

# **The Oxidation of Methanol on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) Single Crystal Surfaces**

by

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## ABSTRACT

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The reaction of methanol with nearly-stoichiometric and oxygen-terminated surfaces of Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}2$ ) was studied using thermal desorption spectroscopy and x-ray photoelectron spectroscopy. Dissociative adsorption of methanol occurs on the nearly-stoichiometric surface and is attributed to the availability of cation-anion site pairs. An array of products including CH<sub>4</sub>, CH<sub>2</sub>O, CO, CO<sub>2</sub>, and H<sub>2</sub> are produced above 550 K on the nearly-stoichiometric surface. Monolayer coverage of methanol yields a 58% conversion to products. Of these products, selectivity to CO is the highest (41%), followed by CH<sub>2</sub>O (28%), CH<sub>4</sub> (24%), and CO<sub>2</sub> (7%). At higher temperatures, methoxides reversibly undergo dehydrogenation and nucleophilic attack from lattice oxygen to create dioxymethylene. Hydrogenation of dioxymethylene back to methoxides leads to the formation of CH<sub>4</sub> and CH<sub>3</sub>OH above 550 K. Formate is formed on the surface by reversible dehydrogenation of dioxymethylene. Formaldehyde is produced via C-O bond cleavage of dioxymethylene and the decomposition of formate yields CO, CO<sub>2</sub>, and H<sub>2</sub> at slightly higher temperatures. The oxygen-terminated surface is unreactive for methanol dissociation due to cation site blocking from terminal chromyl oxygen.

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## TABLE OF CONTENTS

	page
List of Figures	iii.
List of Tables	iv.
Acknowledgements	v.
I Introduction	
i) Reactions of Methanol on Single Crystal Metal Oxides	1.
ii) Reactions of Methanol on Cr <sub>2</sub> O <sub>3</sub> Powders	7.
II The Cr <sub>2</sub> O <sub>3</sub> (10 $\bar{1}$ 2) Surface	9.
III Experimental	11.
IV Results	
i) TDS of Methanol on the Nearly-Stoichiometric Cr <sub>2</sub> O <sub>3</sub> (10 $\bar{1}$ 2) Surface	14.
ii) TDS of Formaldehyde on the Nearly-Stoichiometric Cr <sub>2</sub> O <sub>3</sub> (10 $\bar{1}$ 2) Surface	18.
iii) TDS of Methanol on the Oxygen-Terminated Cr <sub>2</sub> O <sub>3</sub> (10 $\bar{1}$ 2) Surface	21.
iv) XPS of Methanol on the Nearly-Stoichiometric Cr <sub>2</sub> O <sub>3</sub> (10 $\bar{1}$ 2) Surface	23.
V Discussion	
i) Low Temperature Range (< 500 K)	26.
ii) High Temperature Range (500 – 750 K)	26.
VI Conclusions	35.
VII Recommendations for Future Work	36.
References and Notes	39.

## LIST OF FIGURES

	page
1. Intermediates for the reaction of methanol on $\text{ZrO}_2$ (100) and $\text{ZrO}_2$ (111).	4.
2. Ball model representation of the ideal $\text{Cr}_2\text{O}_3$ ( $10\bar{1}2$ ) surface.	10.
3. TDS spectra obtained after exposing the nearly-stoichiometric surface to methanol.	15.
4. TDS spectra of products observed after exposing the nearly-stoichiometric surface to 0.83 L of methanol.	17.
5. TDS spectra of oxygenated products observed after exposing the nearly-stoichiometric surface to 0.4 L of $^{18}\text{O}$ -isotopically labeled methanol; equal distribution of isotopically labeled and unlabeled oxygenated products.	19.
6. TDS spectra of products observed after exposing the nearly-stoichiometric surface to 0.5 L of formaldehyde.	20.
7. TDS spectra obtained after exposing the oxygen-terminated surface to methanol.	22.
8. $\text{C}1\text{s}$ XPS spectra obtained after exposing the nearly-stoichiometric surface to 60 L of methanol.	24.
9. Cartoon illustrating the possible bidentate structure of dioxymethylene on $\text{Cr}_2\text{O}_3$ ( $10\bar{1}2$ ).	29.
10. Reaction scheme for the oxidation of methanol on $\text{Cr}_2\text{O}_3$ ( $10\bar{1}2$ ).	32.

## LIST OF TABLES

	page
1. Table of methanol selectivity on various metal oxide single crystals.	6.

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## I. Introduction

### *Reactions of methanol on single crystal metal oxide surfaces*

The heterolytic dissociative adsorption of methanol on metal oxide single crystal surfaces is typically associated with the presence of cation-anion site pairs [1-11]. Methanol adsorbs on the metal cation (Lewis acid) site from the gas phase and loses a proton to a neighboring oxygen anion (Lewis base), thus forming a surface hydroxide group [1-8, 10, 11], while the conjugate base anion, methoxide ( $\text{CH}_3\text{O}^-$ ), binds to the cation site. An investigation by Vohs and Barteau [6] on the  $(000\bar{1})\text{-O}$  and  $(0001)\text{-Zn}$  polar faces of ZnO revealed that the zinc face of the crystal is active for methanol dissociation and oxidation, while the oxygen face is inactive. The difference in activity of these crystal faces was attributed to site-pair availability, since the zinc face exposed both zinc and oxygen ions while the oxygen face exposed only oxygen anions. For dissociation reactions to occur, it is believed that the surface cations must be coordinatively unsaturated [1], while the coordination of surface oxygen anions is less important [1, 2, 5].

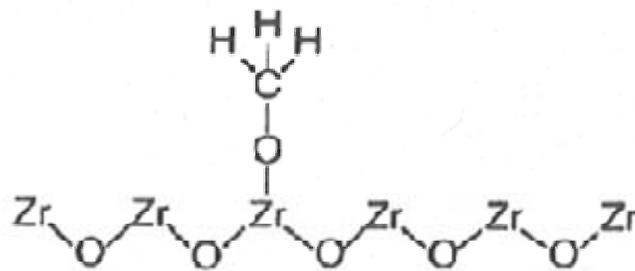
Although these first two conditions are thought to be important for dissociative adsorption of methanol, these conditions alone are not sufficient. The nearly-stoichiometric surfaces of  $\text{SnO}_2$  (110) [5],  $\text{CeO}_2$  (111) [8],  $\text{TiO}_2$  (100) [3, 12], and  $\text{TiO}_2$  (110) [12] contain acid-base site pairs and coordinatively unsaturated surface cations, yet all are nearly inactive for methanol dissociation. While the nearly stoichiometric surfaces of  $\text{SnO}_2$  (110) [5] and  $\text{CeO}_2$  (111) [8] were found to be inactive, reduction of the surfaces exposes cations of different coordination and oxidation states which allow for methanol dissociation. On  $\text{SnO}_2$  (110), methanol dissociation occurs preferentially at 4-coordinate

$\text{Sn}^{2+}$  sites associated with bridging oxygen vacancies, while on  $\text{CeO}_2$  (111) the reaction occurs on 4-coordinate  $\text{Ce}^{4+}$  oxygen deficient sites created by  $\text{Ar}^+$  sputtering. It has been suggested that adsorption of a weaker Brønsted acid (such as methanol) is enhanced by more highly coordinatively unsaturated (more basic) cation sites [11]. While this idea seems to hold for the case of  $\text{CeO}_2$  (111) and  $\text{TiO}_2$  (001), it was determined that further reduction of the active  $\text{SnO}_2$  (110) surface by removal of in-plane oxygen anions caused the surface to become again inactive for methanol dissociation [5]. These observations demonstrate the complexity associated with generalizing the requirements for dissociative adsorption.

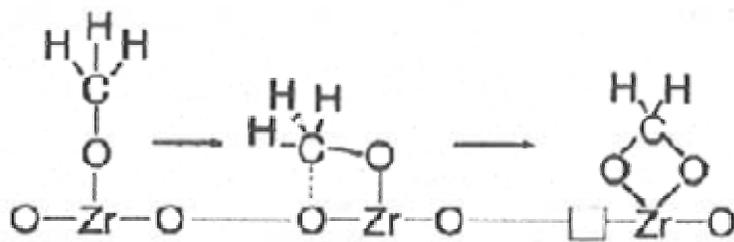
Methoxide ( $\text{CH}_3\text{O}^-$ ) is the key intermediate in the formation of all methanol decomposition products on  $\text{TiO}_2$  (001) [3],  $\text{Cu}_2\text{O}$  (111) and (100) [4],  $\text{SnO}_2$  (110) [5],  $\text{ZnO}$  (0001) [6],  $\text{ZrO}_2$  (100) and (110) [7],  $\text{CeO}_2$  (111) [8], and  $\text{RuO}_2$  (110) [9], having been identified by XPS [3-6, 9] or HREELS [7]. Thermal desorption spectroscopy (TDS) data are also suggestive of methoxide intermediates on these surfaces [3-9]. Upon dissociative adsorption of methanol, methoxide and hydroxide groups are created on oxide surfaces. Heating the surface can cause hydroxides to react with methoxides, reforming methanol [4, 5, 8, 9], or to react with another hydroxide in a disproportionation to form  $\text{H}_2\text{O}$  [3, 6, 9,12]. Another route to methanol formation from a methoxide involves rate-limiting dehydrogenation of methoxide (cleavage of a C-H bond) [4, 5, 8, 9]. This reaction is distinctly apparent from the observation of simultaneous desorption of methanol and formaldehyde ( $\text{CH}_2\text{O}$ ) during TDS [4-9]. Decomposition of methoxide to formaldehyde releases hydrogen to the surface; this hydrogen is then free to react with another methoxide and desorbs as methanol.

Formate ( $\text{HCOO}^-$ ) has been detected by XPS and TPD as a reaction intermediate in the formation of CO and  $\text{CO}_2$  from methanol on ZnO (0001) [6]. This intermediate has also been verified by comparison of XPS spectra for adsorbed methanol and adsorbed formic acid ( $\text{HCOOH}$ ) [6]. The intermediate was derived by lattice oxygen insertion into a methoxide. Formate has not been reported as a stable surface intermediate in methanol oxidation on any other metal oxide single crystal surfaces.

Dioxymethylene ( $\text{CH}_2\text{O}_2$ ) has been identified by high-resolution electron energy loss spectroscopy (HREELS) as a reaction intermediate on  $\text{ZrO}_2$  (110), but not on  $\text{ZrO}_2$  (100) [7]. This species was also derived by lattice oxygen insertion into a methoxide. The difference in reactivity of the (110) and (100) surfaces of  $\text{ZrO}_2$  is attributed to surface structure. On the (110) surface,  $\text{Zr}^{4+}$  cations are 6-fold coordinate ( $\text{ZrO}_2$  has a fluorite structure with Zr cations being a maximum of 8-coordinate in the bulk), while on the (100) surface  $\text{Zr}^{4+}$  cations are only 4-fold coordinate. The (110) surface has a linear array of surface Zr cations and O anions, allowing for possible bonding between methoxide carbon and lattice oxygen. The (100) surface has a zigzag array of surface ions, leading to possible steric hindrance in the formation of  $\text{CH}_2\text{O}_2$  (figure 1). Also worth noting, O anions on the (110) and (100) surfaces are 3 and 4 coordinate, respectively, suggesting that oxygen anions on the (110) surface should be better nucleophiles for the nucleophilic addition of oxygen during  $\text{CH}_2\text{O}_2$  formation. On this surface dioxymethylene decomposes to  $\text{CH}_2\text{O}$ . In general, the formation of  $\text{CH}_2\text{O}$  requires a bi-functional acid-base surface, that is a surface containing mildly basic oxygen species for the transfer of  $\text{H}^+$  from a methoxide and weaker acidic cation sites for the desorption of the product [13].



**ZrO<sub>2</sub> (100)**



**ZrO<sub>2</sub> (110)**

Figure 1. Intermediates in the reaction of methanol on ZrO<sub>2</sub> (100) and ZrO<sub>2</sub> (110). Reproduced from reference 7 with permission.

Table 1 lists selectivity patterns for methanol oxidation over various metal oxide single crystal surfaces. Formaldehyde has been observed as a reaction product during thermal desorption on TiO<sub>2</sub> (001), ZnO (0001), Cu<sub>2</sub>O (100) and (111), SnO<sub>2</sub> (110), ZrO<sub>2</sub> (110), CeO<sub>2</sub> (111), and RuO<sub>2</sub> (110). For the case of TiO<sub>2</sub> (001) studied by Kim and Barteau [3], the {011}-faceted TiO<sub>2</sub> (001) and {114}-faceted TiO<sub>2</sub> (001) surfaces have a higher O/Ti ratio than the unfaceted TiO<sub>2</sub> (001) surface, and both faceted surfaces produce CH<sub>2</sub>O. The {114}-faceted surface has the highest O/Ti ratio and produces the largest amount of CH<sub>2</sub>O, yet a smaller amount of CH<sub>4</sub>, indicating that the reaction is structure sensitive. The {114}-faceted surface is thought to contain 4, 5, and 6-coordinate Ti<sup>4+</sup> cations, while the {011}-faceted surface only contained 5-coordinate Ti<sup>4+</sup> cations. The formation of formaldehyde on TiO<sub>2</sub> (001)-faceted surfaces was attributed to the presence of 5-coordinate Ti<sup>4+</sup> cations.

Dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>) was also identified as a product of the {114}-faceted surface of TiO<sub>2</sub> (001) [3]. This is the only case where CH<sub>3</sub>OCH<sub>3</sub> was observed during methanol oxidation on a metal oxide single crystal surface. The reaction occurs by bimolecular coupling of two methoxides at 4-coordinate Ti<sup>4+</sup> cations, i.e. doubly-coordinatively unsaturated cation sites [1, 2].

Methane (CH<sub>4</sub>) has been observed as a product during thermal desorption experiments on {011} and {114}-faceted TiO<sub>2</sub> (001), reduced TiO<sub>2</sub> (001) [3, 12], ZrO<sub>2</sub> (100), and ZrO<sub>2</sub> (110) [7] surfaces. In these instances, CH<sub>4</sub> formation was attributed to the reaction of a methoxide with an adsorbed hydrogen atom. For TiO<sub>2</sub>, deoxygenation of methoxide to CH<sub>4</sub> occurred at oxygen-deficient Ti cations, and hence cleavage of the C-O bond led to reoxidation of the surface [3, 12]. The same reaction occurred on ZrO<sub>2</sub>,

Table 1. Methanol selectivity on various metal oxide single crystals

Surface	Conversion	Selectivity					Intermediate(s)	Ref.
		CH <sub>2</sub> O	CO	CO <sub>2</sub>	CH <sub>4</sub>	CH <sub>3</sub> OCH <sub>3</sub>		
CeO <sub>2</sub> (111)							CH <sub>3</sub> O	8
annealed	*	100%	---	---	---	---		
Ar <sup>+</sup> -bombarded	+	100%	---	---	---	---		
Cu <sub>2</sub> O (100)	59%	58%	34%	8%	---	---	CH <sub>3</sub> O	4
Cu <sub>2</sub> O (111)	62%	24%	52%	24%	---	---	CH <sub>3</sub> O	4
RuO <sub>2</sub> (110)	87%	28%	26%	46%	---	---	+	9
SnO <sub>2</sub> (110)							CH <sub>3</sub> O	5
stoichiometric	10-20%	100%	---	---	---	---		
reduced	40-50%	100%	---	---	---	---		
less defective	20-50%	100%	---	---	---	---		
more defective	<5%	100%	---	---	---	---		
TiO <sub>2</sub> (001)							CH <sub>3</sub> O	3
{011}-faceted	22%	18%	---	---	82%	---		
{114}-faceted	32%	29%	---	---	38%	33%		
Ar <sup>+</sup> -bombarded	23%	---	26%	---	74%	---		
ZnO (000 $\bar{1}$ )-O	0%	---	---	---	---	---	---	6
ZnO (0001)-Zn	+	13%	43%	44%	---	---	CH <sub>3</sub> O, CHOO	6
ZrO <sub>2</sub> (100)	25%	---	32%	---	68%	---	CH <sub>3</sub> O	7
ZrO <sub>2</sub> (110)	28%	54%	25%	---	21%	---	CH <sub>3</sub> O, CH <sub>2</sub> O <sub>2</sub>	7

+ Information not provided

\* Ordered surface was nearly inactive

but it was reported that oxygen produced in this manner was either incorporated into the lattice or reacted with adsorbed hydrogen to form water [7].

Non-selective oxidation products (CO and CO<sub>2</sub>) are frequently encountered in studies of alcohol oxidation. CO is a reaction product in thermal desorption from ZrO<sub>2</sub> (100) and (110), and Ar<sup>+</sup>-bombarded TiO<sub>2</sub> (001); while CO and CO<sub>2</sub> have both been identified as reaction products from ZnO (0001), Cu<sub>2</sub>O (100) and (111), and RuO<sub>2</sub> (110). On ZnO (0001), CO is formed via two separate reaction pathways: methoxide dehydrogenation and formate decomposition. CO<sub>2</sub> is strictly derived from decomposition of a formate on this surface [6]. For this surface, nearly equal amounts of CO and CO<sub>2</sub> were formed (43% and 44% selective, respectively).

### ***Reaction of methanol on Cr<sub>2</sub>O<sub>3</sub> powders***

IR investigations on Cr<sub>2</sub>O<sub>3</sub> powders prepared by thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> show a methoxide formed upon dissociative adsorption of methanol, indicating an adsorption process similar to that seen on many metal oxide single crystal surfaces [14-17]. On hydroxylated Cr<sub>2</sub>O<sub>3</sub>, methanol is thought to adsorb and react with hydroxyl groups to form methoxide and hydrogen gas [17]. Oxidized Cr<sub>2</sub>O<sub>3</sub> surfaces yield CH<sub>2</sub>O from methanol during thermal desorption experiments [14,18], while hydroxylated [17] and reduced [18] surfaces do not. Reduced, oxidized, and hydroxylated Cr<sub>2</sub>O<sub>3</sub> surfaces all produce CO and CO<sub>2</sub> [15-18]. For the oxidized surface, overall conversion decreased with increasing concentration of pre-adsorbed labile oxygen. This decrease is attributed to competition of methanol and oxygen for the same active sites [18]. Ethylene (CH<sub>2</sub>=CH<sub>2</sub>) and acetylene (CH≡CH) were detected as reaction products during methanol thermal desorption experiments on hydroxylated Cr<sub>2</sub>O<sub>3</sub>

surfaces, but the reaction mechanisms for these products were not described [17]. Dimethyl ether has also been identified as a reaction product from  $\text{Cr}_2\text{O}_3$  in thermal desorption from reduced and hydroxylated  $\text{Cr}_2\text{O}_3$  surfaces [16, 17]. The suggested mechanisms for this product differed between sources; one listing a dehydration reaction of two methanol molecules [16], while the other suggests a coupling reaction of two methoxides [17] as the reaction pathway.

This report focuses on the determination of surface intermediates, reaction pathways, and products for the reaction of methanol on  $\alpha\text{-Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) single crystal surfaces. Thermal desorption spectroscopy (TDS) and x-ray photoelectron spectroscopy (XPS) were employed and the results have been reported herein.

## II. $\text{Cr}_2\text{O}_3(10\bar{1}2)$

$\alpha\text{-Cr}_2\text{O}_3$  is an electrical insulator (band gap = 3.4 eV) with the corundum structure [19,20]. The bulk chromium coordination geometry is a distorted octahedron, while oxygen anions are coordinated in a distorted tetrahedral arrangement of cations. In the corundum structure, one-third of the possible cation sites are vacant and these vacancies are located along the  $(10\bar{1}2)$  plane [21]. A ball model representation of the ideal, stoichiometric  $(10\bar{1}2)$  surface is shown in figure 2. This surface is somewhat wavy due to the alternating tilt of incomplete octahedra relative to the macroscopic plane.

The ideal surface is non-polar and has the lowest energy of any perfect low-index surface of  $\text{Cr}_2\text{O}_3(10\bar{1}2)$  [22]. The topmost 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 periodicity with a ratio of side of  $a/b = 0.94$ . At the surface, all  $\text{O}^{2-}$  anions in the top atomic layer are three coordinate and  $\text{Cr}^{3+}$  cations in the second atomic layer are five coordinate. Both ions have one degree of coordinate unsaturation relative to the bulk [23]. All ions below the top two atomic layers are fully coordinate.

An oxygen-terminated surface may be achieved by capping surface cations of the stoichiometric surface with terminal chromyl oxygen ( $\text{Cr}=\text{O}$ ). This surface can be prepared by successive low-temperature oxygen exposures on the nearly-stoichiometric surface until all of the surface cations are saturated with oxygen [24]. The oxygen-terminated surface exposes both three-coordinate  $\text{O}^{2-}$  anions and terminal chromyl oxygen anions [24].

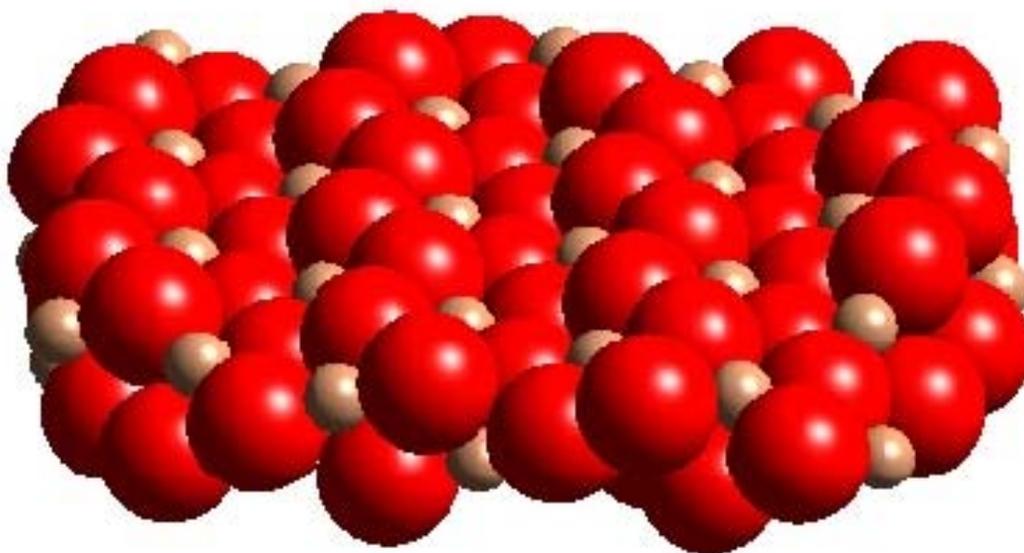


Figure 2. Ball model representation of the ideal  $\text{Cr}_2\text{O}_3$   $(10\bar{1}2)$  surface. The large red balls represent  $\text{O}^{2-}$  anions and the small tan balls represent  $\text{Cr}^{3+}$  cations.

### III. Experimental

Experiments were carried out in two separate stainless steel, ultrahigh vacuum systems. The sample was mechanically clamped to a tantalum mounting piece. The mounting was connected to liquid nitrogen cooled copper electrical feedthroughs on a sample manipulator. The sample temperature was monitored using a type-K thermocouple bonded to the back of the sample with Aremco 569 ceramic cement.

Characterization of the  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) sample has been reported previously [24]. Sample preparation for the nearly-stoichiometric surface consisted of two steps: (1) bombardment with 2 keV  $\text{Ar}^+$  ions for 30 minutes, and (2) annealing at 900 K for 5 minutes. Preparation of the oxygen-terminated surface included an additional step of exposure of the sample to oxygen at a partial pressure of  $10^{-8}$  Torr using a nozzle doser [25] while cycling the sample temperature from 193 K to 353 K three times. Following preparation, low energy electron diffraction (LEED) was performed at 850 K to check the surface periodicity. Elevated temperatures were used to prevent surface charging [24]. Vacuum Generators' three-grid, reverse view, LEED optics were used in both chambers. X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES) was used for characterization of the surface composition prior to, and after thermal desorption experiments.

X-ray photoelectron spectroscopy experiments were carried out in a turbo-pumped, dual-chamber vacuum system. X-rays were produced with a Mg anode and the resulting photoelectrons were analyzed with a Leybold EA-11 hemispherical analyzer. XPS experiments were run at a 60 eV pass energy, which gives an energy resolution of 1.06 eV for the Ag  $3d_{5/2}$  line. Uniform steady-state charging occurs due to the insulating

nature of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> [24]. The Cr 2p<sub>3/2</sub> binding energy was previously determined to be 576.9 ± 0.2 eV for an ion-bombarded and 900 K-annealed (ordered) surface [24]. Experimental binding energy scales were adjusted to align the Cr 2p<sub>3/2</sub> feature to 576.9 eV to compensate for steady state charging. XPS atomic ratios have been corrected with Leybold atomic sensitivity factors.

Thermal desorption spectroscopy (TDS) and Auger electron spectroscopy were performed in an ion-pumped, single-chamber vacuum system equipped with a Perkin-Elmer model 15-155 single-pass, cylindrical mirror analyzer for AES and an Inficon Quadrex 200 mass spectrometers for TDS. Gas exposures were performed by back-filling the chamber through a variable leak valve. Fisher Scientific 99.9% CH<sub>3</sub>OH and Sigma Aldrich 95% CH<sub>3</sub><sup>18</sup>OH were used for this study. Methanol was degassed by three freeze-pump-thaw cycles before use. For thermal desorption experiments, the sample was exposed to methanol at 93 K and heated to 773 K using a linear temperature ramp of 2.5 K/s. The mass spectrometer was equipped with a glass skimmer to minimize the sampling of desorption products from the sample mounting hardware. All reported methanol doses have been corrected for ion gauge sensitivity [26].

Mass spectrometer fragmentation patterns were collected for each suspected desorption product (e.g., CH<sub>3</sub>OH, CH<sub>2</sub>O, CO, CO<sub>2</sub>, and CH<sub>4</sub>). Fragmentation patterns were collected over a pressure range of 10<sup>-10</sup> to 10<sup>-7</sup> Torr for each molecule. Ion gauge sensitivity factors were used to correct the ion gauge reading to the actual pressure. For the products studied, CH<sub>2</sub>O was the only molecule for which an ion gauge sensitivity factor had to be calculated [27]; all others were obtained from the Quadrex 200 manual [26]. Mass spectrometer sensitivity factors were determined for each molecule by

plotting mass spectrometer signal intensity for a particular  $m/z$  ratio versus corrected pressure. The slope of a best fit line was taken as the mass spectrometer sensitivity factor. Product desorption traces were corrected for mass spectrometer sensitivity by dividing the signal intensity by the sensitivity factor [28].

The fragmentation patterns were applied in the analysis of thermal desorption data to determine relative contributions of each product. When multiple molecules contained the same  $m/z$  number in their respective fragmentation patterns, the corresponding spectra for that  $m/z$  was corrected by subtraction of contributions from each molecule. The spectra for  $m/z$  32 were used for  $\text{CH}_3\text{OH}$  with only a correction for mass spectrometer sensitivity since only the methanol fragmentation pattern contains that mass number. The spectra for  $m/z$  29 were used for  $\text{CH}_2\text{O}$  after subtraction of the methanol contribution using the  $m/z$  32 signal scaled according to the methanol cracking pattern. The spectra for  $m/z$  44 were used directly for  $\text{CO}_2$  desorption spectra since only this molecule gave a 44 fragment. Spectra for  $m/z$  28 were corrected for contributions from  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$ , and  $\text{CO}_2$  to yield  $\text{CO}$  spectra. Spectra for  $m/z$  16 were used to track  $\text{CH}_4$  after subtraction of contributions from  $\text{CH}_3\text{OH}$ . Finally, spectra for  $m/z$  2 required corrections from  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$ , and  $\text{CH}_4$  to give the  $\text{H}_2$  spectra.

## IV. Results

### *TDS of methanol reacted on nearly-stoichiometric Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2)*

The reaction of methanol with the nearly-stoichiometric Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) surface was studied using thermal desorption spectroscopy. All feasible C<sub>1</sub> and C<sub>2</sub> hydrocarbons and oxygenates were checked for as reaction products. Formaldehyde (CH<sub>2</sub>O), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and hydrogen (H<sub>2</sub>) were the only observable products. Coupling products such as dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), and acetylene (C<sub>2</sub>H<sub>2</sub>) were checked for but not detected. Water (H<sub>2</sub>O), formic acid (HCOOH), and ethanol (C<sub>2</sub>H<sub>5</sub>OH) were also not observed during thermal desorption.

Figure 3 depicts desorption traces of methanol for a series of methanol exposures. At lower coverages (exposures < 0.1 L), methanol desorbs from the surface in a broad peak over the temperature range of 450 – 700 K. The intensity of this peak increases at 470 K and broadens to lower temperature for exposures greater than 0.3 L. The 470 K peak temperature for CH<sub>3</sub>OH desorption is independent of coverage, indicating a first order kinetic process. Assuming a pre-exponential of 10<sup>13</sup> s<sup>-1</sup> and applying the Redhead analysis [29] for first order kinetics gives an apparent activation energy of 29.5 kcal/mol for a 470 K desorption temperature. Beyond the 470 K main peak, methanol desorption extends out to 700 K. Noticeable within the high temperature tail for exposures greater than 0.5 L is a shoulder at ~ 650 K. A lower temperature peak also appears between 210 – 290 K for exposures greater than 0.5 L. The temperature for this peak is coverage-dependent and is related to molecularly adsorbed methanol based on XPS results (below). Monolayer coverage is defined from observation during TDS of a low temperature peak

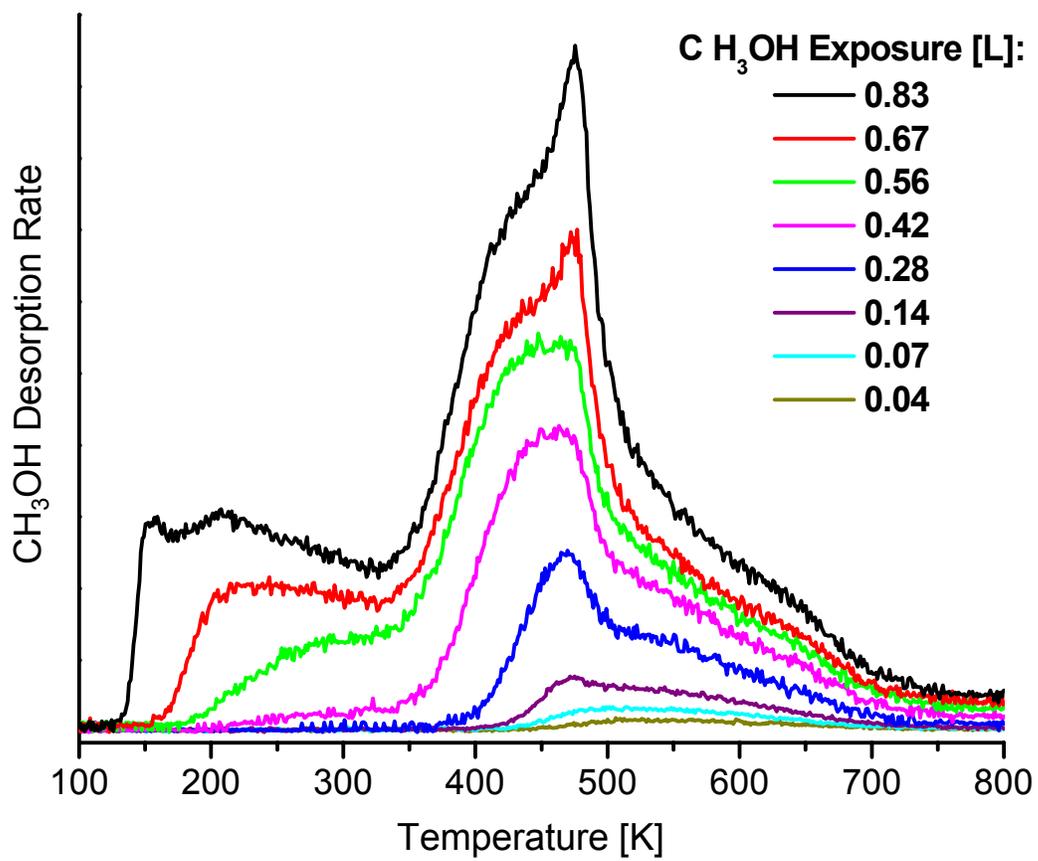


Figure 3. TDS spectra obtained after exposing the nearly-stoichiometric surface to methanol.

that does not saturate with increasing exposure (i.e. multilayer). This peak is first apparent during TDS for a methanol exposure of 0.83 L and appears at 155 K.

Products from the reaction of methanol with the nearly-stoichiometric surface are shown in figure 4 for a 0.83 L (monolayer) dose. The top panel displays the relationship between reaction products and methanol over the entire temperature range of the experiment, while the bottom panel shows the high temperature products on an expanded scale. In the bottom panel of figure 4, the CH<sub>2</sub>O desorption signal is the broadest, and spans essentially the entire temperature range of the other products. The onset of CH<sub>4</sub> desorption is observed at a peak temperature of 680 K; following this peak, CH<sub>2</sub>O, CO, and H<sub>2</sub> desorption occur at a peak temperature of 695 K. Finally, the maximum CO<sub>2</sub> desorption rate is observed at 700 K. The desorption temperatures for CH<sub>2</sub>O, CH<sub>4</sub>, CO, and CO<sub>2</sub> are independent of surface coverage, indicating first order rate-limiting surface reaction steps. Assuming a pre-exponential of 10<sup>13</sup> s<sup>-1</sup> for desorption, application of the Redhead equation [29] for first order kinetics gives an apparent activation energy range of 41.1 - 44.4 kcal/mol for the reaction products.

From the TDS spectra shown in figure 4, monolayer coverage yields a 58% conversion of adsorbed methanol to products. Of the carbon-containing products, selectivity to CO is the highest (41%), followed by CH<sub>2</sub>O (28%), CH<sub>4</sub> (24%), and CO<sub>2</sub> (7%). Experimental variation in selectivity varied ~ 0.5% for monolayer coverage of methanol. It was noted that after the surface was exposed to a total of 3 L of methanol by a series of methanol TDS runs, a sharp feature appears at 475 K within the main methanol desorption peak. The issue of changes in surface condition is addressed in the discussion section of this study.

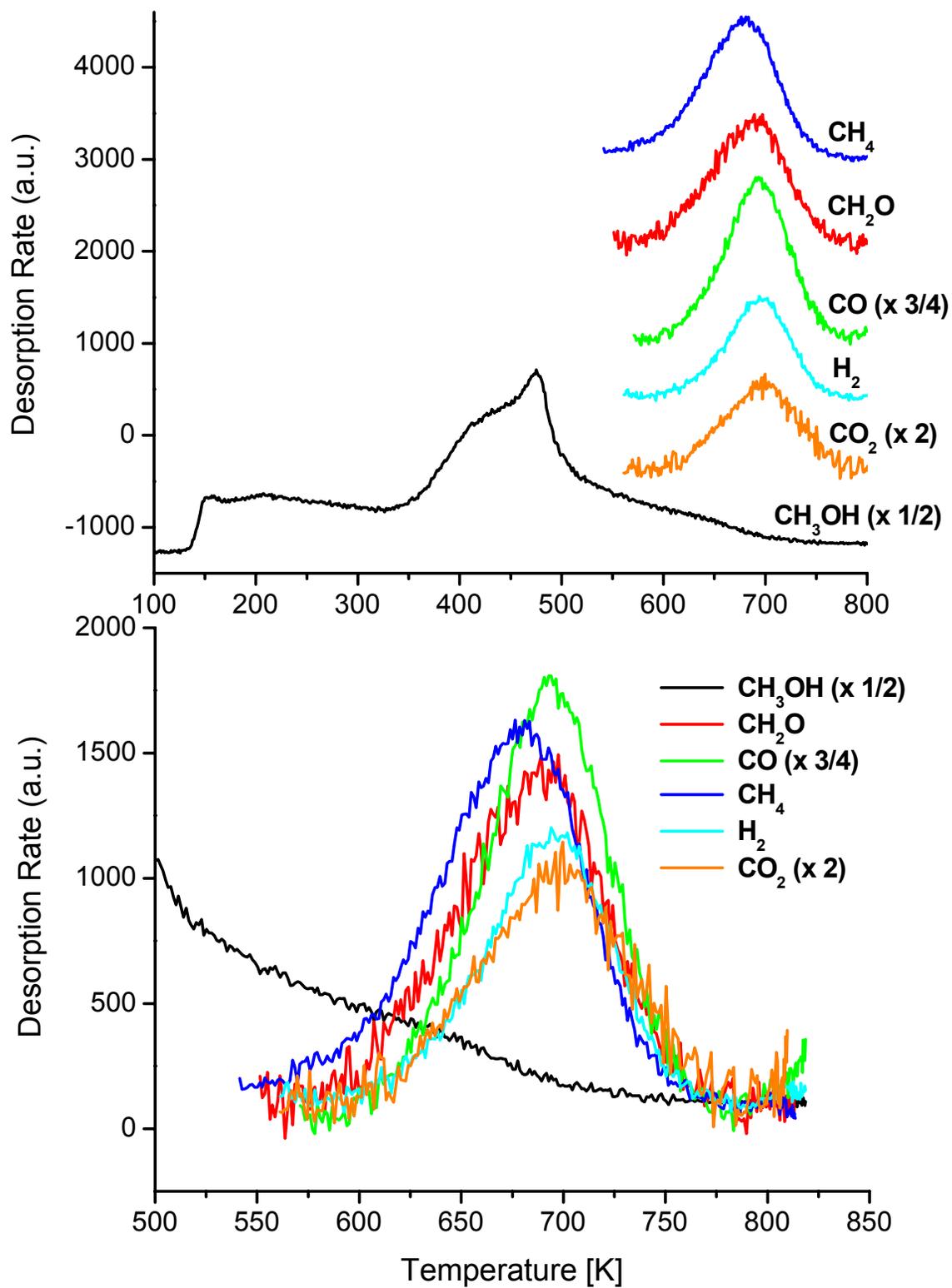


Figure 4. TDS spectra of products observed after exposing the nearly-stoichiometric surface to 0.83 L of methanol.

Figure 5 shows the carbon-containing oxidation products for the reaction of  $\text{CH}_3^{18}\text{OH}$  with the clean, nearly-stoichiometric  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface. Desorption traces for  $\text{CO}$ ,  $\text{C}^{18}\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{CH}_2^{18}\text{O}$ ,  $\text{CO}^{18}\text{O}$ ,  $\text{C}^{18}\text{O}_2$ , and  $\text{CO}_2$  are shown. Formaldehyde ( $\text{CH}_2\text{O}$  and  $\text{CH}_2^{18}\text{O}$ ) and carbon monoxide ( $\text{CO}$  and  $\text{C}^{18}\text{O}$ ) desorb at a peak temperature of  $\sim 690$  K. All three carbon dioxide products ( $\text{CO}_2$ ,  $\text{CO}^{18}\text{O}$ , and  $\text{C}^{18}\text{O}_2$ ) desorb at 700 K. Equal amounts of  $\text{CH}_2\text{O}$  and  $\text{CH}_2^{18}\text{O}$ , as well as equal amounts of  $\text{CO}$  and  $\text{C}^{18}\text{O}$ , are produced. The appearance of  $\text{CO}$ ,  $\text{CH}_2\text{O}$ , and  $\text{CO}^{18}\text{O}$  indicate removal of lattice oxygen since the sample surface remains the only source of  $^{16}\text{O}$  when dosing  $\text{CH}_3^{18}\text{OH}$ . Due to the background of  $m/z$  44 signal in the vacuum system, a low signal-to-noise ratio made it difficult to quantify the relative amount of unlabeled  $\text{CO}_2$  produced.

#### ***TDS of formaldehyde reacted on nearly-stoichiometric $\text{Cr}_2\text{O}_3$ ( $10\bar{1}2$ )***

Some products of interest for the reaction of formaldehyde with the nearly-stoichiometric surface are shown in figure 6. Overall, the reaction of formaldehyde with nearly-stoichiometric  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface yields a multitude of products:  $\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCOOH}$ ,  $\text{C}_2\text{H}_2$ , and  $\text{H}_2$  [30]. This study will focus on the oxygenated products because they aid in determining reaction routes for the oxidation of methanol. Formaldehyde desorbs from the surface in two peaks at 470 and 690 K. The 470 K feature is associated with an adsorbed species not seen from methanol adsorption and will not be discussed here. The high temperature  $\text{CH}_2\text{O}$  desorption (690 K) coincides with the desorption temperature of  $\text{CH}_2\text{O}$  from methanol adsorption. Somewhat surprisingly,  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  were observed desorbing at 655 K, which corresponds to the high temperature shoulder observed in the methanol spectra for methanol adsorption. The desorption of  $\text{CO}$  and  $\text{CO}_2$  occurs at a slightly higher temperature than for methanol

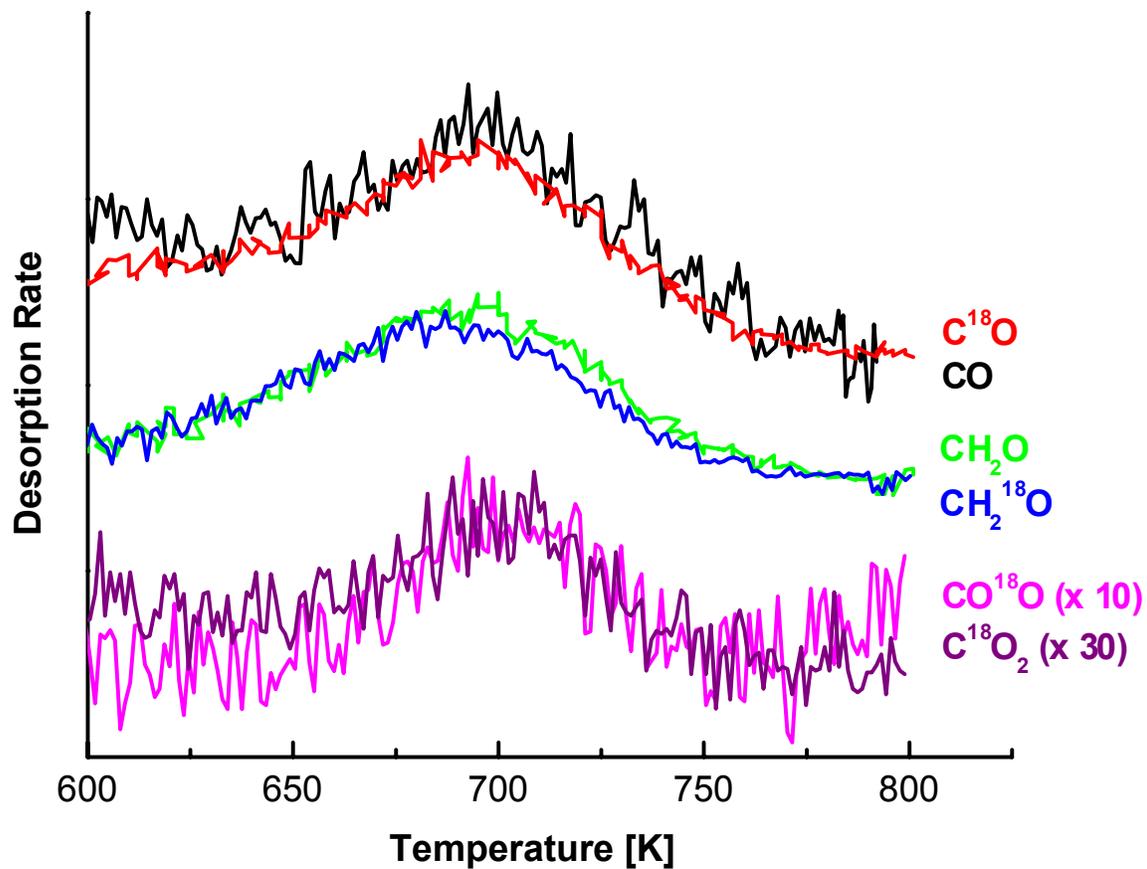


Figure 5. TDS spectra of oxygenated products observed after exposing the nearly-stoichiometric surface to 0.4 L of <sup>18</sup>O-isotopically labeled methanol; equal distribution of isotopically labeled and unlabeled products.

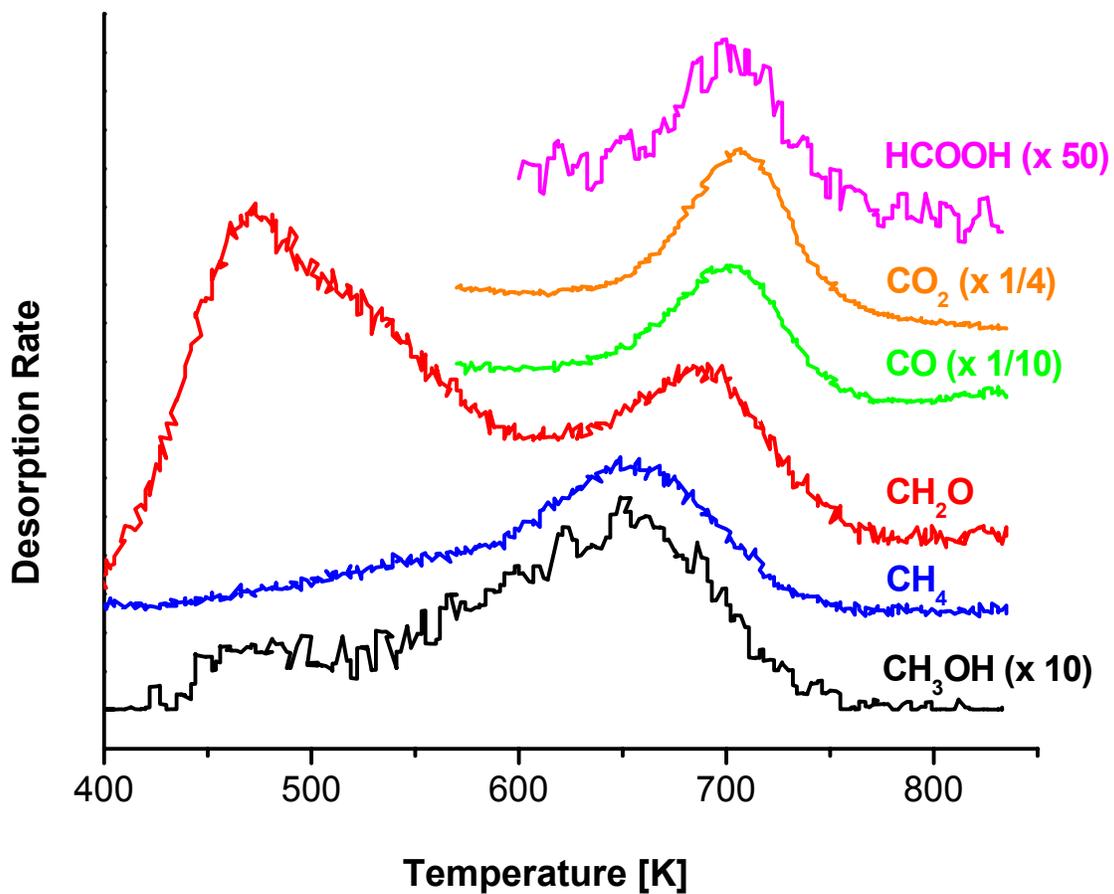


Figure 6. TDS spectra of products observed after exposing the nearly-stoichiometric surface to 0.5 L of formaldehyde.

oxidation (700 and 707 K, respectively) but the temperature difference between CO and CO<sub>2</sub> is the same (7 K). Formic acid (HCOOH) desorbs simultaneously with CO<sub>2</sub> at 707 K, this product was not observed during thermal desorption of methanol.

***TDS of CH<sub>3</sub>OH reacted on oxygen-terminated Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}2$ )***

Figure 7 shows methanol thermal desorption for a series of methanol exposures on the oxygen-terminated Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}2$ ) surface. Methanol is the only observed thermal desorption product. Other products checked for but not detected include: CH<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, HCOOH, and CH<sub>3</sub>OCH<sub>3</sub>. Methanol desorbs from this surface in a sharp peak centered at 480 K. This desorption peak is independent of coverage, indicating a first order desorption process with an apparent first-order activation energy of 30.1 kcal/mol [29]. For the 0.56 L exposure, two other features are observed; a shoulder at 420 K and a peak at 215 K. It has been suggested in prior studies of methanol oxidation on metal oxide single crystal surfaces that methanol desorption below 350 K is from molecularly adsorbed methanol [3, 5, 6], hence, the 215 K desorption peak is attributed to this same species. Multilayer desorption was observed after a 0.70 L exposure of methanol (not shown in figure), and desorbed at 145 K. Since no products were detected for the oxygen-terminated surface and surface cations should be capped with terminal oxygen (no cation-anion site-pairs available), it is likely that only molecular adsorption occurs on this surface. The high temperature desorption of methanol at 480 K and the shoulder at 420 K make this assumption more complicated, therefore further investigation may be needed to fully understand the interaction of methanol with this surface.

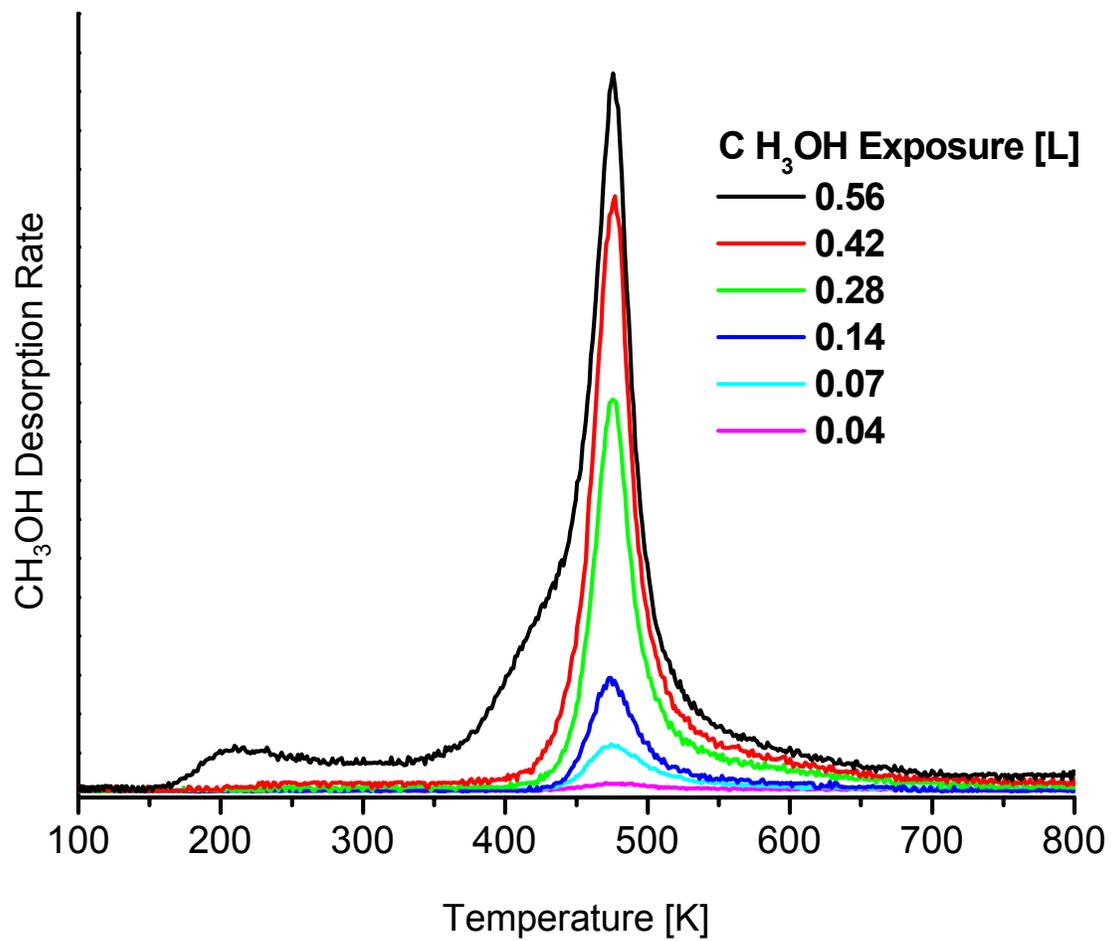


Figure 7. TDS spectra obtained after exposing the oxygen-terminated surface to methanol.

### ***XPS of methanol on nearly-stoichiometric $\text{Cr}_2\text{O}_3$ ( $10\bar{1}2$ )***

Figure 8 depicts C 1s spectra following a 60 L, multilayer coverage, of methanol adsorbed on the nearly-stoichiometric  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface at 120 K. The sample was heated to sequentially higher temperatures, then cooled back to 120 K for XPS. After dosing at 120 K, a symmetrical C 1s peak is observed with a binding energy of 287.5 eV. Based on the observation of multilayer coverage for methanol exposures greater than 1.0 L during TDS, the binding energy of this peak is assigned to molecularly adsorbed methanol. A second peak also appears at 285 eV for the dosed sample, but by applying a bias to the sample it was determined to be signal from the conductive sample mounting. Surface charging for the collection of all other traces separated the signal from the sample mounting and the signal corresponding to the sample by a shift of 6 eV to lower binding energy, moving the signal from the sample mounting outside the range of interest.

Heating to 205 K removes molecularly adsorbed species in the multilayer and leaves a monolayer coverage of methanol. Two overlapping peaks are present in this spectrum. The first is shown as a shoulder at 287.8 eV and represents molecularly adsorbed methanol. The second is shown as a peak centered at 286.5 eV; a 1.0 eV shift from the binding energy of the molecularly adsorbed species. This shift correlates to a change from molecular methanol to methoxides, as was noted by Gercher *et al.* for methanol adsorption on  $\text{SnO}_2$  (110) [5]. Heating to 430 K removes the peak at 287.5 eV and leaves a broad peak centered at 285.7 eV that is  $\sim 1/2$  the intensity of the prior spectrum. The broadness of this spectrum is likely due to the presence of two surface species, methoxides and carbon adatoms (BE range of 284 – 285 eV [31]).

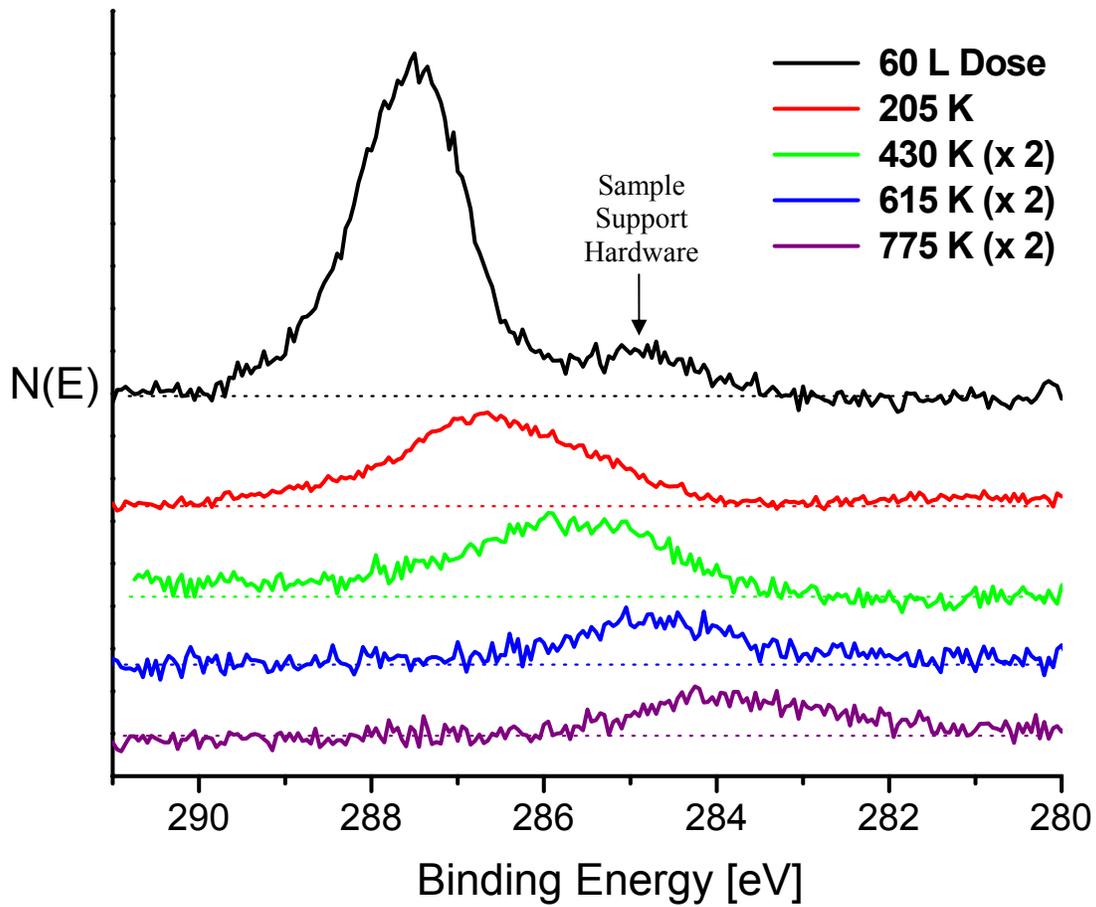


Figure 8. C1s XPS spectra obtained after exposing the nearly-stoichiometric surface to 60 L of methanol.

After heating to 615 K, the peak at 286.5 eV (associated with methoxides) is completely removed, leaving a peak centered at 284.5 eV. The final spectrum for 775 K shows a peak that is slightly shifted to lower binding energy from the prior spectrum. The broadening of this peak to lower binding energy is possibly due to conversion of carbon adatoms to carbides (BE range of 281.5 – 283 eV [31]). Although CO<sub>2</sub> is seen as a desorption product, no positive shift in the C1s XPS spectra, indicative of a COO species on the surface, was observed.

## V. Discussion

### *Low Temperature Range (< 500 K)*

The methanol pretreated, nearly-stoichiometric  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface yields a 58% conversion for a monolayer coverage of methanol. From XPS and TDS results it appears that methanol adsorbs molecularly and dissociatively. XPS results show a symmetric C 1s peak at a binding energy of 287.5 eV after exposing the surface to 60 L of methanol. This peak is associated with molecularly adsorbed methanol, as determined by the observation of multilayer desorption for exposures greater than 1 L during TDS. Heating of the surface to 205 K removes the multilayer and leaves a mixed monolayer coverage of methoxides and molecular methanol. The XPS spectrum for this temperature shows a shoulder for molecularly adsorbed methanol at a binding energy of 287.8 eV, and a peak for dissociatively adsorbed methanol (methoxides) at a binding energy of 286.5 eV.



Heating of the surface to 430 K decreases the peak at 286.5 eV associated with methoxides, and further heating to 615 K completely removes this peak. The removal of methoxides in this temperature range is due to recombination of methoxides with adsorbed hydrogen (as shown in figure 3).



### *High Temperature Range (500 – 750 K)*

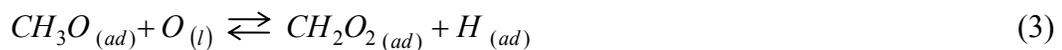
Formation of  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  from methanol was observed within the temperature range of 550 to 750 K for thermal desorption. These products have all been

previously detected during thermal desorption of methanol on metal oxide single crystal surfaces [3-9]. Studies of isotopically labeled  $\text{CH}_3^{18}\text{OH}$  over the nearly-stoichiometric surface yield some insightful results. Equal amounts of  $\text{CO}$  and  $\text{C}^{18}\text{O}$ , as well as  $\text{CH}_2\text{O}$  and  $\text{CH}_2^{18}\text{O}$ , were detected during thermal desorption. This observation signifies that these products were not derived from methoxide decomposition, but from some type of symmetric, bidentate surface intermediate. For a symmetric, bidentate intermediate, there should be an equal probability of cleaving the  $\text{C-O}$  or the  $\text{C-}^{18}\text{O}$  bond, and hence, an equal distribution of isotopically labeled and unlabeled products. The formation of unlabeled products indicates the removal of lattice oxygen since the adsorbed molecule,  $\text{CH}_3^{18}\text{OH}$ , only contains isotopically labeled oxygen.

The production of equal amounts of isotopically labeled and unlabeled formaldehyde and carbon dioxide from  $\text{CH}_3^{18}\text{OH}$  implicates a symmetric surface intermediate such as dioxymethylene ( $\text{CH}_2\text{O}_2$ ) or formate ( $\text{CHOO}^-$ ). For the reaction of methanol on  $\text{ZrO}_2$  (110), Dilara and Vohs determined that adsorbed methoxides underwent nucleophilic attack to form dioxymethylene, which deoxygenated at high temperature and desorbed as  $\text{CH}_2\text{O}$  [7]. On  $\text{ZnO}$  (0001), Vohs and Barteau concluded that formate was formed on the surface from methoxides, and dehydrogenated to  $\text{CO}$  and  $\text{CO}_2$  [6]. The production of  $\text{CH}_2\text{O}$  from this particular surface was attributed to methoxide decomposition, and it was suggested that both formate and methoxide were present on the surface at the same time. Both the  $\text{ZrO}_2$  (110) and the  $\text{ZnO}$  (0001) studies illustrate that bidentate surface intermediates are possible via nucleophilic attack of a lattice oxygen on a methoxide.

Thermal desorption data for the reactions of methanol and formaldehyde with the nearly-stoichiometric surface all show CH<sub>3</sub>OH, CH<sub>2</sub>O, CO, CO<sub>2</sub>, and CH<sub>4</sub> desorbing in the same high temperature range; signifying that the reaction of these two molecules go through the same reaction intermediates. Since formaldehyde desorption occurs at two separate temperatures (470 and 690 K) for the adsorption of formaldehyde, it is feasible to assume that a portion of the reactant is adsorbing molecularly (representing the low temperature desorption product), while the remaining reactant is adsorbing as a bidentate dioxymethylene intermediate (representing the high temperature desorption product). A possible surface structure for dioxymethylene on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) is shown in figure 9. The formation of such a surface intermediate is similar to the report of Abee et al. that CO<sub>2</sub> adsorbs on the nearly-stoichiometric Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) surface as a bidentate carbonate [32]. Both adsorbed species require a cation-anion site-pair with molecular oxygen bound to a surface cation site, with nucleophilic attack of surface lattice oxygen on an electron deficient carbon center.

For methanol adsorption, the desorption products CH<sub>3</sub>OH and CH<sub>4</sub> are typically associated with reaction of surface methoxides [3-8]. If formaldehyde adsorbs as dioxymethylene, the appearance of CH<sub>3</sub>OH and CH<sub>4</sub> as desorption products implies that dioxymethylene must react with hydrogen on the surface to form methoxides. This suggests that, if the adsorption of methanol as methoxides can form dioxymethylene and the adsorption of formaldehyde as dioxymethylene can form methoxides, then the reaction between methoxide and dioxymethylene must be reversible (3).



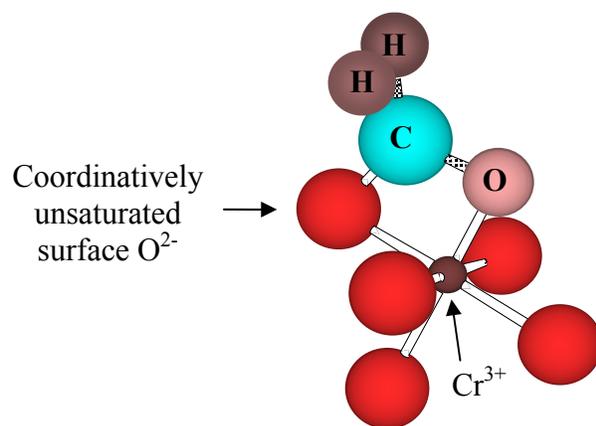


Figure 9. Cartoon illustrating the possible bidentate structure of dioxymethylene on  $Cr_2O_3$  (10 $\bar{1}2$ ). The five oxygen atoms (red) surrounding chromium (brown) represent an incomplete octahedron on the (10 $\bar{1}2$ ) surface.

In comparing methanol and formaldehyde adsorption data, it seems that the high temperature desorption of CH<sub>2</sub>O is a result of dioxymethylene decomposition via cleavage of a C-O bond (4).



For the methanol reactant, hydrogen liberated in the formation of dioxymethylene may react with remaining methoxides to yield CH<sub>3</sub>OH or CH<sub>4</sub> (5). Indication that methoxides, as opposed to methyl fragments, react to form CH<sub>4</sub> is given by a recent study of CH<sub>3</sub>I on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2), which demonstrated that for adsorbed methyl fragments, ethylene (CH<sub>2</sub>=CH<sub>2</sub>) was observed as a product during TDS [30]. In this study of methanol on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2) ethylene was not observed as a desorption product, and hence, methyl fragments are not suggested as a possible surface intermediate.



Thermal desorption of formic acid [30] from this surface yields CO and CO<sub>2</sub> at around 700 K, which coincides with the desorption temperature of these products from methanol and formaldehyde adsorption. It was also observed that only a small fraction of CH<sub>2</sub>O was formed from the adsorption of formic acid. Formic acid is known to dissociatively adsorb as formate (HCOO<sup>-</sup>) on metal oxide single crystals [6], therefore the appearance of CO and CO<sub>2</sub> within the same temperature as was seen for methanol adsorption supports the involvement of surface formate in the reaction of methanol on Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2). The formation of CH<sub>2</sub>O from formic acid is then due to hydrogenation of formate to dioxymethylene during the course of dehydrogenation of other formates to CO or CO<sub>2</sub>, followed by dioxymethylene decomposition. This also implies that the reaction from dioxymethylene to formate is reversible (6).



Even though HCOOH was not detected during thermal desorption of methanol, it was observed at the same temperature for the reactions of formaldehyde and formic acid. Furthermore, evolution of CO and CO<sub>2</sub> was observed at nearly the same temperature (~700 K) for the reactions of methanol, formaldehyde, and formic acid. As already stated, formic acid is known to adsorb dissociatively as formate; therefore it is conclusive to assume that CO and CO<sub>2</sub> are formed by decomposition of surface formates. The evolution of these products is also accompanied by desorption of hydrogen. Figure 10 depicts the reaction route for the oxidation of methanol on the nearly-stoichiometric surface of Cr<sub>2</sub>O<sub>3</sub> (10 $\bar{1}$ 2).



Although thermal desorption data provide a strong case for the formation of dioxymethylene and formate, XPS results did not concur for the adsorption of methanol. TDS results for CH<sub>3</sub><sup>18</sup>OH show that some symmetric COO surface intermediate must be present, but no shift to higher binding energy, indicative of a COO surface species, was observed. Vohs and Barteau reported a +2.5 eV shift in binding energy upon formation of formate from methoxide on ZnO (0001) [6]. At this point it is not clearly understood why the XPS results do not agree with the TDS data. It is possible that differences in the nature of the two experiments lead to this inconsistency. A complete set of XPS experiments took nearly 24 hours, while a typical thermal desorption run took less than

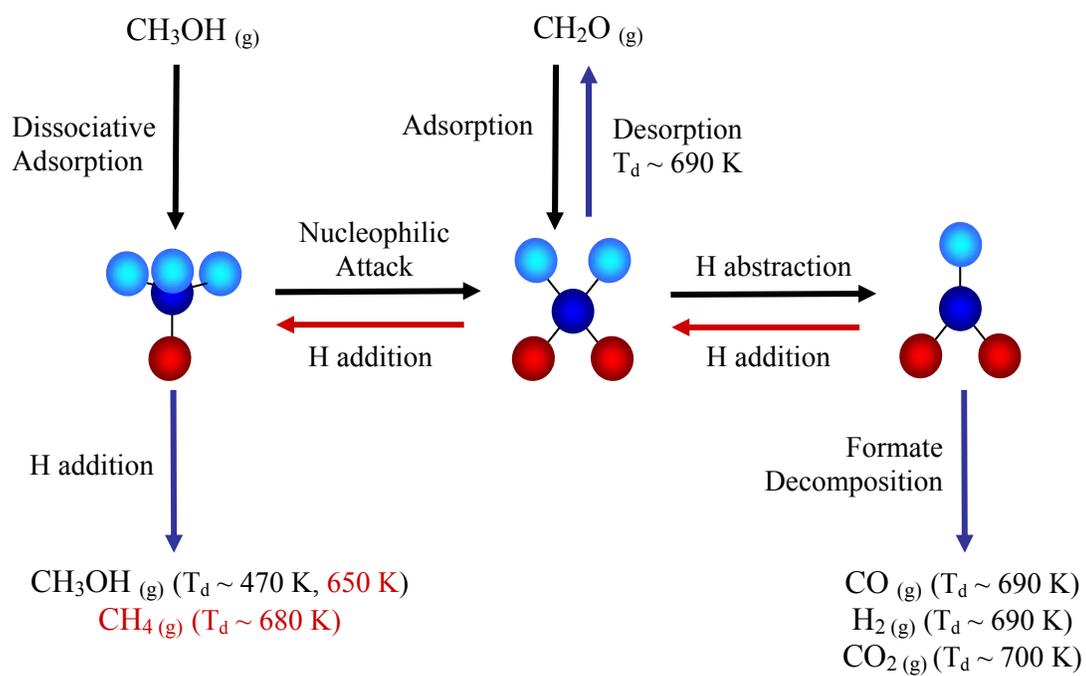


Figure 10. Reaction scheme for the oxidation of methanol on  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ).

15 minutes to perform. Extended exposure of the methanol saturated surface to x-rays might alter the surface chemistry.

Reduction of methoxide to form  $\text{CH}_4$  should leave oxygen bound to the surface, but no clear signs were apparent from either TDS or XPS to support this. On  $\text{ZrO}_2(100)$ , water desorption was observed and was attributed to removal of oxygen left on the surface after  $\text{CH}_4$  desorption. Water was not detected as a reaction product during thermal desorption experiments of methanol on  $\text{Cr}_2\text{O}_3(10\bar{1}2)$ . The relative amount of  $\text{CH}_4$  to  $\text{CO}_2$  was 3:1, indicating that removal of oxygen from the surface via  $\text{CO}_2$  desorption does not compensate for all oxygen left on the surface from the production of  $\text{CH}_4$ . The final possible indicator of an increase in surface oxygen concentration would be observation of surface or chemistry changes with increasing surface exposure to methanol. XPS and AES oxygen to chromium ratios show only slight variation over thermal desorption experimentation and give no definitive results. A series of 0.28 L methanol exposures over the course of three days also showed no change in product selectivity. The only indication of a surface change was the appearance of a sharp peak at 475 K after larger methanol exposures ( $> 3$  L). Reproduction of this surface condition was difficult and it is not yet clear how much methanol the surface must be exposed to before a significant surface change is observed.

From this study, XPS and TDS results indicate that methanol adsorbs molecularly and dissociatively on the nearly-stoichiometric surface of  $\text{Cr}_2\text{O}_3(10\bar{1}2)$ . Classification of adsorption of methanol on the oxygen-terminated  $\text{Cr}_2\text{O}_3(10\bar{1}2)$  surface is somewhat difficult. The desorption temperature for methanol on this surface is 480 K, compared to 470 K for methanol desorption from the nearly-stoichiometric surface. It is not well

understood at this point why methanol desorbs from the oxygen-terminated surface at a higher temperature than on the nearly-stoichiometric surface. XPS was attempted on the oxygen-terminated surface, but only a partially oxygenated surface was achieved in the XPS chamber so the results were inconclusive. Methanol dissociation is thought to require availability of cation-anion site pairs, and in the case of the two surfaces study in this investigation, only the nearly-stoichiometric surface meets this requirement. No reaction products were observed for the oxygen-terminated surface; therefore, the assumption is that only molecular adsorption occurs.

## VI. Conclusions

The reaction of methanol with nearly-stoichiometric and oxygen-terminated surfaces of  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) was studied using thermal desorption spectroscopy and x-ray photoelectron spectroscopy. Dissociative adsorption of methanol occurs on the nearly-stoichiometric surface and is attributed to the availability of cation-anion site pairs. An array of products including  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2$  are produced above 550 K on the nearly-stoichiometric surface. Monolayer coverage of methanol yields a 58% conversion to products. Of these products, selectivity to  $\text{CO}$  is the highest (41%), followed by  $\text{CH}_2\text{O}$  (28%),  $\text{CH}_4$  (24%), and  $\text{CO}_2$  (7%). At higher temperatures, methoxides reversibly undergo dehydrogenation and nucleophilic attack from lattice oxygen to create dioxymethylene. Hydrogenation of methoxides leads to the formation of  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  above 550 K. Formate is formed on the surface by reversible dehydrogenation of dioxymethylene. Formaldehyde is produced via C-O bond cleavage of dioxymethylene, and the decomposition of formate yields  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2$  at slightly higher temperatures. The oxygen-terminated surface is unreactive for methanol dissociation due to cation site blocking by terminal chromyl oxygen.

## VII. Recommendations for Future Work

The reaction of methanol with the nearly-stoichiometric and oxygen-terminated surfaces of  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) has been studied. Recommendations for future studies relating to this study include: (1) characterization of surface intermediates on the nearly-stoichiometric surface; (2) characterization of the adsorbate formed on the oxygen-terminated surface; and (3) studies of the reaction of methanol with a reduced surface. The details of these recommendations follow.

In the case of the nearly-stoichiometric surface, TDS results support the formation of dioxymethylene and formate as reaction intermediates. XPS was attempted in order to verify these two intermediates but the results were inconclusive. A further attempt at characterizing reaction intermediates would help in providing supporting evidence for the intermediates responsible for the formation of products. In the past, HREELS [7] and XPS [3-6, 11] have shown to be useful tools in determining surface intermediates in the reaction of methanol on single crystal metal oxides. An HREELS study on this surface would be complicated due to the insulating nature of  $\alpha\text{-Cr}_2\text{O}_3$ ; XPS is a more appropriate technique for this surface because spectra can easily be corrected for surface charging. The experimental technique used for XPS in this study was to adsorb a multilayer coverage of methanol (60 L) at low temperature (120 K) and then flash the surface to successively higher temperatures while running an XPS analysis in between each heating stage. Adsorbed methanol was on the cold surface approximately 12 hours before the temperature range corresponding to products was reached ( $> 550$  K observed during TDS). Excessive exposure of the surface to x-rays may have altered the surface chemistry; therefore, a recommended technique is to adsorb methanol and heat directly to

the temperature range of observed products. Another approach is to study the adsorption of formaldehyde by XPS. The reaction of methanol and formaldehyde with the nearly-stoichiometric surface yield the same high temperature products during TDS, so analysis of reaction intermediates for either reactant would be useful in determining the reaction mechanism for both molecules. A higher conversion of adsorbate to dioxymethylene is expected for formaldehyde adsorption since the reaction path to this intermediate involves a single step, nucleophilic attack on molecularly adsorbed formaldehyde. Therefore, characterization of dioxymethylene from adsorbed formaldehyde might be easier to achieve due to an increase in the concentration of this species on the surface.

TDS of methanol from the oxygen-terminated surface yields high temperature desorption of methanol. Normally, desorption above 300 K relates to recombination of dissociatively adsorbed methanol. For an oxygen-terminated surface, capping of surface chromium via terminal chromyl (Cr=O) blocks anion-cation site pairs and prevent dissociative adsorption. The results of this study showed that methanol desorbed from the oxygen terminated surface at a higher temperature than was seen for the nearly-stoichiometric surface, 480 K versus 470 K, respectively. Unfortunately, we were unable to completely oxygenate the surface in the XPS chamber and, therefore, do not have a characterization of the adsorbate. A second attempt at characterizing the adsorbate formed upon methanol adsorption is recommended.

Another study that could pose some insightful results is the reaction of methanol with a reduced  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface. The reaction of methanol on  $\text{CeO}_2$  (111) [8],  $\text{SnO}_2$  (110) [5], and  $\text{TiO}_2$  (001) [3,12] was enhanced by controlled reduction of an ordered stoichiometric surface by  $\text{Ar}^+$ -sputtering. For these surfaces, methoxide

decomposition was reported as the intermediate responsible for the formation of products. An increase in  $\text{CH}_4$  selectivity also occurred due to reoxidation of the surface [3]. In the case of  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ), nucleophilic attack of methoxide is thought to lead to dioxymethylene and formate. Reduction of the surface will make the surface more oxophilic and likely decrease conversion of methoxide to dioxymethylene. The difficulty will lie in developing a technique for reducing this surface. Reactions of metal oxides with hydrogen can often remove lattice oxygen via water desorption. Water desorption has not been previously observed as a reaction product from adsorbed hydrogen on  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ), hence hydrogen reduction should be ineffective for this surface. The most common reduction technique for metal oxide single crystals is  $\text{Ar}^+$  bombardment. Henrich found that  $\text{Ar}^+$  bombardment of  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) actually increases the concentration of oxygen on the surface [33]. Unpublished results from our group show that ion bombardment of this surface removes both chromium and oxygen equivalently. At the very least, it is obvious that  $\text{Ar}^+$  bombardment destroys the long range order of the nearly-stoichiometric  $\text{Cr}_2\text{O}_3$  ( $10\bar{1}2$ ) surface, so reduction in this manner may be a good starting point. Further investigation will be needed in determining an appropriate reduction technique for this surface.

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## VITA

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Michael Walter Mensch is the son of Boris and Maureen Sheleg and John and Terry Mensch. Michael was born on January 18<sup>th</sup>, 1978 in Philadelphia, Pennsylvania, but spent most of his life in Merritt Island, Florida. In the fall of 1996, Michael began his studies for a Bachelors of Science degree in Chemical Engineering at Florida Institute of Technology. During his undergraduate studies, Michael completed research projects under the instruction of Professor Manolis Tomadakis and Professor Alan Brown. Michael was an active member of the Florida Tech American Institute of Chemical Engineers chapter and in 1999 he received a 1<sup>st</sup> place award in presentation of the *Autonomous Vehicle Design Competition* at the National AIChE convention. Before graduation, Michael was awarded the chapters "*Most Valuable Member*" for his continued efforts as chapter Vice President. Michael was also the President of the student chapter of the American Chemical Society and organized the 1999 LASER Day chemistry demonstration for visiting high school students.

Michael began work on a Masters of Science degree in Chemical Engineering at Virginia Polytechnic Institute and State University in the fall of 2000. Currently, he is an active member of the Virginia Tech College of Engineering Graduate Student Committee and Big Brothers/Big Sisters of America. After completion of a Master's degree, Michael plans to continue with his studies to complete a Doctor of Philosophy degree in Chemical Engineering at Virginia Tech.

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