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Catalysis Today 85 (2003) 279–289

www.elsevier.com/locate/cattod

Reaction of methanol on stoichiometric and O-terminated α-Cr_2O_3 $(1\,0\,\bar{1}\,2)$: interconversion of oxygenated C_1 surface intermediates

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Abstract

The reaction of methanol on the nearly stoichiometric α-Cr_2O_3 $(1\,0\,\bar{1}\,2)$ surface gives a spectrum of products including CH_4, CH_2O, CO, CO_2 and H_2. These products are all generated in a 200 K temperature range (600–800 K) in thermal desorption through a reaction pathway involving methoxide, dioxymethylene and formate surface intermediates. The interconversion between oxygenated C_1 surface intermediates involves the reversible reaction of methoxide to dioxymethylene via dehydrogenation and nucleophilic attack of surface lattice oxygen. Formate intermediates are subsequently formed by the dehydrogenation of dioxymethylene. Isotopic labeling studies indicate that the precursor to the formaldehyde reaction product is a dioxymethylene intermediate rather than methoxide. The oxygen-terminated surface is completely unreactive, indicating a structure (or composition) sensitive reaction of methanol on the $(1\,0\,\bar{1}\,2)$ surface. Terminal chromyl oxygen acts as a cation site blocker and eliminates the surface cation–anion site pairs necessary for the dissociation and reaction of methanol.

Keywords: Cr_2O_3; Methanol; Methoxide; Dioxymethylene; Formate

1. Introduction

Studies of the reaction chemistry of hydrocarbon oxygenates like alcohols, aldehydes and carboxylic acids can enhance our understanding of the surface chemistry of hydrocarbon oxidation processes. These molecules can provide routes to the formation and subsequent study of oxygenated surface intermediates without the associated requirement of oxygen insertion and C–O bond formation that is necessary for their formation directly from hydrocarbons. For the adsorption of methanol on oxide surfaces, one typically expects heterolytic dissociative adsorption via O–H bond breaking and loss of the acidic proton from this weak Brønsted acid. The site requirements for such a process are thought generally to involve a surface cation–anion site pair with the proton bound to an oxygen anion and the conjugate base anion, methoxide (CH_3O^-), bound to a neighboring cation site [1,2].

Cr_2O_3 is considered an acidic oxide [3,4], but is known to catalyze or promote a variety of reactions including alcohol dehydration and dehydrogenation, methanol synthesis, H_2–D_2 exchange, double bond migration in olefins, ethylene polymerization, oxidative dehydrogenation of alkanes, and hydrocarbon combustion [5–16]. IR investigations of methanol adsorption at room temperature on Cr_2O_3 powders demonstrate that methoxide is formed by dissociative adsorption of methanol [17–19], while adsorption at elevated temperatures (200–400 °C) leads to the formation of formate intermediates [20]. The differences in the IR studies suggest a reaction pathway involving the thermal conversion of methoxide to formate on Cr_2O_3 as proposed by Tamaru and coworkers [20].

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0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00394-8

The (1 0 $\bar{1}$ 2) surface has the lowest energy of any low-index surface of Cr_2O_3 [21], and is the predominant plane exposed on microcrystalline Cr_2O_3 powders [22]. Hence, of all the low-index faces of Cr_2O_3, the (1 0 $\bar{1}$ 2) is the single crystal surface most likely to mimic the behavior of Cr_2O_3 powders. This report is focused on understanding the surface intermediates, reaction pathways, and products for the reaction of methanol on α-Cr_2O_3 (1 0 $\bar{1}$ 2) single crystal surfaces. By comparison of the thermal desorption reaction data for methanol and other C_1 oxygenates, a case is made for the participation of dioxymethylene as a surface reaction intermediate connecting the chemistry of methoxide and formate intermediates in the reaction of methanol.

2. α-Cr_2O_3 (1 0 $\bar{1}$ 2)

The Cr_2O_3 (1 0 $\bar{1}$ 2) surface has been characterized in previous work [23]. A ball model representation of the ideal, stoichiometric surface is shown in Fig. 1. The surface has a rectangular (almost square) periodicity with a ratio of sides of $a/b = 0.94$. The surface is nonpolar, and one full stoichiometric repeating unit normal to the surface contains five atomic layers arranged as {O, Cr, O, Cr, O}. The topmost atomic layer of the ideal surface is composed entirely of oxygen anions. At the ideal (1 0 $\bar{1}$ 2) surface, all O^{2-} anions in the top atomic layer are three-coordinate with a pyramidal local coordination, and the Cr^{3+} cations in the second atomic layer are five-coordinate. Both ions have one degree of coordinate unsaturation relative to their bulk counterparts [24]. The coordinately unsaturated cations at the ideal surface are all subject to an equivalent local coordination environment. All ions below the top two atomic layers are fully coordinated. A nearly stoichiometric surface can be prepared by Ar^+ ion-bombardment and annealing in vacuum at 900 K [23].

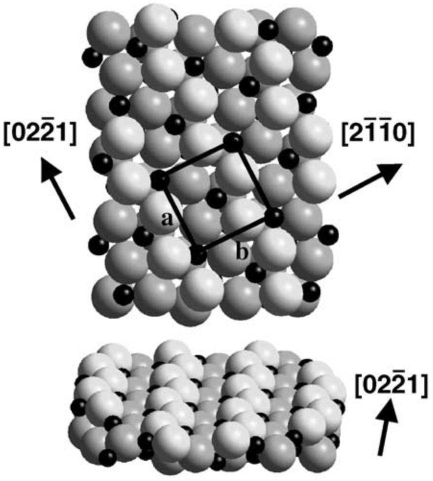

Fig. 1. Ball model representation of the α-Cr_2O_3 (1 0 $\bar{1}$ 2) surface. The top view shows the (1 0 $\bar{1}$ 2) surface parallel to the plane of the page. A surface unit cell is drawn to show the periodicity. The bottom illustration shows a side view of one stoichiometric repeating layer. The smaller black spheres represent the chromium cations, and the oxygen anions are represented by the larger gray spheres.

In addition to the nearly stoichiometric surface, the surface can be prepared with the cations capped with terminal chromyl oxygen (Cr=O). This oxygen-terminated surface is prepared by O_2 exposures on a nearly stoichiometric surface until nearly all surface cations are capped with terminal oxygen [23]. The oxygen-terminated surface exposes both three-coordinate O^{2-} anions and terminal chromyl oxygen (Cr=O) [23].

3. Experimental

The reaction of methanol over stoichiometric and oxygen-terminated (1 × 1) Cr_2O_3 (1 0 $\bar{1}$ 2) surfaces was investigated using thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). Experiments were conducted in an ion-pumped UHV chamber, equipped with a Physical Electronics Model 15-155 single-pass CMA for AES, an Inficon Quadrex 200 mass spectrometer for TDS and a set of Vacuum Generators 3-grid reverse view LEED optics. The base operating pressure for this study was 1×10^{-10} Torr. A broad-beam ion gun was used for sample cleaning.

The crystal was oriented to within 1° of the (1 0 $\bar{1}$ 2) surface using Laue backreflection and polished to a final mirror finish with 0.25 μm diamond paste. The sample was mechanically clamped onto a tantalum stage that was fastened to LN_2-cooled copper electrical conductors. A Type K thermocouple was attached through a hole in the stage to the back of the single crystal using Aremco #569 ceramic cement. This arrangement allowed direct measurement of the sample temperature.

Fisher Scientific 99.9% CH_3OH, Sigma Aldrich 95% $CH_3{}^{18}OH$, Cambridge Isotope Laboratory, Inc. 99% $^{13}CD_3OD$ and Aldrich 95% paraformaldehyde were used for this study. Methanol was degassed by three freeze–pump–thaw cycles before use. Formaldehyde was obtained by thermal decomposition of paraformaldehyde following vacuum degassing of the powder. Gas exposures were performed by back-filling the chamber through a variable leak valve. For thermal desorption experiments, the sample was exposed to the dosed gas at 93 K and heated to 850 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 doses have been corrected for ion gauge sensitivity [25,26].[1] Multiple m/z fragments were monitored simultaneously during the thermal desorption experiments. All desorption traces have been corrected for overlapping cracking patterns, and intensities have been adjusted using experimentally determined mass spectrometer sensitivity factors. In the studies with $CH_3{}^{18}OH$, two products with the same molecular weight, $C^{18}O$ and $CH_2{}^{16}O$, are identified. To track these products, m/z 29 (a major fragment for unlabeled formaldehyde) was used to follow $CH_2{}^{16}O$, while m/z 30 (along with corrections due to overlapping fragments from $CH_2{}^{16}O$ and higher molecular weight products) was used to follow $C^{18}O$.

A nearly stoichiometric (1×1) surface was prepared by ion-bombardment and annealing to 900 K. Preparation of the oxygen-terminated surface [23] includes an additional step of exposure to oxygen at a partial pressure of 1.3×10^{-7} kPa using a nozzle doser [27],[2] while cycling the sample temperature from 193 to 353 K three times. Following preparation, low-energy electron diffraction (LEED) was used to check the surface periodicity, and AES was used to check for surface cleanliness prior to thermal desorption experiments.

4. Results

4.1. Reaction of methanol on nearly stoichiometric Cr_2O_3 $(1\,0\,\bar{1}\,2)$

4.1.1. CH_3OH (and $^{13}CD_3OD$) thermal desorption

The reaction of methanol with the nearly stoichiometric Cr_2O_3 $(1\,0\,\bar{1}\,2)$ surface has been studied with thermal desorption spectroscopy. All C_1 and C_2 hydrocarbons and oxygenates were checked for as reaction products. Formaldehyde, carbon monoxide, carbon dioxide, methane, and dihydrogen are the only observable products. Water is not observed as a reaction product, but was generally checked at lower sensitivity than the other products because of a higher background signal for water in the chamber. Hence, some production of water cannot be completely ruled out. We note, however, that the almost complete absence of water during the interaction of methanol with Cr_2O_3 powders has also been reported [18]. Coupling products such as dimethyl ether, ethane, ethylene, and acetylene were also checked for but not detected. Deuterium and ^{13}C-labeled methanol ($^{13}CD_3OD$) was used to distinguish unambiguously between C_2 hydrocarbon coupling products ($CH_2{=}CH_2$ and $CH_3{-}CH_3$) and C_1 oxygenates (CO and CH_2O) which have overlapping mass spectrometer cracking patterns for the unlabeled methanol reactant. Only the results for unlabeled methanol (CH_3OH) are shown.

Fig. 2 shows methanol desorption traces as a function of CH_3OH exposure on the nearly stoichiometric surface. At lower coverages (exposures <0.1 L), methanol desorbs from the surface in a broad feature 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 feature for CH_3OH desorption is independent of coverage, suggestive of a first order kinetic process. Assuming a pre-exponential of $10^{13}\,s^{-1}$ and applying the Redhead analysis [28] gives an apparent first order activation energy of desorption of 29.5 kcal/mol for the 470 K feature. At the higher coverages, the features above 470 K appears as a long tail to higher temperatures that extends out to 700 K from the main desorption features around 450 K. Noticeable within the high temperature tail (for exposures greater than 0.5 L) is a shoulder at ~650 K.

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[1] The ion gauge sensitivity factor for methanol was taken as 1.8 for methanol as per [25]. The ion gauge sensitivity factor for CH_2O was estimated as 1.6 using the correlation by S. George reported in [26].

[2] The reported local pressure above the sample has been corrected from the chamber background pressure by a doser enhancement factor of 10 that was estimated per [27].

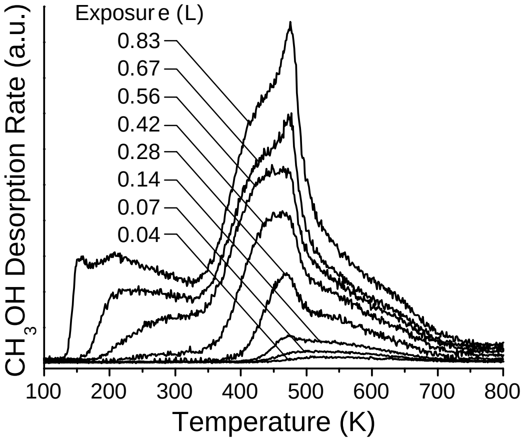


Fig. 2. Methanol thermal desorption spectra for varying exposures on the nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$ surface.

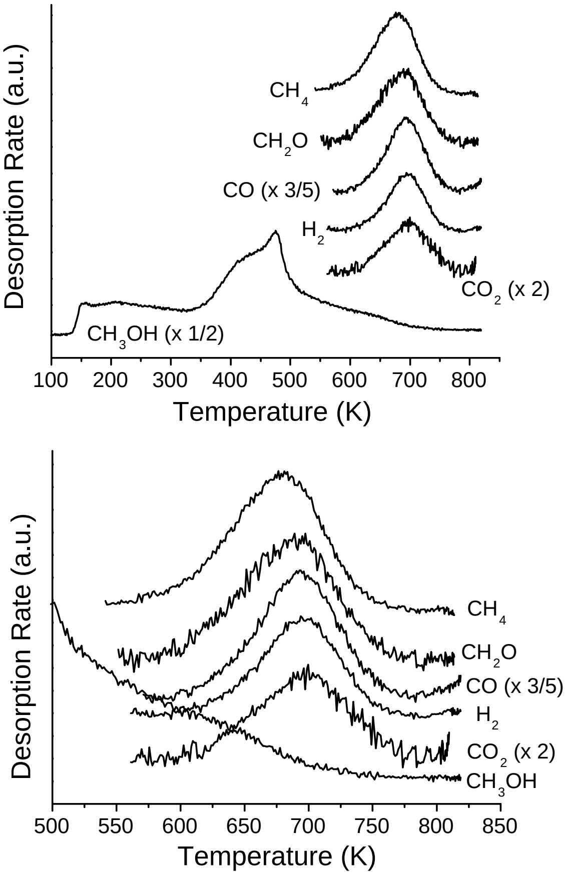


Fig. 3. Thermal desorption spectra from a near monolayer coverage of methanol on the nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$ surface. The top panel illustrates the relationship between the methanol and product desorption traces. The bottom panel gives an expanded view of the temperature range associated with product formation and desorption. The traces have been offset for clarity.

A lower temperature feature extending from 210 to 290 K is also apparent in Fig. 2 for exposures greater than 0.5 L. The temperature for this desorption feature is coverage dependent, and is likely associated with molecularly adsorbed methanol given the low desorption temperature. For exposures of 0.83 L and greater, a multilayer desorption feature appears at 155 K that does not saturate with increasing exposure. The appearance of this feature provides an indication of a near monolayer coverage.

Products from the reaction of CH_3OH with the nearly stoichiometric surface are shown in Fig. 3 for a 0.83 L dose corresponding to a monolayer coverage. The top panel compares the desorption traces of the products and methanol, while the bottom panel shows the high temperature products on an expanded scale. The CH_2O desorption signal appears at ∼690 K and is the broadest of all the desorption traces in the bottom panel in Fig. 3. Normalization of all the product peak heights (not shown) demonstrates that the leading (low temperature) edge of the formaldehyde desorption signal tracks the leading edge of the CH_4 desorption signal which has the lowest desorption temperature of all the products: 680 K. Similarly, the CH_2O desorption trace tracks the trailing (high temperature) edge of the remainder of the products that appear at slightly higher temperatures: 695 K for CO and H_2, and 700 K for CO_2. The formaldehyde trace defines a desorption “envelope”, a range of temperatures within which all the other product desorption features are observed. The temperatures of the desorption features for CH_2O, CH_4, CO, and CO_2 were all found to be independent of surface coverage, indicating first order rate-limiting step(s). Assuming a normal first order pre-exponential of $10^{13}\,s^{-1}$, application of the Redhead equation [28] gives a range of apparent first order activation energies of 43.1–44.4 kcal/mol for the reaction products.

The desorption spectra in Fig. 3 for a monolayer coverage of methanol give approximately 60% conversion of adsorbed methanol to products. Of the carbon-containing products, selectivity to CO is the highest (45%), followed by CH_4 (25%), CH_2O (22%), and CO_2 (8%). Material balances based on the integrated desorption traces fail to account for all the oxygen (∼15% unaccounted for) and hydrogen (∼25 at.% unaccounted for) in the reaction system given the stoichiometry of a methanol reactant, and may indicate some small amount of undetected water or some discrepancy in the ion gauge sensitivity factors used to generate our experimental mass spectrometer sensitivity factors. Additionally, while deoxygenation of the methanol (as indicated by methane formation) and surface oxidation might provide an explanation for some part of the unaccounted for oxygen, post reaction AES analysis shows no increase in the surface O/Cr ratio after many consecutive thermal desorption runs. However, due to the overlap between O and Cr Auger features [23], AES does not provide a particularly sensitive measure of small variations in the amount surface oxygen. Similarly, only trace amounts of surface carbon (<5% of a monolayer) are observed by post reaction AES analysis following many consecutive thermal desorption runs. Given the lack of closure for the material balance, it is important to note that *no significant variation in the apparent conversion or product distribution is observed after many consecutive thermal desorption runs for monolayer coverages of methanol on the stoichiometric surface*. The lack of variation in reactivity suggests no major changes in surface stoichiometry occur as a result of the methanol thermal desorption runs.

4.1.2. $CH_3{}^{18}OH$ thermal desorption

Thermal desorption experiments were also conducted with ^{18}O-labeled methanol as a test of the possibility of oxygen exchange with the surface. Fig. 4 shows the desorption traces of oxygenated products observed for a 0.4 L dose (approximately one-half monolayer coverage) of $CH_3{}^{18}OH$ on a freshly prepared, nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$ surface. Desorption traces for CO, $C^{18}O$, CH_2O, $CH_2{}^{18}O$, and $CO^{18}O$ are shown. Equal amounts of CH_2O and $CH_2{}^{18}O$, as well as equal amounts of CO and $C^{18}O$, are produced. The appearance of unlabeled CO and CH_2O indicates exchange with lattice oxygen since the sample surface is the only source of ^{16}O when dosing $CH_3{}^{18}OH$.

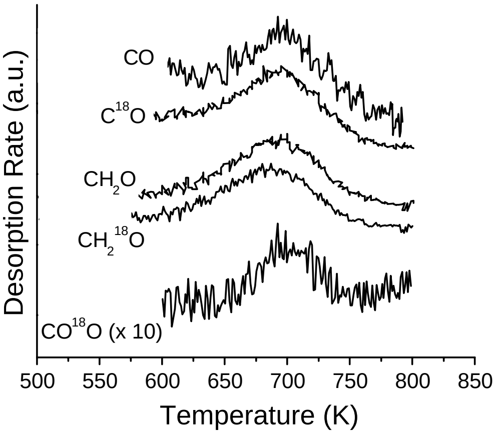


Fig. 4. Thermal desorption spectra for oxygenated products originating from the reaction of ^{18}O-labeled methanol ($CH_3{}^{18}OH$) on the nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$ surface. The traces have been offset for clarity.

4.2. Reaction of other C_1 oxygenates on nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$

The observation of lattice oxygen participation in the surface reaction pathway for methanol over Cr_2O_3 $(10\bar{1}2)$ prompted an investigation of the reaction of formaldehyde and formic acid with the nearly stoichiometric surface. Relevant thermal desorption results for formaldehyde are given below in addition to a brief description of relevant findings for formic acid.

4.2.1. CH_2O thermal desorption

The reaction of CH_2O yields a multitude of products: CH_2O, CH_3OH, CH_4, CO, CO_2, HCOOH, C_2H_2, and H_2 [29]. Products similar to those observed from the reaction of methanol are shown in Fig. 5 for an 0.5 L formaldehyde dose. Formaldehyde desorption occurs in two temperature ranges: at 690 and 470 K. The low temperature feature is associated with chemisorbed formaldehyde and polyoxymethylene (paraformaldehyde) oligomers [29], and is not relevant to the present discussion. The high temperature CH_2O desorption (690 K) coincides with the desorption temperature of CH_2O produced by the reaction of methanol. Similar to the observations for the reaction of methanol, product CH_4 is observed at a lower temperature (655 K) than that for formaldehyde desorption. The product methane desorption signal

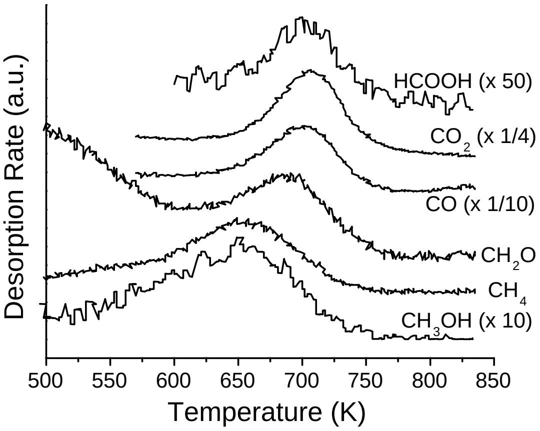


Fig. 5. Thermal desorption traces of carbon-containing products originating from the reaction of formaldehyde (CH_2O) on the nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$ surface. The traces have been offset for clarity.

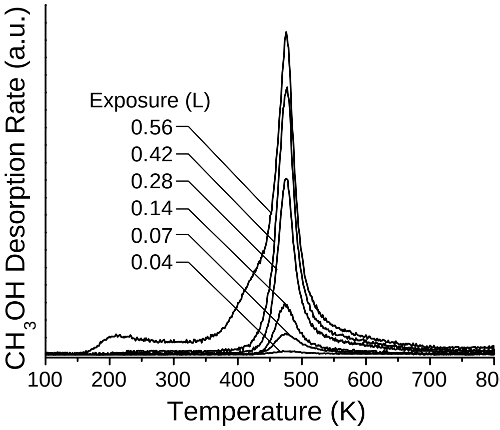


Fig. 6. Methanol thermal desorption spectra for varying exposures on the oxygen-terminated Cr_2O_3 $(10\bar{1}2)$ surface.

appears in coincidence with methanol at 655 K, a temperature which corresponds closely to the shoulder in the high temperature methanol desorption tail observed in Figs. 2 and 3 for the adsorption and reaction of methanol.

Desorption of CO and CO_2 occurs at slightly higher temperatures than the formaldehyde signal, 700 and 705 K, respectively, similar to observations that were made for the production of CO and CO_2 from methanol in Fig. 3. In addition to products observed in common with the reaction of methanol, a trace formic acid (HCOOH) signal is also observed from the reaction of formaldehyde, coincident with the production of CO_2 at 705 K.

For just the desorbing molecules shown in Fig. 5 that are also observed as products from the reaction of methanol, the relative yield of CO is the highest (53%), followed by CO_2 (25%), CH_2O (12%), and CH_4 (10%).

4.2.2. HCOOH thermal desorption

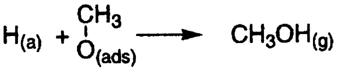
Thermal desorption of formic acid (not shown) from the nearly stoichiometric $(10\bar{1}2)$ surface yields CO, CO_2, H_2 and HCOOH as the primary products at 700 K [29]. In addition, a trace of CH_2O product is also observed in the same temperature range. The desorption temperatures of these species from the reaction of formic acid coincides with the desorption temperature of these products from the reaction of methanol and formaldehyde.

4.3. Reaction of methanol on O-terminated Cr_2O_3 $(10\bar{1}2)$

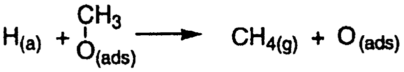
Fig. 6 shows a series of methanol thermal desorption traces for different exposures on the oxygen-terminated Cr_2O_3 $(10\bar{1}2)$ surface. Methanol is the only species observed in thermal desorption. Other products checked for but not detected include: CH_2O, CO, CO_2, CH_4, H_2O, H_2, HCOOH, and CH_3OCH_3. The methanol desorption trace appears as a single sharp feature at 475 K for exposures up to about 0.4 L. 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 [28]. For the 0.56 L exposure, two other features are observed: a shoulder at 420 K and a peak at 215 K. There is no evidence of the higher temperature chemistry observed on the stoichiometric surface. For doses in excess of 0.7 L (not shown), a multilayer desorption feature is observed near 150 K.

5. Discussion

In the reaction of methanol with metal oxides, one typically expects the reaction chemistry to be initiated by the formation of methoxide surface intermediates resulting from the dissociative adsorption of methanol. These expectations hold for chromia powders where dissociation of methanol to methoxides has been observed by IR [17–19]. In our thermal desorption results for the reaction of methanol with the nearly stoichiometric surface, product evolution occurs within a temperature range of 600–800 K. Formaldehyde, a typical reaction product of β-hydride elimination from methoxide, appears over this entire temperature range. In addition, CH_3OH (∼650 K) and CH_4 (680 K) are observed in the lower temperature portion of the desorption envelope mapped out by formaldehyde. The hydrogenation of methoxide to methane has been observed previously on TiO_2 (0 0 1) [30] and ZrO_2 (1 0 0) [31] surfaces during thermal desorption studies of the reaction of methanol. Desorption of methanol in this temperature range can also be attributed to a reaction of methoxide with surface hydrogen, given that a stable molecular methanol adsorbate is highly unlikely at such high temperatures in UHV. Also, since both of these reactions occur at temperatures well above those for the recombination and desorption of atomic hydrogen as H_2 (285 K [32]), the surface hydrogen for these reactions must be produced by the dehydrogenation of some surface intermediate(s). Two parallel reaction steps can describe the chemistry of methoxide hydrogenation in this temperature range:



$$H_{(a)} + \overset{CH_3}{\overset{|}{O_{(ads)}}} \longrightarrow CH_3OH_{(g)} \quad (1)$$



$$H_{(a)} + \overset{CH_3}{\overset{|}{O_{(ads)}}} \longrightarrow CH_{4(g)} + O_{(ads)} \quad (2)$$

While the direct dehydrogenation of methoxide to formaldehyde is a reasonable reaction pathway to formaldehyde, the observation of oxygen exchange with the lattice in the $CH_3{}^{18}OH$ thermal desorption experiments indicates a surface reaction route to formaldehyde that includes an interaction with lattice oxygen. In the thermal desorption studies with ^{18}O-labeled methanol, equal amounts of CH_2O and $CH_2{}^{18}O$ products are detected, as well as equal amounts of CO and $C^{18}O$. These observations suggest the participation of a symmetric, bidentate surface intermediate with the carbon center bonded to the surface through two O atoms—one the ^{18}O atom intrinsic to the adsorbed methanol, and the second a surface lattice oxygen anion. The symmetry of this dioxygenated intermediate is suggested by the equal amounts of labeled (^{18}O) and unlabeled (^{16}O) products of formaldehyde and carbon monoxide, which implies an essentially equal probability of cleaving either C–O bond. The two most likely surface intermediates are formate (HCOO) and dioxymethylene (H_2COO). In either case, the formation of such an intermediate from a surface methoxide involves nucleophilic attack of surface lattice oxygen on the carbon center of methoxide. Such processes have been documented previously for ZnO (0 0 0 1) [33] and ZrO_2 (1 1 0) [31] surfaces, where nucleophilic attack by surface lattice oxygen leads to surface formate and dioxymethylene, respectively.

The local coordination geometry about the chromium cations on the $(1 0 \bar{1} 2)$ surface facilitates this process of nucleophilic attack. On an initially clean, well-ordered stoichiometric surface, the incomplete coordination octahedron of each cation contains two coordinately unsaturated surface anions, represented by the outer atomic layer “zig-zag” rows of anions along the $[0 2 \bar{2} 1]$ direction in Fig. 1. For nucleophilic attack on a methoxide, the cation binding the methoxide and the neighboring coordinately unsaturated anion act as a site pair for the formation of the bidentate surface intermediate. This process is illustrated schematically in Fig. 7a.

The thermal desorption data for the reaction of formaldehyde and formic acid on Cr_2O_3 $(1 0 \bar{1} 2)$ can be used to make a case for the occurrence of both dioxymethylene and formate intermediates in the reaction of methanol. The similarity in the desorption temperatures and reaction products from methanol and formaldehyde indicate that similar surface intermediates are involved in the reaction pathways of both molecules. The formaldehyde desorption profile at 690 K observed following formaldehyde adsorption is similar to that seen for product formaldehyde from the reaction of methanol which involves a bidentate surface intermediate. The similarities argue in favor of a dioxymethylene surface intermediate as the primary bidentate intermediate involved in the reaction of methanol. Dioxymethylene species have been identified or implicated as surface intermediates on a number of metal oxide surfaces, both as a result of formaldehyde adsorption [34–39] and methanol adsorption

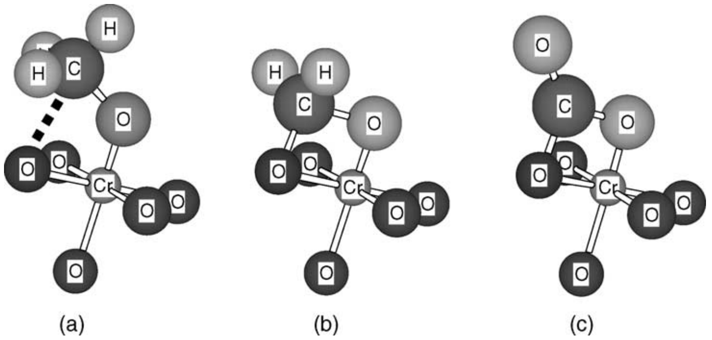
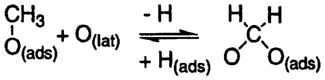


Fig. 7. Illustration of the proposed interaction of adsorbed species with cation–anion site pairs on the stoichiometric Cr_2O_3 $(1 0 \bar{1} 2)$ surface. The site pair involves surface cations and coordinately unsaturated anions: (a) schematic representation of nucleophilic attack of surface lattice oxygen on methoxide leading to the formation of a bidentate intermediate; (b) adsorption of formaldehyde at a site pair gives an adsorbed species with the stoichiometry of dioxymethylene; (c) similar to the proposed adsorption process for formaldehyde, adsorption of CO_2 at a site pair gives a bidentate surface carbonate [42].

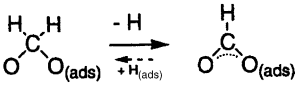
[31,40,41]. Note that adsorption of formaldehyde at a cation–anion site pair yields an adsorbate with the stoichiometry of dioxymethylene. Interaction of the molecular oxygen of formaldehyde with a surface cation site and nucleophilic attack on the carbon center by a neighboring coordinately unsaturated anion yields a dioxymethylene, as illustrated in Fig. 7b. A similar adsorption process (Fig. 7c) involving a cation–anion site pair has been observed previously on this surface where the adsorption of carbon dioxide yields a bidentate surface carbonate [42]. While carbonates are routinely reported for CO_2 adsorption on oxide powders, the stoichiometric Cr_2O_3 $(1 0 \bar{1} 2)$ surface is, to our knowledge, the only well-ordered single crystal oxide surface yet reported to form carbonate species that are stable above room temperature in UHV.

The common link between methanol and formaldehyde through a dioxymethylene surface intermediate is also suggested by the production of methanol and methane from the reaction of formaldehyde. Methanol and methane are produced simultaneously at 655 K from the reaction of formaldehyde in thermal desorption, which indicates that hydrogenation of formaldehyde to methoxide must occur. Given the commonality of these methoxide hydrogenation products and formaldehyde desorption signals for both reactants (formaldehyde and methanol), a reversible reaction linking methoxide and dioxymethylene is implicated. Whether the forward reaction occurs as a single concerted step or separate dehydrogenation and oxygen insertion steps is uncertain:

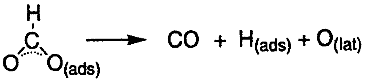


$$\underset{O_{(ads)}}{\overset{CH_3}{|}} + O_{(lat)} \underset{+\,H_{(ads)}}{\overset{-\,H}{\rightleftharpoons}} \overset{H\quad H}{\underset{O\quad O_{(ads)}}{C}} \tag{3}$$

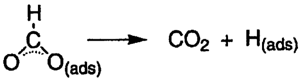
For the production of surface methoxide and its associated hydrogenation products (methanol and methane), a source of surface hydrogen is required. For this process driven by formaldehyde adsorption alone, the source of hydrogen must be the dehydrogenation of adsorbed formaldehyde or the dioxymethylene intermediate formed by formaldehyde adsorption at a cation–anion site pair. Evidence that dioxymethylene dehydrogenation must occur is also apparent on the higher temperature side of the formaldehyde desorption envelope where CO, H_2 and CO_2 desorption features are observed near 700 K from both the reaction of methanol and formaldehyde. These three products are also formed in the same temperature range from the reaction of formic acid, a reactant well known to dissociate to formate species on Cr_2O_3 [20]. Coincident with these desorption features is a product signal for formic acid from both the reaction of formaldehyde (a trace) and formic acid. These product signals are a clear indication of the presence of a formate surface intermediate. CO, CO_2, and H_2 are known decomposition products of formate on Cr_2O_3 [20], and desorption of formic acid in the same temperature range can be attributed to the hydrogenation of formate by hydrogen liberated in the decomposition reaction. Note that the estimated first order activation barrier of ∼44.5 kcal/mol for CO, H_2 and CO_2 production between 695 and 705 K is very similar to the 46 kcal/mol barrier to formate decomposition reported by Tamaru and coworkers [20] for the decomposition of formate to these same three products on Cr_2O_3 powders under vacuum. The reaction sequence in this temperature range is readily explained by the dehydrogenation of dioxymethylene to a bidentate formate, and formate decomposition to CO and CO_2. Note also that the reaction of formic acid produces a trace amount of formaldehyde, suggesting the reverse pathway from formate to dioxymethylene is also operable to a lesser extent:



(4)

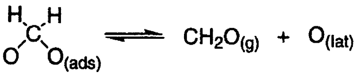


(5)



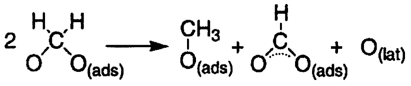
(6)

In addition to the hydrogenation and dehydrogenation of dioxymethylene, an additional thermal decomposition pathway is operable: a deoxygenation route (C–O bond cleavage) to yield gas phase formaldehyde—the reverse of the formaldehyde adsorption reaction. This pathway is indicated clearly by the equal amounts of labeled and unlabeled formaldehyde produced from ^{18}O-labeled methanol, and the similar desorption temperature following formaldehyde adsorption. Similar to the reaction chemistry observed by Dilara and Vohs on ZrO_2 (1 1 0) [31], the precursor to formaldehyde from the reaction of methanol on Cr_2O_3 $(1 0 \bar{1} 2)$ is a dioxymethylene intermediate rather than methoxide:



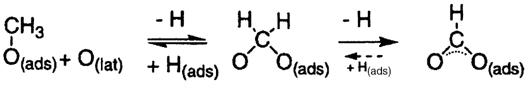
(7)

The link between dioxymethylene, methoxide and formate has been reported previously. For cases of dioxymethylene formation from CH_2O, this link is described typically in terms of a Cannizzaro-type disproportionation of dioxymethylene to methoxide and formate [34–37]:



(8)

Given the obvious route from methoxide to dioxymethylene in the reaction of methanol, it is not clear from our thermal desorption results that equal amounts of methoxide and formate are formed from dioxymethylene, even for the case of formaldehyde adsorption and reaction. However, the existence of a connection between the different oxygenated intermediates is clear. Given the apparent first order kinetics associated with the different products from the reaction of methanol, a kinetic description more related to intermediate decomposition (dehydrogenation) and hydrogen transfer seems appropriate, much in the spirit of earlier descriptions [37]. The observed reaction chemistry linking the oxygenated surface intermediates involved in the reaction of methanol over stoichiometric Cr_2O_3 $(1 0 \bar{1} 2)$ can then be described in terms of a sequence of dehydrogenation and hydrogenation reactions (9) described by the combination of reactions (3) and (4) above. The differences in selectivity between the reaction of methanol and the reaction of formaldehyde support this view. The selectivity for the reaction of formaldehyde is shifted more towards dehydrogenation products, as might be expected for a reactant containing less hydrogen than methanol:



(9)

Unfortunately, our thermal desorption results do not provide a clear indication of the activation barriers to the interconversion of the three oxygenated intermediates in the reaction of methanol on Cr_2O_3. The lowest temperature product, methane, evolves with a desorption peak temperature of 680 K, while the highest temperature product, CO_2, falls at 700 K. With only a 20 K spread in the desorption temperatures, the results suggest some varying population of all three oxygenated intermediates over the 600–800 K temperature range where product evolution occurs.

While a rich reaction chemistry is observed for the interaction of methanol with the stoichiometric Cr_2O_3 $(1 0 \bar{1} 2)$ surface, the O-terminated surface is completely unreactive with methanol. The extreme differences in reactivity indicate a clear structure or composition sensitivity in the reaction chemistry of methanol over Cr_2O_3 $(1\,0\,\bar{1}\,2)$. The O-terminated surface exposes terminal chromyl (Cr=O) oxygen as well as the three-coordinate oxygen anions available on the stoichiometric surface for the dissociation and reaction of methanol. However, the primary difference in the surface condition that impacts the reactivity of methanol is the lack of coordinately unsaturated cations on the O-terminated surface. Terminal oxygen acts as a cation site blocker, eliminating the cation–anion site pairs available on the stoichiometric surface. This observation is in line with suggestions by Barteau [1] that cation–anion site pairs are a necessary site requirement for the dissociation and reaction of Brønsted acids on oxide surfaces.

6. Conclusions

The reaction of methanol on the nearly stoichiometric α-Cr_2O_3 $(1\,0\,\bar{1}\,2)$ surface gives a spectrum of products including CH_4, CH_2O, CO, CO_2 and H_2. These products are all generated in a 200 K temperature range (600–800 K) in thermal desorption through a reaction pathway involving methoxide, dioxymethylene and formate surface intermediates. The interconversion between oxygenated C_1 surface intermediates involves the reversible reaction of methoxide to dioxymethylene via dehydrogenation and nucleophilic attack of surface lattice oxygen. Formate intermediates are formed by the dehydrogenation of dioxymethylene, and formate decomposition appears to be the primary route to CO and CO_2. Isotopic labeling studies indicate that the precursor to the formaldehyde reaction product is a dioxymethylene intermediate rather than methoxide. The oxygen-terminated surface is completely unreactive, indicating a structure (or composition) sensitive reaction of methanol on the $(1\,0\,\bar{1}\,2)$ surface. Terminal chromyl oxygen acts as a cation site blocker and eliminates the surface cation–anion site pairs necessary for the dissociation and reaction of methanol.

Acknowledgements

We gratefully acknowledge financial support by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy through grant DE-FG02-97ER14751.

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