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CO₂ Adsorption on α -Cr₂O₃ (10 $\bar{1}2$) Surfaces

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The basicity of oxide surfaces is often associated with surface lattice oxygen anions. CO₂ is the standard probe molecule for investigating surface basicity, but limited information is available in the surface science literature concerning its interaction with well-defined (single crystal) oxide surfaces. On stoichiometric Cr₂O₃ (10 $\bar{1}2$), CO₂ interacts with cation/anion site pairs to form bidentate carbonates that are stable at room temperature. This site pair consists of five-coordinate Cr³⁺ cations and three-coordinate O²⁻ anions on the clean, stoichiometric, nonpolar (10 $\bar{1}2$) surface. Terminating the surface cations with chromyl oxygen (Cr=O) via dissociative O₂ chemisorption breaks the interaction and gives rise to a weakly bound CO₂ moiety, tentatively identified as a “monodentate” CO₂ adsorbate bound to terminal chromyl oxygen 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 CO₂ and the surface, and no uptake is observed.

I. Introduction

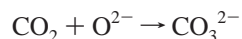
Acid/base characterizations of oxide surfaces have been used often to explain the catalytic behavior of oxide materials. The nature of acidic and basic sites on oxide surfaces can be described in both Lewis and Brønsted terms. For clean metal oxide surfaces (no surface protons), the properties are principally 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.^{1,2} The electron-deficient metal cations exhibit acidic, electron-acceptor character, while the electron-rich oxygen anions exhibit basic, electron-donor character.^{1,2}

This atomic site model of surface acidity and basicity has proven extremely useful for understanding the chemistry of well-defined oxide surfaces. Vohs and Barteau have shown that cation/anion (i.e., acid/base site pair) accessibility is required for the dissociation of Brønsted acids on single-crystal ZnO surfaces.^{1,3–8} The (0001)-Zn surface exposes zinc cations and oxygen anions 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 the dissociation of Brønsted acids because there are no accessible cations to form the acid/base site pairs.^{1,3–8}

Carbon dioxide is used often as an acidic probe molecule for characterizing the basicity of oxide surfaces.^{9–14} CO₂ is traditionally viewed as a weak Lewis acid that probes strong basic sites because of the electropositive nature of the carbon atom.¹⁵ The electrophilic properties of CO₂ 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 linear CO₂ is that anion formation results in changes in molecular geometry that give “bent” chemisorbed species.¹⁶ Stabilization of the anion occurs by distortion of the

molecular geometry to a lower, nonlinear symmetry to split the degeneracy of the CO₂ 2 π_u LUMO, an effect readily illustrated by a Walsh diagram.¹⁷

On oxide surfaces, the adsorption of CO₂ can be viewed simplistically as an acid/base reaction involving the addition of a basic oxide ion to acidic CO₂ to form carbonate:



This view is in line with Tanabe’s definition of the base strength of a solid surface as its ability to convert an adsorbed, electrically neutral molecule into its conjugate base by electron pair donation.^{9,10} However, CO₂ may coordinate to an oxide surface in different ways and form several types of surface species including bent CO₂^{δ-} anions at metal centers, linear unperturbed physisorbates, and monodentate and bidentate carbonate species.^{16,18,19} While the occurrence of these species is widely recognized and methods for their identification (particularly the monodentate and bidentate carbonates) have been reviewed,²⁰ there has been little discussion of how the coordination differences impact the interpretation of site basicity that CO₂ is so often used to probe.

Reports of the interaction of CO₂ with chromia are available for both high surface area particles and more well-defined (ordered) surfaces. In an early study using NEXAFS, Freund and co-workers made a preliminary assignment of bidentate carbonate following CO₂ adsorption on Cr₂O₃ (0001) thin film surfaces epitaxially grown over Cr (110).²¹ On the basis of infrared data, it was later reported that bidentate carbonates were not formed, and strongly adsorbed CO₂ was attributed to a surface carboxylate, described as a bent CO₂^{δ-} species adsorbed at chromium ions on the (0001) surface.¹⁸ These results are in contrast to the infrared observations of bidentate carbonates over α -Cr₂O₃ microcrystalline powders.^{18,22} The differences were attributed to the fact that powders do not expose faces with the (0001) termination as the primary surface.²³

The CO₂–Cr₂O₃ interaction has been well documented over chromia powders.²² Zecchina and co-workers used infrared

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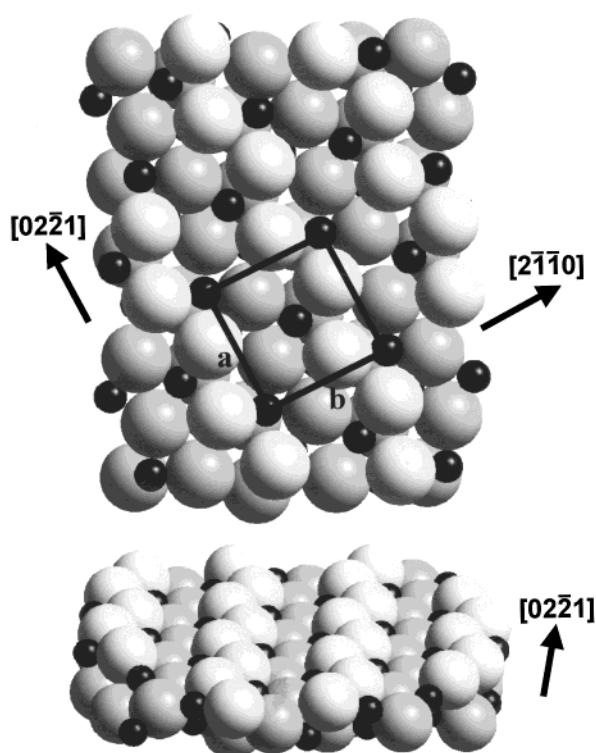


Figure 1. Ball model illustrations of the ideal, stoichiometric, Cr_2O_3 ($10\bar{1}2$) surface assuming no relaxation. The small black balls represent Cr^{3+} cations, while the large gray balls represent O^{2-} anions. The top view is normal to the surface along the $[10\bar{1}2]$ direction and shows the rectangular (nearly square) periodicity expected for a stoichiometric surface. The bottom view gives a perspective across the surface looking down the $[02\bar{2}1]$ direction and shows the corrugation due to the alternating tilt of the incomplete octahedra coordinating the surface Cr^{3+} cations. Increased shading of the anions represents increasing distance away from the surface. For clarity, only the top five atomic layers are shown.

spectroscopy to study CO_2 adsorption over unsupported Cr_2O_3 microcrystalline powders where the predominant surface is the ($10\bar{1}2$),²⁴ and they have shown that CO_2 binds in a bidentate arrangement where the main active sites are the coordinately unsaturated Cr^{3+} and O^{2-} couples.^{18,22} Such site pairs are also available on the ordered, stoichiometric Cr_2O_3 ($10\bar{1}2$) single-crystal surface prepared by ion bombardment and annealing in UHV, where the presence of surface OH, H, and excess O can be minimized.²⁵

In this study, CO_2 adsorption has been studied on the well-defined Cr_2O_3 ($10\bar{1}2$) single-crystal surface to examine the validity of the using CO_2 as a probe of surface basicity. The interaction of CO_2 has been studied on surfaces exposing cation/anion site pairs, oxygen-terminated surfaces exposing terminal chromyl ($\text{Cr}=\text{O}$) and three-coordinate O^{2-} anions, and chlorine-terminated surfaces exposing Cl adatoms and three-coordinate O^{2-} anions.

II. $\alpha\text{-Cr}_2\text{O}_3$ Surfaces Studied

The Cr_2O_3 ($10\bar{1}2$) surface has been characterized in previous work.²⁵ The ideal, stoichiometric surface has only one local coordination environment for the surface cations and anions. A ball model representation of the ideal, stoichiometric surface is shown in Figure 1. The topmost atomic layer of the ideal surface is composed entirely of oxygen anions. One full stoichiometric repeating unit normal to the surface contains five atomic layers arranged as $[\text{O}, \text{Cr}, \text{O}, \text{Cr}, \text{O}]$. The surface has a rectangular (almost square) periodicity with a ratio of sides of $a/b = 0.94$.

At the ideal ($10\bar{1}2$) surface, all O^{2-} anions in the top atomic layer are three-coordinate with a pyramidal local coordination, and the Cr^{3+} cations contained in the second atomic layer are five-coordinate. Both ions have one degree of coordinate unsaturation relative to their bulk counterparts.²⁶ All ions below the top two atomic layers are fully coordinated. A nearly-stoichiometric surface can be prepared by Ar^+ ion bombardment and annealing in a vacuum at 900 K.²⁵

In addition to the nearly-stoichiometric surface, surfaces can be prepared with the cations capped with terminal chromyl oxygen ($\text{Cr}=\text{O}$) or Cl adatoms. An oxygen-terminated surface can be prepared by repeated low-temperature O_2 exposures on a nearly-stoichiometric surface until nearly all surface cations are capped with terminal oxygen.²⁵ The oxygen-terminated surface exposes three-coordinate O^{2-} anions and terminal chromyl oxygen ($\text{Cr}=\text{O}$).²⁵

A chlorine-terminated surface can be prepared by the low-temperature reaction of 1,1,2-trichloro-1-fluoroethane ($\text{CFCl}_2\text{-CH}_2\text{Cl}$) with the nearly-stoichiometric surface. The halocarbon decomposes primarily into $\text{CFCl}=\text{CH}_2(\text{g})$ and adsorbed chlorine on Cr_2O_3 ($10\bar{1}2$).²⁷ The decomposition of $\text{CFCl}_2\text{CH}_2\text{Cl}$ results in the build-up of chlorine on the sample surface with an estimated 1:1 ratio of chlorine adatoms to five-coordinate surface chromium cations.²⁷ The chlorine-terminated surface exposes three-coordinate O^{2-} anions and Cl adatoms.

III. Experimental Section

Experiments were conducted in two different ultrahigh vacuum (UHV) systems. XPS experiments were conducted in a turbo-pumped, dual-chamber vacuum system equipped with a Leybold EA-11 hemispherical analyzer and a dual anode Mg/Al X-ray source. Thermal desorption measurements were conducted in a second ion-pumped, Physical Electronics system equipped with a model 15-155 single-pass CMA for Auger electron spectroscopy (AES). Both systems include an Inficon Quadrex 200 mass spectrometer for thermal desorption spectroscopy (TDS) and a set of Vacuum Generators three-grid, reverse-view, low-energy electron diffraction (LEED) optics.

The Cr_2O_3 crystal was oriented to within 1° of the ($10\bar{1}2$) surface using Laue back-reflection and polished to a final mirror finish with $0.25\ \mu\text{m}$ diamond paste. The sample was mechanically clamped onto a tantalum stage that was fastened to LN_2 -cooled copper electrical conductors. A Type K thermocouple was attached through a hole in the stage to the back of the single crystal using Aremco No. 569 ceramic cement. This arrangement allowed direct measurement of the sample temperature.

Gas exposures were performed by back-filling the chamber through a variable leak valve. The CO_2 used was from AIRCO Gases, grade 5.5 SFC, having less than 5 ppm impurities. For TDS experiments, all surfaces were exposed to CO_2 at 190 K and heated to 700 K using a linear temperature ramp of 2 K/s. The low heating rate was used to minimize the possibility of thermally fracturing the ceramic Cr_2O_3 sample. The mass spectrometer was equipped with a glass skimmer to minimize the sampling of desorption products from the crystal support hardware. The reported doses have been corrected for ion gauge sensitivity.²⁸ During TDS experiments, the background pressure was less than 2×10^{-10} Torr between doses.

Oxidation treatments were performed using Matheson SCF grade O_2 (99.995%) as received. Successive 0.13 L exposures at 190 K followed by heating to 700 K were performed to obtain an oxygen-terminated surface.²⁵ Chlorination treatments were performed using PCR 1,1,2-trichloro-1-fluoroethane (97%) as received. Successive 0.13 L exposures of 1,1,2-trichloro-1-

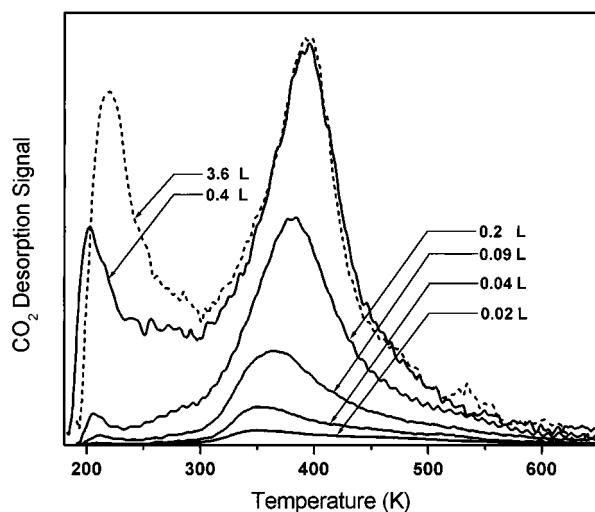


Figure 2. Thermal desorption of CO₂ following adsorption at 190 K on the nearly-stoichiometric surface.

fluoroethane (CFCl₂CH₂Cl) at 190 K with heating to 700 K were used to create a chlorine-terminated surface.²⁷

XPS spectra were collected at 125 K from Cr₂O₃ (10 $\bar{1}2$) surfaces. Uniform steady-state charging occurs due to the insulating nature of Cr₂O₃.²⁵ 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 Cr³⁺ in Cr₂O₃.^{29–31} The binding energy scale of all XPS spectra taken at low temperature 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}.

IV. Results

1. Thermal Desorption Spectroscopy. Variations in CO₂ adsorption at 190 K were examined by TDS for all surface preparations described above. Only CO₂ was observed in TDS following CO₂ adsorption. Desorption of CO was checked for but not observed, hence no reduction of CO₂ to CO was seen. The lack of reaction products suggests no dissociation of CO₂. All desorption features are thought to be first-order, although they do not exhibit simple first-order behavior (i.e., the peak temperatures are not constant for varying coverage). Variations in peak temperatures with coverage suggest more complex desorption kinetics such as coverage-dependent first-order desorption processes as described below.

A. Nearly-Stoichiometric Surface. The coverage dependence of the CO₂ desorption traces from a clean, nearly-stoichiometric surface following adsorption at 190 K is shown in Figure 2. At the lowest dose investigated, 0.02 L (1L \equiv 10⁻⁶ Torr-s), one CO₂ desorption peak is observed with a peak maximum at 350 K. This feature shifts up in temperature to 395 K with increasing coverage and saturates before a CO₂ exposure of 0.36 L. (This increase in desorption temperature with coverage is discussed below.) Also noticeable in the spectrum shown in Figure 2 is a broad, low-temperature feature near 220 K, which grows in at higher surface coverages. For the low-temperature feature, CO₂ desorption was seen immediately upon heating the surface. This observation suggests that an adsorption temperature of 190 K is not low enough to accommodate a fully populated low-temperature adsorption state. Hence, higher CO₂ coverages are

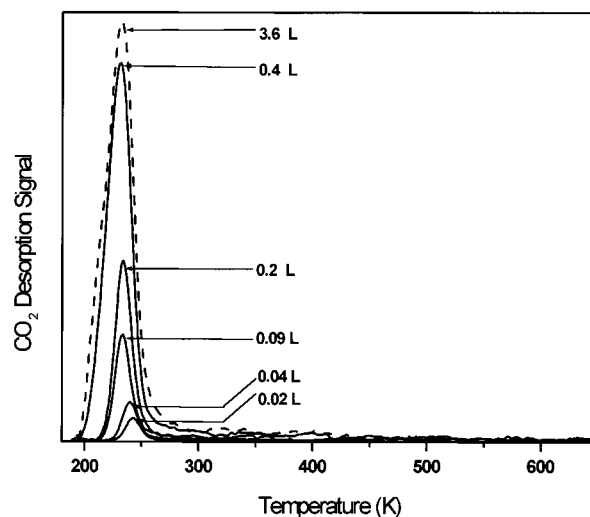


Figure 3. Thermal desorption of CO₂ following adsorption at 190 K on the oxygen-terminated surface.

expected with lower adsorption temperatures. (Note: On Cr₂O₃ (0001) films, in addition to a high-temperature CO₂ desorption feature at 330 K, low-temperature desorption features are observed at 180 and 120 K following adsorption at 90 K.¹⁸) Assuming a normal first-order preexponential of 10¹³ s⁻¹, a range of 21.9–24.8 kcal/mol is found for the apparent first-order activation energy for desorption of the higher-temperature (350–395 K) feature using the Redhead equation.³² No attempt was made to independently determine the preexponential via the method of heating rate variation. The heating rate was kept intentionally low (2 K/s) to avoid the possibility of thermal fracture of the ceramic sample. The 220 and 350 K CO₂ desorption temperatures on the nearly-stoichiometric surface are similar to the CO₂ desorption temperatures of 180 and 330 K reported for Cr₂O₃ (0001) films.¹⁸

B. Oxygen-Terminated Surface. The coverage dependence of the CO₂ desorption traces from an oxygen-terminated surface following adsorption at 190 K is illustrated in Figure 3. At the lowest dose investigated, 0.02 L, one CO₂ desorption peak is observed with a peak maximum at 240 K. This feature shifts down in temperature to 230 K with increasing coverage before approaching saturation near a CO₂ exposure of 0.36 L. For the largest doses, CO₂ desorption again was seen immediately upon heating the surface, which suggests that the adsorption temperature of 190 K is not low enough to populate fully this low-temperature (230 K) feature. Assuming a normal first-order preexponential of 10¹³ s⁻¹, an apparent first-order activation energy for desorption of about 14.6 kcal/mol can be estimated from the Redhead equation [32]. The 230 K CO₂ desorption temperature on the oxygen-terminated surface falls *between* the two desorption features observed from the nearly-stoichiometric surface.

C. Chlorine-Terminated Surface. Very little CO₂ 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 4 L CO₂ exposures on the three surfaces is shown in Figure 4 and demonstrates that CO₂ uptake on the chlorine-terminated surface is greatly suppressed.

2. Coverage Estimates. An upper limit estimate of the coverage of CO₂ as a function of dose at 190 K is shown in Figure 5 for the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated surfaces. To estimate the coverage of CO₂ molecules, an initial sticking coefficient of unity was assumed

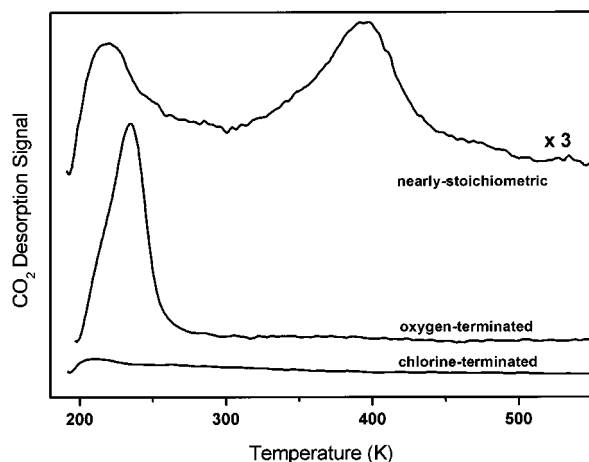


Figure 4. Comparison of thermal desorption spectra following 4 L exposures at 190 K on the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated surfaces.

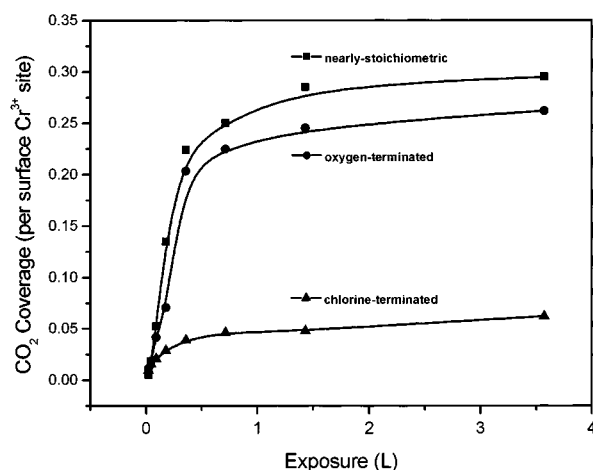


Figure 5. Fractional coverage of CO₂ as a function of dose at 190 K.

for the stoichiometric surface, along with a density of Cr³⁺ sites estimated from the Cr₂O₃ (1012) unit cell parameters. The ideal, stoichiometric surface is estimated to expose 4.86×10^{14} five-coordinate Cr³⁺ sites/cm².²⁵ In Figure 5, a monolayer coverage is defined as the equivalent of one CO₂ molecule per surface cation on the nearly-stoichiometric surface (1 ML $\equiv 4.86 \times 10^{14}$ CO₂ molecules/cm²). At 190 K, the nearly-stoichiometric surface saturates with a CO₂ coverage near 0.3 monolayers.³³ Using the same basis for the definition of a monolayer on the oxygen-terminated surface, a saturation coverage of about 0.26 is observed at 190 K. The saturation coverage of CO₂ at an adsorption temperature of 190 K is similar for both the nearly-stoichiometric and oxygen-terminated surfaces. CO₂ uptake on the chlorine-terminated surface is small in comparison and can be attributed to desorption from the sample support hardware.

3. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was used as a check for carbonate formation following CO₂ adsorption. Surface carbonates and molecularly adsorbed CO₂ are distinguished in XPS by higher binding energies (289–291.5 eV) than most other types of surface carbon species.^{29,31} Carbonates have been reported for Cu (110)–O and ZnO (1010) in the range of 289–290.4 eV.^{19,34} Physisorbed CO₂ has been reported for Cu (110)–O and ZnO (1010) in the range of 291.8–292 eV.^{19,34} The C 1s features following a 7 L CO₂ exposure at 125 K are shown in Figure 6 for the nearly-stoichiometric, oxygen-terminated, and chlorine-terminated surfaces. (Note: The adsorption temperatures for the

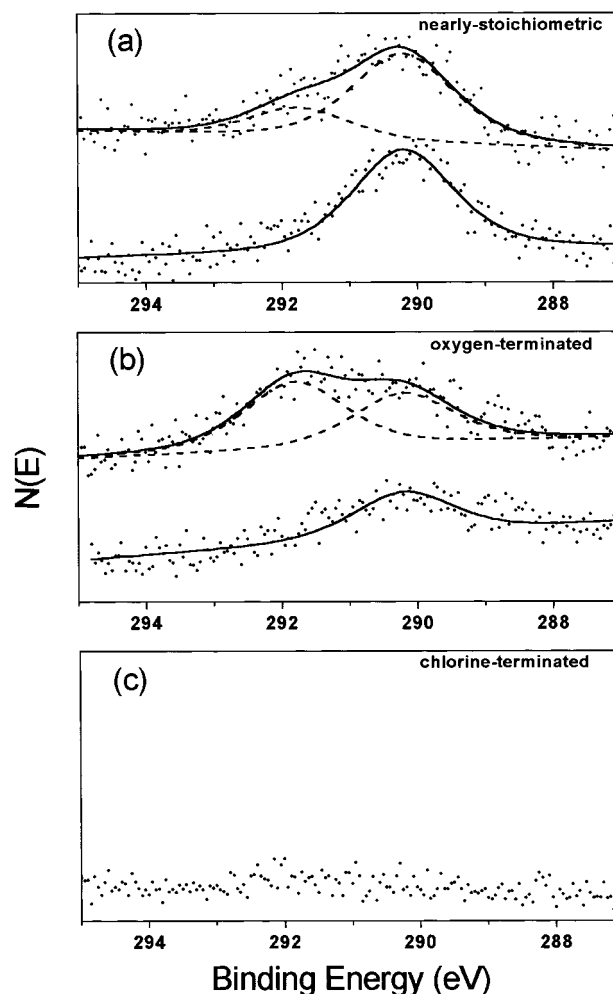


Figure 6. C 1s XPS spectra following 7 L CO₂ exposures at 125 K. (a) nearly-stoichiometric surface following a 7 L dose and annealing to 220 K, (b) oxygen-terminated surface following a 7 L dose and annealing to 200 K, and (c) chlorine-terminated surface following a 7 L dose.

XPS experiments are 65 K lower than those used for the TDS experiments.)

In Figure 6a, the C 1s feature following a 7 L CO₂ dose on the nearly-stoichiometric surface appears as a broad feature with a binding energy centered around 290.5 eV. This broad feature covers a range of binding energies similar to those reported for carbonates and physisorbed CO₂. If the nearly-stoichiometric surface is annealed to 220 K, leaving only CO₂ associated with the 395 K desorption feature observed in TDS, the resulting C 1s feature narrows. Curve fitting suggests two C 1s contributions at 290.2 ± 0.1 eV and 291.7 ± 0.1 eV following the 7 L dose, and a single contribution at 290.2 ± 0.1 eV following annealing to 220 K. The high binding energy XPS feature (291.7 eV) removed by heating to 220 K falls in the range of reported binding energies of physisorbed CO₂, while the lower binding energy feature (290.2 eV) falls in the range reported for carbonates. These XPS data are consistent with an assignment of carbonate for the surface species associated with the high temperature 395 K desorption feature in TDS.

In Figure 6b, the C 1s feature following a 7 L CO₂ exposure on the oxygen-terminated surface is a broad feature with a binding energy centered near 291 eV. As on the nearly-stoichiometric surface, this broad carbon 1s feature on the oxygen-terminated surface extends over a range of binding energies reported for both carbonates and physisorbed CO₂.

Curve fitting again suggests that this broad feature can be fit with two contributions³⁵ at 290.2 ± 0.1 eV and 291.8 ± 0.1 eV. The binding energies of these two features are the same as those observed for the nearly-stoichiometric surface, to within the expected resolution of XPS (± 0.1 eV). The 290.2 eV feature on the oxygen-terminated surface falls in the range of binding energies reported for carbonates, while the 291.8 eV feature falls in the range of physisorbed CO₂. If the oxygen-terminated surface is annealed to 200 K, leaving only CO₂ associated with the 230 K desorption feature observed in TDS, the resulting C 1s feature narrows.³⁵ The C 1s feature at 291.8 eV associated with physisorbed CO₂ decreases, leaving the 290.2 eV feature at lower binding energies that falls in the range associated with carbonate.

For the chlorine-terminated surface shown in Figure 6c, no C 1s feature was detected by XPS following a 7 L dose, in agreement with the lack of uptake observed with TDS.

V. Discussion

1. Chemisorption of CO₂ on the Nearly-Stoichiometric Surface. A variety of adsorbate geometries (carbonates, bent CO₂^{δ-} anions, linear physisorbates) should be considered for the interaction of CO₂ 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 CO₂ carbon to a coordinately unsaturated surface oxygen anion. Formation of a bidentate carbonate species would be expected to involve the coordination of the CO₂ carbon to a coordinately unsaturated surface oxygen anion and one of the molecular oxygen atoms to a coordinately unsaturated surface Cr³⁺ cation.²² CO₂ adsorbed in a nonlinear arrangement is expected to be stabilized by back-bonding into the CO₂ π^* orbitals.^{16,17}

Seiferth et al.¹⁸ observed a 330 K desorption feature for strongly chemisorbed CO₂ on Cr₂O₃ (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 (CO₂^{δ-}) 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.²³ Given the similarity in desorption temperatures (330 K [ref 18] 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 Cr₂O₃ (0001) thin films¹⁸) to require significant π back-bonding from the metal center. However, in previous work on the adsorption of CO (a good π acceptor) on Cr₂O₃ (10 $\bar{1}2$), a desorption temperature of 195 K (first-order E_a for desorption of 12 kcal/mol) was found, suggesting a minimal capacity for π back-donation from the five-coordinate Cr³⁺ cations on the stoichiometric (10 $\bar{1}2$) surface.³⁶

CO₂ bonding in a bidentate carbonate arrangement on Cr³⁺–O²⁻ ion pairs has been observed by infrared spectroscopy over unsupported Cr₂O₃ microcrystalline powders^{18,22} where the predominant exposed crystal planes are (10 $\bar{1}2$),²³ the same as the single-crystal surface used in this study. In the present study, the nearly-stoichiometric surface has both Cr³⁺ cations and O²⁻ anions available for interaction with CO₂.²⁵ The 350–395 K desorption feature on the nearly-stoichiometric surface observed in TDS appears only when there are Cr³⁺ surface sites available for interaction. When surface chromium atoms are terminated by oxygen or chlorine, the high-temperature CO₂ desorption feature observed in TDS disappears, indicating the importance

of coordinately unsaturated Cr³⁺ cations in the formation of this chemisorbed species. Therefore, the 350–395 K CO₂ desorption feature from the nearly-stoichiometric (10 $\bar{1}2$) surface is attributed to a bidentate carbonate, consistent with the literature on chromia powders.^{18,22} 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 was seen in TDS for the strongly chemisorbed CO₂ 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 CO₂ 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 Cr₂O₃ surfaces where submonolayer quantities of impurity adatoms affect the adsorption of other molecules. Freund and co-workers^{37,38} have shown that submonolayer coverages of sodium change the bonding of ethene (CH₂=CH₂) from a π -donor to a di- σ interaction. They suggest that charge redistribution at the surface gives rise to more electron-rich chromium ions in the presence of sodium on Cr₂O₃ (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 (CFCl=CH₂) on Cr₂O₃ (10 $\bar{1}2$) by over 20 K.²⁷ 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.

2. Interaction of CO₂ with Terminal Chromyl Oxygen (Cr=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, CO₂ must interact directly with oxygen sites on the surface in either a bent or linear conformation. The CO₂ 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 CO₂ desorption features of these surfaces are distinctly different, the CO₂ uptake is very similar at 190 K. On the chlorine-terminated surface where all surface Cr sites are terminated with chlorine adatoms, no CO₂ uptake was seen. Therefore, the terminal chromyl oxygens (Cr=O) on the oxygen-terminated surface appear to be directly involved in the CO₂ 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 CO₂ molecule. The interaction between two essentially closed-shell oxygen atoms (terminal oxygen on the surface and molecular oxygen on the CO₂ 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, CO₂ adsorbed on the oxygen-terminated surface is tentatively identified as a “mono-

dentate adsorbate" bound at the terminal chromyl oxygens. Whether the extent of charge transfer is sufficient to give a true monodentate carbonate, a bent CO₂ adsorbate, or a more linear "physisorbate" is not known. The XPS results tend to favor the identification of CO₂ 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 CO₂ physisorbate on oxygen-precovered Cr₂O₃ (0001)/Cr (110) thin films.¹⁸ On the (0001) surface, this weakly bound adsorbate is characterized by a 2352 cm⁻¹ vibrational feature¹⁸ similar to gas-phase CO₂. The similarity in desorption temperature might suggest that the CO₂ adsorbate on the oxygen-terminated Cr₂O₃ (10 $\bar{1}$ 2) surface could be best described as a molecular (nearly-linear) CO₂ adsorbate rather than a carbonate. Vibrational data would be helpful for making this distinction.

3. Basicity of Cr₂O₃ 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,^{1,2} while the metal cations are generally considered to be Lewis acid sites.^{1,2} If the strength of the interaction of CO₂ is taken as a measure of the basicity^{10,11} of the Cr₂O₃ (10 $\bar{1}$ 2) surface, the CO₂ thermal desorption results suggest that the nearly-stoichiometric surface is "more basic" than the oxygen-terminated surface. While this interpretation may fit within the definition of surface basicity as the ability of the surface to convert a neutral molecule to its conjugate base, it does not fit within a simple atomic site model for surface acidity and basicity that attributes acidic properties to cations and basic properties to anions. CO₂ does not interact exclusively with base sites (oxygen anions) on the nearly-stoichiometric Cr₂O₃ (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, CO₂ forms a more weakly adsorbed monodentate species through an interaction with base sites (terminal chromyl oxygens). However, because of the differences in site requirements for the formation of these two surface species, it is clear that CO₂ does not provide a simple measure of the properties of the individual atomic surface oxygen sites. 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 coordinately unsaturated Cr³⁺ ions on Cr₂O₃.^{12,22,39} In this study, the necessity of coordinately unsaturated surface cations for the formation of bidentate carbonates on Cr₂O₃ (10 $\bar{1}$ 2) has been demonstrated, and the ability of five-coordinate cations (one coordination vacancy) to participate in the formation of these species has been confirmed. 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 CO₂ with a basic surface oxygen anion site and the interaction of a basic oxygen atom of CO₂ with an acidic Cr³⁺ site of Cr₂O₃. In such terms, it is perhaps more reasonable to think of CO₂ as an amphoteric probe molecule given its ability to interact with cation/anion (acid/base) site pairs to form bidentate carbonate. For strongly chemisorbed carboxylate species at cations (as reported on Cr₂O₃ (0001)¹⁸) 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 Cr₂O₃ surfaces suggest that one should

not consider CO₂ 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.

VI. Conclusions

On Cr₂O₃ (10 $\bar{1}$ 2), the strongest CO₂-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 Cr³⁺ cations and three-coordinate O²⁻ anions on the stoichiometric, nonpolar (10 $\bar{1}$ 2) surface. Terminating the surface cations with chromyl oxygen (Cr=O) via dissociative O₂ chemisorption prevents this interaction and gives rise to a more weakly bound CO₂ moiety, tentatively identified as a "monodentate" CO₂ 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 CO₂ and the surface, and no uptake is observed.

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References and Notes

- (1) Barteau, M. A. *J. Vac. Sci. Technol. A* **1993**, *11*, 2162.
- (2) Stair, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 4044.
- (3) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1986**, *176*, 91.
- (4) Vohs, J. M.; Barteau, M. A. *J. Phys. Chem.* **1987**, *91*, 4766.
- (5) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1988**, *201*, 481.
- (6) Barteau, M. A.; Vohs, J. M. In *Successful Design of Catalysts*; Inui, T., Ed.; Elsevier: Amsterdam, 1988; p 89.
- (7) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1989**, *221*, 590.
- (8) Vohs, J. M.; Barteau, M. A. *J. Phys. Chem.* **1991**, *95*, 297.
- (9) Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970.
- (10) Tanabe, K.; Misono, M.; Hattori, H. *New Solid Acids and Bases: Their Catalytic Properties*; Elsevier: Amsterdam, 1989; pp 14–17.
- (11) Zhang, G.; Hattori, H.; Tanabe, K. *Appl. Catal.* **1988**, *36*, 189.
- (12) Knozinger, H. *Adv. Catal.* **1976**, *25*, 184.
- (13) Cardona-Martinez, N.; Dumesic, J. A. *Adv. Catal.* **1992**, *38*, 149.
- (14) Auroux, A.; Gervasini, A. *J. Phys. Chem.* **1990**, *94*, 6371.
- (15) Finston, H. L.; Rychman, A. C. *A New View of Current Acid-Base Theories*; John Wiley & Sons: New York, 1982; p 144.
- (16) Freund, H.-J.; Roberts, M. W. *Surf. Sci. Reports* **1996**, *25*, 225.
- (17) Walsh, A. D. *J. Chem. Soc.* **1953**, 2260.
- (18) Seiferth, O.; Wolter, K.; Dillmann, B.; Klivenyi, G.; Freund, H.-J.; Scarano, D.; Zecchina, A. *Surf. Sci.* **1999**, *421*, 176.
- (19) Au, C. T.; Hirsch, W.; Hirschwald, W. *Surf. Sci.* **1988**, *199*, 507.
- (20) Busca, G.; Lorenzelli, V. *Mater. Chem.* **1982**, *7*, 89.
- (21) Kuhlbeck, H.; Xu, C.; Dillmann, B.; Habel, M.; Adam, B.; Ehrlich, D.; Wohlrab, S.; Freund, H.-J.; Ditzinger, U. A.; Neddermeyer, H.; Neuber, M.; Neumann, M. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 15.
- (22) Zecchina, A.; Coluccia, S.; Guglielminotti, E.; Ghiotti, G. *J. Phys. Chem.* **1971**, *75*, 2790.
- (23) Scarano, D.; Spoto, G.; Bordiga, S.; Ricchiardi, G.; Zecchina, A. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64*, 307.
- (24) Scarano, D.; Spoto, G.; Bordiga, S.; Ricchiardi, G.; Zecchina, A. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64*, 307.
- (25) York, S. C.; Abee, M. W.; Cox, D. F. *Surf. Sci.* **1999**, *437*, 386.
- (26) Lad, R. J.; Henrich, V. E. *Surf. Sci.* **1988**, *193*, 81.
- (27) York, S. C.; Cox, D. F., in preparation.
- (28) The ion gauge sensitivity for carbon dioxide was taken as 1.4 per the *Quadrex 200 Technical Manual*, Inficon Leybold-Heraeus.
- (29) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer: Eden Prairie, MN, 1979.

- (30) Foord, J. S.; Lambert, R. M. *Surf. Sci.* **1986**, *169*, 327.
- (31) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D.; Chastain, J. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer: Eden Prairie, MN, 1992.
- (32) Redhead, P. A. *Vacuum* **1962**, *12*, 203.
- (33) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
- (34) Carley, A. F.; Roberts, M. W.; Strutt, J. *J. Phys. Chem.* **1994**, *98*, 9175.
- (35) Supplementary TDS data taken in the XPS system at a CO₂ adsorption temperature of 125 K show an additional desorption feature at 140 K not observed in the TDS data taken following adsorption at 190 K. This additional desorption feature accounts for the observance of two C 1s peaks in the XPS spectra following adsorption at 125 K, while only one desorption feature is observed in TDS (Figure 3) following adsorption at 190 K.
- (36) York, S. C.; Cox, D. F., unpublished data.
- (37) Dillmann, B.; Rohr, F.; Seiferth, O.; Klivenyi, G.; Bender, M.; Homann, K.; Yakovkin, I.; Ehrlich, D.; Baumer, M.; Kuhlbeck, H.; Freund, H. *Faraday Discuss.* **1996**, *105*, 295.
- (38) Freund, H.-J.; Dillmann, B.; Erlich, D.; HaBel, M.; Jaeger, R. M.; Kuhlbeck, H.; Ventrice, C. A., Jr.; Winkelmann, F.; Wohlrab, S.; Xu, C.; Bertrams, Th.; Brodde, A.; Neddermeyer, H. *J. Mol. Catal.* **1993**, *82*, 143.
- (39) Burwell, R. L.; Haller, G. L.; Taylor, K. C.; Read, J. F. *Adv. Catal.* **1969**, *20*, 1.