

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244402784>

BF₃ Adsorption on α -Cr₂O₃ (10 $\bar{1}2$): Probing the Lewis Basicity of Surface Oxygen Anions

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · SEPTEMBER 2001

Impact Factor: 3.3 · DOI: 10.1021/jp011389v

CITATIONS

10

READS

18

2 AUTHORS, INCLUDING:



David F Cox

Virginia Polytechnic Institute and State Univ...

91 PUBLICATIONS 2,024 CITATIONS

SEE PROFILE

BF₃ Adsorption on α -Cr₂O₃ (10 $\bar{1}2$): Probing the Lewis Basicity of Surface Oxygen Anions

Mark W. Abee and David F. Cox*

Department of Chemical Engineering, Virginia Polytechnic Institute & State University,
Blacksburg, Virginia 24061-0211

Received: April 12, 2001; In Final Form: June 22, 2001

Acid/base characterizations of metal oxide surfaces are used often to explain their catalytic behavior. BF₃, a strong Lewis acid, is used in this investigation as a probe molecule to interrogate the basicity of well-defined Cr₂O₃ (10 $\bar{1}2$) surfaces. BF₃ clearly probes differences in oxide ions of different coordination on Cr₂O₃ (10 $\bar{1}2$). The heat of adsorption of BF₃ shows that terminal chromyl oxygens are stronger Lewis bases than three-coordinate oxygen anions on the nearly stoichiometric surface. The trends in basicity found with BF₃ are the opposite of those found from the heat of adsorption of CO₂, a common probe molecule used to investigate the basicity of oxide surfaces. The use of BF₃ as a probe molecule is complicated by some dissociation and the slow build up of surface boron and fluorine during consecutive thermal desorption runs.

I. Introduction

The study of single crystal and oriented thin film oxide surfaces has led to a number of demonstrations of structure sensitivity in oxide surface chemistry. Although these model oxide systems often allow one to control composition, stoichiometry, and cation oxidation state, they also provide an opportunity to expose surface cations and anions in well-defined local coordination geometries. These individual atomic sites are typically described in terms of their coordination numbers or alternately their degree of coordinative unsaturation. Although such descriptions have utility, they often fail to convey a sense of the inherently different chemical nature of the individual atomic sites. This is especially true when one considers surface oxygen anions of varying coordination. To date, there has been no convenient experimental method to probe the chemical nature of surface oxide species in different coordinations and local geometries. This paper demonstrates that a simple thermal desorption experiment with BF₃ probe molecules can provide a site-sensitive measure of the Lewis basicity of surface oxygen species of different coordination.

The adsorption of probe molecules such as ammonia, pyridine, and carbon dioxide is commonly used for acid/base characterizations of surface sites on oxides, and these characterizations in turn have been used often to explain the catalytic behavior of oxide surfaces. The nature of acidic and basic sites on oxide surfaces can be described in Lewis and Brønsted terms. For clean metal oxide surfaces (no surface protons or hydroxyl groups), 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, whereas the oxygen anions are thought of as Lewis base sites.^{1,2} The electron-deficient metal cations exhibit acidic, electron-acceptor character, whereas the electron-rich oxygen anions exhibit basic, electron-donor character.²

Boron halides have been investigated as alternative probe molecules for Lewis basicity because the 2p¹ electronic structure of boron gives a potent Lewis acid when combined with a halogen.³ The boron atom of BF₃ has an empty p_z-like orbital

perpendicular to the molecular plane and has a tendency to accept electron pairs.⁴ Many organic compounds such as alcohols, aldehydes, and ketones can complex with BF₃ via charge donation from the oxygen atom to the boron atom of BF₃.⁴ When BF₃ complexes with a Lewis acid, the molecular geometry changes from planar to tetrahedral. BF₃ was chosen over other boron halides because it is not expected to dimerize like BH₃, polymerize like BI₃, or readily hydrolyze like BBr₃ and BCl₃ in the presence of water.³ To our knowledge, BF₃ has not been used previously to probe the basicity of surface oxygen anions.

II. α -Cr₂O₃ Surfaces Studied

The α -Cr₂O₃ (10 $\bar{1}2$) surface has been characterized in a previous work.⁵ The ideal, stoichiometric surface has only one local coordination environment for the coordinately unsaturated 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 repeat unit normal to the surface contains five atomic layers arranged as [O, Cr, O, Cr, O]. The surface has a rectangular (almost square) periodicity with a ratio of sides of $a/b = 0.94$. At the (10 $\bar{1}2$) surface, all O²⁻ anions in the top atomic layer are three-coordinate with a pyramidal local coordination, and the Cr³⁺ cations contained in the second atomic layer are five-coordinate. Both ions have one degree of coordinate unsaturation relative to their bulk counterparts.⁶ All ions below the top two atomic layers are fully coordinated. A nearly-stoichiometric surface can be prepared by Ar⁺ ion bombardment and annealing at 900 K.⁵

In addition to the nearly-stoichiometric surface, an oxygen-terminated form may also be prepared by repeated low-temperature O₂ exposures. The dissociatively adsorbed oxygen caps nearly all of the chromium cations on the stoichiometric surface with terminal chromyl oxygen (Cr=O). The resulting surface exposes both three-coordinate O²⁻ anions and the singly coordinate terminal chromyl oxygen.⁵

III. Experimental Methods

Experiments were conducted in two different ultrahigh vacuum (UHV) systems. One system is a turbo-pumped, dual-

* To whom correspondence should be addressed. E-mail: dfcox@vt.edu.

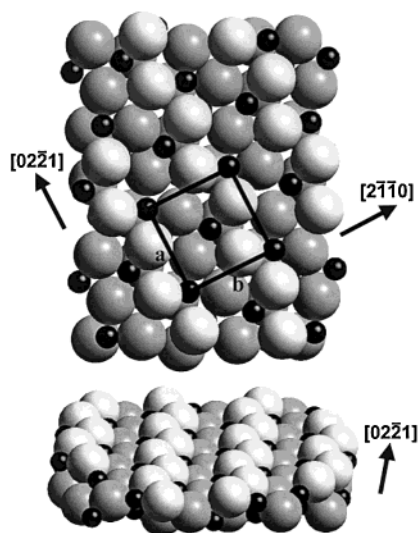


Figure 1. Ball model representation of the Cr_2O_3 ($10\bar{1}2$) surface. The top view shows the ($10\bar{1}2$) surface parallel to the plane of the page. A surface unit cell is drawn to show the periodicity. The bottom illustration shows a side view of one stoichiometric repeating layer. The chromium cations are represented by small black spheres, and oxygen anions are represented by the large gray spheres.

chamber vacuum system equipped with a Leybold EA-11 hemispherical analyzer and a dual anode Mg/Al X-ray source for XPS. The second system is an ion-pumped, Physical Electronics chamber, equipped with a model 15-155 single-pass CMA for Auger electron spectroscopy (AES). Both systems also 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 liquid- N_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 Areenco 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 BF_3 used was from Aldrich, having a purity of 99.5%. For TDS experiments, all surfaces were exposed to BF_3 at 193 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. During TDS experiments, the background pressure was less than 2×10^{-10} Torr between doses. Gas exposures reported in this study have not been corrected for ion gauge sensitivities. Oxidation treatments were performed using Matheson SCF grade O_2 (99.995%) as received. Successive 0.13 L exposures at 193 K and annealing to 700 K were performed to obtain an oxygen-terminated surface.⁵

All reported XPS spectra were collected at 125 K from Cr_2O_3 ($10\bar{1}2$) surfaces. Uniform steady-state charging occurs because of the insulating nature of Cr_2O_3 . 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, as describe elsewhere.⁵ The Cr $2p_{3/2}$ binding energies at 900 K fall at $576.9 \pm 0.2\ \text{eV}$ for a nearly-

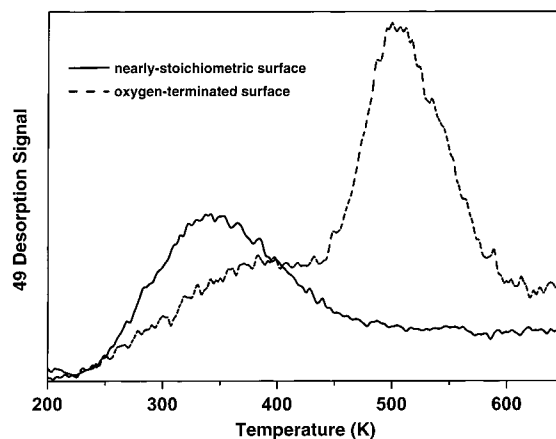


Figure 2. TDS comparison spectra showing desorption intensity versus temperature for BF_3 adsorbed on a nearly-stoichiometric and oxygen-terminated Cr_2O_3 ($10\bar{1}2$) surface after a 0.25 L exposure.

stoichiometric surface. This value is within the range typically attributed to Cr^{3+} in Cr_2O_3 .⁷⁻⁹ The binding energy scale for all reported XPS spectra has been shifted to align the Cr $2p_{3/2}$ peak to 576.9 eV to compensate for the steady-state charging. Detail XPS scans were run at pass energies of 60 eV for the O 1s and F 1s regions and 200 eV for the B 1s region. The larger pass energy was used for boron because B 1s has a small X-ray absorption cross section and a correspondingly low XPS sensitivity factor.¹⁰ The pass energies correspond to Ag $3d_{5/2}$ line widths of 1.06 and 2.1 eV for the 60 and 200 eV pass energies, respectively. All XPS composition ratios were determined by applying Leybold atomic sensitivity factors to integrated peak areas taken from spectra run with 200 eV pass energies.

IV. Results

1. Thermal Desorption Spectroscopy. BF_3 adsorption was examined by TDS for the nearly-stoichiometric and oxygen-terminated surfaces. In simple Lewis acid/base terms, one might expect different basicities for the stoichiometric and oxygen-terminated surfaces because of the different forms of oxygen exposed at the surface. In Figure 2, TDS traces from a 0.25 L ($1\ \text{L} \equiv 10^{-6}\ \text{Torr sec}$) BF_3 exposure are shown for the nearly-stoichiometric and oxygen-terminated surfaces. One BF_3 desorption feature with a peak temperature of 340 K is seen on the nearly-stoichiometric surface. Because the nearly-stoichiometric surface exposes predominately three-coordinate O^{2-} anions, the BF_3 TDS feature is attributed to the adsorption of acidic BF_3 molecules at three-coordinate O^{2-} anions. Two BF_3 desorption features are seen for the oxygen-terminated surface: a peak at 500 K and a shoulder at $\sim 370\ \text{K}$. The BF_3 desorption feature near 370 K is similar in temperature to that seen on the nearly-stoichiometric surface. Therefore, the BF_3 TDS feature at 370 K on the oxygen-terminated surface is also attributed to the adsorption of acidic BF_3 molecules at three-coordinate O^{2-} anions. Because the BF_3 TDS feature at 500 K appears with the introduction of terminal chromyl oxygens on the oxygen-terminated surface, the 500 K feature is attributed to the desorption of acidic BF_3 molecules from the terminal chromyl species ($\text{Cr}=\text{O}$).

The coverage dependences of the BF_3 desorption traces from a nearly-stoichiometric surface and an oxygen-terminated surface are illustrated in Figure 3. TDS spectra are shown only for small BF_3 exposures, 0.03–0.25 L, because of the increasing contribution of BF_3 desorbed from the sample support hardware at

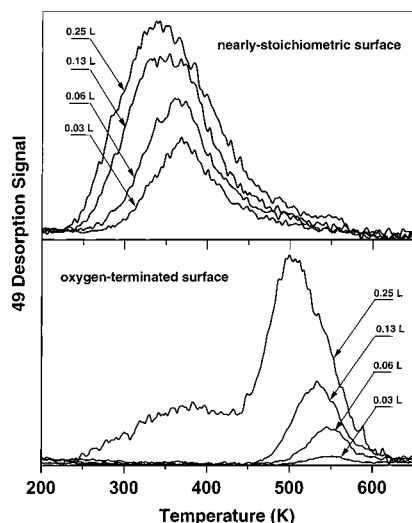


Figure 3. TDS spectra showing desorption intensity versus temperature for BF₃ adsorbed on a nearly-stoichiometric (top) and oxygen-terminated (bottom) Cr₂O₃ (10 $\bar{1}2$) surface.

larger exposures. At the lowest dose investigated, 0.03 L, one BF₃ desorption peak is observed with a peak maximum at 370 K for the nearly-stoichiometric surface and at 550 K for the oxygen-terminated surface. With increasing BF₃ coverages, these features shift down in temperature to 340 K (at 0.25 L) for the nearly-stoichiometric surface and 500 K (at 0.25 L) for the oxygen-terminated surface. The second feature from the oxygen-terminated surface grows in near 370 K for the largest exposure of 0.25 L, near the same temperature of the BF₃ feature seen on the nearly-stoichiometric surface. A decrease in desorption temperature with coverage can be characteristic of a second-order desorption process.¹¹ However, a second-order Redhead analysis of the TDS data shows no linearity suggestive of second-order behavior that might indicate a BF₃ recombination process.¹¹ Hence, all BF₃ desorption features are thought to be first-order and originate from a molecular BF₃ adsorbate. XPS data (below) also suggests a molecular BF₃ adsorbate associated with the BF₃ desorption features. The temperature decrease in TDS is attributed to a variation in the 1st order activation energy for desorption with coverage. Assuming a normal preexponential of 10¹³ s⁻¹, the first-order activation energy for desorption is estimated from the Redhead equation to be 21.3–23.1 kcal/mol for the BF₃ desorption feature on the nearly-stoichiometric surface and a range of 31.8–34.9 kcal/mol for the higher temperature feature seen on the oxygen-terminated surface.¹¹ 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.

Although the BF₃ desorption features are attributed to molecular surface species, BF₃ adsorption on Cr₂O₃ (10 $\bar{1}2$) is not an entirely clean molecular adsorption/desorption process. Trace amounts of HF and F₂ were detected during each BF₃ TDS run. Hence, some BF₃ dissociation occurs. TDS spectra of the reaction products arising from BF₃ on the nearly-stoichiometric and oxygen-terminated surfaces are shown in Figure 4 for a 0.25 L exposure of BF₃. On the nearly-stoichiometric surface, HF desorbs as a broad feature with a peak temperature around 430 K, and trace amounts of F₂ desorb with peak temperatures of 280 and 365 K. On the oxygen-terminated surface, HF desorbs with a peak temperature of 470 K, and trace amounts of F₂ desorb with a peak temperature of

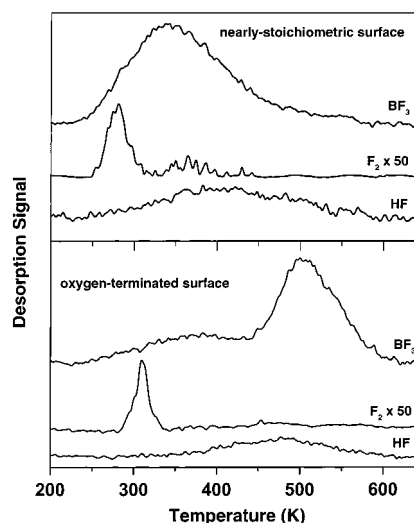


Figure 4. TDS spectra showing desorption intensity versus temperature for a 0.25 L BF₃ exposed nearly-stoichiometric (top) and oxygen-terminated (bottom) Cr₂O₃ (10 $\bar{1}2$) surface and reaction products F₂ and HF.

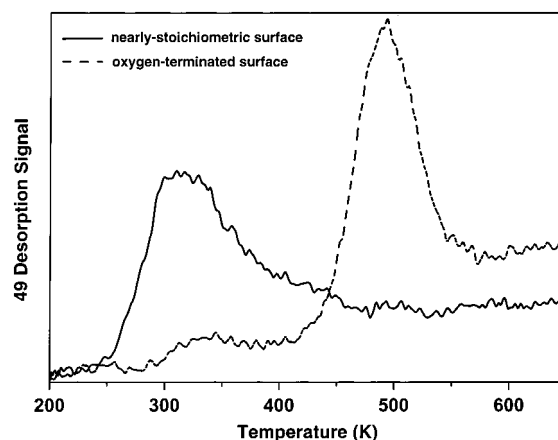


Figure 5. TDS comparison spectra showing desorption intensity versus temperature for BF₃ adsorbed on a BF₃-modified nearly-stoichiometric and BF₃-modified oxygen-terminated Cr₂O₃ (10 $\bar{1}2$) surface for a similar BF₃ coverage seen in Figure 2.

310 K. The hydrogen in HF originates from the uptake of background water in the vacuum system.

Dissociation of BF₃ results in the deposition of boron and fluorine on the surface during successive TDS runs until the concentration of these surface contaminants eventually saturates. On the resulting "BF₃-modified" surfaces, a larger amount of molecular BF₃ desorption is seen for a given exposure. The boron and fluorine left on the surface decreases the probability of BF₃ dissociation in subsequent exposures and results in a higher coverage of reversibly adsorbed BF₃ for a given dose. In Figure 5, BF₃ desorption traces following 0.06 L exposures are shown for BF₃-modified nearly-stoichiometric and oxygen-terminated surfaces. The reversibly adsorbed BF₃ coverages (integrated desorption signals) are similar to those shown in Figure 2 for a clean surface. One BF₃ desorption feature at 320 K is seen on the BF₃-modified nearly-stoichiometric surface, and two BF₃ features at 340 and 495 K are seen on the BF₃-modified oxygen-terminated surface. The shape and desorption temperatures of these TDS features are essentially the same as the TDS features arising from clean (unmodified) surfaces. Hence, the boron and fluorine left on the surface effects the coverage of reversibly adsorbed BF₃ for a given dose, but not the desorption temperature for a given coverage of reversibly

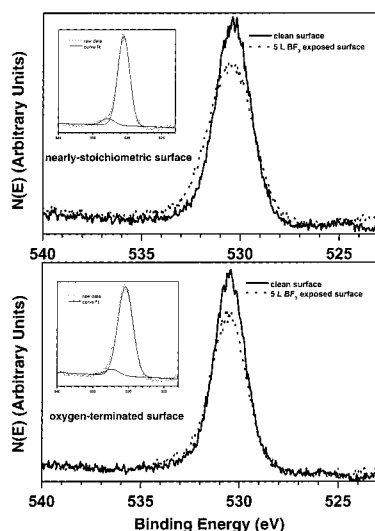


Figure 6. XPS spectra showing the O 1s region of the nearly-stoichiometric surface (top) and the oxygen-terminated surface (bottom) for a clean and 5 L BF_3 exposed surface. Two peaks are resolved by curve fitting where the larger peak represents a clean surface and the smaller peak represents the BF_3 interaction with oxygen sites.

adsorbed BF_3 . Therefore, BF_3 remains a viable probe molecule for Cr_2O_3 (10 $\bar{1}2$) despite the buildup of boron and fluorine on the surface.

2. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was used to study the interaction between BF_3 with the nearly-stoichiometric and oxygen-terminated surfaces. Changes in the O 1s signal upon BF_3 adsorption on the nearly-stoichiometric and oxygen-terminated surfaces are shown in Figure 6. The O 1s features on the nearly-stoichiometric and oxygen-terminated surfaces have a binding energy of 530.4 ± 0.1 eV. When the surfaces are exposed to 5 L of BF_3 , an additional feature in XPS appears at a higher binding energy near 532.8 ± 0.2 eV for the nearly-stoichiometric surface and 532.2 ± 0.2 eV for the oxygen-terminated surface. These higher binding energy features indicate charge transfer from surface oxygen to adsorbed BF_3 and demonstrate a direct interaction of BF_3 with surface oxygen sites.¹² The higher binding energy features disappear when the sample is heated to temperatures where molecular BF_3 is removed from the surface in TDS experiments. Therefore, the higher binding energy O 1s features are indicative of a direct interaction between molecular BF_3 and surface oxygen sites to form Lewis acid/base adducts.

The nature of the adsorbed species was investigated by XPS. The B 1s XPS region is shown in Figure 7 for the nearly-stoichiometric surface (top) and the oxygen-terminated surface (bottom). On the nearly-stoichiometric surface, one broad B 1s feature appears at a binding energy of 194.1 eV with the exposure of 5 L of BF_3 . The B 1s feature shifts down to 193.1 eV upon annealing to 340 K, where all molecular BF_3 is removed from this surface, and the B 1s feature shifts further down to 192.0 eV after annealing to 900 K. On the oxygen-terminated surface, one broad B 1s feature appears at a binding energy of 193.8 eV with the exposure of 5 L of BF_3 . The B 1s feature shifts down to 192.8 eV upon annealing to 500 K, where all molecular BF_3 is removed from this surface. After annealing to 900 K, the B 1s feature shifts down to 192.3 eV. The B 1s features at 194.1 eV (nearly-stoichiometric surface) and 193.8 eV (oxygen-terminated surface) following 5 L BF_3 exposures are attributed to molecular BF_3 at surface oxygen (base) sites because the acid/base adducts $\text{NH}_3\text{:BF}_3$ and $\text{C}_5\text{H}_5\text{N:BF}_3$ have

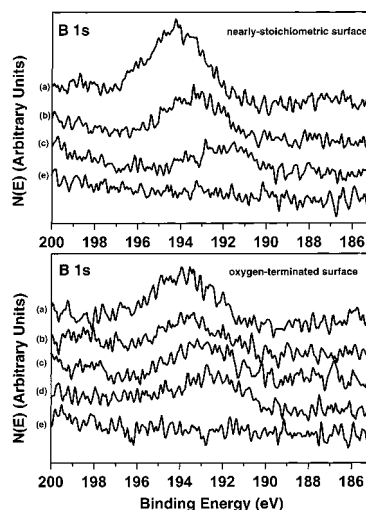


Figure 7. XPS spectra showing the B 1s region of the nearly-stoichiometric surface (top) and the oxygen-terminated surface (bottom) for (a) a 5 L BF_3 exposed surface, (b) a surface annealed to 340 K, (c) a surface annealed to 500 K, (d) a surface annealed to 900 K, and (e) a clean surface.

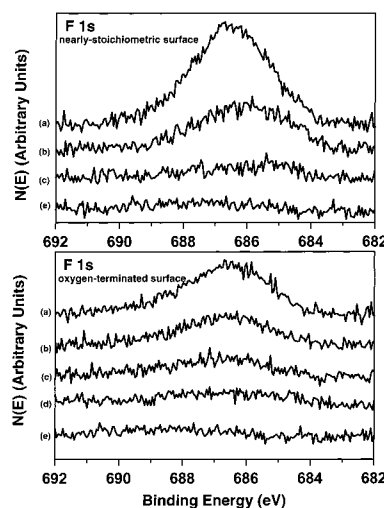


Figure 8. XPS spectra showing the F 1s region of the nearly-stoichiometric surface (top) and the oxygen-terminated surface (bottom) for (a) a 5 L BF_3 exposed surface, (b) a surface annealed to 340 K, (c) a surface annealed to 500 K, (d) a surface annealed to 900 K, and (e) a clean surface.

reported B 1s binding energies of 194.9 and 194.3 eV, respectively.⁹ The 1 eV shift to lower binding energies for the B 1s feature on both surfaces after removing all molecular BF_3 is indicative of a change from molecular to dissociated BF_3 . This lower binding energy feature is attributed to BF_x fragments on the surface. The B 1s features on both surfaces after annealing to 900 K are attributed to deposited boron adatoms.

The fluorine 1s XPS region is shown in Figure 8 for the nearly-stoichiometric surface (top) and the oxygen-terminated surface (bottom). For the nearly-stoichiometric and oxygen-terminated surfaces, one F 1s feature appears at a binding energy of 686.5 eV with the exposure of 5 L of BF_3 . Fluorine in the acid/base adduct $\text{NH}_3\text{:BF}_3$ has a reported F 1s binding energy of 686.6 eV.⁹ Because of the similarity in the fluorine binding energy, the F 1s feature at 686.5 eV is attributed to molecular BF_3 adsorbed at base sites. An XPS spectrum taken after heating to 340 K to remove molecular BF_3 from the nearly-stoichiometric surface shows a shift to a lower binding energy of 685.9 eV for the F 1s feature. This feature falls in the range of a variety

of metal–fluorine compounds such as MnF₂ and CuF₂.⁹ Therefore, some fluorine from dissociated BF₃ remaining on the nearly-stoichiometric surface after 340 K is likely bound at surface metal (i.e., Cr) sites. On the oxygen-terminated surface, the F 1s feature remains around 686.5 eV upon heating to 500 K to remove all molecular BF₃ from the surface. This F 1s feature does not shift down in binding energy because of the unavailability of surface Cr sites.⁵ Although the nature of the binding site for the remaining F is unclear, the signal is likely associated with F adatoms or BF_x fragments on the oxygen-terminated surface.

The amounts of residual boron left on the stoichiometric and oxygen-terminated surfaces after the XPS experiments (5 L BF₃ exposure at 125 K with subsequent heating) are similar to the saturation coverages of residual boron deposited during repeated BF₃ exposures in TDS. These coverages may be estimated from the XPS data using a simple model based on the exponential decay of signal intensity with sampling depth. The estimates are made assuming (1) no diffraction effects, and (2) inelastic mean free paths of 10.0 Å for Cr 2p (KE = 670 eV) and 10.1 Å for O 1s (KE = 720 eV) photoelectrons. Mean free paths were estimated from the “universal” curve in ref 13.

The estimated XPS B/O ratios are insensitive to a variety of assumptions concerning B adatom or molecular BF₃ adsorption sites and bond lengths. Typical B/O ratios of 0.12–0.13 are estimated for a monolayer coverage defined as of two BF₃ molecules per surface unit cell (i.e., one BF₃ molecule per coordinately unsaturated surface oxygen atom). Experimental XPS B/O ratios following the 5 L exposures at 125 K are 0.078 (~0.6 ML) for the nearly-stoichiometric surface, and 0.058 (~0.5 ML) for the oxygen-terminated surface. Following heating to remove molecular BF₃, XPS B/O ratios of 0.035 and 0.024 are found on the nearly-stoichiometric and oxygen-terminated surfaces, respectively. These ratios correspond to coverages of approximately 0.28 and 0.2 ML of residual boron, respectively.

V. Discussion

BF₃ is not a traditional acidic probe molecule for studying the basicity of oxide surfaces. However, the O 1s XPS results in Figure 6 indicate that BF₃ forms an adduct with basic surface oxygen species on Cr₂O₃ (10 $\bar{1}2$). Charge donation from oxygen to BF₃ is accompanied by an increase in the binding energy of the oxygen 1s signal in XPS.¹²

BF₃ clearly probes differences in coordination of oxide ions on Cr₂O₃ (10 $\bar{1}2$). On the nearly-stoichiometric surface where only three-coordinate O²⁻ anions are exposed, TDS of BF₃ (Figure 2) shows only one desorption feature representative of the desorption of a molecular BF₃ adsorbate from these sites. When the Cr cations are terminated with chromyl oxygens, TDS gives an additional high-temperature desorption feature representative of BF₃ desorption from the terminal oxygen species. The two types of surface oxygen sites are clearly distinguished in TDS because of their widely different BF₃ desorption temperatures.

The heats of adsorption of an acidic probe molecule can be interpreted as a measure of the strength of the acid/base interaction.¹⁴ For cases of unactivated adsorption, the activation energy of desorption measured in TDS is indicative of the heat of adsorption. The heat of adsorption of BF₃ on the terminal chromyl oxygens, 31.8 kcal/mol, is larger than the heat of adsorption on three-coordinate O²⁻ anions, 21.3 kcal/mol. Therefore, the BF₃/surface interactions indicate that terminal chromyl oxygens on the oxygen-terminated surface are stronger Lewis base sites than three-coordinate O²⁻ anions on the nearly-

stoichiometric surface. For V₂O₅ (010), Yin et al. found that terminal vanadyl oxygens act as the most favorable adsorption sites among the three types of surface oxygens for the hydrogen bonding of molecular H₂O.¹⁵ Charge donation from the surface oxygen sites to the H₂O molecule was found to correlate directly with adsorption energy in their first-principles calculations using density functional theory (DFT). Their results indicate that terminal vanadyl oxygens are better charge donors than two- and three-coordinate surface oxygen on V₂O₅ (010).¹⁵ A similar result is found here experimentally for terminal chromyl oxygen on Cr₂O₃ (10 $\bar{1}2$); the highest BF₃ heat of adsorption is associated with terminal oxygen that appears to be the stronger of the two Lewis base sites.

Although the heats of adsorption of molecular BF₃ measured in TDS demonstrate that terminal oxygen on Cr₂O₃ (10 $\bar{1}2$) is a stronger Lewis base than three-coordinate surface oxygen anions, the O 1s XPS results for the higher binding energy features seen upon BF₃ adsorption show the opposite trend one would expect. The O 1s binding energy for the BF₃:O_(s) complex is higher for three-coordinate oxygen than for terminal oxygen, suggesting a greater degree of charge transfer from the three-coordinate oxygen species. We believe, however, that the O 1s XPS results are an indication of differences in the electronic properties of the surface oxygen atoms associated with the two adsorption sites, and not a simple measure of the extent of charge transfer from the oxygen atom to the adsorbed Lewis acid. One potential explanation for the apparent discrepancy between the O 1s binding energies and the heat of adsorption at the different binding sites could involve differences in the extent of charge transfer from Cr to O following BF₃ adsorption. The Cr=O bond associated with the terminal oxygen should be significantly more covalent than the Cr–O bonds associated with the three-coordinate surface lattice oxygen. Charge transfer from the Cr to the terminal oxygen following BF₃ adsorption could account for a lower *net* charge transfer from the terminal oxygen that would show up as a smaller binding energy shift for the O 1s XPS feature. The differences in B 1s binding energies observed following BF₃ adsorption on the stoichiometric and oxygen terminated surfaces lend some support to this view. There is evidence from gas-phase photoemission studies that the B 1s binding energy in BF₃ acid/base adducts tracks the extent of charge transfer to B from the associated Lewis base.¹⁶ Although the B 1s XPS features observed immediately following a BF₃ dose cannot be unambiguously attributed to a single type of molecularly adsorbed species, the 0.3 eV lower binding energy observed initially for the O-terminated surface suggests greater charge transfer to boron for adsorbed BF₃ at terminal oxygen sites than from three coordinate oxygen anion sites on the stoichiometric surface. A computational investigation of this adsorption system would be useful as it could shed light on the relative importance of steric and electronic effects in determining the heat of adsorption at the two different types of surface oxygen sites.

The use of BF₃ as a probe molecule is complicated by some dissociation and buildup of boron and fluorine on the surface after a BF₃ exposure. The nature of the dissociation process is unclear at this time. The possibility of dissociative electron attachment driven by the availability of low energy electrons from ion gauges, mass spectrometer ionizers, and the photoemission process has not been ruled out. Regardless of the cause, under the experimental conditions used in this study BF₃ dissociates on Cr₂O₃ and forms HF and F₂ as products. The hydrogen in the HF product originates from the uptake and dissociation of small amounts of water from the background

vacuum. Some fluorine and boron adatoms from dissociated BF_3 remain on Cr_2O_3 (10 $\bar{1}2$) surfaces after annealing to 900 K. On Cr_2O_3 (10 $\bar{1}2$) it has been observed that a number of halogenated compounds will dissociate and react, leaving halogen at surface chromium sites.¹⁷ Similarly, the residual fluorine from dissociated BF_3 is associated with surface chromium sites if available on Cr_2O_3 , whereas the residual boron from dissociated BF_3 remains as boron adatoms on the surface after annealing to 900 K.

In TDS, the BF_3 desorption features shift to lower temperatures with increasing exposures for both the nearly-stoichiometric and oxygen-terminated surfaces. Molecular BF_3 is expected to change from a planar molecular geometry to a tetrahedral geometry when bound to a Lewis base.⁴ Hence, the BF_3 adsorbates are expected to acquire a dipole moment upon interaction with basic surface sites. Repulsive interactions between the dipoles of BF_3 in the adlayer are the likely cause of the BF_3 desorption features shifting to lower temperatures with increasing coverage.

To our knowledge, BF_3 has not been used previously as a probe of surface basicity. Conversely, CO_2 is the most common probe molecule used to investigate surface basicity.¹⁸ BF_3 and CO_2 interact very differently on Cr_2O_3 (10 $\bar{1}2$) surfaces. The heats of adsorption of BF_3 and CO_2 show opposite trends between the nearly-stoichiometric and oxygen-terminated surfaces.¹⁹ The heats of adsorption of BF_3 on Cr_2O_3 indicate that terminal chromyl oxygens on the oxygen-terminated surface are stronger Lewis base sites than the three-coordinate O^{2-} anions on the nearly-stoichiometric surface, whereas the heats of adsorption of CO_2 are larger on the nearly-stoichiometric surface.¹⁹ These differences are primarily due to variations in the CO_2 coordination geometry with surface condition. BF_3 interacts directly with the oxygen anions on both Cr_2O_3 surfaces, but the interaction of CO_2 is not as straightforward. CO_2 forms a bidentate carbonate on the nearly-stoichiometric surface, which requires an interaction with cation/anion (acid/base) site pairs.¹⁹ On the oxygen-terminated surface, a monodentate adsorbate is formed with the predominant interaction between terminal oxygen and the carbon atom of CO_2 to form more weakly adsorbed CO_2 surface species.¹⁹ Because of differences in the coordination geometry, CO_2 does not probe the same types of surface sites on the two surfaces. Because the bidentate carbonate involves the adsorption of CO_2 at a cation/anion site pair, it is clear that CO_2 is not a simple probe of the basicity of surface oxide ions.

VI. Conclusions

BF_3 , although not a standard probe molecule, has been tested as a probe of the surface Lewis of oxide ions on Cr_2O_3 (10 $\bar{1}2$)

surfaces. BF_3 clearly probes differences in three-coordinate O^{2-} anions and terminal chromyl oxygen ($\text{Cr}=\text{O}$) on Cr_2O_3 (10 $\bar{1}2$). Heats of BF_3 adsorption show that terminal chromyl oxide anions are stronger Lewis bases than three-coordinate O^{2-} anions. BF_3 adsorbates interact directly with surface oxygen making it a direct probe of oxygen "base" sites on Cr_2O_3 . The use of BF_3 as a probe molecule is complicated by some dissociation and the slow build up of surface boron and fluoride during consecutive thermal desorption runs, although the heat of adsorption is not changed significantly with the deposition of $\text{F}_{(\text{s})}$ and $\text{B}_{(\text{s})}$. Heats of adsorption of BF_3 show an opposite trend for characterizing the apparent basicity of Cr_2O_3 surfaces than the heats of adsorption of CO_2 .

Acknowledgment. The authors gratefully acknowledge financial support by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy through Grant DE-FG02-97ER14751. Professor Brian Hanson (VPI-Chemistry) is gratefully acknowledged for helpful discussions.

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) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1999.
- (4) Booth, H. S. *Boron Trifluoride and Its Derivatives*; John Wiley & Sons: New York, 1949.
- (5) York, S. C.; Abee, M. W.; Cox, D. F. *Surf. Sci.* **1999**, *437*, 386.
- (6) Lad, R. J.; Henrich, V. E. *Surf. Sci.* **1988**, *193*, 81.
- (7) 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.
- (8) Foord, J. S.; Lambert, R. M. *Surf. Sci.* **1986**, *169*, 327.
- (9) 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.
- (10) The Leybold sensitivity factor for B 1s is 0.101.
- (11) Redhead, P. A. *Vacuum* **1962**, *12*, 203.
- (12) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
- (13) Riggs, W. M.; Parker, M. J. In *Methods of Surface Analysis*; Czanterna, A. W., Ed.; Elsevier: Amsterdam, 1975; p 103.
- (14) Tanabe, K.; Morrison, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*; Elsevier: New York, 1989.
- (15) Yin, X.; Fahmi, A.; Hahn, H.; Endou, A.; Ammal, S. S. C.; Kubo, M.; Teraishi, K.; Miyamoto, A. *J. Phys. Chem. B* **1999**, *103*, 3218.
- (16) Barber, M.; Connor, J. A.; Guest, M. F.; Hillier, I. H.; Schwarz, M.; Stacey, M. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 551.
- (17) York, S. C.; Cox, D. F. Unpublished data.
- (18) Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970.
- (19) Abee, M. W.; York, S. C.; Cox, D. F. *J. Phys. Chem. B* **2001**, *105*, 7755.