Geometric and Electronic Structure Sensitivity of Methyl and Methylene Reactions on $\alpha$-Cr$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ surfaces

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ABSTRACT

Structural and electronic effects in hydrocarbon reactions over metal oxides have been examined by comparing the reactions of methyl (-CH₃) and methylene (=CH₂) fragments on three different oxide single crystal surfaces: α-Cr₂O₃(10̅12), α-Cr₂O₃(0001), and α-Fe₂O₃(10̅12). The intermediates have been generated through the decomposition of halogenated hydrocarbons.

The primary reactions of methyl and methylene over α-Cr₂O₃ are methyl dehydrogenation to methylene, and methylene coupling (C-C bond formation) to ethylene (CH₂=CH₂). The different surface geometric structures of α-Cr₂O₃(10̅12) and (0001) lead to an increase in the activation barrier for methylene surface migration, a critical step in the coupling reaction, of 5.9 kcal/mol over the (0001) surface. For methyl dehydrogenation, differences in the local site pair (cation/anion) geometry and the proximity of surface lattice oxygen to the methyl group do not result in a significant difference in the barrier for dehydrogenation, suggesting that the surface anions play a minor role in the dehydrogenation of methyl on these surfaces.

Electronic differences in the Fe³⁺ (d⁵) and Cr³⁺ (d³) cations on structurally-similar α-Cr₂O₃(10̅12) and α-Fe₂O₃(10̅12) surfaces lead to major differences in reaction selectivity. α-Cr₂O₃(10̅12) is nonreducible under the reaction conditions of this study, but α-Fe₂O₃(10̅12) is highly reducible due to the difference in the d electron configuration. Hydrocarbons are formed over α-Cr₂O₃(10̅12), but nonselective oxidation products (CO₂, CO, H₂O) are formed over the stoichiometric α-Fe₂O₃(10̅12) surface along with surface reduction. Reduction of the α-Fe₂O₃(10̅12) leads to a shift in the product selectivity towards formaldehyde (CH₂O) and ethylene.

For the limited number of systems examined in this study, examples of geometric structure sensitive (methylene coupling) and structure insensitive (methyl dehydrogenation) reactions have been found on α-Cr₂O₃, and electronic effects are observed for the reactions on α-Cr₂O₃(10̅12) and α-Fe₂O₃(10̅12). For the structure sensitive reaction, the differences in surface geometry impact the reactions kinetics over Cr₂O₃ but not the types of products formed, while the electronic differences give rise to dramatic changes in the selectivity associated with the very different products formed over α-Cr₂O₃(10̅12) and α-Fe₂O₃(10̅12).
Dedication

Dedicated to my parents: Ockmi Kim and Jong-in Dong.
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Chapter 1.

Introduction

1.1. Key Elements of Metal Oxide Surface Chemistry

Surface geometric and electronic structures are key factors that determine the reactivity of a surface. Numerous studies have been done in which reactivity differences have been seen on different planes of the same material that expose different surface structures [1-3], indicating that the surface geometric structure can play an important role in surface reactivity [4-6]. For example, Fe(111), Fe(100), and Fe(110) surfaces show different reactivities for ammonia synthesis, as an effect of the different surface structures. The oxidation state of the reaction centers in supported catalysts is the center of attention in catalysis literature because different oxidation states of the reaction center result in different reactivity [7-9], indicating that the surface electronic structure plays an important role in surface reactivity. For example, the active center for the dehydrogenation of alkane into alkenes on supported chromia catalysis is known to be Cr$^{3+}$, and the presence of other oxidation states is related with the reduction of reactivity [10].

These factors apply to metal oxide surface chemistry, with the key concepts for describing the metal oxide surfaces being the coordination environment and the oxidation states of the surface cations [11]. Metal cations, which are isolated by oxygen linkages, are generally the reaction centers for reactions on metal oxide surfaces, and the coordination vacancy of a metal cation corresponds to the number of missing $M^{n+}-O^{m-}$ bonds compared to its bulk counterpart. The extent of coordinative unsaturation is known to play an important role in the
reaction chemistry of metal oxide surfaces. For example, surfaces with coordinatively saturated cations are typically inert [12-15], since all possible bonds of the surface cations are occupied, and adsorbates are not able to bind to the cations. It is generally thought that adsorbates go through unimolecular reactions on surfaces that expose cations with a single coordination vacancy [11], since only one adsorbate is likely to bind on the reaction sites. Surfaces with multiple coordination vacancies are thought to be capable of carrying out coupling (bond making) reactions, because they are able to accommodate multiple ligands on a single cationic site. The application of these concepts is the basis for the pioneering work of Barteau and coworkers [11]. Multiple coordinative unsaturation of surface cations was found to be necessary for C-C bond forming (coupling) reactions, based on studies done with carboxylates and alcohols on a number of metal oxide surfaces [16-21]. Additionally, cations can have a range of possible oxidation states depending on the preparation method of the metal oxide surfaces, unlike on metal surface where only zero-valent metals exist. Surface reactions may be strongly dependent on the oxidation state of the surface metal cation.

1.2. Previous Studies of Hydrocarbon Fragments on α-Cr₂O₃(1012)

Supported chromia is a well-known catalyst for the selective dehydrogenation of alkanes such as isobutane and propane to the corresponding alkenes [10, 22-24]. The catalysts show high selectivities for the reactions, with the selectivity of the industrial process CATOFIN™ having selectivity as high as 90+ mol% for the dehydrogenation of isobutane to isobutylene. The active catalytic site for these reactions are thought to be coordinatively unsaturated Cr³⁺ cations [10]. The high selectivities of these reactions have led to a series of ultra-high vacuum (UHV) surface science studies of C₁ and C₂ hydrocarbon intermediates on the α-Cr₂O₃(1012) single crystal
surface [25-30] in an effort to mimic the catalytic surface reactions of the simplest hydrocarbon intermediates. Interesting results have been found with C\textsubscript{1} hydrocarbon intermediates which were expected to be coke (carbonaceous residue) formers through simple dehydrogenation reactions. Indeed, ethylene and methane were produced from both methyl (−CH\textsubscript{3}) and methylene (=CH\textsubscript{2}) intermediates with minimal surface carbon formation.

The ideal, stoichiometric α-Cr\textsubscript{2}O\textsubscript{3}(10\overline{1}2) surface has cations that are singly undercoordinated compared to their bulk compartments. According to the study of Barteau and coworkers [11], a multiple coordinative unsaturation of surface cations is thought to be necessary for C-C bond forming (coupling) reactions to happen. The observation that C\textsubscript{1} species couple to form C\textsubscript{2} products on this metal oxide surface with singly-undercoordinated surface cations is at variance with what is currently understood about C-C bond making chemistry on metal oxide surfaces.

According to the experimental and computational studies on α-Cr\textsubscript{2}O\textsubscript{3}(10\overline{1}2), surface methylene migrates (Figure 1.1) and couples with one another to produce ethylene, or inserts into methyl groups forming surface ethyl (1.2), then go through a β-H elimination to form ethylene (1.3). Methyl intermediates dehydrogenate to form methylene intermediates (1.4) which go through reactions (1.2) and (1.3), producing ethylene. The liberated hydrogens from the dehydrogenation of methyl groups react with the remaining methyl groups to produce methane (1.5), or couple with one another to produce H\textsubscript{2} (1.6). The migration of methylene species across the surface to couple with surface methylene or methyl is a phenomenon reported on metal surfaces, but to our knowledge, not observed previously on metal oxide surfaces.

\[
=\text{CH}_2(\text{ads}) + =\text{CH}_2(\text{ads}) \rightarrow \text{CH}_2=\text{CH}_2(\text{gas}) \quad (1.1)
\]
Figure 1.1. Two methylene migration pathways on α-Cr₂O₃(1012) found by DFT studies. The yellow route represents the path that goes through the valleys of the corrugated surface by direct migration between neighboring cations. The blue route represents the migration path that goes over the hills of oxygen to the nearest neighboring cation on the other side of the oxygen. (a) Tilted view. (b) Side view.
\[=\text{CH}_2\text{(ads)} + \text{CH}_3\text{(ads)} \rightarrow \text{CH}_2\text{CH}_3\text{(ads)} \quad (1.2)\]

\[\text{CH}_2\text{CH}_3\text{(ads)} \rightarrow \text{CH}=\text{CH}_2 + \text{H}\text{(ads)} \quad (1.3)\]

\[\text{CH}_3\text{(ads)} \rightarrow =\text{CH}_2\text{(ads)} + \text{H}\text{(ads)} \quad (1.4)\]

\[\text{CH}_3\text{(ads)} + \text{H}\text{(ads)} \rightarrow \text{CH}_4\text{(g)} \quad (1.5)\]

\[\text{H}\text{(ads)} + \text{H}\text{(ads)} \rightarrow \text{H}_2\text{(g)} \quad (1.6)\]

Two pathways for the migration of methylene have been found with density functional theory (DFT)-based calculations: one that goes through the valleys of the corrugated surface by direct migration between neighboring cations, and one that goes over the ridges of coordinatively unsaturated oxygen anion to the nearest neighboring cation on the opposite side of the ridge (Figure 1.1) [31]. This chemistry is possible because the stoichiometric \(\alpha\)-\(\text{Cr}_2\text{O}_3\)\((10\bar{1}2)\) is highly non-reducible and therefore does not produce oxygen-containing oxidation products.

1.3. Purpose & Methods of this Study

With the observation of coupling reactions on a surface with singly-coordinated cations, the question arises if the nature of the coordination environment is important in directing these reactions, or if the electronic structure of the surface a more important factor. Such considerations in heterogeneous catalysis are traditionally referred to as either “structural” or “electronic” effects. To address these issues in the case of methyl and methylene reactions, a comparison study has been done on the \(\alpha\)-\(\text{Cr}_2\text{O}_3\)\((0001)\) and \(\alpha\)-\(\text{Fe}_2\text{O}_3\)\((10\bar{1}2)\) surfaces for comparison to the previous studies of \(\alpha\)-\(\text{Cr}_2\text{O}_3\)\((10\bar{1}2)\).

Particular questions and details to address are as follows:
1) Are multiple coordination vacancies of surface cations critical for the coupling reactions on metal oxide surfaces?

The metal cations of the ideal, stoichiometric $\alpha$-Cr$_2$O$_3$ surface have one coordination vacancy while they have three coordination vacancies on the $\alpha$-Cr$_2$O$_3$(0001) surface (Table 1.1). By examining the reaction chemistry of methylene and methyl intermediates on the $\alpha$-Cr$_2$O$_3$(0001) and comparing to previous results from the $\alpha$-Cr$_2$O$_3$(1012) surface, this question can be addressed. In particular, whether there are any significant differences in catalytic selectivity (product distributions) or kinetics (activation barriers).

2) Does the geometrical proximity of surface lattice oxygen with a hydrocarbon adsorbate make dehydrogenation more favorable?

In addition to the difference in coordination vacancies, the local site-pair geometries of the cations are also different on the $\alpha$-Cr$_2$O$_3$(1012) and $\alpha$-Cr$_2$O$_3$(0001) surfaces (Table 1.1). On the $\alpha$-Cr$_2$O$_3$(1012) surface, the outermost atomic layer consists of coordinatively unsaturated oxygen anions that are more accessible to adsorbates, while on the $\alpha$-Cr$_2$O$_3$(0001) surface, surface oxygen sits below a surface Cr layer making them less accessible to the adsorbates. According to a general notion in the field of catalysis by metal oxides, surface oxygen facilitates the abstraction of hydrogen from adsorbates. We can test this concept by comparing the activation energies for methyl dehydrogenation on these two surfaces.

3) Does the surface electronic environment affect the surface reactions?

The $\alpha$-Cr$_2$O$_3$(1012) and $\alpha$-Fe$_2$O$_3$(1012) surfaces have similar surface geometric structures in that they are the same termination of the bulk materials with the corundum
Table 1.1. Comparison of coordination environment, local site-pair geometry, and the number of $d$ electrons of surface metal cations of $\text{Cr}_2\text{O}_3(10\bar{1}2)$, $\text{Cr}_2\text{O}_3(0001)$, and $\text{Fe}_2\text{O}_3(10\bar{1}2)$ surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\text{Cr}_2\text{O}_3(0001)$</th>
<th>$\text{Cr}_2\text{O}_3(10\bar{1}2)$</th>
<th>$\text{Fe}_2\text{O}_3(10\bar{1}2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination Environment of Surface Metal Cations</td>
<td>3-fold coordinated to oxygen anions</td>
<td>5-fold coordinated to oxygen anions</td>
<td>5-fold coordinated to oxygen anions</td>
</tr>
<tr>
<td>Local Site-pair Geometry</td>
<td>coordinatively unsaturated surface oxygens are below surface cations</td>
<td>coordinatively unsaturated surface oxygens are in the outermost atomic layer</td>
<td>coordinatively unsaturated surface oxygen are in the outermost atomic layer</td>
</tr>
<tr>
<td>Electronic Cation Configuration</td>
<td>$3d^3 \text{Cr}^{3+}$</td>
<td>$3d^3 \text{Cr}^{3+}$</td>
<td>$3d^6 \text{Fe}^{3+}$</td>
</tr>
</tbody>
</table>
structure, and the lattice constants are similar for both materials. However, the surface cations have different 3\(d\) electron densities, so the surfaces have different electronic structures (Table 1.1). The Cr\(^{3+}\) cations of the \(\alpha\-\text{Cr}_2\text{O}_3(10\bar{1}2)\) surface have three 3\(d\) electrons, while the Fe\(^{3+}\) cations of the \(\alpha\-\text{Fe}_2\text{O}_3(10\bar{1}2)\) surface have five 3\(d\) electrons. By comparing the reaction chemistry of the methylene and methyl intermediates on these two surfaces, the effect of the different electronic structure (an electronic effect) can be isolated with no significant variation in surface structure. This can be achieved by seeing if there are any differences in the types of products formed (selectivity), and if there are any difference in the reaction kinetics. Since the effect of different 3\(d\) electron density makes \(\alpha\-\text{Fe}_2\text{O}_3\) a reducible oxide (while \(\alpha\-\text{Cr}_2\text{O}_3\) is a non-reducible oxide), special attention will be paid to differences in selectivity to oxygen containing products(e.g., CO, CO\(_2\), and H\(_2\)O) on the \(\alpha\-\text{Fe}_2\text{O}_3(10\bar{1}2)\) surface. No such products were observed in the earlier studies on \(\alpha\-\text{Cr}_2\text{O}_3(10\bar{1}2)\).

To this end, methylene and methyl intermediates have been generated through the thermal or electron-stimulated decomposition of adsorbed halogenated hydrocarbons such as dichloromethane (CH\(_2\)Cl\(_2\)) and iodomethane (CH\(_3\)I). The low barriers to the C-X (X \(\equiv\) halogen) bond breaking compared to C-H bond breaking allow for the formation of the required hydrocarbon intermediates. Studies show that metal cation Lewis acid sites promote the removal of the halogen from the haloalkanes [32-37]. Reaction products and reaction orders of the rate-limiting surface reaction steps have been investigated with temperature-programmed desorption (TPD). X-ray photoelectron spectroscopy (XPS) has been used to monitor the dissociation of carbon-halogen bonds, identify reaction intermediates, and determine the location of surface hydrocarbon fragments: whether they are cation or anion centered. Density functional theory
(DFT) calculations have been used for the prediction of the adsorbate geometry, adsorption sites and reaction pathways.

1.4. Bulk Properties

\[ \alpha\text{-Cr}_2\text{O}_3 \text{ and } \alpha\text{-Fe}_2\text{O}_3 \text{ crystals both have the corundum bulk structure} \text{[38, 39].} \text{ In a crystal of corundum structure, metal cations are surrounded by six oxygen anions in a distorted octahedra, while each anion is surrounded with a tetrahedron of four metal cations (Figure 1.2). Among the possible cation sites, one-third of the sites are vacant [40]. Cleavage of the crystal along the vacancies results in the \( (10\bar{1}2) \) plane which is the primary cleavage plane for most metal oxides with corundum structure [40]. This is presumably because it cleaves only one oxygen ligand per metal cation, reducing the coordination number of the cation by the smallest amount [40].}

Both \( \alpha\text{-Cr}_2\text{O}_3 \text{ and } \alpha\text{-Fe}_2\text{O}_3 \text{ are antiferromagnetic insulators with band gaps of } \approx 3.4 \text{ eV and } \approx 2 \text{ eV, respectively} \text{[41-45].} \text{ The Néel temperatures}\footnote{The Néel temperature is the temperature above which an antiferromagnetic material becomes paramagnetic—that is, the thermal energy becomes large enough to destroy the macroscopic magnetic ordering within the material.} \text{ are 308 and 955 K, respectively. Figure 1.3 shows the minimum energy antiferromagnetic spin ordering of the metal cation layers along the } [0001] \text{ direction as determined by density functional theory (DFT): } +\text{-}+\text{-} (+ \text{ for spin up, - for} \text{ spin down) for } \text{Cr}_2\text{O}_3 \text{ and } +\text{+}+- \text{ for } \text{Fe}_2\text{O}_3 \text{[46, 47]. Spectroscopic experiments characterize } \alpha\text{-Fe}_2\text{O}_3 \text{ as a charge transfer (CT) insulator, while } \alpha\text{-Cr}_2\text{O}_3 \text{ is considered to be a borderline case between a CT and Mott-Hubbard (MH) insulator [48]. } \alpha\text{-Fe}_2\text{O}_3 \text{ allows surface electron spectroscopic experiments without significant modifications [43, 49, 50], while the strongly insulating property of } \alpha\text{-Cr}_2\text{O}_3 \text{ results in significant charging effects during investigations using} \]
Figure 1.2. Corundum structure. Small spheres represent $M^{3+}$ cations and big spheres represent $O^{2-}$ anions.

Figure 1.3. The bulk antiferromagnetic ordering of the spin of the metal cation layers along the [0001] direction of $\alpha$-Cr$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$. $+$ represents spin up unpaired electrons on the cations and $-$ represents spin down.
X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

1.5. **Surface Properties**

1.5.1. **The α-Cr$_2$O$_3$(10$\overline{1}$2) surface**

The α-Cr$_2$O$_3$(10$\overline{1}$2) surface is the energetically most favored termination for α-Cr$_2$O$_3$ [51]. A ball model illustration of the ideal, stoichiometric surface is shown in Figure 1.4. The surface Cr$^{3+}$ cations are 5-fold coordinated with oxygen anions. The cations are separated by about 3.65 Å, providing some isolation of likely reaction sites. The surface has a rectangular periodicity with a ratio of sides a/b = 0.94. The ideal, stoichiometric surface terminates with a [O,Cr,O,Cr,O] stoichiometric repeat unit of the bulk. The dipole moments between the layers of the repeat units cancel, making this a non-polar surface [52]. It has been shown that a nearly-stoichiometric surface can be reproducibly prepared by Ar$^+$ ion bombardment and annealing at 900 K in ultra-high vacuum [53].

1.5.2. **The α-Cr$_2$O$_3$(0001) surface**

The cleavage of the crystal through the plane between the closely-lying Cr layers in the [0001] direction yields the α-Cr$_2$O$_3$(0001) surface with 3-fold coordinated cations (Figure 1.5). The stoichiometric repeat unit is [Cr, 3O, Cr] along the direction perpendicular to the surface for the ideal, stoichiometric surface. The dipole moments are canceled out, forming a non-polar surface. The surface cations are separated by 4.9 Å, further isolating the reaction sites. This surface has a hexagonal periodicity.
Figure 1.4. The ideal, stoichiometric (10\bar{1}2) model surface. The grey, small spheres are $M^{3+}$ cations and the red, big spheres are $O^{2-}$ anions. (a) Two-dimensional view. \(a:b\) is 0.94 for $Cr_2O_3(10\bar{1}2)$ and 0.93 for $Fe_2O_3(10\bar{1}2)$. (b) The tilted view shows the corrugation of the surface with the outermost oxygen layer showing a zig-zag pattern.
The α-Cr₂O₃(0001) surface has been prepared by different groups on surfaces formed by molecular beam epitaxy or the direct oxidation of Cr(110). Nearly-stoichiometric thin film surfaces were prepared by 500 eV Ar⁺ ion bombardment and annealing at 850 K of the crystal formed by molecular beam epitaxy on an α-Al₂O₃ substrate [54], or the oxidation of Cr(110) with 10 to 20 L of oxygen at 625 K followed by annealing in vacuum at 925 K [55, 56].

According to a study of water molecules on these surfaces, dissociative and molecular adsorption of water molecules have been seen on terrace sites [54], as well as dissociative adsorption on defect sites [55]. Studies of water on this surface have been done in our lab on a single crystal surface cleaned by 2 keV Ar⁺ ion sputtering, oxidation, mild sputtering and annealing to create a nearly-stoichiometric surface following the recipes of the Henderson et al., and also on a surface simply prepared by sputter-cleaning with 2 keV Ar⁺ ions then annealing at 900 K to order the surface [30]. The result has shown water desorption from the molecular and dissociated forms of water from both surfaces, consistent with the studies of the previous groups. In addition, traces of D₂ desorption have been seen from the sputtered and annealed surface, due to some defect sites which comprises less than 1% of the total surface Cr site density. The sputtered-annealed surface is thought to be identical to the nearly-stoichiometric surface except for the 1% of defect sites. The sputter-anneal preparation method has been therefore utilized in this study due to the simplicity of treatment, and since it keeps the background pressure of the chamber low.

1.5.3. The α-Fe₂O₃(1012) surface

The ideal, stoichiometric α-Fe₂O₃(1012) surface is structurally similar to the Cr₂O₃(1012) surface. The surface Fe³⁺ cations are 5-fold coordinated with oxygen anions with the cations separated by 3.71 Å. The surface has a rectangular periodicity with a ratio of sides
Figure 1.5. Top view of the ideal, stoichiometric $\alpha$-Cr$_2$O$_3$(0001) model surface.
a/b=0.93. The ideal, stoichiometric surface terminates the [O,Fe,O,Fe,O] repeat unit of the bulk, forming a non-polar surface.

A bulk terminated α-Fe₂O₃(10̅12)-(1×1) surface can be prepared by ion bombardment and annealing in a background of O₂ [50, 57, 58]. However, α-Fe₂O₃ is more reducible than α-Cr₂O₃, and heating in vacuum above 700 K induces a (2×1) reconstruction associated with the reduction of Fe³⁺ surface cations to Fe²⁺ [50, 57, 58]. The structure of the (2x1) reconstructed surface is thought to be associated with one oxygen vacancy for every two surface unit cells along the direction perpendicular to the zig-zag rows of the outermost oxygen layer, resulting in the reduction of the underlying Fe³⁺ cations to Fe²⁺ [50, 57]. However, no detailed atomic-resolution STM study of this surface is available in the literature.

1.6. Methods

1.6.1. Experimental

Most experiments were conducted in an ion-pumped, ultra-high vacuum chamber with a base operating pressure of 1 × 10⁻¹⁰ Torr. The chamber is equipped with a Physical Electronics model 15-555 single-pass CMA for Auger electron spectroscopy (AES), an Inficon Quadrex 200 mass spectrometer for thermal desorption experiments, and a Princeton Research Instruments model RVL 8-120 reverse view low-energy electron diffraction (LEED) optics. A primary electron energy of 5 keV was used for AES, and the measurements were collected at 850 K to compensate for charging on the α-Cr₂O₃(0001) surface, while they were collected at room temperature for the α-Fe₂O₃(10̅12) surface. A broad-beam ion gun was used for sample cleaning.
The crystals were oriented to within 1° of the (0001) surface using Laue backreflection and polished to a final mirror finish with 0.25 μm diamond paste. The samples were mechanically clamped onto a tantalum stage that was fastened to LN₂-cooled copper conductors. Direct sample temperature measurement was achieved with a type K thermocouple attached to the back of the single crystals through a hole in the stage using an Areco No. 569 ceramic cement. A heating ramp of 2.5 K/s was used in temperature-programmed desorption (TPD).

Soft X-ray photoelectron spectroscopy (XPS) has been performed for the reactions on the α-Cr₂O₃(0001) surface in a separate vacuum system at the U12a beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. C 1s and Cl 2p photoemission spectra were collected at an instrumental resolution of 0.5 eV using 350 eV photons while I 3d spectra were collected using 700 eV photons. The spectra are referenced to a Cr 2p₃/₂ binding energy of 576.9 eV [59]. For the data taken at \( h\nu = 350 \) eV, the Cr 3p photoemission feature was used as an internal reference and compared to the Cr 2p₃/₂ feature in separate runs using \( h\nu = 650 \) eV. Compensation for surface charging during the XPS was achieved with a Gammadata Scienta FG-300 flood gun using 0.5 eV electrons. The base operating pressure for this system was \( 1 \times 10^{-10} \) Torr.

A nearly-stoichiometric α-Cr₂O₃(0001) surface was prepared by 2 keV Ar⁺ ion-bombardment and annealing at 900 K. Following the preparation, AES was used to check for surface cleanliness and LEED was used to confirm the hexagonal (1x1) periodicity characteristic of a simple bulk termination of the bulk material (Figure 1.6). AES spectra were collected at 850 K and LEED was done at 600 K to avoid sample charging.
Figure 1.6. (a) AES spectrum of the prepared nearly-stoichiometric $\alpha$-Cr$_2$O$_3$(0001) surface which shows that the surface is clean after the treatment. Spectrum has been collected at 800 K to avoid sample charging. (b) LEED of the prepared nearly-stoichiometric $\alpha$-Cr$_2$O$_3$(0001) surface shows hexagonal (1x1) periodicity. Picture is the diffraction pattern observed at 600 K to avoid sample charging with 93 eV beam energy.
A nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2)-(1×1) surface was prepared by 500 eV Ar$^+$ ion bombardment and annealing of the single crystal in a background of $1.0 \times 10^{-6}$ torr O$_2$ at 700 K, following the preparation method of Henderson et al. [60] Following the preparation, AES was used to check for surface cleanliness and LEED was used to confirm the rectangular (1x1) periodicity characteristic of a simple bulk termination of the bulk material (Figure 1.7).

Gas dosing was accomplished by backfilling the chamber through a variable leak valve, and the reported dose sizes have been corrected for ion gauge sensitivity. The ion gauge sensitivities of the dosed molecules were calculated using an empirical formula from S. George and reported in the work of Brainard and Madix [61], which is based on the total number of electrons for hydrocarbons and alkyl halides. However, the accuracy of this correlation may depend on the molecule and the number of halogen atoms contained therein, and no further information is available about the correlation. It should be noted that uncertainty in the ion gauge sensitivity leads to some uncertainty in the dose size.

The activation barriers for first-order processes have been estimated throughout this document using Redhead method assuming a first-order pre-exponential of $10^{13}$ s$^{-1}$. This “normal” pre-exponential for first-order processes has been used due to a lack of knowledge about the pre-exponential factors for reactions such as methylene migration and methyl dehydrogenation. This leads to uncertainty in the activation barriers calculated due to the assumed pre-exponential factor: a change in the pre-exponential of three orders of magnitude may result in a change in the barrier by about 6 kcal/mol for a peak centered at 480 K.
Figure 1.7. (a) AES spectrum of the prepared nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(10\bar{1}2) surface which shows that the surface is clean after the treatment. Spectrum has been collected at room temperature. (b) LEED of the prepared nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(1012) surface shows rectangular (1x1) periodicity. Picture is the diffraction pattern observed at room temperature with 52 eV beam energy.
Normally, pre-exponential factors may be estimated by varying the heating rate and plotting against the peak temperatures using the Redhead analysis. However, this method was not used for this study since fast heating of the metal oxide samples may result in thermal fracture, while the heating rates need to be varied by at least two orders of magnitude for a reasonable accuracy for the pre-exponential [49].

1.6.2. Computational

Computational investigations have been done for the study of the reactions on the α-Cr$_2$O$_3$(0001) surface. All calculations were performed using the projector-augmented-wave method [62, 63] within the Vienna Ab-initio Simulation Package (VASP) of Kresse and Hafner [64-66]. The Perdue-Burke-Ernzerhof (PBE) approximation was used to treat exchange and correlation utilizing a standard generalized gradient approximation (GGA) of Perdew and Wang [67, 68].

The zero-pressure minimum-energy volume was found for the bulk cell by varying both cell edges and the positions of the non-equivalent atoms for a 120-atom primitive unit cell which is six stoichiometric [Cr, 3O, Cr] repeat units deep. A geometry-optimized 80-atom unit cell with a vacuum gap of 20 Å was used for all subsequent surface geometry optimizations. For all calculations, the $k$-point sampling was generated using a Monkhorst-Pack scheme [69]. A 3×3×3 mesh has been found to be sufficient to ensure convergence of the structure and energy for bulk structure calculations, while a 2×2×1 mesh was found to be sufficient for surface calculations considering the limitation of computing time needed for the calculation of the minimum-energy pathways. For all geometry optimized structures, the forces on the individual atoms is less than 0.01 eV/Å. The unit cell includes four surface unit cells and is four stoichiometric [Cr, 3O, Cr]
repeat units deep, with the two lower repeat units fixed at bulk positions. The initial magnetic moments of the Cr$^{3+}$ cations ($d^3$) were set as [+3, -3, +3, -3] in the direction going into the bulk perpendicular to the surface, following the antiferromagnetic order of the crystal [70], which is also calculated to be the ground-state magnetic order using DFT calculations within the GGA [45]. The minimum energy pathways (MEPs) for surface reactions were investigated using the climbing-image nudged elastic band method (CI-NEB) [71-74].

DFT calculations are known to have difficulties in predicting the properties of strongly correlated oxide materials, often greatly underevaluating the band gap [75-77]. It has been shown that this problem can be overcome with the inclusion of on-site Coulomb repulsion (DFT+U) [78]. A DFT study using VASP demonstrates this for α-Cr$_2$O$_3$ and α-Fe$_2$O$_3$ systems [45]. The study shows that an on-site potential of U=5.0 and J=1.0 leads to an acceptable compromise between the structural and electronic properties for the bulk α-Cr$_2$O$_3$. In the current study, calculation results for both DFT and DFT+U are presented for comparison. The DFT+U method in the form proposed by Dudarev et al. [79] has been used. It must be pointed out, however, that the optimal value of the on-site potential for the bulk may not strictly apply to the surface [45].

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Chapter 2.

Reactions of methylene groups on a model chromia surface: A study of dichloromethane on stoichiometric α-Cr₂O₃(0001)

2.1. Introduction

Studies of the reaction of methylene (=CH₂) on metal surfaces indicate that CH₂ decomposition to surface carbon (2.1) is the dominant reaction pathway on most transition metal surfaces. CH₂ hydrogenation to methane (2.2) has been reported for a number of surfaces [1-9], and methylene coupling to form ethylene is also observed [3, 5, 7, 9-11]. Studies of methyl and methylene species on copper surfaces indicate that methylene migrates on the surface to couple directly with other methylene forming ethylene (2.3), or couple with methyl groups formed by the hydrogenation of methylene to form adsorbed ethyl groups (2.4), which go through β-H elimination to produce ethylene and adsorbed hydrogen (2.5) [10, 11].

\[ =\text{CH}_2\,\text{(ads)} \rightarrow \text{C}\,\text{(ads)} + 2\,\text{H}\,\text{(ads)} \quad \text{(2.1)} \]

\[ =\text{CH}_2\,\text{(ads)} + 2\,\text{H}\,\text{(ads)} \rightarrow \text{CH}_4\,\text{(gas)} \quad \text{(2.2)} \]

\[ =\text{CH}_2\,\text{(ads)} + =\text{CH}_2\,\text{(ads)} \rightarrow \text{CH}_2=\text{CH}_2\,\text{(gas)} \quad \text{(2.3)} \]

\[ =\text{CH}_2\,\text{(ads)} + =\text{CH}_3\,\text{(ads)} \rightarrow =\text{CH}_2\text{CH}_3\,\text{(ads)} \quad \text{(2.4)} \]

\[ =\text{CH}_2\text{CH}_3\,\text{(ads)} \rightarrow \text{CH}_2=\text{CH}_2\,\text{(gas)} + \text{H}\,\text{(ads)} \quad \text{(2.5)} \]

It has been proposed that the rate of ethylene formation is controlled by the rate of CH₂ diffusion [11]. Bond-order/Morse potential calculations predict a near zero activation energy for CH₂ coupling on Cu(111), which implies that the measured activation energy for the reaction is attributable to methylene surface diffusion [12, 13]. Methane, surface carbon, and H₂ are formed.
through the dehydrogenation of methylene in addition to the formation of ethylene [5, 6, 11, 14, 15]. Methylene hydrogenation to methane requires the formation of a methyl intermediate in the reaction pathway. The dehydrogenation of methylene has been proposed as the rate-limiting step for methane production from methylene intermediates, and is the source of hydrogen for the hydrogenation of methylene [5, 6, 11, 15].

Dehydrogenation of surface methylene can be expected to form either methylidyne intermediates (≡CH$_\text{ads}$) or surface carbon. On Ni(111) the reaction of methyl fragments to acetylene is thought to occur through methylidyne coupling [15]. On Al(111), surface methylidyne formed by methyl fragment dehydrogenation undergoes dehydrogenation to H$_2$ and surface carbon [16].

In a previous study from our group on a model α-Cr$_2$O$_3$(10̅12) single crystal surface [17], it has been found that methylene intermediates migrates across the surface to couple with one another to produce ethylene (2.3), or can insert into methyl groups forming surface ethyl (2.4), then go through a β-H elimination to form ethylene (2.5). They also couple with surface hydrogen to produce methane (2.2). Two pathways for the migration of methylene on α-Cr$_2$O$_3$(10̅12) have been found with DFT calculations: one that goes through the valleys of the corrugated surface by direct migration between neighboring cations, and one that goes over the hills of coordinatively unsaturated oxygen anions to the nearest neighboring cation on the other side of the oxygen ridge (Figure 1.1) [18]. The migration of methylene species across the surface to couple with surface methylene or methyl is a phenomenon reported on metal surfaces, but to our knowledge, not observed previously on metal oxide surfaces.
In this chapter, the reaction chemistry of methylene intermediates will be studied on the \(\alpha\text{-Cr}_2\text{O}_3(0001)\) surface by the reaction of dichloromethane (\(\text{CH}_2\text{Cl}_2\)). The reaction of methylene intermediates on this surface will be compared to the reaction on the \(\alpha\text{-Cr}_2\text{O}_3(10\overline{1}2)\) surface to determine if the reactions are structure sensitive, and investigate the effect of multiple coordination vacancies on methylene coupling as described in Chapter 1.

### 2.2. Experimental

Sigma-Aldrich dichloromethane (\(\text{CH}_2\text{Cl}_2\)), anhydrous \(\geq 99.8\ %\), Sigma-Aldrich “100 %”, 99.96 atom % D dichloromethane-d\(_2\) (\(\text{CD}_2\text{Cl}_2\)), Matheson CP grade 99.7 % deuterium (D\(_2\)), and Aldrich 99.9 atom % D deuterium oxide (D\(_2\)O) were used as received. Gas dosing was accomplished by backfilling the chamber through a variable leak valve. The reported dose sizes have been corrected for ion gauge sensitivity, and all desorption traces and quantities have been corrected for mass spectrometer sensitivity.\(^2\) The nearly-stoichiometric surface has been prepared by 2 keV \(\text{Ar}^+\) ion-bombardment of the \(\alpha\text{-Cr}_2\text{O}_3(0001)\) single crystal and annealing at 900 K. The temperature ramp for TPD starts from 90 K and is linearly increased with a rate of 2.5 K/sec up to 830 K.

### 2.3. Results

Thermal desorption experiments for adsorbed dichloromethane result in two gas phase products: ethylene (\(\text{CH}_2=\text{CH}_2\)) and methane (\(\text{CH}_4\)). Multiple \(m/z\) signals were monitored simultaneously during the thermal desorption experiments, then compared to the mass

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\(^2\) An ion gauge sensitivity of 6.2 was used for dichloromethane using a correlation by S. George as reported by Brainard and Madix [19]. It should be noticed that this method is not strictly accurate, and there is an uncertainty associated with the calibration of the dosage. Relative mass spectrometer sensitivity factors of 0.15 for methyl chloride (\(m/z\ 84\)), 0.23 for ethylene (\(m/z\ 27\)), and 0.66 for methane (\(m/z\ 16\)) were determined experimentally.
spectrometer fragmentation patterns of the suspected molecules to identify the products. $m/z$ signal of 84 and 49 were used to identify the dosed CH$_2$Cl$_2$ molecule while $m/z = 28, 27, 26, 25$ were used for the identification of ethylene, and $m/z = 16, 15, 14$ were used to identify methane. Contributions of the dosed molecule signal to the product signals were corrected by subtracting the signal out according to the mass spectrometer fragmentation pattern of the dosed molecule. Other products were excluded by checking $m/z$ values in the range of 2 to 200. No CO, CO$_2$, or chlorinated gas phase reaction products were observed, indicating that the surface is non-reducible.

2.3.1. TPD of CH$_2$Cl$_2$

Figure 2.1 shows the thermal desorption of products after a 0.05 L (1 L = 1×10$^{-6}$ Torr·sec) dose of CH$_2$Cl$_2$ on a clean, nearly-stoichiometric (0001) surface at 90 K that was heated linearly up to 830 K. A small dose size is used to minimize the effect of adsorbed chlorine on the kinetics and selectivity of the methylene reaction. The products observed are ethylene and methane with unreacted CH$_2$Cl$_2$ desorbing around 290 K. Two features of ethylene are seen around 300 and 480 K, and methane is produced at 510 K with a shoulder about 50 K higher. The lack of any singly-chlorinated reaction products is one of the indications that methylene is formed by the cleavage of both C-Cl bonds of CH$_2$Cl$_2$.

2.3.1.1. Ethylene production

Ethylene dosed directly on this surface desorbs in TPD around 300 K (not shown), indicating that the ethylene production from CH$_2$Cl$_2$ (Figure 2.1) at 300 K is desorption-limited. Taking account of the small dose size, the reaction-limited ethylene peak at 480 K is thought to
Figure 2.1. TPD following a 0.05 L dose of CH₂Cl₂ on the clean, nearly-stoichiometric α-Cr₂O₃(0001).
be formed by a diffusion-limited process where methylene species migrate across the surface to couple with one another to form ethylene. In support of this idea, it is noted that computational studies on Cu(111) suggest a near-zero activation energy for the coupling of methylene intermediates bound on a metal site [12, 13]. DFT studies on α-Cr₂O₃(0001) (described below) also indicate a near-zero activation energy for coupling of two methylenes at a cation site on this surface. Therefore, the rate-limiting step for the ethylene production at 480 K is assigned to be the migration of methylene species rather than the coupling (C-C bond formation) step. The apparent first-order activation energy barrier calculated using Redhead method is 30.3 kcal/mol (1.31 eV) assuming a pre-exponential factor of 10¹³ s⁻¹[20]³. The desorption-limited ethylene at 300 K is therefore thought to arise from a methylene coupling pathway that does not require the migration of methylene: most likely the coupling of two methylenes bound at a single chromium center given the multiple coordination vacancies available at the surface chromium cations.

In addition to the data for the small 0.05 L doses shown in Figure 2.1, the thermal desorption behavior has been examined over a range from 0.05 L to 0.5 L doses sizes. No significant variation in the ethylene desorption temperature is observed, indicating that the desorption temperature is independent of coverage, and the rate-limiting step is therefore first-order [20].

2.3.1.2. Methane production

Methane is formed with a maximum rate at 510 K, with a shoulder about 50 K higher (Figure 2.1). The methane peak at 135 K is attributed to the desorption of physisorbed methane formed in the ion pump from the dosed gas. For methane to be generated from methylene, the

³ A “normal” arbitrary pre-exponential factor of 10¹³ s⁻¹ has been used to estimate the activation energy for a given peak temperature for first-order processes. The uncertainty in the activation barrier due to the unavailability of the exact pre-exponential factor for methylene migration should be recognized.
expected route would be the dehydrogenation of methylene to form surface H, with the
subsequent hydrogenation of the methylene groups with the liberated hydrogen to form surface methyl and methane. Methylene dehydrogenation is expected to have a higher activation barrier
than methyl dehydrogenation. However, the peak temperature of 510 K is near the temperature
where methyl dehydrogenation occurs (see Chapter 3), raising suspicion that methylene
dehydrogenation is not the source of the hydrogen for methane production from methylene. In
addition, no H\textsubscript{2} desorption (another likely reaction product of surface H atoms) is observed.
Lastly, complete dehydrogenation to form surface carbon might be expected if the
dehydrogenation of methylene occurs, however, no surface carbon is observed in post reaction
AES (to be shown below).

\subsection*{2.3.2. TPD of CD\textsubscript{2}Cl\textsubscript{2} and side reaction chemistry}

To examine the source of hydrogen for the formation of methane, a TPD study of the
reaction of CD\textsubscript{2}Cl\textsubscript{2} has been performed. If the methane formed from this reactant is CD\textsubscript{4}, it
would indicate that the hydrogen source for the hydrogenation of methylene to methane is the
dehydrogenation of methylene. Otherwise, if the methane formed contains H atoms rather than D
atoms, it would indicate a different hydrogen source.

Figure 2.2 shows the types of methanes formed from the reaction of CD\textsubscript{2}Cl\textsubscript{2}. The
majority of the methane produced is CD\textsubscript{2}H\textsubscript{2} at 510 and 575 K, similar to the CH\textsubscript{4} production
from CH\textsubscript{2}Cl\textsubscript{2} (Figure 2.1). A smaller desorption feature for CD\textsubscript{3}H appears to be a combination of
two peaks aligned at the main methane peak temperature (510 K) and the shoulder temperature
(575 K), while an even smaller feature of CD\textsubscript{4} is seen primarily at 575 K. This dataset indicates
that the source of hydrogen for the formation of the majority of methane formed from methylene
Figure 2.2. Methane production from the reaction of an 0.05 L dose of CD₂Cl₂ on the clean, nearly-stoichiometric α-Cr₂O₃(0001).
is a source other than the D atoms expected from dehydrogenation of deuterated methylene from the dosed CD₂Cl₂ molecule.

In a separate set of D₂ TPD experiments (not shown), D₂ desorbs from the clean, nearly-stoichiometric surface at 100 K. This weak interaction of D₂ (or H₂) suggests that background H₂ is not the likely source of the H atoms for the formation of methane from methylene. That leaves background water as the likely source of hydrogen. H₂O is known to adsorb in both dissociative and molecular forms on the Cr₂O₃(0001) surface according to a study by Henderson et al. [21] Furthermore, a recent study in our lab identified trace amounts of D₂ production around 800 K from D₂O TPD on Cr₂O₃(0001), a process thought to be due to a small concentration of surface defects [22].

In a separate TPD experiment, D₂O was preadsorbed then heated to 600 K, a temperature that is higher than the desorption temperatures of molecular and dissociative D₂O, but lower than the D₂ desorption attributed to surface defects (800 K). The sample was then cooled and a CH₂Cl₂ TPD run was done. The preadsorption was done in an effort to generate surface species from D₂O molecules bound to defect sites that are responsible for trace D₂ production. If these species are responsible for the methane production, the resulting methane formed from the =CH₂ intermediate would be CD₂H₂. CD₂H₂ was produced around 490 K (not shown), indicating that the origin of the hydrogen for methane formation from methylene (=CH₂) is likely background water.

Coming back to the discussion of CD₂Cl₂ TPD, the main peak temperature of 515 K for the CD₂H₂ production (Figure 2.2) is around the temperature for methyl dehydrogenation (see Chapter 3). It is presumed that surface H adds to =CD₂ to form −CD₂H (2.6), which goes through
a dehydrogenation step to liberate either H (2.7a) or D (2.7b), then combines with the remaining –CD₂H to form CD₂H₂ (2.8) or CD₃H (2.9).

\[ =\text{CD}_2\text{(ads)} + \text{H (ads)} \rightarrow -\text{CD}_2\text{H (ads)} \]  
(2.6)

\[ -\text{CD}_2\text{H (ads)} \rightarrow =\text{CD}_2\text{(ads)} + \text{H (ads)} \quad \text{(rate-limiting step)} \]  
(2.7a)

\[ -\text{CD}_2\text{H (ads)} \rightarrow =\text{CDH (ads)} + \text{D (ads)} \quad \text{(rate-limiting step)} \]  
(2.7b)

\[ -\text{CD}_2\text{H (ads)} + \text{H (ads)} \rightarrow \text{CD}_2\text{H}_2 \text{(gas)} \]  
(2.8)

\[ -\text{CD}_2\text{H (ads)} + \text{D (ads)} \rightarrow \text{CD}_3\text{H (gas)} \]  
(2.9)

The rate-limiting step for methane production is the dehydrogenation of –CD₂H (2.7a), (2.7b) for the production of methane at 515 K since it is near the methyl dehydrogenation temperature (Chapter 3). The calculated semiclassical ratio of the rate constants for the C-H bond scission and C-D bond scission, \( \frac{k_\text{H}}{k_\text{D}} \), is 2.86 at 515 K. Since –CD₂H has two deuterium and a single hydrogen, the rate of H elimination should be approximately 1.43 times the rate of D elimination. Therefore, the amount of CD₂H₂ formed at 515 K should be 1.43 times the amount of CD₃H formed at 515 K. However, the experimental value is 4.3. This indicates the possibility of H/D exchange between a D atom on a methylene/methyl intermediate and surface H atoms, possibly forming –CDH₂. In the case of –CDH₂ dehydrogenation only, the calculated release of H atoms should be 5.72 times faster than the production of D atoms. The experimental ratio of CD₂H₂ and CD₃H production amount is 4.3, which is between 1.43 and 5.72, consistent with the presumption that hydrogen-deuterium exchange may occur on the surface.

A separate experiment has been done with ethyl chloride (CH₃CH₂Cl) to investigate the reaction chemistry of ethyl (–CH₂CH₃) intermediates on the Cr₂O₃(0001) surface. The result
shows two β-H elimination routes at 390 and 560 K to produce ethylene. The shoulder temperature of 565 K for the formation of CH$_4$ from =CH$_2$ (Figure 2.1) coincides with the higher temperature β-H elimination route from surface ethyl, and the shoulder temperature of 575 K for the formation of CD$_2$H$_2$ from =CD$_2$ is also within the same range. Isotopically-labeled methyl (−CD$_3$) and methylene (=CH$_2$) studies are reported in Chapter 3 in order to investigate the mechanisms that produces ethylene from methyl fragments. This study confirms a route for methylene insertion into surface methyl groups to form ethyl intermediates (2.10), then the β-H elimination of the ethyl groups to produce ethylene (2.11).

\[ =\text{CH}_2\text{(ads)} + \text{−CH}_3\text{(ads)} \rightarrow \text{−CH}_2\text{CH}_3\text{(ads)} \quad (2.10) \]

\[ \text{−CH}_2\text{CH}_3\text{(ads)} \rightarrow \text{CH}_2=\text{CH}_2\text{(gas)} + \text{H}\text{(ads)} \quad (2.11) \]

The methane shoulder at 575 K from =CD$_2$ is explained by this mechanism. =CD$_2$ migrates and inserts into −CD$_2$H forming −CD$_2$CD$_2$H (2.10), which goes through a rate-limiting β-H elimination (2.13a), (2.13b) via the high temperature route at 560 K seen from the ethyl chloride experiments. −H and −D are liberated from this process, then combines with −CD$_2$H to produce CD$_2$H$_2$ and CD$_3$H via reactions (2.8) and (2.9).

\[ =\text{CD}_2\text{(ads)} + \text{−CD}_2\text{H}\text{(ads)} \rightarrow \text{−CD}_2\text{CD}_2\text{H}\text{(ads)} \quad (2.12) \]

\[ \text{−CD}_2\text{CD}_2\text{H}\text{(ads)} \rightarrow \text{CD}_2=\text{CD}_2\text{(gas)} + \text{H}\text{(ads)} \quad \text{(rate-limiting step)} \quad (2.13a) \]

\[ \text{−CD}_2\text{CD}_2\text{H}\text{(ads)} \rightarrow \text{CDH}_2=\text{CD}_2\text{(gas)} + \text{D}\text{(ads)} \quad \text{(rate-limiting step)} \quad (2.13b) \]

\[ =\text{CD}_2\text{H}\text{(ads)} + \text{−H}\text{(ads)} \rightarrow \text{CD}_2\text{H}_2\text{(gas)} \quad (2.8) \]

\[ =\text{CD}_2\text{H}\text{(ads)} + \text{−D}\text{(ads)} \rightarrow \text{CD}_3\text{H}\text{(gas)} \quad (2.9) \]
The ethylene products formed in thermal desorption of CD$_2$Cl$_2$ are shown in Figure 2.3. In addition to the production of CD$_2$=CD$_2$ expected from the direct coupling of two methylenes (=CD$_2$) bound at the same Cr site (300 K) and the migration and coupling of methylenes (480 K), CDH=CD$_2$ is also produced at 515 K with a shoulder at 570 K. The production of CDH=CD$_2$ around 515 K is evidence for reactions (2.7a) and (2.7b): =CD$_2$ and =CDH intermediates are formed by the dehydrogenation of –CD$_2$H intermediates, and they migrate and couple to form CD$_2$=CD$_2$ and CD$_2$=CDH. The temperature of the slight shoulder of CDH=CD$_2$ around 570 K corresponds well to the high temperature route for β-H elimination (560 K) seen from ethyl chloride experiments. Therefore, the shoulder is evidence for the route of =CD$_2$ insertion into –CD$_2$H for the formation of –CD$_2$CD$_2$H (2.12), and the rate-limiting β-H elimination (2.13b).

Reaction (2.7b) does not seem to occur sufficiently to produce enough surface D to add to =CD$_2$ to form –CD$_3$ then CD$_4$ since no CD$_4$ is detected at 515 K (Figure 2.2). However, together with reaction (2.13b), enough D is liberated that CD$_4$ is produced in a detectable amount at 580 K (2.14), (2.15).

\[ =\text{CD}_2 \, (_{\text{ads}}) + \, \text{D} \, (_{\text{ads}}) \rightarrow -\text{CD}_3 \, (_{\text{ads}}) \]  
\[ (2.14) \]

\[ -\text{CD}_3 \, (_{\text{ads}}) + \, \text{D} \, (_{\text{ads}}) \rightarrow \text{CD}_4 \, (_{\text{gas}}) \]  
\[ (2.15) \]

2.3.3. Sequential CH$_2$Cl$_2$ doses: TPD and AES analysis

Figure 2.4 shows the AES spectrum of a clean, nearly stoichiometric Cr$_2$O$_3$(0001) (Figure 2.4 (a)), and the spectrum taken after a series of 0.05 L TPD runs CH$_2$Cl$_2$ with an accumulated dose of 7.15 L (Figure 2.4 (b)). Figure 2.4(a) shows the typical fingerprint of a clean Cr$_2$O$_3$ surface with Cr and O features in the range of 470-550 eV, and no signals for carbon or chlorine. Figure 2.4(b) shows a Cl LMM feature characteristic of Cl adatoms left on the surface following
Figure 2.3. Ethylene production from the reaction of an 0.05 L dose of CD\textsubscript{2}Cl\textsubscript{2} on the clean, nearly-stoichiometric α-Cr\textsubscript{2}O\textsubscript{3}(0001).
Figure 2.4. AES of the (a) clean Cr$_2$O$_3$(0001) surface before exposure to CH$_2$Cl$_2$ and (b) after CH$_2$Cl$_2$ TPD with a total exposure of 7.15 L.
the reaction of CH₂Cl₂ in TPD. No carbon signal is detected, indicating that complete
dehydrogenation of surface methylene to surface carbon does not occur to a significant extent.

Figure 2.5 shows the AES Cl/Cr ratio corrected by the sensitivity factors⁴ as a function of
total dose for a sequence of consecutive TPD runs beginning on a initially clean surface. The
Cl/Cr ratio increases with exposure to CH₂Cl₂ and levels out at a value around 0.22 (±0.02) for a
total dose of 0.5 L of CH₂Cl₂ or greater. This Cl/Cr value corresponds to a nearly monolayer
coverage of one Cl adatom per one surface Cr site (Cl/Cr=0.22).⁵

Figure 2.6 shows the integrated TPD signals corrected for mass spectrometer sensitivity
for each product for consecutive 0.05 L CH₂Cl₂ TPD runs as a function of the cumulative
CH₂Cl₂ exposure. The ethylene production decreases linearly with consecutive doses of CH₂Cl₂
over the range of doses where the Cl coverage increases linearly (Figure 2.6). The decrease in
ethylene production with increasing surface Cl coverage indicates reactive site blocking by Cl
adatoms. Methane production also decreases, but is relatively insensitive to the Cl coverage for
earlier doses. The fraction of carbon dosed as CH₂Cl₂ that becomes methane is 0.21 for the first
dose.

⁴ Due to the overlap between the primary peaks Cr L₂M₂3M₄5 (529 eV) and O KLL (503 eV), the intensity of the Cr
L₂3M₂3M₄₃ (489 eV) peak is used for the calculation of Cr signal intensity for quantification purposes [23]. The Cr
L₂3M₂3M₄₅ / Cr L₂3M₂3M₄₃ peak ratio from a standard Cr metal spectrum [24] is applied to the sensitivity factor of
the Cr L₂3M₂3M₄₅ peak to obtain the sensitivity factor for Cr L₂3M₂3M₄₅ (0.225). Cl KLL sensitivity factor of 1.03
was used [24].

⁵ The Cl/Cr ratio corresponding to a monolayer is estimated using an exponential decay method for signal intensity
with depth into the bulk for a 42⁰ emission off the surface normal (corresponding to the analyzer collection
geometry), assuming a mean free path of 10 Å for O KLL and Cr LMM AES features at kinetic energies of 503 and
489 eV estimated using the ‘universal’ curve [25].
Figure 2.5. AES Cl/Cr ratio for different amounts of exposure to CH$_2$Cl$_2$ for TPD on Cr$_2$O$_3$(0001). The error bar represents the error in Cl/Cr ratio measured after the same amount of CH$_2$Cl$_2$ dosed in different sets of the TPD experiment.

Figure 2.6. Integrated signals for each product for consecutive 0.05 L CH$_2$Cl$_2$ TPD runs as a function of cumulative CH$_2$Cl$_2$ exposure.
To demonstrate the effect of surface Cl adatoms on the reaction kinetics, the TPD signals of ethylene (Figure 2.7 (a)) and methane (Figure 2.7 (b)) are shown for five consecutive 0.05 L doses of CH$_2$Cl$_2$ starting on a clean, nearly-stoichiometric surface. According to the AES studies of the surface after consecutive TPD runs, the Cl coverages increase for each run. The peak temperatures of ethylene and methane do not show a significant shift for different Cl coverages, indicating that the surface Cl does not have a significant impact on the kinetics. However, the reaction probability is decreased with higher Cl coverage, yielding less reaction products due to the site-blocking of CH$_2$Cl$_2$ dissociation by Cl adatoms.

2.3.4. X-ray photoelectron spectroscopy

Figure 2.8 shows the synchrotron-based photoemission results (h$\nu$ = 350 eV) for the reaction of adsorbed dichloromethane. The clean, nearly-stoichiometric surface was dosed with 10 L of dichloromethane at 110 K, heated to the consecutively higher temperatures, and cooled between heatings to near 110 K for photoemission in an attempt to isolate the surface intermediates formed during the thermally-induced surface reaction of CH$_2$Cl$_2$.

C 1s XPS spectra are shown in Figure 2.8(a). The spectrum taken directly after dosing 10 L of dichloromethane at 110 K shows a single peak at a 287.4 eV binding energy. The high binding energy of this feature is attributed to the doubly chlorinated carbon of molecular CH$_2$Cl$_2$ [26, 27]. After heating the sample to 200 K to remove the multilayers, the feature is reduced in intensity while shifting to 286.9 eV, and a lower binding energy peak is formed at 284.0 eV which is within the range for a metal-bound hydrocarbon. With further heating of the sample to 270 and 300 K, the molecular CH$_2$Cl$_2$ feature is seen at 287.2 eV, and further decreases in intensity with only a small amount remaining for the 300 K spectrum. There is little change in
Figure 2.7. Change of signals for (a) ethylene and (b) methane for consecutive 0.05 L CH$_2$Cl$_2$ TPD runs.
Figure 2.8. (a) C 1s and (b) Cl 2p XPS spectra of Cr$_2$O$_3$(0001) dosed with 10 L CH$_2$Cl$_2$ at 110 K and heated to according temperatures ($h\nu = 350$ eV).
intensity of the low binding energy feature at 284.0 eV. Heating the surface further to 800K results in the loss of all but a trace C 1s features over the temperature range associated with product desorption observed in the thermal desorption experiments.

The Cl 2p spectra shown in Figure 2.8(b) exhibit a similar trend to the C 1s data. A partially resolved doublet of Cl 2p is observed with a 2p_{3/2} binding energy of 200.3 eV upon dosing at 110 K. This signal is assigned to the Cl atoms of molecular CH₂Cl₂ [26]. This feature decreases as the sample is heated and the multilayers are removed, while a feature for a lower energy doublet appears with a Cl 2p_{3/2} binding energy near 198.3 eV. The molecular (200.3 eV) contribution is mostly gone by 300 K, which is the temperature where CH₂Cl₂ desorption is observed in TPD for small doses, while the 198.3 eV doublet feature remains after heating the sample to 800 K. The low binding energy of the remaining Cl 2p doublet is characteristic of metal chloride [26], and is assigned to Cl adatoms bound at surface Cr sites, consistent with the site blocking effect by Cl seen in TPD experiments.

The C 1s and Cl 2p spectra clearly demonstrate that C-Cl bond cleavage occurs between 110 and 200 K since they both show the decrease in signals that correspond to the CH₂Cl₂ molecule and an increase in signals for surface-bound species. The C 1s spectra do not show any signal of singly-chlorinated carbon (285.5-286.5 eV, [27-29]), but only show that the unchlorinated carbon feature (284.0 eV) appears as the doubly-chlorinated carbon feature (287.4 eV) decreases for higher temperatures. This indicates that complete C-Cl bond dissociation of dichloromethane takes place forming surface methylene intermediates. Therefore, the metal-bound carbon feature at 284.0 eV is attributed to methylene bound at Cr sites. The binding energy of the C 1s features at 287.2 eV for the spectra taken at 270 and 300 K is within the range for both oxygenated carbons and chlorinated carbons. However, the majority of the signal left by
300 K is metal-bound carbon, and the Cl 2p spectra at 270 K shows that some small Cl contribution due to molecular CH$_2$Cl$_2$ remains on the surface. Therefore, the C 1s feature at 287.2 eV is attributed to a submonolayer coverage of molecular CH$_2$Cl$_2$ on the surface. The shift in the binding energy of this feature is presumably due to different binding modes of molecular CH$_2$Cl$_2$, also seen as multiple peaks of CH$_2$Cl$_2$ in thermal desorption for large dose sizes (not shown).

### 2.3.5. DFT simulations

Geometry optimization of methylene on different surface sites has been done on the 80-atom unit cell mentioned previously (Chapter 1) in the computational methods section. Three configurations were examined: methylene bound on top of a Cr center (atop methylene), methylene that bridges between a Cr and a neighboring O (short-bridging methylene), and methylene that bridges between a Cr and a second-nearest neighboring O (long-bridging methylene) (Figure 2.9). Methylene was not found to stabilize between two surface oxygens or at a 3-fold hollow site of O atoms with (DFT) or with the use of an on-site potential (DFT+U).

Figure 2.10 shows the relative free energies and magnetic moments of the binding configurations in Figure 2.9. The calculation without the on-site potential predicts that the atop methylene is the most stable configuration with the short-bridging and long-bridging configurations being 0.33 and 0.68 eV higher in energy, respectively. DFT+U predicts the short-bridging methylene to be the most stable configuration with the atop and long-bridging methylene being 0.78 and 0.28 eV higher in energy, respectively. The XPS result presented earlier indicates that the majority of the methylene is metal bound, indicating a preference for atop methylene.
Figure 2.9. Three possible configurations of methylene on the α-Cr₂O₃(0001) surface determined with DFT: (a) atop configuration, (b) short-bridging configuration, and (c) long-bridging configuration. Small blue spheres represent Cr cations, large red spheres O anions, small grey spheres carbon, and the white spheres hydrogen atoms.
Figure 2.10. (a) Relative free energies and (b) magnetic moments of the different methylene configurations on the 80-atom surface unit cell calculated with and without on-site potential for Cr.
The magnetization represents a change from the antiferromagnetic ground state (magnetization of zero) due to a change in the number of unpaired electrons caused by the binding of the adsorbate. The magnetization value of the atop methylene is 2.0000, characteristic of the double bond between the Cr and the =CH₂ carbene which results in two fewer unpaired electrons. The magnetic moment calculated for the short-bridging methylene was 1.0625 with DFT, and 0 with DFT+U, while both calculations for the long-bridging configuration agreed on a magnetization value of 0. The free energy of each configuration has been calculated with several manually set values of the different magnetic moments (e.g., mag = 0, 1, 2), and it has shown that the magnetization described above corresponds to the DFT ground state for each binding configuration.

The methylene migration pathway was examined using the climbing-image nudged elastic band (CI-NEB) method [30-33]. A single route for migration was found along the line that connects two neighboring Cr atoms (Figure 2.11). The migration involves the transition between the atop and the short-bridging, short-bridging and the long-bridging, and long-bridging and atop methylene configurations. Figure 2.12 shows the minimum energy pathway of the potential energy surface for the migration of methylene. The highest barrier transition states occur between the long-bridging and the atop configurations with overall activation barriers of 1.28 with DFT and 1.51 with DFT+U. The activation barrier calculated without the inclusion of on-site potential is in better agreement with the activation energy calculated from the TPD of CH₂Cl₂ using the Redhead method for a pre-exponential factor of 10¹³ (1.31 eV).
Figure 2.11. (a) Top view of the methylene migration pathway. Small blue balls represent Cr$^{3+}$, and large red balls correspond to O$^{2-}$. (b) The transition between methylene configurations along the methylene migration pathway.
Figure 2.12. The minimum energy pathway (MEP) calculated using the climbing-image nudge elastic band method calculated (a) without the on-site potential, and (b) with the on-site potential. The changes in net magnetization are shown on the secondary axis on the right hand side.
2.4. Discussion

2.4.1. The reaction chemistry of CH$_2$Cl$_2$ on α-Cr$_2$O$_3$(0001)

The lack of singly chlorinated species in TPD and XPS clearly demonstrates that both C-Cl bonds of dichloromethane are thermally cleaved, forming methylene intermediates and surface Cl adatoms. The small dose size used for the TPD experiment suggest that the reaction-limited ethylene peak at 480 K is formed by methylenes bound at different sites which migrate across the surface to couple with one another. DFT calculations demonstrate that the migration mechanism between atop cation sites is mediated by surface oxygen.

The chlorine adatoms deposited on the surface have little effect on the activation barriers for the production of ethylene and methane. However, the reaction probability is decreased with higher Cl coverage, yielding less reaction products due to the cation site-blocking of CH$_2$Cl$_2$ dissociation by Cl adatoms. The saturation AES Cl/Cr ratio of 0.22 is noticeable in that the reaction stops at a value that corresponds to one Cl per one surface Cr site, unlike the expectation that the surface cations might bind multiple Cl adatoms because of the multiple coordination vacancies available. This is presumably because Cl bound on Cr sites changes the oxidation state of the cations from Cr$^{3+}$ to Cr$^{4+}$ which prefers tetrahedral coordination rather than the octahedral coordination [34].

DFT calculations with and without the inclusion of on-site potential predict different trends for the relative free energy of the methylene binding configurations as well as the overall activation barrier for the methylene migration process. DFT predicts that the atop methylene is the most stable configuration, while DFT+U predicts that the short-bridging methylene is the most stable configuration. Using the activation barrier values from the DFT calculations, the
equilibrium fraction of the different methylene binding configurations as a function of temperature have been calculated for both case of DFT and DFT+U, assuming equal pre-exponentials in the forward and reverse directions (Figure 2.13). Up to the temperature where the reaction of methylene is completed in TPD (about 650 K), the prediction using the activation barrier from DFT suggests a fraction of both short and long bridging methylene of less than 1%. On the other hand, the result using the DFT+U prediction of the activation barrier yields a fraction of more than 99% for the methylene species in the short-bridged configuration for the temperature range associated with the reaction seen with TPD.

According to the XPS result, the majority of methylene exists in the form of atop methylene as seen in the C 1s spectrum at 300 K, more in agreement with the DFT prediction. In addition, the activation energy barrier for methylene migration calculated with DFT (1.28 eV) is closer to the experimental value calculated from the TPD data (1.31 eV) than that calculated with DFT+U (1.51 eV). These results show that the inclusion of the on-site potential is not beneficial for describing the chemical behavior of methylene on the α-Cr₂O₃(0001) surface. These results are contrary to the other studies in which the inclusion of the on-site potential significantly improves the predictions for the electronic properties such as band gap of the bulk and the surface of strongly correlated oxide materials [35, 36]. It is also contrary to our own results from a separate study in which the on-site potential is necessary in explaining the binding site of methyl species on this same surface (Chapter 3). The results imply that the inclusion of the on-site potential in compensating the d-electron delocalization caused by the self-interaction error may not be suitable for predicting the chemistry of adsorbed carbene species.

The activation barriers for surface diffusion between the atop and bridging configurations are much higher than the barriers between the short and long bridging configurations for both
Figure 2.13. Equilibrium fraction of the different methylene configurations calculated using the activation energies from (a) DFT and (b) DFT+U assuming equal pre-exponentials in the forward and reverse directions of the equilibrium.
DFT and DFT+U calculations. The transition state between the atop and bridging configurations involves a thermally driven rehybridization between sp² and sp³ methylene binding configurations. While the barrier to thermal rehybridization driving the surface diffusion of methylene is significant, it is seen from experiment to be clearly lower than the barrier to methylene dehydrogenation. Hence, the migration and coupling of methylene to ethylene is favored over the dehydrogenation of methylene to surface carbon.

2.4.2. Structure sensitivity of methylene reactions

On the α-Cr₂O₃(10̄12) surface, two methylene migration routes were found at 300 and 390 K (activation barriers of 18.7 and 24.4 kcal/mol). The low-barrier route is attributed by DFT investigations to the direct migration between two Cr cations, while the high-barrier route is attributed to an oxygen-mediated path. On the α-Cr₂O₃(0001) surface, a single oxygen-mediated migration route is found at 480 K (activation barrier of 30.3 kcal/mol), because paths between neighboring Cr’s are equivalent in all directions (Figure 2.14), and the long Cr-Cr distance (4.9 Å) disables direct Cr to Cr migration. The barriers of the oxygen-mediated migration paths are related to the rehybridization of the methylene between the sp² and sp³ configurations, and the higher barrier for methylene migration occurs on the α-Cr₂O₃(0001) surface. Direct coupling of methylene bound to a single cation site only occurs on the α-Cr₂O₃(0001) surface since the surface cations have multiple coordination vacancies, in contrast to the cations on the α-Cr₂O₃(10̄12) surface which have a single coordination vacancy. Since most of the methane produced from methylene on the two surfaces is the result of the interaction with background water, the selectivity between ethylene and methane does not have a significant meaning as it varies depending on the amount of background water in the chamber. Hence, a direct comparison of the selectivity of products from methylene is not particularly informative.
Figure 2.14. Ball model illustration of the ideal nearly-stoichiometric $\alpha$-Cr$_2$O$_3$ (0001) surface showing straight lines between a Cr and neighboring Cr’s that are equivalent in all directions. Small grey spheres represent Cr$^{3+}$ cations and the large red spheres represent the O$^{2-}$ anions.
The structural differences of the two surfaces cause a 5.9 kcal/mol difference\(^6\) in the activation barrier for the oxygen-mediated methylene migration. However, the difference in the number of coordination vacancies of surface cations does not seem to play a crucial role in directing the production of ethylene. It appears that the similarity in the electronic configuration of the surface cations (\(d^3\)) resulted in the two surfaces producing the same kind of products via similar mechanisms.

2.5. Conclusions

Dichloromethane goes through a thermally-induced C-Cl bond cleavage to form methylene intermediates on \(\alpha\)-Cr\(_2\)O\(_3\) (0001). CH\(_2\)Cl\(_2\) TPD and DFT calculations show the first reported mechanism for methylene migration on an oxide surface. The calculations predict a migration route that involves a rehybridization from sp\(^2\) to sp\(^3\) binding modes of methylene that is mediated by surface oxygen anions. XPS results indicate that the lowest energy binding sites for methylene species are Cr cations. Comparison of the experimental and computational results indicates that DFT without the inclusion of on-site potential provides the best model for the chemistry of this adsorbed carbene species on \(\alpha\)-Cr\(_2\)O\(_3\) (0001). The observation of some desorption limited ethylene at 300 K in TPD also suggests that ethylene can be formed from direct coupling of methylene bound at a single surface Cr. In addition, methylene intermediates couple with hydrogen atoms from adsorbed water to form methane. Chlorine adatoms that are deposited during the reaction deactivate the surface by Cr site blocking.

\(^6\) This difference in activation energy barriers affects the rate of reaction by influencing the exponential parts of the rate constants (\(k = A \exp(-E_a/RT)\), k: rate constant, A: pre-exponential factor, \(E_a\): activation energy, R: gas constant, T: temperature). The exponential part of the rate constant is higher on \(\alpha\)-Cr\(_2\)O\(_3\) (1012) compared to that on \(\alpha\)-Cr\(_2\)O\(_3\) (0001) by about 2000 times at 390 K and 500 times at 480 K. In other words, the ratio of the rate constants are \(k_{10\overline{1}2}/k_{0001} = 2000 \cdot A_{10\overline{1}2}/A_{0001}\) at 390 K and \(k_{10\overline{1}2}/k_{0001} = 500 \cdot A_{10\overline{1}2}/A_{0001}\).
The comparison of the methylene reaction chemistry on $\alpha$-Cr$_2$O$_3$(0001) to that on $\alpha$-Cr$_2$O$_3$(1012) shows that the difference in the surface geometric structure affects the activation barrier for the oxygen-mediated methylene migration path. However, the two surfaces produce the same product slate through similar mechanisms, implying that the surface geometric structure does not play a critical role directing the production of ethylene although the kinetics of methylene are altered.

2.6. References


Chapter 3.

Reactions of methyl groups on a model chromia surface: A study of iodomethane on stoichiometric $\alpha$-Cr$_2$O$_3$(0001)

3.1 Introduction

Ultra-high vacuum surface science studies of the reaction of methyl, $\text{CH}_3$, intermediates on metal surfaces show that the most common reaction pathways of methyl are hydrogenation to produce methane and decomposition to surface carbon and hydrogen [1]. C-C bond formation to produce ethane is seen on silver and gold surfaces [2-4], while ethylene is produced on copper surfaces by the migration of methylene (=CH$_2$) intermediates formed from the dehydrogenation of methyl [5-7]. The methylene intermediates migrate across the surface to couple with one another, or insert into the remaining methyl groups to form ethyl, then go through a $\beta$-H elimination to produce ethylene.

In a previous study from our group on a model $\alpha$-Cr$_2$O$_3$(10\overline{1}2) single crystal surface [8], it has been found that surface methyls go through a rate-limiting dehydrogenation to form surface methylenes (3.1) which migrate across the surface to couple with one another to produce ethylene (3.2), or insert into methyl groups forming surface ethyl (3.3), which undergoes a $\beta$-H elimination to form ethylene (3.4), similar to earlier observations on metals. The liberated hydrogens from the dehydrogenation of methyl groups react with the remaining methyl groups to produce methane (3.5), or couple with one another to produce H$_2$ (3.6). No oxygenated products are observed because $\alpha$-Cr$_2$O$_3$(10\overline{1}2) is highly non-reducible.
\[-\text{CH}_3 \text{ (ads)} \rightarrow \text{=CH}_2 \text{ (ads)} + \text{H} \text{ (ads)}\]  
(3.1)

\[\text{=CH}_2 \text{ (ads)} + \text{=CH}_2 \text{ (ads)} \rightarrow \text{CH}_2=\text{CH}_2 \text{ (gas)}\]  
(3.2)

\[\text{=CH}_2 \text{ (ads)} + \text{=CH}_3 \text{ (ads)} \rightarrow \text{=CH}_2\text{CH}_3 \text{ (ads)}\]  
(3.3)

\[\text{=CH}_2\text{CH}_3 \text{ (ads)} \rightarrow \text{CH}_2=\text{CH}_2 \text{ (gas)} + \text{H} \text{ (ads)}\]  
(3.4)

\[\text{=CH}_3 \text{ (ads)} + \text{H} \text{ (ads)} \rightarrow \text{CH}_4 \text{ (gas)}\]  
(3.5)

\[\text{H} \text{ (ads)} + \text{H} \text{ (ads)} \rightarrow \text{H}_2 \text{ (gas)}\]  
(3.6)

In this chapter, the reaction chemistry of methyl intermediates will be studied on the $\alpha$-Cr$_2$O$_3$(0001) surface by the reaction of iodomethane (CH$_3$I). The reaction on this surface will be compared to the earlier results on the $\alpha$-Cr$_2$O$_3$(10T2) surface to determine if the reactions are structure-sensitive. Especially, the effect of geometrical proximity of surface lattice oxygen on the dehydrogenation of surface methyl, and the effect of the cation coordination environment on the coupling (C-C bond formation) reactions will be examined.

### 3.2 Experimental

Sigma-Aldrich iodomethane (CH$_3$I) 99.5 %, iodomethane-d$_3$ (CD$_3$I) 99.5 atom% D, Sigma-Aldrich dichloromethane (CH$_2$Cl$_2$), anhydrous $\geq$ 99.8 %, and Matheson CP grade 99.7 % deuterium ($\text{D}_2$) were used as received. Gas dosing was accomplished by backfilling the chamber through a variable leak valve. The reported dose sizes have been corrected for ion gauge sensitivity, and all desorption traces and quantities have been corrected for mass spectrometer sensitivity.\(^7\) The nearly-stoichiometric surface has been prepared by 2 keV Ar$^+$ ion-bombardment

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\(^7\) An ion gauge sensitivity of 9.5 was used for CD$_3$I using a correlation by S. George as reported by Brainard and Madix [9]. It should be noticed that this method is not strictly accurate, and there is an uncertainty associated with the calibration of the dosage. Relative mass spectrometer sensitivity factors of 0.05 for CD$_3$I (m/z = 145), 0.23 for CD$_2$=CD$_2$ (m/z = 32), and 0.66 for the methanes (m/z = 20 and 19) were determined experimentally.
of the α-Cr₂O₃(0001) single crystal and annealing at 900 K. A 2.5 K/sec temperature ramp was used for most TPD runs with a range from 90 K to 830 K.

3.3 Results

The reaction of CD₃I on the nearly-stoichiometric α-Cr₂O₃(0001) surface results in three gas phase products and a residual surface product: CD₂=CD₂, CD₄, CD₃H and surface I adatoms. Multiple m/z signals were monitored simultaneously during the thermal desorption experiments, then compared to the mass spectrometer fragmentation patterns of the suspected molecules to identify the products. A m/z signal of 142 was used to track the desorption of the dosed CD₃I molecule, while m/z = 32, 30, 28 were used for the identification of CD₂=CD₂, and m/z = 20, 19, 18, 17 for methane species. Contributions of the dosed molecule signal to the product signals were corrected by subtracting the m/z 142 signal from the desorption trace using an intensity based on the mass spectrometer fragmentation pattern of the dosed molecule. Other products were excluded by checking m/z values in the range of 2 to 200. No ethane (CD₃-CD₃), CO, CO₂, or chlorinated gas phase products were observed.

3.3.1 TPD of CD₃I

Figure 0.1 shows the thermal desorption traces following a 0.1 L dose of CD₃I on the freshly prepared, nearly stoichiometric surface at 90 K that was heated linearly up to 830 K. The peaks for the products CD₄, ethylene (CD₂=CD₂), CD₃H and D₂ occur simultaneously around 490 K with slight shoulders around 590 K, while the reactant molecule desorbs around 265 K. In addition, sharp methane features are seen around 110 K.

Ethylene, D₂, and methane dosed directly on the surface desorb in TPD around 300, 100,
Figure 0.1. TPD of 0.1 L CD$_3$I on the nearly-stoichiometric α-Cr$_2$O$_3$(0001).
and 110 K (not shown), respectively, indicating that the production of these molecules at 490 K from CD$_3$I are reaction limited. The simultaneous production of CD$_2$=CD$_2$, CD$_4$ and D$_2$ at 490 K suggests that they originated from a common surface intermediate with the same rate-limiting step. A rate-limiting step that can lead to the production of ethylene and methane from methyl species is the dehydrogenation of methyl: the methyl species dehydrogenate to methylene and surface deuterium atoms (3.7). A separate study of methylene species on this surface (Chapter 2) shows that methylene intermediates migrate across the surface to couple with one another to form ethylene at 480 K [10]. Thus, two methylene moieties formed by the dehydrogenation of methyl species may couple with one another to form ethylene (3.8). Another route for the production of ethylene from methyl and methylene intermediates exists, and will be discussed below in the coadsorption section (3.1.2). Methane (CD$_4$) is formed by the reaction of liberated deuterium with a remaining methyl group (3.9).

\[ \text{−CD}_3 \text{(ads)} \rightarrow =\text{CD}_2 \text{(ads)} + \text{−D (ads)} \]  
(rate-limiting) (3.7)

\[ =\text{CD}_2 \text{(ads)} + =\text{CD}_2 \text{(ads)} \rightarrow \text{CD}_2=\text{CD}_2 \text{(gas)} \]  
(3.8)

\[ \text{−CD}_3 \text{(ads)} + \text{−D (ads)} \rightarrow \text{CD}_4 \text{(gas)} \]  
(3.9)

In addition to the 0.1 L dose size illustrated in Figure 0.1, larger doses up to 0.5 L (not shown) were also examined. No variation in the product desorption temperature is seen for the varying coverages, indicating first-order kinetics of the rate-limiting dehydrogenation step. The activation energy barrier for the dehydrogenation of methyl at 490 K calculated using the Redhead method [11] for first-order kinetics is 30.9 kcal/mol (1.34 eV) assuming a normal pre-
exponential factor of $10^{13}$ s$^{-1}$.\textsuperscript{8} The methane desorption features near 110 K are due to the desorption of physisorbed methanes formed by the ionization and reaction of the CD$_3$I dosed molecules in the ion pump during the dosing procedure. Ethane (CD$_3$-CD$_3$) is not produced, indicating no direct coupling of methyl groups.

The origin of the hydrogen, H, for the formation of CD$_3$H must be a substance other than the dosed molecule (CD$_3$I) present on the surface. A separate study of methylene (≡CD$_2$) hydrogenation on this surface (Chapter 2) has shown CD$_2$H$_2$ production that is due to coupling with H atoms derived from adsorbed background water in the vacuum system [10]. Accordingly, the source of hydrogen for the formation of CD$_3$H from −CD$_3$ in the current study is also thought to be adsorbed background water. The coupling of −CD$_3$ and −H to form CD$_3$H occurs gradually over a wide range of temperatures beginning at the dosing temperature. The reason that a peak exists that aligns with the methyl dehydrogenation temperature (490 K) may be related to the exchange of hydrogen/deuterium between the deuterated surface methyl and the hydrogen from adsorbed water seen in Chapter 2: deuterated methyl, −CD$_3$, may undergo hydrogen-deuterium exchange to become −CD$_2$H.

Figure 0.2 shows the change of the integrated area for each reaction product with consecutive 0.1 L doses. The signals of the products CD$_4$ and CD$_2$≡CD$_2$ drop off for later runs, most likely due to a site-blocking effect by surface iodine adatoms. Iodine could not be detected with AES due to the overlap of the signal with the Cr LMM feature from the crystal. However, surface iodine is clearly seen in the XPS experiments described below. In a separate study of methylene reactions on this surface from the reaction of CH$_2$Cl$_2$ (Chapter 2), the reactivity is

\textsuperscript{8} A “normal” arbitrary pre-exponential factor of $10^{13}$ s$^{-1}$ has been used to estimate the activation energy for a given peak temperature for first-order processes. The uncertainty in the activation barrier due to the unavailability of the exact pre-exponential factor for methyl dehydrogenation should be recognized.
Figure 0.2. Integrated signals for each product for consecutive 0.1 L CD$_3$I TPD runs as a function of cumulative CD$_3$I exposure.
mostly gone by an AES Cl/Cr ratio that corresponds to a near monolayer coverage of one Cl per surface Cr site. It is presumed that this would be the case with changing iodine coverages during CD₃I TPD. The selectivity among the products from a clean surface for a 0.1 L dose is CD₄: CD₂=CD₂ = 1:0.6.

Considering the fact that it takes two methyl or methylene intermediates to produce an ethylene molecule, the probability of a methyl group producing either product is similar.

CD₃I TPD runs with different final ramp temperatures show that the maximum temperature of the run impacts the intensity of the product desorption signal for the subsequent run. When the final ramp temperature is lowered from 830 K to 700 K, there are larger decreases in the signal intensities for each successive run (not shown). This behavior is most possibly due to some unobserved desorption of iodine that happens at the higher temperature end of the TPD ramp that decreases the iodine coverage, thus site-blocking for the next TPD run. The desorption of iodine at high temperature may inhibit the iodine coverage from reaching saturation coverage of one I per surface Cr, explaining why the reactions do not completely shut down for later runs, as seen in Figure 0.2.

3.3.2 Methyl and methylene coad sorption study

As mentioned above, methyl intermediates undergo a rate-limiting dehydrogenation to methylene and surface deuterium (3.7), leading to the production of CD₄ and CD₂=CD₂.

$$-\text{CD}_3\,(\text{ads}) \rightarrow \text{=CD}_2\,(\text{ads}) + -\text{D}\,(\text{ads}) \quad \text{(rate-limiting)} \ (3.7)$$

There are, however, two possible pathways to produce ethylene from the dehydrogenation of methyl groups. As seen with the study of methylene species on this surface (Chapter 2), ethylene
can be produced by the migration of methylene intermediates that subsequently couple with one another (3.8). Another possibility is that the methylene species migrate and insert into the surface-carbon bond of remaining methyl groups to form surface ethyl (3.10), with these ethyl groups undergoing a subsequent $\beta$-D elimination process produce ethylene (3.11), as observed on metal surfaces [1].

$$\text{=CD}_2\text{(ads)} + \text{=CD}_2\text{(ads)} \rightarrow \text{CD}_2\text{=CD}_2$$ (3.8)

$$\text{=CD}_2\text{(ads)} + \text{=CD}_3\text{(ads)} \rightarrow \text{=CD}_2\text{CD}_3\text{(ads)}$$ (3.10)

$$\text{=CD}_2\text{CD}_3\text{(ads)} \rightarrow \text{CD}_2\text{=CD}_2 + \text{=CH}_2\text{(ads)}$$ (3.11)

To test whether the insertion pathway (3.10 and 3.11) is operable on this surface, an isotopically labeled coadsorption study has been done. 0.05 L CD$_3$I was dosed to form $\text{=CD}_3$ methyl fragments, and 0.05 L CH$_2$Cl$_2$ was dosed to form $\text{=CH}_2$ methylene fragments. A CH$_2$=CD$_2$ product would indicate the occurrence of the insertion and $\beta$-D elimination pathway since this product can be made by the insertion of $\text{=CH}_2$ into the $\text{=CD}_3$ carbon/surface bond forming $\text{=CH}_2\text{CD}_3$ (3.12). A final $\beta$-deuterium elimination step would then produce CH$_2$=CD$_2$ (3.13).

$$\text{=CH}_2\text{(ads)} + \text{=CD}_3\text{(ads)} \rightarrow \text{=CH}_2\text{CD}_3\text{(ads)}$$ (3.12)

$$\text{=CH}_2\text{=CD}_2\text{(ads)} \rightarrow \text{CD}_2\text{=CH}_2 + \text{=D}_2\text{(ads)}$$ (3.13)

The result (Figure 0.3) shows that CH$_2$=CH$_2$ and CD$_2$=CD$_2$ are produced at 465 and 490 K, similar to the temperatures where they are formed from CH$_2$Cl$_2$ and CD$_3$I, respectively. CD$_2$=CH$_2$ is also produced at 465 K at the same temperature as the CH$_2$=CH$_2$ production. This
temperature is lower than the −CD₃ dehydrogenation temperature, implying a coupling pathway associated with the diffusion of surface methylene (−CH₂).

Ethyl chloride TPD is compared in Figure 0.3 as a grey trace to demonstrate the reaction pathways of ethyl species on the surface. Two peaks of ethylene are seen at 395 and 555 K, representing two distinct reaction pathways associated with β-H elimination from ethyl on this surface. The origin of the two reaction channels is not well understood, but considering that there is only one pathway for β-H elimination on the Cr₂O₃(1012) surface, the multiple pathways are thought to be related somehow to the multiple coordination vacancies available on Cr₂O₃(0001) cation reaction sites. The CD₂=CH₂ peak temperature from the coadsorption experiment is higher than the 395 K pathway for β-H elimination of ethyl groups, but aligns with the methylene migration-limited CH₂=CH₂ production at 465 K. This suggests that the migration of methylene to find a methyl fragment is rate-limiting, rather than the insertion of methylene into the methyl groups or the β-H of ethyl groups. It is also notable that the bump on the high temperature side of the CD₂=CH₂ trace aligns with the 555 K pathway of the β-H elimination of ethyl groups. These results indicate that part of the ethyl formed via coupling goes through the high temperature β-H elimination channel. In this case, the rate limiting step is the β-H elimination.

3.3.3 X-ray photoelectron spectroscopy

Figure 0.4 shows the synchrotron-based photoemission results for the adsorbed iodomethane. The nearly-stoichiometric surface was dosed with 10 L of iodomethane at 110 K, heated to the listed temperatures, then cooled for the photoemission measurements in an attempt to isolate the surface intermediates formed during the thermally-induced surface reaction of CH₃I. Experiments were done separately to obtain the C 1s and the I 3d spectra since different
Figure 0.3. Ethylene products for 0.05 L CH$_2$Cl$_2$ and 0.05 L CD$_3$I coadsorption TPD. The grey line represents ethylene production from CH$_3$CH$_2$Cl TPD.
monochromator gratings were required for the selected photon energies. Is only one pathway for β-H elimination on the Cr₂O₃(1012) surface, the multiple pathways are thought to be related somehow to the multiple coordination vacancies available on Cr₂O₃(0001) cation reaction sites. The CD₂=CH₂ peak temperature from the coadsorption experiment is higher than the 395 K pathway for β-H elimination of ethyl groups, but aligns with the methylene migration-limited CH₂=CH₂ production at 465 K. This suggests that the migration of methylene to find a methyl fragment is rate-limiting, rather than the insertion of methylene into the methyl groups or the β-H of ethyl groups. It is also notable that the bump on the high temperature side of the CD₂=CH₂ trace aligns with the 555 K pathway of the β-H elimination of ethyl groups. These results indicate that part of the ethyl formed via coupling goes through the high temperature β-H elimination channel. In this case, the rate limiting step is the β-H elimination.

### 3.3.4 X-ray photoelectron spectroscopy

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C 1s XPS spectra for a photon energy of 350 eV are shown in Figure 0.4(a). The spectrum taken directly after dosing 10 L iodomethane at 110 K shows a single sharp peak at 285.0 eV binding energy. The high binding energy of this feature is attributed to the iodized
Figure 0.4. (a) C 1s and (b) I 3d$_{5/2}$ XPS spectra of Cr$_2$O$_3$(0001) dosed with 10 L CH$_3$I at 110 K and heated to according temperatures.
carbon of molecular CH₃I [2, 4, 12]. The feature broadens and decreases in intensity upon heating to 200 K to desorb multilayer CH₃I. Two apparent contributions are seen after heating to 325 K to desorb the remaining molecular CH₃I adsorbate. A broadened asymmetric feature extending from about 287 to 282 eV is seen following heating to 325 K, with a maximum at 286.0 eV. Since binding energies near 286 eV are typical of methoxy groups (-O-CH₃) [13], the XPS suggests some methyl fragments bind at surface oxygen anion sites. The low BE feature that ranges from 282 to 284 eV is attributed to Cr-bound methyls since typical binding energies for oxygenated carbons are 286 eV or higher [14]. A peak at 284.0 eV remains after heating to 425 K, indicating that surface methyl is mostly Cr-bound prior to the dehydrogenation reaction which occurs at 490 K. The data suggest that the oxygen-bound methyls may form, but likely migrate to adjacent lower-energy Cr sites. These possibilities will be addressed in the section describing DFT calculations. Heating the sample further to 700 K results in the loss of all but a trace amount of carbon over the temperature range associated with product desorption in TPD.

The I 3d₅/₂ spectra for a photon energy of 700 eV are shown in Figure 0.4(b). A sharp I 3d₅/₂ feature is observed at a binding energy of 620.9 eV upon dosing at 110 K, characteristic of I in molecular CH₃I [2, 4]. This feature decreases as the sample is heated and the multilayers are removed, while a lower binding energy feature appeared at 619.5 eV. The molecular (higher binding energy) contribution is mostly gone by 330 K, while the lower binding energy feature remains after heating the sample to 700 K. This low binding energy of the remaining I 3d₅/₂ feature is characteristic of a metal iodide [14], and is assigned to I adatoms bound at surface Cr sites, explaining the site blocking effect seen in TPD experiments.
3.3.5 DFT calculation results

Geometry optimization of surface methyl on different adsorption sites has been done on the 80-atom unit cell described previously (Chapter 1) in the computational methods section. Stable bonding configurations were found to vary with the type of calculation performed. Calculations done without the on-site potential predict that the methyl group is only stable on a surface cationic site (Figure 0.5a) with a Cr-C bond length of 2.0 Å. Methyl groups do not form a stable, methoxy-like intermediate on oxygen anion sites. On the other hand, DFT+U calculations yield stable binding configurations for Cr-bound methyl (Figure 0.5b, Cr-C bond length of 2.0 Å) and O-bound methyl (Figure 0.5c, O-C bond length of 1.5 Å), with the Cr-bound configuration more stable by 0.12 eV than O-bound methyl. This result is in line with the O-bound methyl observed with XPS, supporting the DFT+U results, and indicating that on-site coulomb repulsion is needed to correctly predict the binding modes of the methyl radical for this system. However, it has a limitation that the optimal value of the on-site potential for the bulk does not strictly apply to the surface, and the predictions using DFT+U may not be more qualitative than quantitative.

3.4 Discussion

Methyl groups on the \(\alpha\)-Cr\(_2\)O\(_3\)(0001) surface undergo nearly identical reaction pathways as methyl groups on the \(\alpha\)-Cr\(_2\)O\(_3\)(10\(\bar{1}\)2) surface in CD\(_3\)I TPD [8]. The methyl dehydrogenation temperatures on the two surfaces are similar, 490 K on (0001) and 510 K on (10\(\bar{1}\)2), indicating a similar activation barrier (1.3 kcal/mol difference) for the dehydrogenation reaction despite the different local site-pair geometry of the cationic reaction center and the surrounding oxygen anions. The (10\(\bar{1}\)2) surface terminates with coordinatively unsaturated oxygen anions in the
Figure 0.5. Configurations of methyl on the α-Cr$_2$O$_3$(0001) surface calculated with DFT: (a) Cr-bound methyl calculated without the on-site potential, (b) Cr-bound methyl calculated with DFT+U, and (c) O-bound methyl calculated with DFT+U. Small blue spheres represent Cr cations, large red spheres O anions, small grey spheres carbon, and the white spheres hydrogen.
outermost layer where they are geometrically more available to assist in the abstraction of hydrogen from the methyl bound on the cation (Figure 0.6(a), O-H distance of 2.7 Å). On the other hand, oxygen anions on the (0001) surface sit below the surface Cr$^{3+}$ cations, making them less available to methyl groups (Figure 0.6(b), O-H distance of 3.3 Å). However, the experimental activation barriers for dehydrogenation are similar on the two surfaces, indicating that the geometric availability of the oxygen sites does not play a crucial role in the dehydrogenation reaction barrier. The comparison suggests instead that the surface anions play a minor role in methyl dehydrogenation, acting more like simple “parking spots” for the hydrogen following the decomposition of the methyl species.

Selectivities among the main reaction products CD$_4$ and CD$_2$=CD$_2$ are 57:43 on the (10\(\overline{1}\)2) surface and 63:37 on the (0001) surface for the first 0.1 L dose of CD$_3$I. The values are within the same range with the (0001) surface being more selective to CD$_4$. However, it is difficult to draw a conclusion from the values since CD$_3$H was also made from the side reaction with adsorbed water on the (0001) surface.

It should also be noted that ethane (CD$_3$-CD$_3$) is not produced from surface methyl on \(\alpha\)-Cr$_2$O$_3$(0001), as well as on the \(\alpha\)-Cr$_2$O$_3$(10\(\overline{1}\)2). This result indicates that two methyls do not adsorb on a single cation site to couple directly to form ethane on \(\alpha\)-Cr$_2$O$_3$(0001), implying that multiple coordination vacancies of the surface cations does not play a crucial role in the coupling of methyls. It also implies that the barrier for the methyls to migrate between different Cr sites to couple with one another is higher than the barrier for the dehydrogenation of methyls, so that methyl migration is not observed on \(\alpha\)-Cr$_2$O$_3$(0001).
Figure 0.6. Illustration of the availability of surface anions to the hydrogen on the methyl groups bound on Cr sites on (a) $\alpha$-Cr$_2$O$_3$(1012) and (b) $\alpha$-Cr$_2$O$_3$(0001).
3.5 Conclusions

The reaction of surface methyl was investigated on the nearly-stoichiometric $\alpha$-Cr$_2$O$_3$(0001) surface via dissociative adsorption of CD$_3$I. Reaction products seen are methane, ethylene, hydrogen and surface I adatoms. The rate-limiting step for the reaction is the dehydrogenation of methyl groups to methylene. The methylene intermediates formed from the dehydrogenation of methyl migrate across the surface to couple with one another or insert into the remaining methyl intermediates to form surface ethyl, which goes through a $\beta$-H elimination to produce ethylene. Surface hydrogen also combines with methyl groups to form methane, while some methane is also made from hydrogen originating from adsorbed background water. Iodine adatoms from the dissociation of CD$_3$I deactivated the surface by simple cation site blocking. Comparison of the result with the dehydrogenation on the Cr$_2$O$_3$̅(10$ar{1}$2) surface suggests that for the dehydrogenation of methyl groups, the cation-anion site-pair geometry is not a controlling factor for the reaction chemistry.

3.6 References


Chapter 4.

Reactions of Formic Acid and Formaldehyde on $\alpha$-Fe$_2$O$_3$(1012)

4.1 Introduction

For the understanding of the chemistry of methyl and methylene intermediates on the $\alpha$-Fe$_2$O$_3$(1012) surface, the reaction chemistry of C$_1$ oxygenates needs to be studied since the surface is a reducible surface, and oxygenated compounds are produced from the C$_1$ hydrocarbon intermediates. In this chapter, the reaction chemistry of formic acid (HCOOH) and formaldehyde (CH$_2$O) on the $\alpha$-Fe$_2$O$_3$(1012) surface is discussed.

Studies of formic acid with single-crystal metal oxide surfaces have shown that formic acid adsorbs either molecularly or dissociatively, with dissociation occurring via deprotonation on cation-anion site pairs to form adsorbed formates and surface hydroxyl groups [1-6]. The ability of metal oxides to dissociate formic acid most likely reflects the basicity of the surface [1]. Surface formates are generally stable up to about 600 K, and they decompose to produce CO$_2$, CO, water, and H$_2$. It has been suggested that the ratio of CO$_2$ and CO products depends on the ease of reduction of the oxide during formate decomposition: more easily reduced oxides produce more CO$_2$ [4].

A simultaneous hydrogenation and oxidation of formaldehyde into surface methoxy and formate, respectively, is reported on single-crystal metal oxide surfaces [6-8] and oxygen covered metal surfaces [9-13], as initially reported by Busca et al. in a study of adsorbed formaldehyde on metal-oxide powders [14]. A nucleophilic attack of surface oxygen occurs at
the carbonyl carbon with hydride transfer to a second adsorbed formaldehyde molecule to produce surface formate and methoxy (Figure 4.1), commonly described as a Cannizzaro-type disproportionation reaction [7, 8, 14].

Methoxide intermediates formed from formaldehyde adsorption dehydrogenate to formaldehyde and carbon monoxide, and hydrogenate to form methanol and methane [7, 8, 11]. The production of formic acid, CO, CO₂ and formaldehyde was also reported as a result of formate decomposition from adsorbed formaldehyde [6-10, 12, 13]. At higher coverages, the polymerization of formaldehyde into paraformaldehyde is reported on metal surfaces [10, 15-18], oxygen covered metal surfaces [9, 12, 13] and metal oxide powders [19-22]. Paraformaldehyde decomposes and produces formaldehyde in thermal desorption experiments [10, 15-18].

4.2 Experimental

Experimental equipment and preparation techniques are described in Chapter 1. Experiments have been done on the nearly-stoichiometric α-Fe₂O₃(1012) surface prepared by ion bombardment and annealing of the single crystal in a background of oxygen following the preparation method of Henderson et al [23]. Formaldehyde was obtained by the thermal decomposition of paraformaldehyde powder (Aldrich, 95 %), and Sigma-Aldrich reagent grade formic acid (HCOOH, ≥ 95 %) was used as received. The reported dose sizes have been corrected for ion gauge sensitivity, and all desorption traces and quantities have been corrected for mass spectrometer sensitivity. Multiple m/z signals were monitored simultaneously during the thermal desorption experiments, then compared to the mass spectrometer fragmentation

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9 Ion gauge sensitivities 1.98 and 3.28 were used for formaldehyde and formic acid using a correlation by S. George as reported by Brainard and Madix [24]. It should be noticed that this method is not strictly accurate, and there is an uncertainty associated with the calibration of the dosage. Relative mass spectrometer sensitivity factors of 0.14 for
Figure 4.1. A depiction of the Cannizzaro-type disproportionation reaction of formaldehyde on metal oxide surfaces (adapted from reference[25])

formaldehyde (m/z 30), 0.30 for CO₂ (m/z 44), and 0.78 for CO (m/z 28), 0.80 for H₂O (m/z 18), 1.60 for H₂ (m/z 2), 0.0039 for HCOOH (m/z 46) were determined experimentally.
patterns of the suspected product molecules. $m/z$ signal of 30 and 29 were used to identify CH$_2$O, while $m/z = 46$ was used for the identification of HCOOH, $m/z = 44$ for CO$_2$, $m/z = 28$ for CO, $m/z = 18$ for H$_2$O, and $m/z = 2$ for H$_2$. Contributions from different molecules to the product signals were corrected by subtracting the signal out according to the mass spectrometer fragmentation pattern of the corresponding molecule. Other products were excluded by checking $m/z$ values in the range of 2 to 100.

4.3 Results

4.3.1 TPD of HCOOH

Figure 4.2 shows the thermal desorption of the reaction products after a 0.2 L dose of formic acid on a clean, nearly-stoichiometric surface following adsorption at 90 K. The products observed are CO$_2$, formic acid, CO, water, H$_2$, and trace amounts of formaldehyde. CO$_2$ and formic acid desorbs as a combined feature of two peaks centered around 570 and 605 K with almost identical shapes. CO is produced with a peak at 560 K and a broad feature of H$_2$ is seen at a range of 450-670 K with a peak temperature of 540 K. H$_2$O is produced as a combination of features centered around 570 and 605 K following the trend of CO$_2$ and formic acid. The majority of water desorbs in a broad peak around 160-180 K. The contribution centered around 180 K aligns with low temperature desorption features for formic acid and formaldehyde.

Figure 4.3 shows the changes of product signals for consecutive doses and TPD runs of 0.2 L of formic acid. The high temperature peaks for CO$_2$ and formic acid that were partially resolved combine to give single features centered around 590 K by the second run. The desorption traces for CO$_2$ and formic acid remains similar for later runs. The small formic acid peak near 185 K in the first run disappears by the second run. The CO peak which originally
Figure 4.2. Thermal desorption of 0.2 L HCOOH on the nearly-stoichiometric α-Fe₂O₃(10\(\overline{1}2\)).
Figure 4.3. Change of signals for (a) CO\(_2\), (b) formic acid, (c) CO, (d) H\(_2\), (e) H\(_2\)O and (f) formaldehyde for consecutive 0.2 L HCOOH TPD runs done on \(\alpha\)-Fe\(_2\)O\(_3\)(10\(\overline{1}2\)).
aligned with the lower temperature features of CO$_2$ and formic acid at 570 K shifts to 600 K by the second run. H$_2$ shows a rather steady trace with the peak centered around 545 K for all runs. The low-temperature water peak around 170 K decreases with consecutive TPD of formic acid. A broad contribution for water ranging from 190 to 480 K remains for later runs with possible peaks around 210, 360, and 410 K. The higher temperature water feature shows a similar trend with the CO$_2$ and formic acid: the partially resolved peaks appear as one feature centered around 605 K for later runs. The low-temperature formaldehyde contribution at 180 K disappears by the second run, similar to what is seen for the HCOOH and water features, and a broad formaldehyde desorption feature is left in the region from 215 to 380 K. A peak at 580 K appears for the second dose and remains for later runs.

Figure 4.4 shows the desorption traces for all molecules following the 5$^{th}$ TPD run of 0.2 L formic acid. The CO$_2$, formic acid, and water peaks around 600 K that consisted of two partially resolved features now appear as one feature. However, the H$_2$O peak temperature is slightly shifted towards high temperature from the CO$_2$ and formic acid features. The CO feature around 600 K now aligns better with the CO$_2$ and HCOOH. The low temperature features around 190 K for H$_2$O, formic acid and formaldehyde seen in the first dose are no longer apparent, but a new formaldehyde peak is seen around 580 K. A broad contribution for water ranging from 190 to 480 K is seen with possible peaks around 210, 360, and 410 K and a broad feature of H$_2$ is seen around 530 K.

4.3.2 TPD of CH$_2$O

Figure 4.5 shows the thermal desorption of the products after a 0.1 L dose of CH$_2$O on a clean, nearly-stoichiometric surface following adsorption at 90 K. The products observed are formaldehyde, CO$_2$, CO, and H$_2$O. Formaldehyde desorbs around 350 K, while CO$_2$ and CO are
Figure 4.4. 5th TPD run of 0.2 L HCOOH done on the nearly-stoichiometric α-Fe₂O₃(10\overline{1}2) surface.
Figure 4.5. Thermal desorption of 0.1 L CH$_2$O on the nearly-stoichiometric α-Fe$_2$O$_3$(10$ar{1}$2) surface.
produced around 620 and 605 K, respectively. H₂O is seen as a bump over a wide range (300-600 K).

Figure 4.6 shows the change in the formaldehyde signal for consecutive doses and TPD runs of 0.1 L formaldehyde. A small contribution at the higher-temperature-end of the 350 K peak of CH₂O slowly grows in for later doses around 390 K. Figure 4.7 shows the change of CO and CO₂ signals for the consecutive 0.1 L CH₂O TPD runs. Both signals gradually decrease for later runs, with the CO signal reducing to an undetectable amount by the 6th dose.

4.4 Discussion

4.4.1 The reaction chemistry of formic acid

The simultaneous production of formic acid and carbon dioxide from formic acid at 570 and 605 K suggest the involvement of formate intermediates [2-4]. CO₂ is produced by the dehydrogenation of formate, forming surface hydrogen (4.1), and the adsorbed hydrogen can then combine with the remaining formates to produce formic acid (4.2) with the rate-limiting step being the dehydrogenation of the formate species.

\[
\text{HCOO}_{(\text{ads})} \rightarrow \text{CO}_2 + \text{H}_{(\text{ads})} \quad (4.1) \text{ (rate-limiting)}
\]

\[
\text{H}_{(\text{ads})} + \text{HCOO}_{(\text{ads})} \rightarrow \text{HCOOH} \quad (4.2)
\]

The existence of two peaks of CO₂ and formic acid suggests the possibility of two different kinds of formates. CO is also produced mostly at 560 K with a shoulder around 610 K from the decomposition of formate intermediates (4.3) to a smaller extent compared to the decomposition of formates into CO₂.

\[
\text{HCOO}_{(\text{ads})} \rightarrow \text{CO} + \text{H}_{(\text{ads})} + \text{O}_{(\text{ads})} \quad (4.3)
\]
Figure 4.6. Change of formaldehyde desorption for consecutive 0.1 L CH₂O TPD runs done on α-Fe₂O₃(1012).

Figure 4.7. Change of signals for (a) CO and (b) CO₂ for consecutive 0.1 L CH₂O TPD runs done on α-Fe₂O₃(1012).
It has been suggested that the ratio of CO$_2$ and CO produced from formate intermediates depends on the ease of reduction of the oxide during formate decomposition [4]. The high CO$_2$:CO production ratio of 8.01 from this surface is in line with the fact that the stoichiometric $\alpha$-Fe$_2$O$_3$(1012) surface is reducible.

Formate intermediates are formed by the deprotonation of the organic acid to give the conjugate base anion formate (4.4), with the proton likely binding to a surface oxygen anion site forming surface hydroxyl.

\[
\text{HCOOH} \rightarrow \text{HCOO}^{-(\text{ads})} + \text{H}^+\text{(ads)} \quad (4.4)
\]

Reactions of formic acid on other metal oxide surfaces have shown that the formic acid either dissociates immediately to form formate and surface hydroxyl, or adsorbs molecularly at low temperatures and dissociates to form formate and hydroxyl species upon heating [5, 6, 26]. It is believed that the difference in the ability of different metal oxides to dissociate formic acid most likely reflects the basicity of the surface [5, 6]. However, the temperature range for dissociation temperature of formic acid on this surface is not known from the current TPD experiments.

Water is formed around the same temperatures that CO$_2$, HCOOH, and CO are formed (520-630 K), by the combination of the surface H formed by reactions (4.1) and (4.3) with surface lattice oxygen. Trace amounts of H$_2$ is also formed by the simple combination of the surface H. Generally, formic acid dehydrogenation (-H$_2$) yields CO$_2$, and dehydration (-H$_2$O) yields CO. However, since the surface is readily reducible and the surface H adatoms can combine with lattice oxygen to produce water, the hydrogen formed by the dehydrogenation of formic acid for the production of CO$_2$ can also be associated with the production of water. The
amount of H₂ seen in this experiment is small, and the majority of the hydrogen formed from the decomposition of the formic acid is found to be desorbed in the form of water.

Formic acid and water are also produced around the same low temperature range (170 K) in the first TPD runs of formic acid. The hydrogen adatoms formed from the dissociation of formic acid (4.4) are thought to recombine with the formate species formed, producing formic acid, or combine with surface lattice oxygen to produce water.

The C:O ratio of the products is 1:2.6 for the first dose (Figure 4.8), indicating that the reaction involves the reduction of the surface, when compared to the C:O ratio of 1:2 in the reactant molecule formic acid. Water is the main product that causes the change of stoichiometry since other products maintain (CO₂, HCOOH, and H₂) or decrease (CO and CH₂O) the C:O ratio. Further reduction of the surface may also be induced by the heating, since this surface is known to be reduced by heating in vacuum above 700 K. Nevertheless, the major cause of the change in selectivity is the reduction of the surface. As the surface gets reduced (i.e., as the reactive surface oxygen anions are consumed), the overall C:O ratio of products decreases for later runs and stabilize at a value around 2.22 (Figure 4.8), which is close to the value for the reactant molecule formic acid. The reduced surface binds more formates in the form that decomposes at higher temperature (605 K), so the CO₂ and formic acid production at 605 K increases for later runs, resulting in an unresolved single feature together with the 570 K peak. CO is also produced more at 600 K than 560 K as the surface is reduced, and more of the higher-temperature-dissociating formates are formed.

The intensities of the formic acid and water desorption features around 170 K decrease as the surface is reduced. A broad water feature that ranges from 190 to 480 K is left, consistent
Figure 4.8. The overall C:O ratio of products for consecutive runs of 0.2 L HCOOH TPD done on α-Fe₂O₃(1012).
with the desorption of molecular and dissociative forms of adsorbed water from both the ideal and reduced surface. The water adsorption study of Henderson et al. shows that the molecular and dissociated water desorbs at 160 and 350 K, respectively on the $\alpha$-Fe$_2$O$_3$(1012)-(1×1), but at 230 and 405 K on the reduced $\alpha$-Fe$_2$O$_3$(1012)-(2×1) surface [23]. The big decrease in the water desorption intensity at 170 K on the reduced surface compared to the nearly-stoichiometric surface is also seen in their work. The water desorption traces from later formic acid TPD runs are comprised of contributions at 210, 360, and 410 K, showing water desorption characteristics of stoichiometric and reduced surface domains.

Relatively small peaks of CH$_2$O are observed at 580 K after the first dose, coincident with the formate decomposition temperature. It is believed that the surface hydrogen formed by formate decomposition can hydrogenate remaining formate into adsorbed formaldehyde species, then desorb as formaldehyde from the reduced surface.

4.4.2 The reaction chemistry of formaldehyde

The 350 K desorption temperature of formaldehyde is associated with the desorption of molecularly-bound formaldehyde. The increased C:O stoichiometry of the product CO$_2$ (1:2) compared to the reactant CH$_2$O (1:1) implies that oxygen is incorporated from a source other than the dosed CH$_2$O molecule: lattice oxygen from the reduction of the surface. The changes of product signals for consecutive TPD runs are associated with this reduction of surface. The higher temperature shoulder of the formaldehyde desorption peak at 350 K is barely noticeable for the first dose, but grows for later doses. This feature is attributed to surface sites produced by the surface reduction; the heat of adsorption is higher on these reduced sites, resulting in a higher temperature desorption. As more TPD runs are done, more reduced sites are formed as oxidation products are generated, and this higher temperature formaldehyde feature also increases. On the
other hand, as the surface gets reduced, there is less oxygen available for the production of oxidation products, so the production of CO$_2$ and CO decreases for later runs.

The production of CO$_2$ from formaldehyde indicates the formation of formate intermediates. The mechanism for the production of CO$_2$ and CO from formaldehyde can be understood with the comparison to the formic acid chemistry. The CO$_2$ and CO production temperature (620 and 605 K) aligns with the higher temperature feature of their production from formic acid (605 and 610 K) which was attributed to formate decomposition. This suggests formate decomposition as the rate-limiting step for the production of CO$_2$ and CO from formaldehyde. Formate species can be formed through the dehydrogenation of dioxymethylene intermediates which results from nucleophilic attack of surface lattice oxygen on adsorbed formaldehyde (Figure 4.9). Dioxymethylene species have been seen in FTIR [14], and proposed in thermal desorption experiments over various metal-oxide single crystal surfaces from adsorbed formaldehyde [7-9, 12]. The formation of dioxymethylene species occurs via the direct adsorption of formaldehyde with an available cation/anion site pair (Figure 4.9). The nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(10$\overline{1}$2) surface contains adjacent, coordinately unsaturated surface cations and anions which can provide such a site pair.

The Cannizzaro-type disproportionation reaction is a common reaction observed for adsorbed formaldehyde or dioxymethylene species as mentioned in the introduction (Section 4.1., Figure 4.1). Chemistry related to both methoxide and formate decomposition should be observed if the Cannizzaro disproportionation is operable on this surface, and the reaction products of methoxide are methane and/or methanol. However, neither of these products are seen in our current study of the reaction of formaldehyde on $\alpha$-Fe$_2$O$_3$(10$\overline{1}$2), indicating that the Cannizzaro-type disproportionation reaction does not occur.
Figure 4.9. Illustration of the formation of dioxymethylene species by the direct adsorption of formaldehyde with an available cation/anion site pair.
The production of CO$_2$ and CO from formaldehyde accompanies the formation of surface hydrogen. These hydrogen adatoms are desorbed in TPD in the form of water as a broad feature. As it is the case seen with the formic acid reaction, water is thought to be produced by the combination of the hydrogen adatoms with surface oxygen on this surface.

### 4.5 Conclusions

Formic acid deprotonates to surface formate, which decompose into CO$_2$ and CO on both the nearly-stoichiometric and the reduced surfaces $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2). Hydrogen released by the dissociation of formic acid desorb mostly as water by the combination with surface lattice oxygen, which causes the reduction of the surface. Most of the formaldehyde dosed on the $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2) surface desorb molecularly around 350 K on the ideal sites, and 390 K on the reduced sites. Nucleophilic attack of surface lattice oxygen on adsorbed formaldehyde also leads to the formation of surface formate, which decompose into CO$_2$ and CO.

### 4.6 References


Chapter 5.

The reaction of methylene and methyl on an iron oxide surface:

Diiodomethane and iodomethane on $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2)

5.1 Introduction

The studies of the reaction of methylene and methyl intermediates on metal surfaces have been introduced in Chapter 2 and 3. The studies in this chapter are done in an effort to examine the effect of surface electronic structure on the reaction of methylene and methyl species through a comparison to earlier studies done on the $\alpha$-Cr$_2$O$_3$(10$\bar{1}$2) surface. Fe$^{3+}$ cations on the $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2) surface have different electronic configuration ($3d^5$) than the Cr$^{3+}$ cations on the $\alpha$-Cr$_2$O$_3$(10$\bar{1}$2) surface ($3d^3$). Since both materials have the same crystal structure, this work provides an opportunity to examine a purely electronic effect in surface chemistry.

Studies of methyl radicals on iron oxide surfaces have been done by Stair et al. [1, 2]. Their study has shown that little or no methyl radical adsorption is seen experimentally on the $\alpha$-Fe$_2$O$_3$(0001) surface, while Fe$_3$O$_4$(111) adsorbs methyl radicals to form methoxy groups. The methoxy reacts on heating by dissociation of the C-O bond to directly form gas phase methyl radicals in two temperature regimes. Small amounts of ethane production were also found on the Fe$_3$O$_4$(111) at saturation coverage.

Methyl radicals have also been studied on oxygen-covered metal surfaces by Friend et al. [3-5]. Methoxy intermediates were formed by the direct addition of methyl radicals on surface oxygen. These studies observed direct desorption of methyl radical from the methoxy formed on
the O-covered Mo(110), and CO$_2$, CO and formaldehyde production on the O-covered Rh(111) surface. On the O-covered Mo(110), methoxy formation involves the adsorption of methyl radicals on the quasi-threefold (bridging) oxygen sites, and it formation does not directly involve terminal Mo=O sites [5].

5.2 Experimental

Experimental equipment and preparation techniques are described in Chapter 1. The nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(10$\bar{2}$) surface was prepared by ion bombardment and annealing of the single crystal in a background of oxygen following the preparation method of Henderson et al [6]. Sigma-Aldrich 99% diiodomethane (CH$_2$I$_2$), dichloromethane (CH$_2$Cl$_2$) and iodomethane (CH$_3$I) were used as received. A Kimball Physics FRA-2X1-2 electron gun was used to promote the reaction of CH$_3$I via electron-induced dissociation. An electron energy of 80 eV was used since it resulted in a reasonable amount of product formation. The measured current between the surface and ground was in the range of 18 to 21 $\mu$A, and the sample was irradiated for 5 minutes. The reported dose sizes have been corrected for ion gauge sensitivity, and all desorption traces and quantities have been corrected for mass spectrometer sensitivity.\textsuperscript{10} Multiple $m/z$ signals were monitored simultaneously during the thermal desorption experiments, then compared to the mass spectrometer fragmentation patterns of the suspected product molecules to monitor the products. $m/z$ signal of 141 was used to identify CH$_2$I$_2$, $m/z = 142$ for CH$_3$I, $m/z = 30$ and 29 for CH$_2$O, $m/z = 46$ for HCOOH, $m/z = 44$ for CO$_2$, $m/z = 28$ for CO, $m/z = 18$ for H$_2$O, and $m/z = 2$ for H$_2$ were used for the identification of the corresponding molecules. Contributions

\textsuperscript{10} Ion gauge sensitivity 17.9 and 9.5 were used for diiodomethane and iodomethane using a correlation by S. George as reported by Brainard and Madix [7]. It should be noticed that this method is not strictly accurate, and there is an uncertainty associated with the calibration of the dosage. Relative mass spectrometer sensitivity factors of 0.04 for diiodomethane ($m/z$ 141), 0.052 for iodomethane, 0.14 for formaldehyde ($m/z$ 30), 0.30 for CO$_2$ ($m/z$ 44), and 0.78 for CO ($m/z$ 28), 0.80 for H$_2$O ($m/z$ 18), 1.60 for H$_2$ ($m/z$ 2), 0.0039 for HCOOH ($m/z$ 46) were determined experimentally.
from different molecules to the product signals were corrected by subtracting the signal out according to the mass spectrometer fragmentation pattern of the corresponding molecule. Other products were excluded by checking $m/z$ values in the range of 2 to 150.

5.3 Results

5.3.1 TPD of CH$_2$I$_2$

The reaction of methylene intermediates on the $\alpha$-Fe$_2$O$_3(10\bar{1}2)$ has been examined with the reaction of CH$_2$I$_2$. The use of iodized hydrocarbon has a shortcoming in that the deposited iodine adatoms cannot be detected by AES which is the characterization method available for the vacuum system used in this set of experiments. However, CH$_2$Cl$_2$ did not show any reactivity on this surface in TPD other than simple desorption of the dosed molecule. Thus, CH$_2$I$_2$ has been used for the formation of methylene intermediates, since the weaker C-I bond compared to the C-Cl bond strength allows for thermal dissociation (C-I bond cleavage) of the molecule.

Figure 5.1 shows the thermal desorption of the reaction products after a 0.2 L dose of CH$_2$I$_2$ on a clean, nearly-stoichiometric $\alpha$-Fe$_2$O$_3(10\bar{1}2)$ surface at 90 K. CO$_2$ is the main product and smaller amounts of CO, formaldehyde and trace amounts of ethylene are observed. CO$_2$ and CO are produced in a similar temperature range with peak temperatures of 625 and 635, respectively. Formaldehyde is produced at 395 K, and ethylene is produced in a broad feature ranging from about 160 to 375 K in what appears to be contributions from multiple peaks. Water is also produced in a broad feature ranging from about 250 to 600 K. The dosed molecule CH$_2$I$_2$ is desorbed as a combination of two peaks centered around 265 and 305 K. No singly-iodized reaction products are found.
Figure 5.1. Thermal desorption following a 0.2 L dose of CH$_2$I$_2$ on the clean, nearly-stoichiometric α-Fe$_2$O$_3$(1012).
Figure 5.2 shows the changes of product signals for consecutive doses and TPD runs of 0.2 L CH₂I₂. The production of nonselective oxidation products CO₂ and CO at 625 and 635 K decrease with successive dose and eventually disappear (Figure 5.2 (a) and (b)). The small feature of formaldehyde at 395 K seen in the first dose grows larger for later doses and stabilizes in intensity while the peak temperature shifts slightly down to 365 K (Figure 5.2(c)). The trace amount of ethylene produced in the first run increases in later runs, with contributions at 205 and 275 K becoming apparent (Figure 5.2(d)). The desorption traces of water do not show an obvious trend with successive doses of CH₂I₂ (Figure 5.2(e)). The CH₂I₂ desorption which is seen as a combination of two peaks at 265 and 305 K in the first run becomes a single asymmetric feature which tails on the high temperature side in later runs with a peak temperature of 245 K (Figure 5.2(f)). The intensity of the peak remains steady for the consecutive TPD runs.

The 5th consecutive run of 0.2 L CH₂I₂ TPD (Figure 5.3) illustrates the shift in reaction selectivity due to the changes in the surface condition during consecutive doses. The main products are formaldehyde and ethylene, in contrast to the first run where CO₂ and CO production are more dominant. Almost none of the nonselective oxidation products CO₂ and CO are produced for this run.

Figure 5.4 shows the integrated signal intensity of products for the consecutive runs. The reaction selectivity shifts from CO₂ to CH₃O and CH₂=CH₂ with successive doses. No obvious trend is seen with the signal intensities of the dosed molecule, diiodomethane, and the sum of the product signals for carbon-containing products for successive doses. The ratio of the C and O content of the overall products is plotted in Figure 5.5 for the consecutive TPD runs. The initial O/C ratio of 1.7 indicates significant reduction of the surface due to the consumption of surface lattice oxygen since the reactant methylene does not include any oxygen (O/C ratio of zero). The
Figure 5.2. Change of signals for (a) CO₂, (b) CO, (c) formaldehyde, (d) ethylene, (e) water and (f) diiodomethane for consecutive TPD runs of 0.2 L CH₂I₂.
Figure 5.3. 5th thermal desorption run of 0.2 L dose of CH$_2$I$_2$ on the clean, nearly-stoichiometric α-Fe$_2$O$_3$(10$ar{1}$2).
Figure 5.4. Integrated signals for each product for consecutive 0.2 L CH$_2$I$_2$ TPD runs as a function of cumulative CH$_2$I$_2$ exposure.
Figure 5.5. The overall C:O ratio of products for consecutive runs of 0.2 L CH₃I₂ TPD done on α-Fe₂O₃(1012).
ratio decreases for later TPD runs, reaching 0.52 for the fifth run. These results indicate that the shift in selectivity is associated with a decrease in the availability of surface lattice oxygen due to surface reduction.

No carbon is observed by AES after the series of TPD runs, indicating that the carbonaceous species completely react away. The coverage of iodine on the surface could not be determined in AES due to the overlap of the I MNN and O KLL signals.

5.3.2 TPD of CH$_3$I

The fact that CH$_2$Cl$_2$ does not dissociate on α-Fe$_2$O$_3$(1012) as mentioned in the previous section automatically excludes the use of CH$_3$Cl for the formation of methyl groups on this surface, since singly-halogenated carbon centers are known to have stronger carbon-halogen bonds compared to doubly-halogenated carbon centers. Instead, iodomethane was chosen in this study for the formation of methyl groups due to the weaker bond strength of C-I bond compared to C-Cl bond. Adsorbed iodomethane does not show any thermal reactivity other than simple molecular adsorption and desorption in TPD, but has shown reactivity when an electron gun is used to promote the reaction of CH$_3$I via electron-induced dissociation (EID). In earlier work by Liu et al. [8] on the reaction of ethyl chloride on Ag(111), electron-induced dissociation C-Cl bond cleavage was used to promote the reaction of thermally unreactive ethyl chloride molecules in UHV. Their study examined electron energies in the range of 0-130 eV, with a dose of 1.61×10$^{16}$ electrons. As a function of electron energy, the C-Cl bond dissociation cross section drops by more than an order of magnitude between 0.5 and 3 eV. It rises again by an order of magnitude between 8 and 12 eV, and then rises slowly to 50 eV. In this study, electron energies in the range of 5-130 eV and electron doses of 9×10$^{14}$ to 7.2×10$^{16}$ have been examined.
Increasing amounts of dissociation have been seen for increasing energy and electron dose. An electron energy of 80 eV and $3.6 \times 10^{16}$ (20 µA for 5 minutes) electron dose has been chosen because it results in a sufficient amount of dissociation of CH$_3$I, and to avoid possible side effects of using higher beam energy such as electron-stimulated desorption and the dissociation of background molecules.

Figure 5.6 shows the thermal desorption trace of the reaction products after a 0.2 L dose of CH$_3$I and electron-induced dissociation (C-I bond cleavage) on a clean, nearly-stoichiometric surface at 90 K. The products observed are CO$_2$, CO, formaldehyde, and trace amounts of water. CO$_2$ and CO are produced at a similar range with peak temperatures of 630 and 620, respectively. Formaldehyde is produced at 355 K, tailing to the higher temperature side, and a small but broad feature of water is seen with a peak at 450 K. The dosed molecule CH$_3$I is produced as a combination of two peaks centered around 260 and 195 K.

Figure 5.7 shows the changes of product signals for consecutive doses and TPD runs of 0.2 L CH$_3$I. The production of CO$_2$ and CO at 630 and 620 K declines with successive doses, and the CO peak eventually disappears. The small feature of formaldehyde at 355 K seen in the first dose grows larger for later doses and stabilizes in intensity while the peak temperature shifts to 380 K. A small amount of water is produced steadily around 430 K. Trace amounts of ethylene begin to be produced in the later runs with peaks around 210 and 270 K. The total intensities of the CH$_3$I desorption peaks at 260 and 195 K remain steady, although the two peaks smear out for later doses.

The 5$^{th}$ consecutive run of 0.2 L CH$_3$I TPD (Figure 5.8) illustrates the changed reaction selectivity on the reduced surface compared to the reaction on the nearly-stoichiometric surface.
Figure 5.6. Thermal desorption following a 0.2 L dose of CH$_3$I on the clean, nearly-stoichiometric α-Fe$_2$O$_3$(1012).
Figure 5.7. Change of signals for (a) CO$_2$, (b) CO, (c) formaldehyde, (d) ethylene, (e) water and (f) iodomethane for consecutive TPD runs of 0.2 L CH$_3$I.
Figure 5.8. 5th thermal desorption run of 0.2 L dose of CH$_3$I on the clean, nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(10\overline{1}2).
The main product is formaldehyde in this run, instead of CO$_2$, which was the main product in the first run. No detectable amount of CO is produced, while trace amounts of ethylene are produced in this run.

Figure 5.9 shows the integrated signal intensity of products for the consecutive runs. The reactivity shifts from CO$_2$ and CO to CH$_2$O with successive doses. No obvious trend is seen with the signal intensities of the dosed molecule, iodomethane, and the sum of the carbon-containing product signals for successive doses. The ratio of C and O in the overall products is plotted on Figure 5.10 for the consecutive TPD runs. The initial O/C ratio of 1.78 indicates significant reduction of the surface due to the consumption of surface lattice oxygen since the reactant methyl does not include any oxygen (O/C ratio of zero). The ratio decreases for later TPD runs, reaching 1.26 for the fifth run. These results indicate the shift in selectivity is due to a decrease in the availability of surface lattice oxygen due to surface reduction.

No carbon is observed in AES after the series of TPD runs, indicating that the carbonaceous surface species have completely reacted out into gas phase. The coverage of iodine on the surface could not be examined with AES due to the overlap of the I MNN and O KLL signals.

5.4 Discussion

5.4.1 CH$_2$I$_2$ reaction chemistry

The lack of singly iodized species in TPD indicates that both C-I bonds of diiodomethane are thermally cleaved prior to product formation, likely forming methylene intermediates and surface I adatoms. The main product of the reaction of methylene species on the nearly-
Figure 5.9. Integrated signals for each product for consecutive 0.2 L CH$_3$I TPD runs as a function of cumulative CH$_3$I exposure.
Figure 5.10. The overall C:O ratio of products for consecutive runs of 0.2 L CH₃I TPD done on α-Fe₂O₃(1012).
stoichiometric $\alpha$-Fe$_2$O$_3$(10\overline{1}2)$ surface is CO$_2$. While the peak temperatures differ slightly for CO$_2$ and CO production, both products occurs over the same temperature range, suggesting that they originate from two parallel reaction channels for the same surface intermediate. The peak temperature for the production of CO$_2$ at 625 K from the CH$_2$I$_2$ TPD is close to the temperature for CO$_2$ production from formic acid (the higher temperature feature at 605 K) and formaldehyde (605 K) seen in Chapter 4, which have been attributed to the decomposition of formate species. CO is also produced with a peak temperature (635 K) that is close to the CO production temperatures in Chapter 4 seen for the reaction of formic acid and formaldehyde (610 K) reactions. Thus, the rate-limiting step for the production of CO$_2$ and CO is attributed to the decomposition of formate species.

$$\text{HCOO(ads)} \rightarrow \text{CO}_2 + \text{H(ads)}$$  \hspace{1cm} (5.1)

$$\text{HCOO(ads)} \rightarrow \text{CO} + \text{H(ads)} + \text{O(ads)}$$  \hspace{1cm} (5.2)

These results indicate nucleophilic attack of methylene by surface lattice oxygen, along with one C-H bond breaking event to generate surface formate. In the absence of other data, the ordering of these processes and the temperatures at which they occur is unclear. Formate species then decompose via parallel reaction channels to give mostly CO$_2$ with a little CO. The CO$_2$ and CO peaks have a typical 1$^{st}$-order shape that is asymmetric, and has a steeper slope at the high-temperature side. This again supports the assignment of the formate decomposition reaction which is a 1$^{st}$-order reaction as the rate-limiting step. The hydrogen adatoms deposited on the surface by this process also react with lattice oxygen to form water. The reducible nature of the surface leads to water formation rather than H atom coupling to H$_2$.
The production of the nonselective oxidation products CO₂ and CO decreases rapidly with later TPD runs as the surface lattice oxygen is consumed and the surface is reduced, with formate formation becoming less prevalent. The selectivity change is reflected in the change of O/C ratio of overall products (Figure 5.5), with higher O/C ratio representing more CO₂ production and low O/C ratio representing less production of oxygenated products. The ratio changes faster for CH₂I₂ reaction than for formic acid and formaldehyde reactions with successive doses (Chapter 4). This is because the methylene reaction reduces the surface more, since more surface oxygen incorporation is needed for the production of the same kind of products since the reactant molecule does not include any oxygen.

Formaldehyde is produced in small amounts for the first run, then grows in intensity, becoming the main product on the reduced surface. In Chapter 4, two desorption features of formaldehyde (at 355 and 390 K) are seen when formaldehyde is dosed directly for TPD. The two features have been attributed to the desorption of formaldehyde adsorbed on the ideal (355 K) and reduced (390 K) sites of the surface. Taking into account the center (360 K) and the shape of the formaldehyde desorption feature from the reaction of CH₂I₂ in the current chapter, it appears that the desorption feature consist of the two desorption contributions (at 355 and 390 K) seen from the formaldehyde TPD. This suggests that the desorption of formaldehyde is the rate-limiting step. Formaldehyde is thought to be formed by the adsorption of methylene species on the surface lattice oxygen sites.

\[
=\text{CH}_2(\text{ads}) + \text{O}_{(\text{lattice})} \rightarrow \text{CH}_2\text{O(ads)} \tag{5.3}
\]

Ethylene is produced in considerable amounts only after reduction of the surface, most probably because it is more favorable for methylene to form oxygen-bound intermediates and
desorb as oxygenates when the surface is not reduced. After surface reduction, ethylene is produced with two obvious contributions at 205 and 270 K on the reduced surface. Ethylene can be produced from methylene by the coupling of two methylene species.

\[
=\text{CH}_2_{\text{(ads)}} + =\text{CH}_2_{\text{(ads)}} \rightarrow \text{CH}_2=\text{CH}_2 \quad (5.4)
\]

Taking account of the small dose size used for the experiment, it is considered that the ethylene is formed by the migration of methylene across the surface and coupling with one other. Ethylene dosed directly on the \(\alpha-\text{Fe}_2\text{O}_3\) surface reduced by five doses and TPD runs of 0.2 L of \(\text{CH}_2\text{I}_2\) desorb at 185 K. Therefore, the ethylene production at 205 and 270 K (corresponds to an activation barrier of 12.6 and 16.7 kcal/mol assuming first-order kinetics using the Redhead method [9] assuming a pre-exponential factor of \(10^{13}\)\(^{11}\) from the \(\text{CH}_2\text{I}_2\) reaction is reaction-limited. Studies of methylene migration on metal surfaces have shown that the barrier for the migration of methylene is as low as 12-20 kcal/mol [10, 11], in contrast to the high barrier seen with the oxygen-mediated migration seen on the \(\alpha-\text{Cr}_2\text{O}_3\) metal oxide surface in Chapter 2 (a barrier of 30 kcal/mol). The barrier seen on the \(\alpha-\text{Fe}_2\text{O}_3\) surface is closer to the barrier seen on metal surfaces, suggesting a possibility that the methylene intermediates migrate directly between the surface metal cations on the reduced surface. However, the extent of reduction of the surface during these reactions is currently not known.

The hydrogen atoms produced from the dehydrogenation of methylene intermediates desorb as water by the combination of the hydrogen adatoms with surface lattice oxygen. However, Figure 5.4 clearly shows that the amount of water produced does not match the amount of \(\text{CO}_2\) produced, especially for the first few doses. The difficulty in closing the

\(^{11}\) A “normal” arbitrary pre-exponential factor of \(10^{13}\) s\(^{-1}\) has been used to estimate the activation energy for a given peak temperature for first-order processes. The uncertainty in the activation barrier due to the unavailability of the exact pre-exponential factor for methylene migration should be recognized.
hydrogen material balance is not unusual in the study of metal oxide surfaces, and it is thought to be due to the relatively high background pressure of water and hydrogen in the chamber that inhibits the detection of small intensities or broad features of the signal.

The integrated signals for the dosed molecule CH₂I₂ and the sum of the carbon containing product signal on a C₁ basis do not show any obvious trend. Studies have been done previously in our lab (in addition to the studies shown in earlier chapters of this dissertation) showing increasing signal intensities of the dosed halogenated molecules, and decreasing signal intensities of product signals for consecutive TPD runs [12-14]. These changes have been attributed to the site blocking of the reactive surface sites by the deposited halogen adatoms which inhibits reactant dissociation. More of the unreacted dosed molecules desorb, and less intermediates are available for the reaction, resulting in the decrease of product formation. The fact that the dosed molecule signal and the sum of the product signal do not show a significant change with consecutive TPD runs suggests the possibility that some of the iodine adatoms formed from the dissociation of CH₂I₂ desorb. However, no significant signal for iodine desorption from the mass spectrometer signal is seen. This may be due to the limitation for detecting I₂ molecules, since the main signal of m/z = 254 is out of the range of detection of the mass spectrometer used in the current study, and m/z = 127 for I⁺ does not have a significant contribution in the mass spectrometer cracking pattern of I₂ [15]. Auger spectra of the surface after the TPD experiments also fail to provide information of iodine coverage due to the overlap of signals between the IMNN and O KLL signals. However, the fact that the change of CH₂I₂ signal and product sum does not change gives a good implication that some iodine likely desorbs.

After seven 0.2 L doses of CH₂I₂ and TPD runs, a TPD run was made to a lower final temperature of 560 K in contrast to the other runs in which the sample is heated to 750 K. After
five TPD runs, there are minimal amounts of CO$_2$ or CO production, so if iodine desorbs in the
temperature range of 560 to 750 K, more iodine adatoms will remain on the surface after the
shorter TPD run. The CH$_2$I$_2$ TPD after the run to 560 K shows lower reactivity (less production
of formaldehyde and ethylene), and more desorption of the unreacted dosed molecule. The
production of formaldehyde and ethylene only decrease in intensity. The apparent higher iodine
coverage does not affect the barrier for the reactions. These results indicate that surface halogen
affects the chemistry primarily by simple site-blocking. It is noted, however, that given the
changing surface condition due to reduction, the effects of I on the reactivity cannot be easily
separated.

No carbon is found after the reaction unlike the experiments on α-Cr$_2$O$_3$\(\{10\bar{1}2\}\) where
trace amounts of carbon was found with AES [16]. This is due to the reactivity of the surface
lattice oxygen on the α-Fe$_2$O$_3$\(\{10\bar{1}2\}\) surface that burns off any surface carbon by oxidation into
nonselective oxidation products CO$_2$ and CO.

Complete extinction of oxygen-containing products arising from the complete surface
reduction is not seen in the current study. This observation is likely due to the migration of
oxygen from bulk to surface expected at the elevated temperatures at the end of the TPD runs.
An indication of the migration of bulk oxygen to the surface can be found from preliminary
sputter and annealing studies (not shown) with AES. A surface that has been sputtered and
annealed to the final temperature of the TPD ramp, 750 K, shows a higher O/Fe ratio (1.7)
compared to the sputtered surface (1.2). These results indicate that the 750 K temperature is
sufficient to drive mass transfer and reoxidation of the surface via either the outward diffusion of
bulk oxygen or inward diffusion of iron.
5.4.2 CH$_3$I reaction chemistry

The products seen from the reaction of CH$_3$I are assigned to be the result of the reaction of surface methyl species formed from the dissociation (C-I bond cleavage) of CH$_3$I since the gas phase reaction products do not include iodine. The CH$_3$I TPD shows no reaction without the electron-induced dissociation, demonstrating that the products are a result of the reaction electron-induced C-I bond cleavage, rather than a thermal CH$_3$I reaction.

The reaction of methyl on the α-Fe$_2$O$_3$(10ȇ2) surface results in the same products with similar kinetics as observed for the reaction of methylene. As seen for the reaction of methylene, the main product on the nearly-stoichiometric surface is CO$_2$, which is produced by the formate decomposition along with CO around 620-630 K. Formaldehyde production becomes dominant for later doses as the surface is more reduced. The fact that ethylene is produced at a similar range that it was formed from methylene species suggests that methylene species are formed at a temperature as low as 200 K by the dehydrogenation of methyl species, then the methylene intermediates go through the same coupling reaction as seen with the CH$_2$I$_2$ reaction and discussed above.

The change in O/C ratio of overall carbonaceous products for consecutive doses (Figure 5.10, 1.78 for the first run to 1.26 for the fifth run) is slower than observed for CH$_2$I$_2$ (Figure 5.5, 1.75 for the first run to 0.58 for the fifth run). This is likely because the degree of surface reduction due to the reactant oxidation by surface lattice oxygen is lesser with CH$_3$I. In other words, less CH$_3$ intermediates are reacted into oxygenates for each TPD run, resulting in less reduction of the surface. Since the change in surface is less, the change in product distribution changes less for consecutive runs. This trend is evident when the sum of the product signals of
the reactions of CH$_2$I$_2$ (Figure 5.4) and CH$_3$I (Figure 5.9) are compared. The sum of the signals is about four times higher with the CH$_2$I$_2$, indicating that more methylene is converted than methyl. This may be due to a difference in sticking coefficient between the two molecules (the Cl sum for methyl iodide is lower than for diiodomethane), and possibly a lower extent of dissociation of CH$_3$I via electron-induced dissociation.

### 5.4.3 Comparison to the reactions on α-Cr$_2$O$_3$ surfaces

On the α-Cr$_2$O$_3$(10$ar{1}$2) and α-Cr$_2$O$_3$(0001) surfaces, the major reaction pathway for the reaction of methylene is migration and coupling into ethylene, and that for methyl is the dehydrogenation into methylene that leads to the production of ethylene and methane. The products formed from the reaction of methyl and methylene on α-Fe$_2$O$_3$(10$ar{1}$2) such as CO$_2$, CO, and formaldehyde are totally different than the hydrocarbon products formed on α-Cr$_2$O$_3$(10$ar{1}$2). The difference in the selectivities of the methylene and methyl reactions on α-Cr$_2$O$_3$(10$ar{1}$2) and α-Fe$_2$O$_3$(10$ar{1}$2) is more drastic than the small difference in the activation barrier for methylene migration on the α-Cr$_2$O$_3$(10$ar{1}$2) and α-Cr$_2$O$_3$(0001) surfaces. These results illustrate that the electronic property of the surfaces play a more critical role on the reactivity of surface methylene and methyl species than the geometric differences between the (10$ar{1}$2) and (0001) corundum structure surfaces of α-Cr$_2$O$_3$.

The surface lattice oxygens on α-Fe$_2$O$_3$(10$ar{1}$2) are thought to be more reactive due to the extra electrons that the Fe$^{3+}$ cations ($d^5$) have compared to the Cr$^{3+}$ cations ($d^3$) on the α-Cr$_2$O$_3$(10$ar{1}$2) surface. A simple understanding of this can be achieved through the adaption of crystal field theory of octahedral arrangement of ligands as a simplification of the distorted octahedral structure of the crystals. According to crystal field theory, the five $d$ orbitals in a
transition metal surrounded by an octahedral arrangement of charges result in the splitting of the orbitals into three lower energy orbitals referred to as $t_{2g}$ and two higher energy orbitals called $e_g$. For a $d^5$ configuration, each of the five $d$ electrons fills the separate orbitals in a high-spin configuration, whereas for the $d^3$ configuration, the three electrons occupy the three $t_{2g}$ orbitals (Figure 5.11). In the case of the $d^5$ configuration, the population of the antibonding $e_g$ orbitals causes a decrease in the metal-oxygen bond strength, making the $\alpha$-Fe$_2$O$_3$ surface more reducible and the surface lattice oxygen more reactive to adsorbates. Oxygen removal via surface reduction further populates the $t_{2g}$ bonding orbitals, and stabilizes the remaining metal-oxygen bonds.

Another difference to note in the reactions of methylene and methyl species on $\alpha$-Cr$_2$O$_3$(10$\bar{1}$2) and $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2) is the methyl dehydrogenation temperature. On the $\alpha$-Cr$_2$O$_3$(10$\bar{1}$2) surface, the methyl dehydrogenates at a relatively high temperature of 510 K. On the other hand, methyl seems to be dehydrogenated at temperatures lower than 200 K on the $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2) surface, although direct evidence is limited to the partially-reduced surface as seen by the production of ethylene. This may also be related to the difference in the reactivity of oxygen: the higher reactivity of surface oxygen on $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2) may assist the breaking of the C-H bond of the methyl due to a higher preference for the formation of surface hydroxyl.

5.5 Conclusions

The main product CO$_2$ is produced together with CO from methyl and methylene on the nearly-stoichiometric $\alpha$-Fe$_2$O$_3$(10$\bar{1}$2) surface through the decomposition of formate species formed by the nucleophilic attack of surface oxygen along with on C-H bond breaking. This reaction induces a reduction of the surface, with the liberated hydrogens desorbing in the form of water. On the reduced surface, the selectivity changes, and formaldehyde production becomes
Figure 5.11. $d^5$ (high-spin) and $d^3$ configurations of transition metals split in an octahedral ligand field.
prevail by the adsorption of methylene on oxygen sites, while ethylene is also formed by the
migration and coupling of methylene. Methyl intermediates dehydrogenate into methylene at a
low temperature and undergo the same set of reactions as methylene intermediates.

The reaction of methyl or methylene on $\alpha$-Fe$_2$O$_3$(1012) shows a significantly different
selectivity than the reaction on $\alpha$-Cr$_2$O$_3$(1012) towards the production of oxygenated products.
This is due to the extra electrons that the surface Fe$^{3+}$ cations have ($d^5$) compared to Cr$^{3+}$ ($d^3$),
which results in the weak Fe-O bond and a more reducible surface. These results, compared to
the reaction chemistry of methylene and methyl on $\alpha$-Cr$_2$O$_3$ (0001), illustrates that the electronic
differences between Fe$^{3+}$ and Cr$^{3+}$ are more critical than the geometric effects observed on $\alpha$-
Cr$_2$O$_3$ for the methylene and methyl reactions on these metal oxide surfaces.

5.6 References

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Chapter 6.

Conclusions and Recommendations for Future Work

6.1 Conclusions

The different geometric structures of the α-Cr₂O₃(10̅12) and α-Cr₂O₃(0001) surfaces leads to a difference in the activation barrier of methylene migration across the surface (5.9 kcal/mol difference). DFT calculations indicate that this difference is due to a higher barrier for the transition from atop (sp²) to bridging (sp³) configurations of methylene on the α-Cr₂O₃(0001) surface. A minor reaction channel for the direct coupling of methylene bound to a single cation site only occurs on the α-Cr₂O₃(0001) surface since the surface cations have multiple coordination vacancies, in contrast to the cations on the α-Cr₂O₃(10̅12) surface which have a single coordination vacancy.

The difference in the geometrical proximity of surface lattice oxygen does not result in a significant difference in the barrier for the methyl dehydrogenation reaction (1.3 kcal/mol difference), suggesting that the surface anions play a minor role in the dehydrogenation of methyl on these surfaces, with surface lattice oxygen acting more like simple “parking spots” for the hydrogen following the decomposition of the methyl species.

Due to the side reactions with background water that produce methane, a direct comparison of selectivities of methylene and methyl reactions on the α-Cr₂O₃(10̅12) and α-Cr₂O₃(0001) surfaces is not particularly meaningful. However, it is noticeable that the
selectivities among the main reaction products CD$_4$ and CD$_2$=CD$_2$ for the first 0.1 L dose of CD$_3$I are similar: 63:37 on the (10\bar{1}2) surface and 57:43 on the (0001) surface.

The carbon-containing products formed from the reaction of methyl or methylene on \( \alpha\text{-Fe}_2\text{O}_3(10\bar{1}2) \) (CO$_2$, CO, and formaldehyde) are totally different than the products formed on \( \alpha\text{-Cr}_2\text{O}_3(10\bar{1}2) \) (methane and ethylene). This result is due to the extra electrons that the surface Fe$^{3+}$ cations have \( (d^5) \) compared to Cr$^{3+}$ \( (d^3) \), which results in the weaker Fe-O bond that impacts the reducibility of the surface and reactivity of surface lattice oxygen to incorporate into reaction products.

The difference in the selectivities of the methylene and methyl reactions on \( \alpha\text{-Cr}_2\text{O}_3(10\bar{1}2) \) and \( \alpha\text{-Fe}_2\text{O}_3(10\bar{1}2) \) is more drastic than the difference in the activation barrier of the methylene migration seen on the \( \alpha\text{-Cr}_2\text{O}_3(10\bar{1}2) \) and \( \alpha\text{-Cr}_2\text{O}_3(0001) \) surfaces. In other words, the “electronic effect” is more critical than the “geometric effect” for the methylene and methyl reactions on these metal oxide surfaces.

6.2 Recommendations for future work

6.2.1 DFT Calculation of halogen on \( \alpha\text{-Cr}_2\text{O}_3(0001) \)

In Chapter 2, it has been shown that the reactivity of the surface shuts down at an AES Cl/Cr ratio that corresponds to one Cl per one surface Cr site, despite the multiple coordination vacancies available on the surface cationic sites of the \( \alpha\text{-Cr}_2\text{O}_3(0001) \) surface. This has been attributed to the change of the oxidation state of the cation from Cr$^{3+}$ to Cr$^{4+}$ when a halogen is bonded to surface cations, leading to a preferred tetrahedral coordination, rather than the octahedral coordination. The trend that the cationic sites avoid the binding of multiple Cl
adatoms can be monitored by DFT calculations for this surface. Such calculations were made in the early stages of this study for a ferromagnetic spin configuration in $\alpha$-Cr$_2$O$_3$(0001). The heat of adsorption calculated for a Cl adatom significantly decreases when multiple Cl adatoms are bound on a cationic site. Moreover, the barrier for the diffusion of a single Cl from a doubly-chlorinated site to a vacant surface cation is 0.24 eV, and is exothermic by over 1.6 eV. This is in contrast with the process of single Cl diffusion from a singly-occupied cation site, which has a barrier of 1.38 eV, and is, therefore, only operable at the higher temperature end of the TPD experiment. These calculations were not reported in this dissertation because they were done prior to a recognition that the antiferromagnetic ground state is most appropriate for $\alpha$-Cr$_2$O$_3$. These calculations should be redone for $\alpha$-Cr$_2$O$_3$(0001) with the correct antiferromagnetic spin arrangement. Although similar results are expected, these calculations need to be redone to predict the correct heats of adsorption for various numbers of Cl bound to a cationic site, and the barrier for the Cl migration to understand why the reaction shuts down at one Cl per one surface Cr. However, these calculations have not been done due to the limitation in computing resources on campus which have caused significant delays in the computational studies.

6.2.2 Calculation of methylene dehydrogenation barrier on $\alpha$-Cr$_2$O$_3$(0001)

DFT calculations of the methylene migration process on the $\alpha$-Cr$_2$O$_3$(0001) surface have shown that the rehybridization between sp$^2$ (atop) and sp$^3$ (bridging) configurations of methylene is directly related to the barrier of methylene migration. It is thought that the methylene migration and coupling into ethylene is favored over the dehydrogenation into surface carbon because this rehybridization process has a lower barrier than the methylene dehydrogenation process. This reasoning can be verified if a potential energy surface for methylene dehydrogenation is performed for a direct comparison to the values for the methylene migration
These calculations also have not been done due to the limitation in computing resource as mentioned in the previous section.

### 6.2.3 XPS, NEXAFS, and DFT study of C\textsubscript{1} intermediates on α-Fe\textsubscript{2}O\textsubscript{3}(10\overline{1}2)

Although the reaction studies of CH\textsubscript{2}I\textsubscript{2} and CH\textsubscript{3}I provide information about the reaction mechanism of methylene and methyl reactions on the α-Fe\textsubscript{2}O\textsubscript{3}(10\overline{1}2) surface, direct evidence of the binding configurations of the C\textsubscript{1} intermediates is not available. An XPS study of the adsorption of CH\textsubscript{2}I\textsubscript{2} and CH\textsubscript{3}I on this surface will aid greatly in identifying reaction intermediates, determining the location of surface hydrocarbon fragments, and monitoring the dissociation of carbon-halogen bonds. Most importantly, it can be found if the surface iodine deposited by the dissociation of the dosed molecules desorb during the temperature range of the TPD experiments, which has not been possible with the use of AES due to the overlap between the I MNN and O KLL signals.

The use of NEXAFS could also be helpful for the identification of intermediates with intra-molecular resonances (formate) and pi bonds (formaldehyde). A DFT study will also be helpful in finding the energetics of the binding sites of the surface intermediates. The previous XPS examination of the reactions on the α-Cr\textsubscript{2}O\textsubscript{3}(0001) surface has been done at a beamline of a synchrotron light source, however, the facility has not been available for the examination of the reactions on the α-Fe\textsubscript{2}O\textsubscript{3}(10\overline{1}2) for the past year although requests have been made. Moreover, the low beam intensity of the in-house XPS equipment together with the low sensitivity for carbon inhibits the acquisition of quality C 1s spectra with a reasonable signal-to-noise ratio and resolution, and the small size of the iron oxide crystal (0.5 cm × 0.5 cm) compared to the
sampling area of our laboratory spectrometer does not allow for an accurate characterization of the surface.