Methylene migration and coupling on a non-reducible metal oxide:
the reaction of dichloromethane on stoichiometric α -Cr₂O₃(0001)

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ABSTRACT

The reaction of CH_2Cl_2 over the nearly-stoichiometric $\alpha\text{-Cr}_2\text{O}_3(0001)$ surface produces gas phase ethylene, methane and surface chlorine adatoms. The reaction is initiated by the decomposition of CH_2Cl_2 into surface methylene and chlorine. Photoemission indicates that surface cations are the preferred binding sites for both methylene and chlorine adatoms. Two reaction channels are observed for methylene coupling to ethylene in temperature-programmed desorption (TPD). A desorption-limited, low-temperature route is attributed to two methylenes bound at a single site. The majority of ethylene is produced by a reaction-limited process involving surface migration (diffusion) of methylene as the rate-limiting step. DFT calculations indicate the surface diffusion mechanism is mediated by surface oxygen anions. The source of hydrogen for methane formation is adsorbed background water. Chlorine adatoms produced by the dissociation of CH_2Cl_2 deactivate the surface by simple site-blocking of surface Cr^{3+} sites. A comparison of experiment and theory shows that DFT provides a better description of the surface chemistry of the carbene intermediate than DFT+U using reported parameters for a best representation of the bulk electronic properties of $\alpha\text{-Cr}_2\text{O}_3$.

1. Introduction

Hydrocarbon surface intermediates occur in a variety of heterogeneous catalytic processes. Among the multitude of possible intermediates, methylene ($=\text{CH}_2$) is the simplest carbene, and is thought to be an active species for C-C bond formation in the Fischer-Tropsch reaction [1] and in the synthesis of formaldehyde from methane [2]. In one of the dominant reaction pathways over well-defined transition metal surfaces [3], methylene acts as a coke former by undergoing complete dehydrogenation. Additional reactions on transition metal surfaces include hydrogenation to methane [4-9], and methylene coupling to form ethylene [4-6,9]. On copper surfaces, the migration (surface diffusion) of methylene has been reported, and can result in either the coupling of the methylene species to produce ethylene, or insertion into surface metal-alkyl bonds [3,5,6], similar to the chain growth step in Fischer-Tropsch chemistry. Following the reports for copper surfaces, additional examples of the migratory coupling and/or insertion of methylene have been reported [10-14], including a thorough RAIRS investigation of the insertion step on Ag(111) [11].

Studies of the reactions of methylene on well-defined oxide-like surfaces have been limited to a few studies on oxygen-covered metal surfaces. The partial oxidation of methylene to formaldehyde was reported on oxygen-covered Rh(111) [15]. On oxygen-covered Mo(100), methylene is found to hydrogenate to methane by reaction with surface hydrogen, while oxygen acts as a site-blocker in comparison to the reaction on the clean Mo(100) [16]. C-C bond formation is also seen on oxygen-covered Mo(100) surfaces [12], with higher coverages of oxygen suppressing the migratory insertion reaction.

Supported chromia is a well-known catalyst for the selective dehydrogenation of alkanes such as isobutane and propane to the corresponding alkenes [17-20]. For example, the industrial

CATOFINTM process has a selectivity as high as 90+ mol% for the dehydrogenation of isobutane to isobutylene. The active reaction centers in these catalysts are thought to be coordinatively unsaturated Cr³⁺ cations [20]. Supported chromia is also the active component in the Phillips catalyst for olefin polymerization [21]. While there has been controversy over the oxidation state of Cr at the active site [21], recent work from the Scott group [22] indicates a three-coordinated Cr²⁺ center may be the precursor for the polymerization-active sites.

This study reports the migratory coupling of methylene on a well-defined, model, metal oxide surface, α -Cr₂O₃(0001). Methylene intermediates are generated through the thermal dissociation of dichloromethane (CH₂Cl₂), and studied experimentally with temperature-programmed reaction and X-ray photoelectron spectroscopy. First-principles calculations have also been used to examine the mechanism of methylene surface diffusion and coupling.

2. α -Cr₂O₃(0001)

α -Cr₂O₃ has a corundum bulk structure and is an insulator with a band gap of 3.2 eV [23-26]. Cr³⁺ cations in the bulk are surrounded with six O²⁻ anions in distorted octahedra, while each anion is surrounded with a tetrahedron of four metal cations. Among the possible cation sites, one-third of the sites are vacant along the $[10\bar{1}2]$ direction [27]. Along the [0001] direction, three atomic planes provide a stoichiometric repeating unit with compositions of [Cr, 3O, Cr]. Cleavage between the planes of closely-lying Cr layers yields a hexagonal, non-polar, stoichiometric α -Cr₂O₃(0001) surface (Figure 1). The resulting surface exposes 3-fold coordinated cations (three coordination vacancies) and 3-fold coordinated anions (one coordination vacancy). On the ideal unrelaxed surface, the cations are separated by 4.9 Å, effectively isolating the metal reaction centers.

3. Methods

3.1. Experimental Methods

Reaction experiments were conducted in an ion-pumped ultra-high vacuum chamber with a base operating pressure of 1×10^{-10} Torr. The chamber was equipped with a Physical Electronics model 15-555 single-pass CMA for Auger electron spectroscopy (AES), an Inficon Quadrex 200 mass spectrometer for temperature programmed desorption (TPD) experiments, and a Princeton Research Instruments model RVL 8-120 reverse view low-energy electron diffraction (LEED) optics.

Soft X-ray photoelectron spectroscopy (XPS) was performed in a separate cryopumped vacuum system at the U12a beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. All photoemission spectra were collected at an instrumental resolution of 0.5 eV using 350 eV photons. The spectra are referenced to a Cr $2p_{3/2}$ binding energy of 576.9 eV [28]. 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 $2p_{3/2}$ feature in separate runs using $h\nu = 650$ eV. Compensation for surface charging during the XPS was achieved with a Gammapdata Scienta FG-300 flood gun using 0.5 eV electrons. The base operating pressure for this system was 1×10^{-10} Torr.

The α -Cr₂O₃ crystal boule was purchased from a Japanese jewelry company, St. Omer. The principle impurity, potassium, was depleted from the crystal by extended Ar ion bombardment in UHV at elevated temperatures. The sample was cut and oriented to within 1° of the (0001) surface using Laue back-reflection and polished to a final mirror finish with 0.25 μ m diamond paste. The sample was 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 crystal through a hole in the stage using Aremco No. 569 ceramic cement.

α -Cr₂O₃(0001) surfaces described in the literature have been prepared by the direct oxidation of Cr(110) with 10 to 20 L of oxygen at 625 K followed by annealing in vacuum at 925 K [29] and by molecular beam epitaxy on α -Al₂O₃ substrates [30]. For the epitaxial thin films, Henderson and Chambers [30] were able to prepare stoichiometric surfaces by 500 eV Ar⁺ ion bombardment and annealing at 850 K. Using adsorbed water as a probe, they demonstrated that dissociative and molecular adsorption of H₂O occurs on terrace sites [30,31], and gives a characteristic fingerprint for water desorption from the stoichiometric surface.

The studies reported here were conducted on a (0001)-terminated bulk single crystal of α -Cr₂O₃. Several different surface preparations have been examined that give water desorption traces similar to those reported by Henderson and Chambers [30], including treatments involving a 2 keV argon ion bombardment cleaning, oxidation, milder sputtering (500 eV Ar⁺), and annealing [32]. For this study, we used a simpler procedure involving 2 keV ion bombardment and annealing at 900 K in vacuum to clean and order the surface. This treatment produces water desorption traces characteristic of a stoichiometric surface, with an additional (small) signal at higher temperatures for trace hydrogen desorption corresponding to the reoxidation of reduced sites by water. The hydrogen generated is attributable to less than 1 % of the total surface Cr site density [32]. This preparation method (2 keV ion bombardment and annealing at 900 K in vacuum) has been utilized because of its simplicity, and because a lower background pressure is realized in the vacuum chamber in the absence of an oxidation step in the preparation procedure. Following sample cleaning and ordering, AES was used to check for surface cleanliness, and LEED was used to confirm the hexagonal (1x1) periodicity characteristic of a simple termination

of the bulk material. AES spectra were collected at a primary beam energy of 5 keV. To avoid sample charging due to impinging electron beams, AES was done at 850 K, and LEED was done at 600 K.

Sigma-Aldrich dichloromethane (CH_2Cl_2), anhydrous $\geq 99.8\%$, Sigma-Aldrich “100 %”, 99.96 atom % D dichloromethane- d_2 (CD_2Cl_2), Matheson CP grade 99.7 % deuterium (D_2), and Aldrich 99.9 atom % D deuterium oxide (D_2O) were used as received. Gas dosing was accomplished by backfilling the chamber through a variable leak valve. The mass spectrometer used for TPD is fitted with a quartz skimmer to enhance the signal from the sample surface, and cover the ionizer to minimize sampling from non-sample surfaces in TPD. In addition, desorption traces were checked from non-sample surfaces (such as the clamps that fasten the sample to the holder) to ensure that these background signals make no significant contribution to the reported data. The reported dose sizes have been corrected for ion gauge sensitivity, and all desorption traces and quantities have been corrected for mass spectrometer sensitivity.¹ For TPD, all doses were made at a sample temperature of 90 K, and linear heating ramps were run at 2.5 K/s up to a sample temperature of 830 K. The low heating rate was used to decrease the possibility of thermal fracture of the ceramic sample.

3.2. Computational Methods

All calculations were performed using the projector-augmented-wave method [34,35] within the Vienna Ab-initio Simulation Package (VASP) [36-38]. The Perdue-Burke-Ernzerhof (PBE) approximation was used to treat exchange and correlation utilizing a standard generalized gradient approximation (GGA) [39].

¹ An ion gauge sensitivity of 6.2 was used for dichloromethane based on a correlation by S. George reported by Brainard and Madix in Ref 33. Relative mass spectrometer sensitivity factors of 0.15 for dichloromethane (m/z 84), 0.23 for ethylene (m/z 27), and 0.66 for methane (m/z 16) were determined experimentally.

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 super cell that is six stoichiometric [Cr, 3O, Cr] repeat units deep in the [0001] direction. For all calculations, the k -point sampling was generated using a Monkhorst-Pack scheme [40]. A $3\times3\times3$ mesh was sufficient to ensure convergence of the structure and energy for the bulk calculations. For all geometry optimized structures, the forces on the individual atoms are less than 0.01 eV/Å. An 80-atom slab with a vacuum gap of 20 Å was used for all subsequent surface calculations. The 80-atom cell is four stoichiometric [Cr, 3O, Cr] repeat units deep and exposes a (2×2) surface mesh. The atoms in the two lower stoichiometric repeat units were fixed at bulk positions. For all calculations, the initial magnetic moments of the Cr³⁺ cations (d^3) were set following the known antiferromagnetic order of the crystal [41], which is also found to be the ground-state magnetic order using DFT calculations within the GGA [42]. The minimum energy pathways (MEPs) for methylene migration/coupling and Cl migration processes were investigated using the climbing-image nudged elastic band method (CI-NEB) [43-45].

DFT calculations are known to have difficulties in predicting the electronic properties of strongly correlated oxide materials, often greatly under-evaluating the band gap [42]. It has been shown that this problem can be overcome with the inclusion of on-site Coulomb repulsion (DFT+U) [46,47]. A DFT+U of α -Cr₂O₃ [42] 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 -Cr₂O₃. In the current study, results for both DFT and DFT+U are presented for comparison. The DFT+U method in the form proposed by Dudarev *et al.* [47] has been used. It is pointed out, however, that the optimal value of the on-site potential for the bulk may not strictly apply to the surface, as mentioned in the study of this surface by Rohrbach *et al* [42].

4. Results

Reaction experiments (TPD) for adsorbed dichloromethane results in two gas phase products, ethylene ($\text{CH}_2=\text{CH}_2$) and methane (CH_4), and desorption of unreacted dichloromethane (CH_2Cl_2). Post-reaction surface analysis (AES and XPS) indicates adsorbed chlorine as a surface reaction product. Surface Cl was subsequently removed by Ar ion bombardment as part of the standard surface cleaning and ordering procedure described above. 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 for identification. m/z signal of 84 and 49 were used to identify the dosed CH_2Cl_2 molecule while $m/z = 28, 27, 26, 25$ were used for the identification of ethylene and $m/z = 16, 15, 14$ for methane. Contributions of the signal for the dosed reactant molecule (CH_2Cl_2) in 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 under these reaction conditions.

4.1. Thermal desorption

Figure 2 shows the thermal desorption traces for an 0.05 L ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{sec}$) dose of CH_2Cl_2 on a clean, nearly-stoichiometric surface at 90 K with heating up to 830 K. A small dose size is chosen to minimize the effect of adsorbed chlorine on the kinetics and selectivity of the methylene reaction, and to decrease the contribution of unreacted CH_2Cl_2 that desorbs around 290 K. Two features for the ethylene product 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 thermal cleavage of both C-Cl bonds in CH_2Cl_2 .

4.1.1. Ethylene production

The production of ethylene from CH_2Cl_2 implies the coupling of two methylenes, and the observation of two ethylene desorption peaks in TPD indicates two different rate limiting steps to methylene coupling. When ethylene is directly dosed onto a clean $\alpha\text{-Cr}_2\text{O}_3(0001)$ surface, it desorbs around 300 K (not shown). Therefore, the ethylene production from CH_2Cl_2 (Figure 2) at 300 K is considered desorption-limited, and the production at 480 K is reaction-limited.

Desorption limited ethylene indicates the formation of ethylene below 300 K with an activation barrier lower than that for the desorption of ethylene. A possible route for this process is the direct coupling of two methylenes that are bound to a single site. Previously, computational studies on Cu(111) have suggested a near-zero activation energy for the coupling of methylene intermediates bound on a metal site [48,49], and the DFT investigation of methylene coupling on $\alpha\text{-Cr}_2\text{O}_3(0001)$ described below also indicates near-zero activation energy for the coupling of two methylenes bound in close proximity to a single chromium center.

Following this argument and taking into account the small dose size and limited adsorbate coverage, the dominant reaction-limited contribution to ethylene production at 480 K is thought to be the result of a diffusion-limited process where methylene migration across the surface controls the coupling kinetics. A DFT examination of this process is described below. In addition to the data for the 0.05 L dose shown in Figure 2, the thermal desorption behavior has been examined over a range of dose sizes from 0.05 L to 0.5 L. No significant variation in the reaction-limited ethylene desorption temperature (480 K) is observed, indicating that the desorption temperature is independent of coverage, and the rate-limiting step is nominally first-

order. The apparent first-order activation energy for the 480 K reaction channel is estimated at 30.3 kcal/mol (1.31 eV) using the Redhead method and assuming a normal pre-exponential factor of 10^{13} s^{-1} [50].

4.1.2. Methane production

Methane is formed with a maximum rate at 510 K with a shoulder about 50 K higher (Figure 2). The methane peak at 135 K is attributed to the desorption of physisorbed methane formed in the ion pump from the dosed gas, [and is consistent with other reports for the desorption of molecularly adsorbed methane on oxide surfaces \[51,52\]](#). For methane to be generated from methylene, the expected route might be the dehydrogenation of methylene to form surface H, with the subsequent hydrogenation of remaining methylene groups with the liberated hydrogen to form surface methyl and eventually methane. However, methylene dehydrogenation is expected to have a higher activation barrier than methyl dehydrogenation, but the 510 K peak temperature is near that observed for methyl dehydrogenation on this surface (490 K) [53], raising suspicion that methylene dehydrogenation is not the source of hydrogen for methane production from methylene in our experiments. In addition, no H_2 desorption (another likely reaction product of surface H atoms formed from the dehydrogenation step) 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 (shown below).

4.2. Thermal desorption of CD_2Cl_2 and side reaction chemistry

To examine the source of hydrogen for the formation of methane, a TPD study of CD_2Cl_2 has been performed. If the methane formed from this reactant is CD_4 , it would indicate that the source of hydrogen 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 3 shows the isotopic forms of methanes produced from the reaction of CD_2Cl_2 . The majority of the methane produced is CD_2H_2 at 515 and 575 K, similar to the CH_4 production seen from CH_2Cl_2 (Figure 2). A smaller desorption feature for CD_3H appears to be a combination of two peaks aligned at the main methane peak temperature (515 K) and the shoulder temperature (575 K), while an even smaller feature of CD_4 is seen primarily at 575 K. This dataset indicates that the source of hydrogen for the formation of the majority of methane from methylene is a source other than the D atoms expected from dehydrogenation of deuterated methylene.

In another separate set of D_2 TPD experiments (not shown), D_2 desorbs from the clean, nearly-stoichiometric surface at 100 K. This weak interaction of D_2 (or H_2) suggests that background H_2 is not the likely source of the H atoms for the formation of methane, leaving background water as a likely source of hydrogen. As shown by Henderson and Chambers [30], H_2O is known to adsorb in dissociative and molecular forms on $\alpha\text{-Cr}_2\text{O}_3(0001)$. Furthermore, a recent study in our lab identified trace amounts of D_2 production from D_2O TPD on $\alpha\text{-Cr}_2\text{O}_3(0001)$, a process thought to be due to a small concentration of surface defects [32].

In Figure 3, the main peak temperature of 515 K for CD_2H_2 production is near the methyl dehydrogenation temperature of 490 K [53], suggesting a rate-limiting dehydrogenation of methyl ($-\text{CD}_2\text{H}$) formed by the addition of surface H (from dissociated water) to methylene, $=\text{CD}_2$. The shoulder of the methane peak at 575 K is assigned to the rate-limiting production of surface H by $\beta\text{-H}$ elimination from ethyl fragments formed by the insertion of methylene into surface-methyl bonds. This additional reaction pathway is addressed in detail elsewhere [53,54]

by examining the coadsorption and reaction of methyl and methylene. We note also that a small portion of ethylene is produced by this same process in the high temperature tail of the ethylene desorption signal.

4.3. Sequential CH₂Cl₂ doses: TPD and AES analysis

Figure 4 shows the AES spectrum of a clean, nearly stoichiometric α -Cr₂O₃(0001) (Figure 4(a)), and the spectrum taken after a series of CH₂Cl₂ TPD runs with an accumulated total exposure of about 7 L (Figure 4(b)). Figure 4(a) shows the typical fingerprint of a clean α -Cr₂O₃ surface with Cr and O features in the range of 470-550 eV, with no signals for carbon or chlorine. Figure 4(b) shows a Cl LMM feature characteristic of Cl adatoms left on the surface following 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 detectable extent.

Figure 5 shows the AES Cl/Cr ratio corrected by AES sensitivity factors² as a function of total dose for a sequence of consecutive TPD runs beginning on an initially clean surface. The Cl/Cr ratio increases with each TPD run, and levels out at a value around 0.22 (± 0.02) for a total exposure of 0.5 L of CH₂Cl₂ or greater. The Cl/Cr value corresponds to a nearly monolayer coverage of one Cl adatom per one surface Cr site.³

Figure 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 nearly linearly with consecutive doses of CH₂Cl₂ over the range of doses where the Cl coverage increases linearly (Figure 5). The decrease

² Due to the overlap between the primary peaks Cr L₃M_{2,3}M_{4,5} (529 eV) and O KLL (503 eV), the intensity of the Cr L_{2,3}M_{2,3}M_{2,3} (489 eV) peak is used for the calculation of Cr signal intensity for quantification purposes as described in Ref. 55. The Cr L_{2,3}M_{2,3}M_{4,5} / Cr L_{2,3}M_{2,3}M_{2,3} peak ratio from a standard Cr metal spectrum in Ref. 56 is applied to the sensitivity factor of the Cr L_{2,3}M_{2,3}M_{4,5} peak to obtain the sensitivity factor for Cr L_{2,3}M_{2,3}M_{2,3}.

³ The Cl/Cr ratio corresponding to a monolayer is estimated using an exponential decay model for signal intensity with depth into the bulk for 42° 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 from the ‘universal’ curve in Ref 57.

in ethylene production with increasing surface Cl coverage indicates site blocking by Cl adatoms. Methane production also decreases, but is relatively insensitive to the Cl coverage for earlier doses.

To demonstrate the effect of surface Cl adatoms on the reaction kinetics, the TPD signals of ethylene (Figure 7(a)) and methane (Figure 7(b), respectively) are shown for five consecutive TPD runs of 0.05 L doses of CH_2Cl_2 starting on a clean, nearly-stoichiometric surface. AES (Figure 5) shows that the Cl coverage increases for each run. The peak temperatures of ethylene and methane do not change significantly for different Cl coverages, indicating that the surface Cl does not have a significant impact on the surface methylene reaction kinetics. However, the reaction probability decreases with higher Cl coverage, yielding less reaction products due to the site-blocking for CH_2Cl_2 dissociation and reaction by Cl adatoms.

4.4. X-ray photoelectron spectroscopy

Figure 8 shows the synchrotron-based photoemission results ($h\nu = 350$ eV) for the reaction of adsorbed dichloromethane. The clean, nearly-stoichiometric sample 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 the photoemission measurements in an attempt to isolate the surface intermediates formed during the thermally-induced surface reaction of CH_2Cl_2 .

C 1s XPS spectra are shown in Figure 8(a). The spectrum taken directly after dosing 10 L 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_2Cl_2 [28,58]. 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 expected for a metal-bound methylene fragment [9,59]. With further heating to

270 and 300 K, some high binding energy feature is left at 287.2 eV, and further decreases in intensity with only a small contribution remaining for the 300 K spectrum. There is little change in intensity of the low binding energy feature at 284.0 eV. Heating the surface to 800K through the temperature range associated with product desorption in TPD results in the loss of all but a trace C 1s signal. We note that no signal for molecularly adsorbed methane (as seen in TPD) is expected in these experiments because the chamber on the beamline is cryopumped.

The Cl 2p spectra shown in Figure 8(b) exhibit similar trend with 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 CH_2Cl_2 [28]. This feature decreases as the sample is heated and the multilayers are removed, while 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 corresponds to the desorption temperature of CH_2Cl_2 in TPD, while the 198.3 eV doublet feature remains after heating the sample to 800 K. This low binding energy of the remaining Cl 2p doublet is characteristic of metal chloride [28], 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 begins between 110 and 200 K since both cation-bound hydrocarbon and chlorine adatom signals appear by 200 K. The C 1s spectra do not show a signal for singly-chlorinated carbon (285.5-286.5 eV, [58,60,61]), but only show the unchlorinated carbon feature (284.0 eV) appearing as the doubly-chlorinated (molecular CH_2Cl_2) carbon feature (287.4 eV) decreases for higher temperatures. These results indicate complete C-Cl bond breaking in the CH_2Cl_2 reactant, leading to the

formation of a metal-bound hydrocarbon fragment at 284.0 eV attributed to methylene bound at Cr cation 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 C 1s signal left by 300 K is that of a metal-bound hydrocarbon fragment, and the Cl 2p spectra at 270 K shows a small Cl contribution due to molecular CH₂Cl₂. A similar but smaller contribution is also apparent after heating to 300 K as shown in Figure 8(c) by comparison to the 800 K Cl 2p spectrum. The spectrum taken after heating to 800 K is characteristic of only Cl adatoms since TPD indicates the complete reaction of CH₂Cl₂ by 700 K. The comparison in Figure 8(c) shows an additional higher binding energy Cl 2p contribution attributable to molecular CH₂Cl₂ for the 300 K spectrum following normalization on the low binding energy 2p_{3/2} peak. These results indicate that the small C 1s feature at 287.2 eV for the 300 K spectrum is likely attributable to a small coverage of molecular CH₂Cl₂ rather than an oxygenated surface intermediate.

4.5. DFT simulations

4.5.1. Methylene binding

The optimized geometries of surface methylene for three different initial configurations are shown in Figure 9: methylene bound on top of a Cr center (atop methylene), methylene that bridges between a Cr and a nearest neighbor O anion (short-bridging methylene), and methylene that bridges between a Cr and a second-nearest neighbor O (long-bridging methylene). No stable methylene configuration was found that bridged between two surface oxygen anions or occupied a 3-fold hollow site of O atoms using either DFT or DFT+U.

Figure 10 shows the relative free energies and [net magnetization of the unit cell](#) for the configurations shown in Figure 9. The calculation without the on-site potential predicts that the on-top 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 that the short-bridging methylene is 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 indicates a majority of the methylene is metal bound, suggesting a preference for the atop configuration of methylene and better agreement of the DFT results (rather than DFT+U) with experiment.

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 [associated with a decrease in spin for the cations binding the fragment](#). The calculated magnetization of the system for atop methylene is 2.0000, characteristic of a π bonded methylene, $=CH_2$, leading to two fewer unpaired electrons. The [magnetization](#) calculated for the short-bridging methylene was 1.0625 with DFT, and 0.0000 with DFT+U, while both calculations give a value of 0.0000 for the long-bridging configuration. The free energy of each configuration was calculated for several fixed integer values of the [magnetization](#) (*e.g.*, $mag = 0, 1, 2$), to ensure that the values described above corresponds to the DFT ground state for each binding configuration.

4.5.2. Methylene migration

The methylene migration pathway was examined using the climbing-image nudged elastic band (CI-NEB) method [44,45,62,63]. A single route for migration was found along the line that connects two neighboring Cr cations (Figure 11). The migration involves the movement between minima on the potential energy surface associated with the three methylene binding

configurations in Figure 11(b): atop to short-bridging, short-bridging to long-bridging, and long-bridging to atop methylene configurations. Figure 12 shows the potential energy surface with no zero point corrections for methylene migration between neighboring surface cations. The transition state for the rate-limiting surface diffusion step occurs between the long-bridging and the atop configurations with overall activation barriers of 1.28 eV for DFT and 1.51 eV for DFT+U. The activation barrier calculated without the inclusion of on-site potential is in better agreement with the experimental apparent first-order activation energy of 1.31 eV for the reaction-limited production of ethylene attributed to the rate-limiting migration of methylene.

While DFT suggests the possibility of a bridge bonded species, our XPS data show no clear indication of such a surface intermediate. Note that the single C–O bond in a bridge bonded species would be expected to give an XPS feature with a binding energy similar to that of the oxygenated C in an alkoxide, i.e., around 286.4 eV. Because of the lack of experimental evidence for such a species in XPS, we have used the barriers between minima in the DFT potential energy surface in Figure 12(a) to estimate the equilibrium fraction of the different methylene binding configurations as a function of temperature (Figure 13) assuming equal pre-exponentials in the forward and reverse directions. Up to the temperature where the reaction of methylene is completed in TPD (about 650 K), the predicted fraction of both short and long bridging methylene of less than 1 %, a fraction we are unlikely to detect in XPS.

4.5.3. Methylene coupling to ethylene

TPD of CH_2Cl_2 shows that part of the ethylene is produced through a desorption-limited reaction channel at 300 K, indicating a pathway to methylene coupling that does not require migration. Given the multiple coordination vacancies of the surface chromium cations, the coupling of two methylenes bound at a single chromium center could be a reasonable possibility.

Attempts to geometry optimize various configurations of two methylenes bound at a single chromium center led directly to a stable configuration involving ethylene bound at a chromium cation site, indicating a near-zero activation energy for the coupling of methylene to ethylene, similar to the observations for methylene coupling over Cu(111) [48,49]. Given the better agreement between experiment and DFT in previous sections, DFT+U was not used to examine the methylene coupling reaction.

Due to the near-zero barrier for coupling and the lack of stable configurations for two methylene species bound to a single cation, a NEB calculation which resembles the coupling reaction at the end of the methylene diffusion process was examined with DFT. Figure 14(a) shows the minimum energy pathway for the coupling of two methylenes bound at neighboring Cr sites, one bound in an atop configuration and the other bound in the long-bridging configuration to a neighboring cation and an O anion nearest neighbor to the atop species. Figure 14(b) shows the associated structures at several points along the potential energy surface. DFT gives an activation barrier of 0.56 eV to break the Cr-C bond of the long-bridging methylene to form a formaldehydic transition state, and shows no further barrier for coupling into ethylene once the two species are in the vicinity of a cationic site. [With the barrier for coupling being lower than the barrier for methylene diffusion \(1.28 eV\), the diffusion of methylene is the rate-limiting step for the overall process of migration and coupling process.](#)

4.5.4. Binding and diffusion of Cl adatoms

Given the experimental observation of a limiting coverage of one Cl adatom per surface Cr cation, DFT has been used to examine the binding and diffusion of Cl adatoms on the α -Cr₂O₃(0001) surface. The preferred binding geometry of a single Cl adatom is an atop configuration over a surface Cr cation, in agreement with the XPS observations, with a heat of

adsorption of 2.15 eV. The heat of adsorption per Cl adatom decreases greatly when multiple cations are bound to a single cation site. The heat of adsorption decreases from 2.15 to 1.16 and 0.77 eV per Cl adatom for one, two and three chlorine atoms, respectively, bound to a single Cr site. In all cases, examination of the system magnetization indicates that the binding of each Cl adatom decreases the number of unpaired d electrons by one. [There is no indication from the simulations of site exchange of O and Cl during the chlorine surface diffusion process.](#)

Cl surface diffusion has been investigated for two specific situations: (1) diffusion of a single Cl adatom between two equivalent Cr sites, and (2) Cl diffusion from a doubly-occupied cation site to a neighboring vacant cation site. For both cases, the Cl adatom is directly transferred between Cr cations, unlike the case of methylene migration which is mediated by surface oxygen. Additionally, the system magnetization is constant across the potential energy surface, suggesting the Cl-surface bond order is conserved in the diffusion process.

Figure 15 shows the potential energy surface for case (1): the diffusion of a Cl adatom from a singly occupied Cr site to a neighboring vacant site. The barrier to surface diffusion predicted by DFT is 1.40 eV, slightly higher than the predicted barrier of 1.28 eV for methylene migration. The transition state is a Cl adatom symmetrically bridged between the two neighboring surface cations for this athermal reaction.

The second case is illustrated in Figure 16 for the diffusion of a Cl adatom from a Cr cation binding two chlorines to a neighboring vacant cation site. The predicted barrier to diffusion is small, 0.18 eV, and the reaction is exothermic by 1.9 eV. An early transition state is found (Figure 16), as might be expected for this exothermic reaction based on the Hammond-Leffler postulate [64,65].

5. Discussion

The lack of singly chlorinated products in TPD and singly chlorinated surface intermediates in XPS clearly demonstrates that both C-Cl bonds in dichloromethane are thermally cleaved, forming methylene intermediates and surface Cl adatoms. Experimental and computational results suggest two different rate-limiting processes for ethylene formation from methylene: a desorption-limited process involving the coupling of methylenes bound at a single site, and a diffusion-limited migration and coupling of methylenes with a higher activation energy. DFT calculations indicate a methylene migration mechanism between atop cation sites that is mediated by surface oxygen anions, allowing several bridging configuration for methylene between surface cations and anions. The methylene surface diffusion/migration process can be viewed as a thermally driven rehybridization between sp^2 (π bonded methylene in an atop site on a surface Cr cation) and sp^3 (bridge bonded 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 complete dehydrogenation of methylene to surface carbon.

The chlorine adatoms deposited on the surface have little effect on the activation barriers for the production of ethylene and methane. However, the CH_2Cl_2 dissociation and reaction probability decreases with increasing Cl coverage, yielding less reaction products due to the blocking of Cr cation sites by Cl adatoms. The observation that the surface Cl saturates and the reactivity shuts down at a coverage near one Cl adatom per surface Cr cation was unexpected given the multiple coordination vacancies for Cr cations on the stoichiometric (0001) surface. This result can be understood in terms of the chemistry of tetravalent chromium. The binding of a single Cl adatom at a Cr cation site changes the formal oxidation state of the cation from Cr^{3+}

to Cr^{4+} and increases the surface cation coordination from three to four, leaving the cation in the nominally tetrahedral coordination environment preferred by tetravalent chromium [66]. We note, however, that there is no clear evidence for a change in Cr oxidation state from an examination of the Cr 2p features in XPS. The preference for one Cl adatom per surface Cr cation is also apparent in our DFT calculations. Given the similarities in the predicted barriers to surface diffusion for Cl (1.40 eV) and methylene (1.28 eV), it is likely that both species are mobile in the temperature range for the reaction-limited production of ethylene.

DFT calculations with and without the inclusion of the 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. Based on the experimental XPS result, the majority of methylene binds at surface cation sites, in agreement with the DFT prediction. Since the on-site potential in DFT+U promotes electron localization [67], it appears to overestimate electronic configurations with localized electrons such as bridged methylene that interacts with the cation centers through a σ bond compared to more delocalized configurations such as π -bonded atop methylene. The results imply that the inclusion of an on-site potential appropriate for the bulk electronic structure is not necessarily suitable for predicting the surface chemistry of adsorbed species such as carbenes.

In addition, the activation barrier for methylene migration calculated with DFT (1.28 eV compared to 1.51 eV with DFT+U) is closer to the apparent first-order activation energy of 1.31 eV determined from the TPD experiments. While there are significant differences in the predicted activation barriers and relative adsorption energies of the stable species predicted by

the two methods, both methods give similar insight into the structural evolution of methylene during the surface diffusion process.

6. Conclusions

Dichloromethane undergoes thermally-induced C-Cl bond cleavage at low temperatures to form methylene intermediates on α -Cr₂O₃(0001). XPS results indicate that the lowest energy binding sites for methylene species are Cr cations, suggesting an sp², π -bonded surface intermediate. 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 α -Cr₂O₃(0001). A mechanism for the reaction-limited coupling of methylene to ethylene is proposed that invokes a rate-limiting surface migration of methylene. DFT calculations suggest a migration route that involves a thermally driven rehybridization of methylene between sp² and sp³ binding modes that is mediated by surface oxygen anions. The observation of some desorption limited ethylene at 300 K in TPD also suggests that ethylene can be formed by the 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.

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FIGURE CAPTIONS

Figure 1. Ball model illustration of the ideal nearly-stoichiometric α -Cr₂O₃(0001) surface. Small grey spheres represent Cr³⁺ cations and the large red spheres represent the O²⁻ anions.

Figure 2. TPD following a 0.05 L dose of CH₂Cl₂ on the clean, nearly-stoichiometric α -Cr₂O₃(0001).

Figure 3. Methane production from the reaction of an 0.05 L dose of CD₂Cl₂ on the clean, nearly-stoichiometric α -Cr₂O₃(0001).

Figure 4. AES of the (a) clean α -Cr₂O₃(0001) surface before exposure to CH₂Cl₂ and (b) after CH₂Cl₂ TPD with a total exposure of 7.15 L.

Figure 5. AES Cl/Cr ratio for different amounts of exposure to CH₂Cl₂ for TPD on α -Cr₂O₃(0001). The error bar represents the error in Cl/Cr ratio measured after the same amount of CH₂Cl₂ dosed in different sets of the TPD experiment.

Figure 6. Integrated signals for each product for consecutive 0.05 L CH₂Cl₂ TPD runs as a function of cumulative CH₂Cl₂ exposure.

Figure 7. Change of signals for (a) ethylene and (b) methane for consecutive 0.05 L CH₂Cl₂ TPD runs.

Figure 8. (a) C 1s and (b) Cl 2p XPS spectra of α -Cr₂O₃(0001) dosed with 10 L CH₂Cl₂ at 110 K and heated to according temperatures (h ν = 350 eV). (c) comparison of Cl 2p spectra for 300 K and 800 K (normalized).

Figure 9. Three possible configurations of methylene on the α -Cr₂O₃(0001) surface determined with DFT: (a) atop configuration, (b) short-bridging configuration between a cation and nearest neighbor O anion, and (c) long-bridging configuration between a cation and a second nearest neighbor O anion. Small blue spheres represent Cr cations, large red spheres O anions, small grey spheres carbon, and the white spheres hydrogen.

Figure 10. (a) Relative free energies and (b) unit cell magnetization of the different methylene configurations on the 80-atom surface unit cell calculated by DFT and DFT+U.

Figure 11. (a) Top view of the methylene migration pathway. Small blue balls represent Cr³⁺, and large red balls correspond to O²⁻. (b) The transition between methylene configurations along the methylene migration pathway.

Figure 12. Minimum energy pathway for methylene migration calculated using CI-NEB (a) using DFT (without the on-site potential), and (b) DFT+U (with the on-site potential). The changes in net magnetization are shown on the secondary axis on the right hand side.

Figure 13. Expected equilibrium fraction of the different methylene configurations calculated using the predicted activation barriers from DFT assuming equal pre-exponentials in the forward and reverse directions.

Figure 14. (a) The potential energy surface and (b) the associated adsorbate geometries for the coupling of two methylenes bound at neighboring Cr sites, one bound in an atop configuration and the other bound in the long-bridging configuration to a neighboring cation and an O anion nearest neighbor to the atop species.

Figure 15. Minimum energy pathway for the diffusion of a single Cl between neighboring Cr cation sites.

Figure 16. Minimum energy pathway for the diffusion of a single Cl from a doubly-chlorinated Cr site to a vacant Cr.

Figure(s)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

(a)

(b)

Figure 11

(a) DFT

(b) DFT+U

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16