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Methylene migration and coupling on a non-reducible metal oxide: The reaction of dichloromethane on stoichiometric α-Cr_2O_3(0001)

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ABSTRACT

The reaction of CH_2Cl_2 over the nearly-stoichiometric α-Cr_2O_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 α-Cr_2O_3.

1. Introduction

Hydrocarbon surface intermediates occur in a variety of heterogeneous catalytic processes. Among the multitude of possible intermediates, methylene ($=CH_2$) 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 CATOFIN™ 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 Cr^{3+} 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 Cr^{2+} 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-Cr_2O_3(0001). Methylene intermediates are generated through the thermal dissociation of dichloromethane (CH_2Cl_2), 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.

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2. α-Cr_2O_3(0001)

α-Cr_2O_3 has a corundum bulk structure and is an insulator with a band gap of 3.2 eV [23–26]. Cr^{3+} cations in the bulk are surrounded with six O^{2-} 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 $\left[10\bar{1}2\right]$ 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-Cr_2O_3(0001) surface (Fig. 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 Gammadata Scienta FG-300 flood gun using 0.5 eV electrons. The base operating pressure for this system was 1×10^{-10} Torr.

The α-Cr_2O_3 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 μm diamond paste. The sample was mechanically clamped onto a tantalum stage that was fastened to LN_2-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.

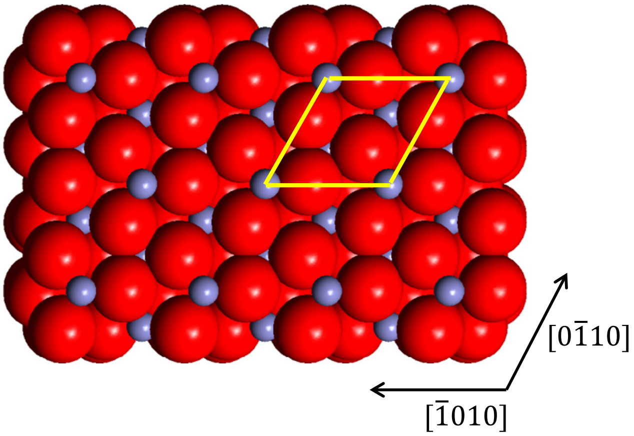

Fig. 1. Ball model illustration of the ideal nearly-stoichiometric α-Cr_2O_3(0001) surface. Small grey spheres represent Cr^{3+} cations and the large red spheres represent the O^{2-} anions.

α-Cr_2O_3(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-Al_2O_3 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 H_2O 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-Cr_2O_3. 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 ≥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].

The zero-pressure, minimum-energy volume was found for the bulk cell by varying both cell edges and the positions of the non-equivalent

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[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.