**Figure 5.3 Comparison of TDS spectra of 5 L exposures showed on the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated Cr<sub>2</sub>O<sub>3</sub> surfaces.**



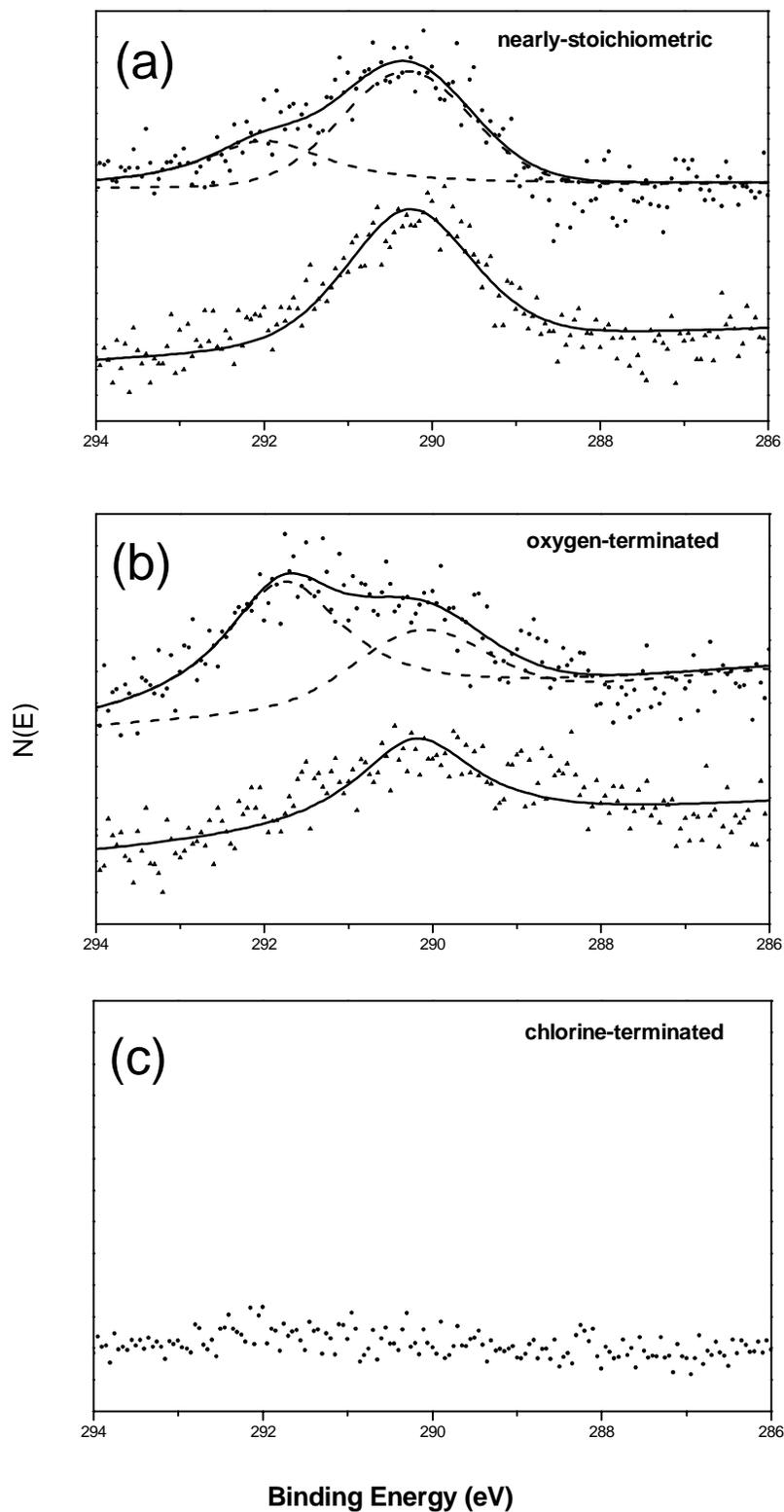
**Figure 5.4** CO<sub>2</sub> coverage per surface Cr<sup>3+</sup> cation as a function of exposure shown for the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated Cr<sub>2</sub>O<sub>3</sub> surfaces.

molecules/cm<sup>2</sup>). At 190 K, the nearly-stoichiometric surface saturates with a CO<sub>2</sub> coverage near 0.3 monolayers [27]. Using the same basis for the definition of a monolayer on oxygen-terminated surface, saturation coverage of about 0.26 is observed at 190 K. The saturation coverage of CO<sub>2</sub> at an adsorption temperature of 190 K is similar for both the nearly-stoichiometric and oxygen-terminated surfaces. From the TDS data, CO<sub>2</sub> desorption is seen immediately upon heating the surface. Hence, a higher CO<sub>2</sub> coverage could be stabilized with a lower adsorption temperature. CO<sub>2</sub> uptake on the chlorine-terminated surface is small in comparison and is attributed to desorption from the sample support hardware.

### **5.3.3 X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) was used as a check for carbonate formation following CO<sub>2</sub> adsorption on Cr<sub>2</sub>O<sub>3</sub> surfaces. Surface carbonates are distinguished in XPS by higher binding energies (289-292 eV) than other forms of surface carbon species reported on other surfaces [23,25]. Carbonates have been reported for Cu (110)-O and ZnO (10 $\bar{1}$ 0) in the range of 289-290.4 eV [20,28]. Physisorbed CO<sub>2</sub> has been reported for Cu (110)-O and ZnO (10 $\bar{1}$ 0) in the range of 291.8-292 eV [20,28]. The C 1s features following 7 L CO<sub>2</sub> exposures at 125 K are shown in Figure 5.5 for the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated surfaces. (Note: The adsorption temperatures of the XPS experiments are 65 K lower than those used for the TDS experiments.)

In Figure 5.5 (a), the C 1s feature for the nearly-stoichiometric surface is a broad feature with a binding energy centered around 290 eV. This broad feature falls in the



**Figure 5.5** XPS spectra show the C 1s region of CO<sub>2</sub> adsorbate on the (a) nearly-stoichiometric Cr<sub>2</sub>O<sub>3</sub> surface and surface annealed to 220 K, (b) oxygen-terminated Cr<sub>2</sub>O<sub>3</sub> surface, and (c) chlorine-terminated Cr<sub>2</sub>O<sub>3</sub> surface.

range of reported binding energies of carbonates and physisorbed CO<sub>2</sub>. If the nearly-stoichiometric surface is annealed to 220 K leaving only CO<sub>2</sub> associated with the 395 K desorption feature from TDS, the resulting C 1s feature narrows with a binding energy around 289 eV (shown in Figure 5.5 (a)). This feature at 289 eV is representative of a surface carbonate associated with the 395 K desorption feature on the nearly-stoichiometric surface. The CO<sub>2</sub> that is associated with the 220 K (or lower) desorption feature on the nearly-stoichiometric surface is likely representative of physisorbed CO<sub>2</sub>. In Figure 5.5 (b), the C 1s feature following a 7 L CO<sub>2</sub> exposure on the oxygen-terminated surface is a broad feature with a binding energy centered near 291.5 eV. This broad carbon 1s feature on the oxygen-terminated surface extends over the range of binding energies for both reported carbonates and physisorbed CO<sub>2</sub>. Therefore, the CO<sub>2</sub> associated with the 230 K (or lower) desorption feature on the oxygen-terminated surface can not be unambiguously identified with XPS. For the chlorine-terminated surface, no carbon 1s peak was detected by XPS, in agreement with the lack of uptake seen with TDS.

## 5.4 Discussion

### 5.4.1 Strong chemisorption of CO<sub>2</sub> on the nearly-stoichiometric surface

A variety of adsorbate geometries (carbonates CO<sub>3</sub><sup>2-</sup>, bent CO<sub>2</sub><sup>δ-</sup> anions, linear unperturbed physisorbates) should be considered for the interaction of CO<sub>2</sub> with chromia surfaces. For carbonate formation, two types must be considered: monodentate and bidentate. A monodentate surface carbonate species would be expected to form by the coordination of the CO<sub>2</sub> carbon to a coordinately-unsaturated surface oxygen anion.

Formation of a bidentate carbonate species would be expected to involve the coordination of the CO<sub>2</sub> carbon to a coordinately-unsaturated surface oxygen anion and one of the molecular oxygen atoms to a coordinately-unsaturated surface Cr<sup>3+</sup> cation [2]. CO<sub>2</sub> adsorbed in a non-linear arrangement is expected to be stabilized by backbonding into the CO<sub>2</sub> π\* orbitals [17,18].

Seiferth *et al.* [19] observed a 330 K desorption feature for strongly chemisorbed CO<sub>2</sub> on Cr<sub>2</sub>O<sub>3</sub> (0001) thin films that is blocked by oxygen predosing, similar to the 350-395 K desorption feature observed in this study. On the basis of infrared data, they assigned the adsorbate to a carboxylate (CO<sub>2</sub><sup>δ-</sup>) surface species at coordinately-unsaturated cation sites, and they noted that the (0001) surface is not the predominant surface on powders which expose primarily (10 $\bar{1}2$ ) planes [21]. Given the similarity in desorption temperatures (330 K [ref.19] vs 350-395 K [this study]) a similar assignment might seem reasonable for the (10 $\bar{1}2$ ) surface. One would expect the formation of a strongly chemisorbed carboxylate at a surface chromium site (as observed on Cr<sub>2</sub>O<sub>3</sub> (0001) thin films [19]) to require significant π-backbonding from the metal center. However, in previous work on the adsorption of CO (a good π acceptor) on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}2$ ), a desorption temperature of 195 K (first-order E<sub>a</sub> for desorption of 12 kcal/mol) was found suggesting a minimal capacity for π backdonation from the five-coordinate Cr<sup>3+</sup> cations on the (10 $\bar{1}2$ ) surface [31].

CO<sub>2</sub> bonding in a bidentate carbonate arrangement on Cr<sup>3+</sup>-O<sup>2-</sup> ion pairs has been observed by infrared spectroscopy over unsupported Cr<sub>2</sub>O<sub>3</sub> microcrystalline powders [2,19] where the predominant exposed crystal planes are (10 $\bar{1}2$ ) [21], the same as the single-crystal surface used in this study. In the present study, the nearly-stoichiometric

surface has both  $\text{Cr}^{3+}$  cations and  $\text{O}^{2-}$  anions available for interaction with  $\text{CO}_2$  [22]. The 350 - 395 K desorption feature on the nearly-stoichiometric surface seen in TDS only appears when there are  $\text{Cr}^{3+}$  surface sites available for interaction. When surface chromium atoms are terminated by oxygen or chlorine, the high temperature  $\text{CO}_2$  desorption feature observed in TDS disappears, indicating the importance of coordinately unsaturated  $\text{Cr}^{3+}$  cations in the formation of this chemisorbed species. Therefore, the 350-395 K  $\text{CO}_2$  desorption feature from the nearly-stoichiometric  $(10\bar{1}2)$  surface is attributed to a bidentate carbonate, consistent with the literature on chromia powders [2,19]. The XPS results are also consistent with carbonate formation for this higher temperature feature observed in TDS.

For the nearly-stoichiometric surface, a 45 K upward shift in the peak desorption temperature with coverage is seen in TDS for the strongly chemisorbed  $\text{CO}_2$  species attributed to bidentate carbonates. Such increases in desorption temperature are typically associated with attractive interactions between adsorbate molecules in an adlayer. However in the present case, the uptake of  $\text{CO}_2$  is limited to about 0.3 monolayers at 190 K on the nearly-stoichiometric surface, and only about 60% of that total (around 0.2 monolayers) is associated with the bidentate carbonate species. If attractive interactions between the adsorbate species were responsible for the increase in the desorption temperature, one would not expect such a low limiting coverage.

Two examples exist for well-defined  $\text{Cr}_2\text{O}_3$  surfaces where submonolayer quantities of impurity adatoms affect the adsorption of other molecules. Freund and coworkers [29,30] have shown that sub-monolayer coverages of sodium change the bonding of ethene ( $\text{CH}_2=\text{CH}_2$ ) from a  $\pi$ -donor to a di- $\sigma$  interaction. They suggest that

charge redistribution at the surface gives rise to more electron-rich chromium ions in the presence of sodium on  $\text{Cr}_2\text{O}_3$  (0001) thin film surfaces. It has also been observed that the addition of halogen to surface chromium sites at up to 1/3 of a monolayer coverage increases the desorption temperature of 1-chloro-1-fluoroethene ( $\text{CFCl}=\text{CH}_2$ ) on  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) by over 20 K [31]. Given the differences in the sign of the expected charge on the sodium and chlorine adatoms, it is likely that they have an opposite effect on the charge of neighboring cations. While the nature of these through-surface effects is not well understood, it is suggested that the charge transfer associated with bidentate carbonate formation gives rise to a charge redistribution that affects the strength of the adsorbate/surface interaction at neighboring cation/anion site pairs via some related through-surface process.

#### 5.4.2 Interaction of $\text{CO}_2$ with terminal chromyl oxygen ( $\text{Cr}=\text{O}$ )

On the oxygen-terminated surface, surface Cr sites are capped with terminal chromyl oxygen, leaving only surface oxygen exposed as possible adsorption sites. Therefore,  $\text{CO}_2$  must interact directly with oxygen sites on the surface in either a bent or linear conformation. The  $\text{CO}_2$  desorption feature on the oxygen-terminated surface falls distinctly between the desorption temperatures of the two TDS features seen for the nearly-stoichiometric surface. Even though the  $\text{CO}_2$  desorption features of these surfaces are distinctly different, the  $\text{CO}_2$  uptake is very similar at 190 K. On the chlorine-terminated surface where all surface Cr sites are terminated with chlorine adatoms, no  $\text{CO}_2$  uptake is seen. Therefore, the terminal chromyl oxygens ( $\text{Cr}=\text{O}$ ) on the oxygen-terminated surface appear to be directly involved in the  $\text{CO}_2$  adsorption process.

It is most reasonable to expect that terminal surface oxygen should interact with the electropositive carbon atom rather than an oxygen atom of a CO<sub>2</sub> molecule. The interaction between two essentially closed-shell oxygen atoms (terminal oxygen on the surface and molecular oxygen on the CO<sub>2</sub> molecule) is not expected to give rise to any significant attractive interaction, and would more likely give a short-range interaction that is repulsive in nature. For these reasons, CO<sub>2</sub> adsorbed on the oxygen-terminated surface is tentatively identified as a “monodentate adsorbate” bound at the terminal chromyl oxygens. Whether the extent of charge transfer is sufficient to give a true monodentate carbonate, a bent CO<sub>2</sub> adsorbate, or a more linear “physisorbate” is not known. The XPS results tend to favor the identification of CO<sub>2</sub> adsorbed at terminal oxygens as a monodentate carbonate, but the C 1s binding energies do not provide definitive proof for such a species. It is noted that the low (230 K) desorption temperature is similar to the 190 K desorption temperature observed with IRAS by Seiferth *et al.* for a CO<sub>2</sub> physisorbate on oxygen-precovered Cr<sub>2</sub>O<sub>3</sub> (0001)/Cr (110) thin films [19]. On the (0001) surface, this weakly bound adsorbate is characterized by a 2352 cm<sup>-1</sup> vibrational feature [19] similar to gas phase CO<sub>2</sub>. The similarity in desorption temperature might suggest that the CO<sub>2</sub> adsorbate on the oxygen-terminated Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) surface could be best described as a molecular (nearly-linear) CO<sub>2</sub> adsorbate rather than a carbonate. Vibrational data would be helpful for making this distinction.

### 5.3 Basicity of Oxide Surfaces

Surface base sites on oxides are typically considered to be electron-rich surface oxygen anions that can donate electronic charge or bind acidic protons to form surface

hydroxyl groups [8,9], while the metal cations of metal oxides are generally considered the acid sites [8,9]. Attempts to study surface basicity typically employ acidic probe molecules, of which  $\text{CO}_2$  is the most common [7,32]. If the strength of the interaction of  $\text{CO}_2$  is taken as a measure of the basicity of the  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface, the  $\text{CO}_2$  thermal desorption results suggest that the nearly-stoichiometric surface is “more basic” than the oxygen-terminated surface. However,  $\text{CO}_2$  does not interact exclusively with base sites (oxygen anions) on the nearly-stoichiometric  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface, but with an acid (cation) and base (anion) site pair to form a bidentate carbonate. On the oxygen-terminated surface where cation/anion site pairs are not available,  $\text{CO}_2$  forms a weakly-adsorbed monodentate species, which directly interacts with base sites (terminal chromyl oxygens). Hence,  $\text{CO}_2$  probes base sites (terminal oxygen atoms) on the O-terminated surface. Because of the differences in site requirements for the formation of these two surface species, it is clear that  $\text{CO}_2$  does not provide a simple probe of surface oxygen species. Differences in the coordination of these adsorbate species make the heats of adsorption a poor measure of the basicity of surface oxide ions.

It has long been suggested that bidentate carbonate formation on chromia requires the participation of the coordinately unsaturated  $\text{Cr}^{3+}$  ions on  $\text{Cr}_2\text{O}_3$  [2,33,34]. In this study, the necessity of coordinately-unsaturated surface cations for the formation of bidentate carbonates on  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) has been clearly demonstrated. If the formation of a bidentate carbonate is to be considered in acid/base terms, it can be thought of as the interaction of an acidic carbon atom of  $\text{CO}_2$  with a basic surface oxygen anion site, and the interaction of a basic oxygen atom of  $\text{CO}_2$  with an acidic  $\text{Cr}^{3+}$  site of  $\text{Cr}_2\text{O}_3$ . In such terms, it is perhaps more reasonable to think of  $\text{CO}_2$  as an amphoteric probe molecule

capable of interacting with cation/anion (acid/base) site pairs when considering a bidentate carbonate. For strongly chemisorbed carboxylate species at cations (as reported on  $\text{Cr}_2\text{O}_3$  (0001) [19]) or monodentate species formed by an interaction with surface lattice oxygen, the primary interaction likely occurs at the molecular carbon, but the nature of the interaction is dependent on the nature of the coordinating surface site. These results from well-defined  $\text{Cr}_2\text{O}_3$  surfaces suggest that one should not consider  $\text{CO}_2$  to be a simple acidic probe molecule for characterizing the basicity of oxide surfaces without first considering the resulting adsorbate conformation and the nature of the interrogated surface site.

## 5.5 Conclusions

On  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ), the strongest  $\text{CO}_2$ -surface interaction occurs with cation/anion site pairs to form bidentate carbonates that are stable at room temperature. These sites are associated with five-coordinate  $\text{Cr}^{3+}$  cations and three-coordinate  $\text{O}^{2-}$  anions on the stoichiometric, non-polar ( $10\bar{1}2$ ) surface. Terminating the surface cations with chromyl oxygen ( $\text{Cr}=\text{O}$ ) via dissociative  $\text{O}_2$  chemisorption prevents this interaction and gives rise to a weakly-bound  $\text{CO}_2$  moiety, tentatively identified as a “monodentate”  $\text{CO}_2$  adsorbate bound to terminal chromyl oxygen surface sites. Differences in the coordination of these species make the heats of adsorption a poor measure of the basicity of surface oxide ions. Terminating the surface cations with chlorine adatoms blocks the interaction between  $\text{CO}_2$  and the surface.

## 5.6 References

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