

CHAPTER 3

Halogen-Oxygen Exchange on Cr₂O₃ (10 $\bar{1}$ 2) Single Crystal Surfaces

3.1 Introduction

The photolysis of fully halogenated chlorofluorocarbons (CFC) in the stratosphere, and their role in ozone depletion is of great global concern [1]. The phaseout of the production of CFC's is well underway, in developed countries, with significant amounts of time and money being spent on the development of CFC alternatives. CFC substitutes must offer the same inertness, stability, and low toxicity as CFC's with significantly shorter atmospheric lifetimes. The ideal replacement would be a hydrofluorocarbon (HFC) therefore eliminating the possibility of starting a chlorine atom-initiated ozone destruction cycle. Temporary solutions may include chlorine containing hydrofluorochlorocarbons (HCFC) which have atmospheric lifetimes of 25 years or less, leaving very little to enter the stratosphere [1].

Chromia catalysts have proven effective in a variety of halocarbon reactions, including halogen exchange, isomerization, and disproportionation. Several key CFC alternatives have been produced using chromium(III) oxide based catalysts including 1,1,1,2,-tetrafluoroethane (HFC-134a) [2], 1,1,1,-trifluoro-2,2-dichloroethane (HCFC-123) [3], and pentafluoroethane (HFC-125) [4].

No studies have been published regarding the activation of well-characterized Cr₂O₃, single crystal surfaces for any of these reactions. However, a number of studies

have been completed investigating the catalytic activation of powdered Cr_2O_3 samples [5-9]. Isotopic labeling techniques have been used by Webb, Winfield and co-workers to examine catalytic activation and halogenation of chlorofluoroethanes on the chromia surface [6-8]. Pretreatment with ^{18}F - and ^{36}Cl - labeled hydrogen halides and CFC's is believed to involve the replacement of chemisorbed hydroxyl groups with halogen on the catalyst surface ($\text{Cr}^{3+}\text{-OH}$ by $\text{Cr}^{3+}\text{-X}$, where $\text{X} = ^{18}\text{F}$ or ^{36}Cl). Reaction of CFC's with these catalytically active metal-halogen sites resulted in halogenation of the chlorofluorocarbon through a halogen-exchange reaction. The presence of ^{18}F and ^{36}Cl in the products indicates the halogen is not irreversibly bound to the surface. Additionally, the formation of an inactive halogen surface species that is inert towards reaction is reported [7]. The catalytically inactive species supposedly results from the gradual replacement of lattice $\text{Cr}^{3+}\text{-O}$ by $\text{Cr}^{3+}\text{-X}$ (where $\text{X} = \text{F}$ or Cl) and represented approximately 15-25% of the halogen uptake during pretreatment.

Coulson, *et al.* have suggested that the activation of chromia catalyst towards HCFC disproportionation and isomerization occurs in a two step process [9]. The first step involves the reduction of surface chromia to a Cr^{3+} oxidation state. The second step involves the creation of catalytically active halogen-metal bonds at coordinatively unsaturated Cr^{3+} sites. Active sites on the chromium oxide surface can be created by pretreatment with a number of halogenated compounds including CHF_3 , CF_3Cl , and HF , and destroyed by oxidation with O_2 , through a completely reversible cycle [9]. The current study represents the first time a well characterized single crystal sample was used to study the reversible halogenation and oxidation of the chromia surface.

The Cr_2O_3 (10 $\bar{1}$ 2) surface is nonpolar and has the lowest energy of any low

index Cr_2O_3 surface [10]. A ball model diagram of the ideal, stoichiometric surface is shown in Figure 3.1.

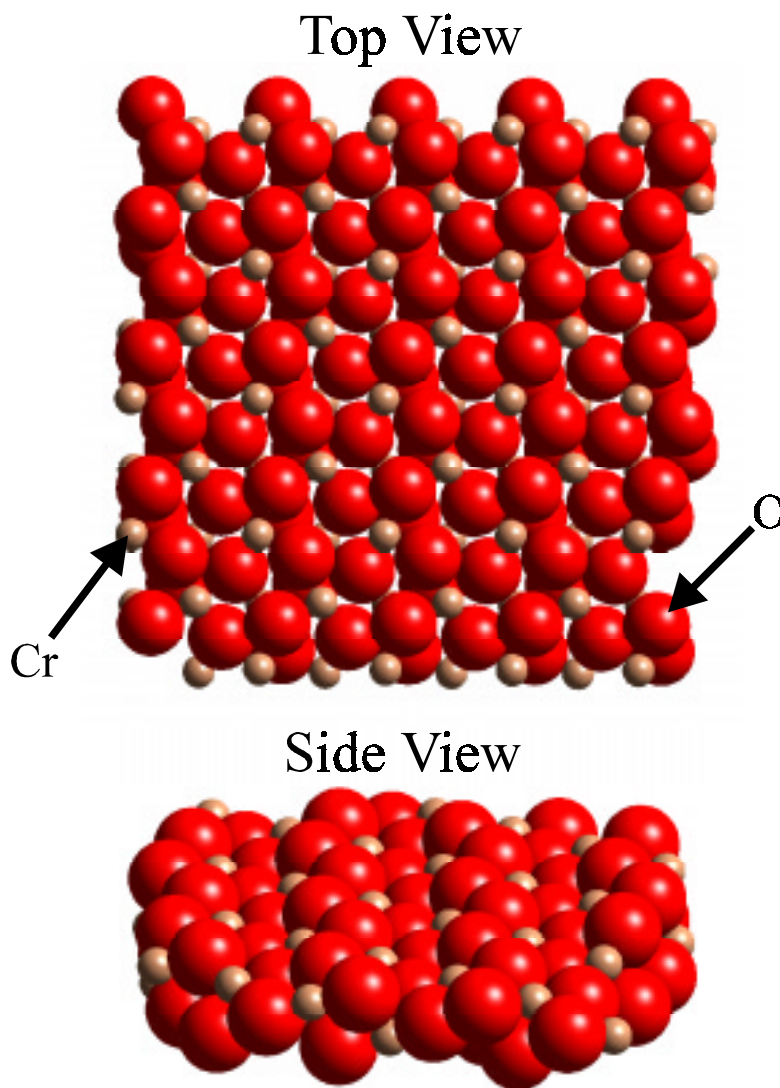


Figure 3.1: Ball model illustration of the ideal, stoichiometric Cr_2O_3 ($10\bar{1}2$) surface.

The topmost atomic layer of the stoichiometric Cr_2O_3 ($10\bar{1}2$) surface is composed entirely of three coordinate oxygen anions, and the second layer contains Cr^{3+} cations that are five coordinate. The topmost oxygen anions and the second layer chromium cations each have one degree of coordinative unsaturation relative to their counterparts in the bulk.

All atoms below the first two atomic layers are fully coordinated.

3.2 Experimental

All experiments were conducted in an ion-pumped, single chamber, stainless steel ultra-high vacuum (UHV) system equipped with a Perkin Elmer model 15-155 single-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), a broad beam ion gun for sample sputtering, and a set V.G. 3-grid reverse view LEED optics. The base pressure of the UHV system is 1×10^{-10} Torr. AES experiments were performed using an incident electron beam energy of 5 keV with spectra being collected in an N(E) mode and differentiated numerically. An Inficon Quadrex 200 mass spectrometer was used for thermal desorption spectroscopy (TDS).

Gas exposures were performed by backfilling the chamber through a variable leak valve. Matheson research purity oxygen (>99.998%) and PCR 1,1,2-trichloro-1-fluoroethane (HCFC-131a) were used as received. A 2 K/s linear temperature ramp was used in all TDS experiments. The low heating rate was used to minimize the possibility of thermal fracture of the Cr_2O_3 sample. The mass spectrometer was equipped with a quartz skimmer to minimize the contribution to the desorption signal from the sample hardware.

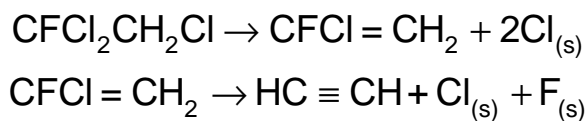
The single crystal Cr_2O_3 sample was oriented using Laue backreflection, and mechanically polished to within 1° of the (10 $\bar{1}$ 2) plane. The sample has an exposed surface area of approximately 77 mm^2 and an average thickness of 1 mm. The sample was mounted on a tantalum holder which acted as an indirect heating and cooling source. The sample holder assembly was mechanically attached to an XYZ rotary sample manipulator. The sample temperature was monitored using a type K thermocouple attached, through a hole in the back of the sample holder, to the rear of the sample using

AREMCO #569 ceramic cement. The sample could be cooled to 130 K, using a liquid nitrogen cooled heat sink, and heated to 1100 K.

The clean, nearly-stoichiometric Cr_2O_3 (10 $\bar{1}$ 2) surface was prepared by ion bombardment with 2 keV Ar^+ and annealing at 900 K for five minutes in UHV [12]. The clean surface exhibits a (1x1) low-energy electron diffraction (LEED) pattern. XPS analysis confirms the presence of chromium in the 3⁺ valence state with an O:Cr ratio of 1.5 ± 0.1 [9]. The clean surface O:Cr ratio as measured using Auger electron spectroscopy (AES) at 873 K and corrected for atomic sensitivities was 0.70 ± 0.03 . AES must be done at high temperature where the material conductivity is sufficient to prevent charging by the primary electron beam. Overlap of the primary oxygen and chromium peaks and distortion of the peak shapes at elevated temperatures makes it difficult to obtain a more accurate estimate of the O:Cr ratio with AES. However, the ratio of 0.70 is characteristic of a stoichiometric surface as seen by comparison to the XPS results. Progressive changes in the surface oxygen and chlorine concentration can be easily monitored using AES. Details of the surface characterization are found elsewhere [12].

An oxygenated surface was prepared by repeatedly exposing the clean Cr_2O_3 (10 $\bar{1}$ 2) surface to oxygen at 173 K, heating linearly at 2 K/s to 723 K, and then manually heating to 873 K for AES [12]. The O:Cr ratio for an oxygen-saturated surface as measured using AES at 873 K and corrected for atomic sensitivities is 0.80 ± 0.03 [12].

AES was used to study the progressive chlorination of the stoichiometric Cr_2O_3 (10 $\bar{1}$ 2) surface following repeated room temperature exposures of $\text{CFCl}_2\text{CH}_2\text{Cl}$ [12]. The catalytic decomposition of HCFC-131a on Cr_2O_3 (10 $\bar{1}$ 2) proceeds in the following manner [13],



with chlorine and fluorine being deposited on the surface. Fluorine and chlorine undergo electron stimulated desorption during AES [13]. Electron stimulated desorption of fluorine is so rapid, at the AES temperature of 873 K, it is impossible to quantify the surface fluorine concentrations with AES. Electron stimulated desorption of chlorine proceeds at a slower pace, making it possible to determine the concentration of chlorine on the Cr_2O_3 surface with AES at 873 K. The effect of electron stimulated desorption of chlorine can be minimized by performing only a single scan, and by sampling a different position on the surface with each AES measurement. The Cl:Cr ratio varies from 0.00 for the stoichiometric surface to 0.30 ± 0.03 for the chlorine-saturated surface [12]. The surface oxygen to chromium ratio was unchanged, from the stoichiometric value of 0.70 ± 0.03 , following exposure of the clean surface to HCFC-131a.

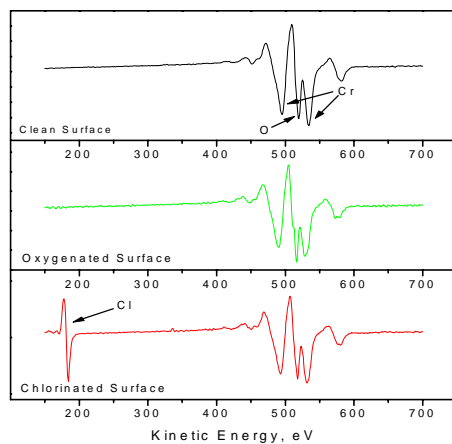


Figure 3.2: AES spectra for the three types of surface preparations (clean, oxygenated, and chlorinated) studied.

3.3 Results

3.3.1 Oxygen-Halogen Exchange on a Chlorinated Surface

The exchange of oxygen with chlorine on a chlorine-saturated surface was examined using AES and TDS. The chlorinated surface was exposed to O₂ through a series of 0.13 L doses of O₂ at 173 K, heated linearly at 2 K/s to 723 K, and then manually heated to 873 K for AES. The progressive oxygenation and dechlorination of the surface is illustrated in Figure 3.3 with a series of O:Cr and Cl:Cr ratios obtained from AES.

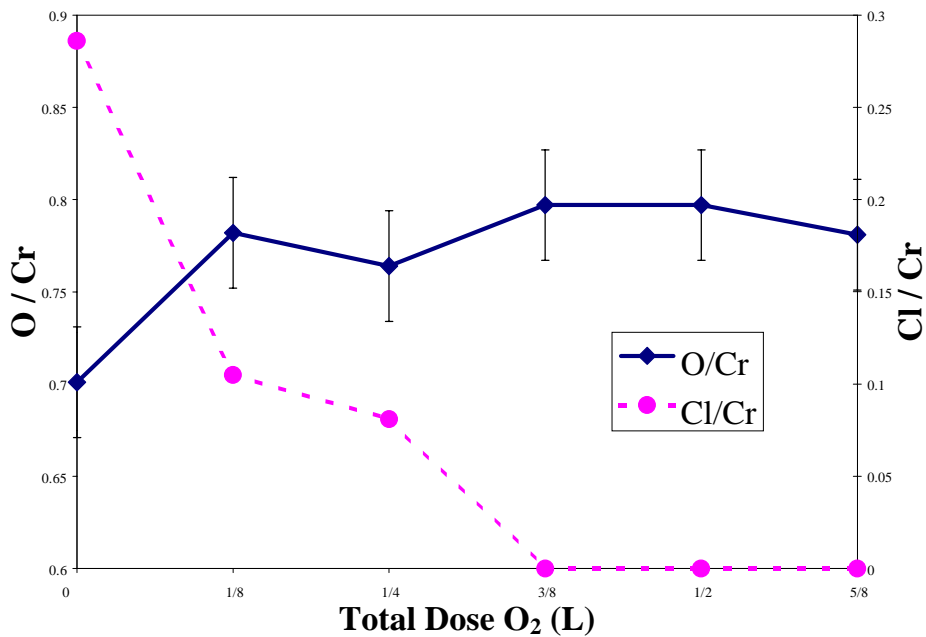


Figure 3.3: AES O:Cr and Cl:Cr ratios following consecutive 1/8 L oxygen exposures at 173 K on a chlorinated surface.

Chlorine is completely removed from the surface following a maximum of three 0.13 L exposures of O₂. No chlorinated desorption products were observed during TDS

including ClO, ClO₂, Cl₂O, Cl₂, HCl, and CrCl₂. A single set of TDS experiments were conducted where the linear temperature ramp was extended to 873 K, the AES temperature. This would account for any desorption between the end of the TDS temperature ramp and the AES temperature. The higher final TDS temperature was not consistently used because of the significant strain it placed on the sample mounting hardware. As before, no chlorinated products were observed during this high temperature TDS experiment. No atomic chlorine ($m/z = 35$) desorption signal was observed during any of the TDS runs. It is assumed that a small atomic chlorine contribution would be included in the cracking pattern of any chlorinated desorption product. Following three 1/8 L doses of O₂, the O:Cr ratio increased from the stoichiometric value of 0.70 ± 0.03 to 0.80 ± 0.03 , consistent with an oxygen-saturated surface.

3.3.2 Halogen-Oxygen Exchange on an Oxygenated Surface

AES and TDS were used to study the exchange of chlorine with oxygen on the oxygenated Cr₂O₃ (10 $\bar{1}$ 2). A oxygen-saturated surface was exposed to chlorine through a series of 0.13 L doses of CFCl₂CH₂Cl (HCFC-131a) at 173 K, heated linearly at 2 K/s to 723 K, and then manually heated to 873 K for AES. The progressive chlorination of the oxygenated surface is illustrated with a series AES surface compositions shown in Figure 3.4. The O:Cr ratio of the oxygenated surface was reduced from 0.82 ± 0.03 to 0.72 ± 0.03 following a total HCFC-131a exposure of 0.38 L. The O:Cr ratio was unchanged following additional 0.13 L HCFC-131a exposures. The final AES O:Cr ratio, 0.72 ± 0.03 , is consistent with a stoichiometric or chlorine-saturated surface.

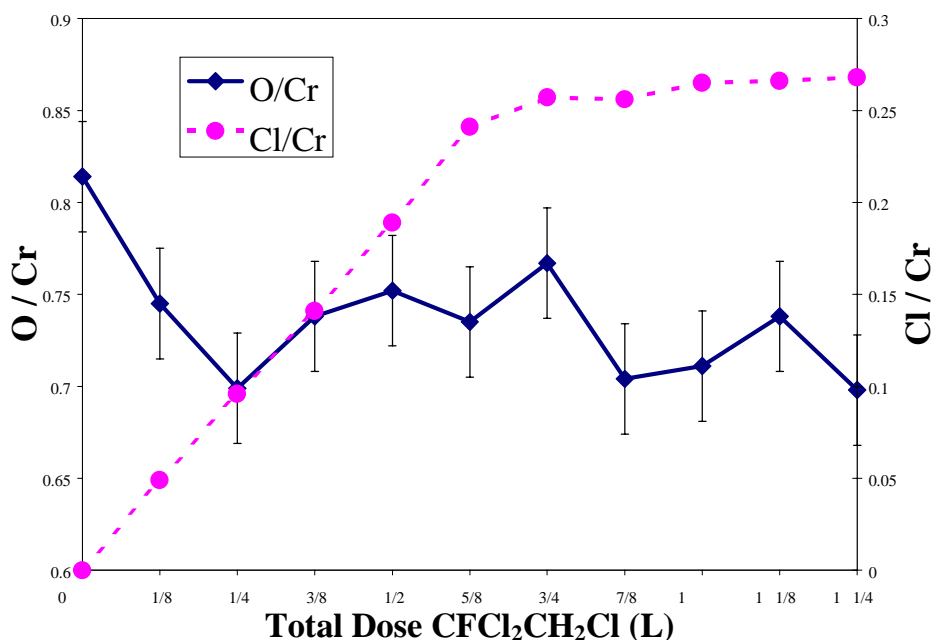


Figure 3.4: AES O:Cr and Cl:Cr ratios following consecutive 1/8 L CFCl₂CH₂Cl exposures at 173 K on an oxygenated surface.

Oxygen desorption was not observed during TDS. The only desorption products identified during TDS resulted from the decomposition of HCFC-131a, including CFCl=CH₂ and HC≡CH [13]. However, it is possible that other oxidation products went undetected because of the complexity of the CFC cracking pattern. The decrease in surface oxygen concentration was accompanied by an increase in chlorine concentration. A saturation chlorine coverage, Cl:Cr ratio of 0.27 ± 0.03 , was obtained following a total HCFC-131a exposure of 0.75 L. The final Cl:Cr ratio, 0.27 ± 0.03 , was consistent with a chlorine-saturated surface.

The progressive chlorination of clean and oxygenated Cr₂O₃ (10 $\bar{1}$ 2) following exposure to CFCl₂CH₂Cl is illustrated in Figure 3.5.

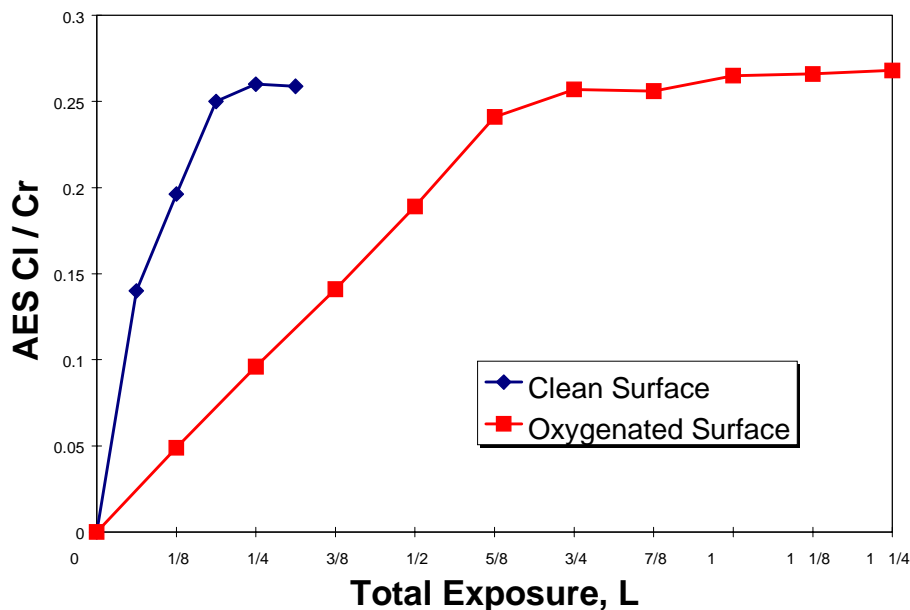


Figure 3.5: AES Cl:Cr ratio following consecutive 1/8 L $\text{CFCl}_2\text{CH}_2\text{Cl}$ exposures at 173 K on clean and oxygenated surfaces.

The final AES Cl:Cr ratio, 0.27 \pm 0.03, was the same for each starting surface. An exposure of approximately 3/16 L of $\text{CFCl}_2\text{CH}_2\text{Cl}$ was required to saturate the clean surface. The oxygenated surface required an exposure of nearly 3/4 L to obtain saturation.

3.3.3 Thermally Activated Diffusion of Oxygen

Thermally activated diffusion and electron stimulated desorption of oxygen into the bulk was studied on an oxygen saturated Cr_2O_3 (10 $\bar{1}$ 2) surface using AES. The AES O:Cr ratio was used to monitor the disappearance of oxygen from the surface via diffusion or desorption. The migration of oxygen into the bulk was not observed during 20 minute cycles over a temperature range of 873-1023 K. Additionally, electron stimulated desorption of oxygen was not observed for an oxygen saturated surface

continuously exposed to the AES electron beam for 20 minutes at 873K. For each set of experiments, no statistically significant change in the AES O:Cr ratio was observed.

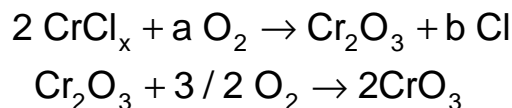
3.4 Discussion

The exchange of chlorine and oxygen was found to be reversible on Cr₂O₃ (10 $\bar{1}$ 2). Exposure of CFCl₂CH₂Cl resulted in the formation of a chlorine-saturated surface regardless of the condition of the starting surface, clean or oxygenated. Similarly, exposing a clean or chlorinated surface to oxygen resulted in the formation of an oxygen-saturated surface.

3.4.1 Oxygen-Halogen Exchange

Two mechanisms are likely for the removal of chlorine from a chlorinated Cr₂O₃ (10 $\bar{1}$ 2) surface following exposure of O₂. The first involves the formation of a chlorinated product that was undetected during TDS. No chlorinated desorption products were observed during TDS including Cl, ClO, ClO₂, Cl₂O, Cl₂, HCl, and CrCl₂. Desorption of chlorine may have proceeded through an undetermined chlorinated product, although it appears unlikely since no contribution was observed with a *m/z* of 35 (Cl⁺) during TDS.

The second mechanism involves chlorine migration into the bulk. Thermally activated diffusion of chlorine into the bulk has been observed previously on the Cr₂O₃ (10 $\bar{1}$ 2) surface [13]. An energy of activation for chlorine diffusion into the bulk of 45 kcal/mol was determined experimentally [13]. An estimate of the heat of reaction (ΔH_R), at 298 K, associated with transformation from chlorinated Cr₂O₃ to an oxidized surface can be made using the following simplified model,



where $\Delta H_R = -72.4$ kcal/mol when $x=2$, and $\Delta H_R = -9.4$ kcal/mol when $x=3$. The chlorinated Cr_2O_3 surface is approximated with chromium chlorides and the oxidized surface is assumed to consist of chromium only in the +6 oxidation state as CrO_3 . Although this model provides only a gross approximation, the exothermic nature of this transformation provides a possible source for the generation of energy required to initiate chlorine migration (45 kcal/mol) into the bulk. The diffusion of chlorine into the bulk is a likely explanation for the disappearance of surface chlorine, especially since no chlorinated desorption products were observed during TDS.

The total elimination of chlorine from the surface following oxygen exposure was a somewhat surprising result following previously published studies on powdered Cr_2O_3 surfaces [6,7,8]. Webb, Winfield, and co-workers observed the creation of a halogenated catalytically inactive species that was retained by the catalyst following oxidation in air [7]. The halogenated species was postulated to result from the slow, gradual replacement of lattice $\text{Cr}^{3+}\text{-O}$ with $\text{Cr}^{3+}\text{-X}$ (where $\text{X}=\text{Cl}$ or F) [6]. It is likely that the creation of lattice $\text{Cr}^{3+}\text{-X}$ (where $\text{X}=\text{Cl}$ or F) bonds resulted from the slow migration of halogen into the bulk. As mentioned previously, chlorine diffusion into the bulk has been observed on the chlorinated Cr_2O_3 (10 $\bar{1}$ 2) surface, at temperatures between 923 K and 1023 K [13]. The rate of chlorine migration is dependent on sample temperature, over the temperature range studied, 923 K to 1023 K, chlorine was completely removed from a chlorine-saturated surface in a matter of minutes. The experiments of Webb and Winfield involved catalytic studies between 4 and 24 hours at reaction temperatures of 623 K to 808 K [7]. The longer reactions times may have been sufficient to initiate halogen diffusion away from the surface at temperatures between 623 and 808 K. 15-25% of the

halogen was retained by the powdered Cr_2O_3 following a complete catalytic study and exposure to moist air for 48 hours [7]. Techniques used in determining the remaining halogen content on powdered Cr_2O_3 catalysts were not surface sensitive and hence could not differentiate between halogen chemisorbed on the surface or diffused a few atomic layers below the surface [7]. In this study on single crystal Cr_2O_3 (10 $\bar{1}$ 2), the complete removal of chlorine from the surface could easily be detected using AES, a surface sensitive technique. In the current study chemisorbed halogen was completely replaceable, suggesting that the inactive species proposed by Webb, Winfield, and coworkers results from halogen thermally diffused into the bulk.

3.4.2 Halogen-Oxygen Exchange

Two likely explanations exist for the reduction of surface oxygen concentration to that of the clean surface following exposure of $\text{CFCl}_2\text{CH}_2\text{Cl}$. The first possibility is oxygen diffusion away from the surface into the bulk. Oxygen migration into the bulk seems unlikely given the endothermic nature (9.4 -72.4 kcal/mol) of the reduction and chlorination of the surface, obtained from the reverse of the surface transformation outlined earlier. Additionally, thermally activated diffusion of oxygen into the bulk has not been observed for oxygen-saturated Cr_2O_3 (10 $\bar{1}$ 2) surfaces at temperatures up to 1023 K.

Reduction of the surface most likely proceeded through the desorption of an undetermined oxygenated product. An increased oxygen exposure of over 300% was required to oxygenate a chlorinated surface relative to a clean surface. It is likely that the chlorine that was deposited on the surface following HCFC-131a decomposition

subsequently combined with the chemisorbed oxygen to form an oxygen and chlorine containing desorption product. Emphasis was placed on monitoring the $\text{CFCl}_2\text{CH}_2\text{Cl}$ decomposition products during TDS, so the desorption of oxidation products may have gone undetected because of the complexity of the CFC cracking patterns.

3.4.3 Comparison to Powder Studies

Parallels can be drawn regarding the exchange of halogen and oxygen on Cr_2O_3 (10 $\bar{1}$ 2) surface and observations made previously by Coulson, *et. al.* [9] on the activation and deactivation of chromia catalysts. Coulson proposed that the creation of active sites on chromium oxide proceeds, following pretreatment with a halogenated compound, initially with the reduction of the surface chromia to Cr^{3+} followed by the creation of chromia-halogen bonds. [9]. In the current study a similar process was noted following pretreatment with a halogenated compound, in this case $\text{CFCl}_2\text{CH}_2\text{Cl}$. The O:Cr ratio of an oxidized surface was reduced to that of the stoichiometric surface, Cr^{3+} oxidation state, and halogen was deposited on the surface. The destruction of active sites on chromium oxide is accomplished by oxidizing in O_2 [9]. The destruction of active sites on the chromia surface is likely due to the complete removal of halogen from the surface accompanied by oxidation, as observed in the current study. Coulson observed that the activation and deactivation of the chromium oxide surface is completely reversible [9]. Similarly, the exchange of halogen and oxygen was shown to be completely reversible under well-defined conditions on single crystal Cr_2O_3 (10 $\bar{1}$ 2).

3.5 Conclusions

The exchange of chlorine and oxygen was found to be reversible on the Cr_2O_3 (10 $\bar{1}$ 2) surface. Chlorine was completely removed from the Cr_2O_3 (10 $\bar{1}$ 2) surface with oxygen exposure. The rate of chlorination, following $\text{CFCl}_2\text{CH}_2\text{Cl}$ exposure, was significantly reduced by pretreatment of the surface with oxygen. Exposure of $\text{CFCl}_2\text{CH}_2\text{Cl}$ was found to be an effective means of reducing the surface oxygen concentration to that of stoichiometric Cr_2O_3 (10 $\bar{1}$ 2). The exchange of halogen with oxygen appears to involve only chemisorbed surface oxygen, not bulk lattice oxygen.

3.6 References

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