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Reactions of methyl groups on a non-reducible metal oxide: The reaction of iodomethane on stoichiometric α-Cr_2O_3(0001)

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ABSTRACT

The reaction of iodomethane on the nearly stoichiometric α-Cr_2O_3(0001) surface produces gas phase ethylene, methane, and surface iodine adatoms. The reaction is initiated by the dissociation of iodomethane into surface methyl fragments, $-CH_3$, and iodine adatoms. Methyl fragments bound at surface Cr cation sites undergo a rate-limiting dehydrogenation reaction to methylene, $=CH_2$. The methylene intermediates formed from methyl dehydrogenation can undergo coupling reactions to produce ethylene via two principle reaction pathways: (1) direct coupling of methylene and (2) methylene insertion into the methyl surface bond to form surface ethyl groups which undergo β-H elimination to produce ethylene. The liberated hydrogen also combines with methyl groups to form methane. Iodine adatoms from the dissociation of iodomethane deactivate the surface by simple site blocking of the surface Cr^{3+} cations.

1. Introduction

Methyl is a common intermediate encountered in the catalysis of hydrocarbons and has been shown to be an active species in the partial oxidation of methane [1] and the coupling of methane into higher hydrocarbons [2,3]. Ultra-high vacuum studies of methyl intermediates on metal surfaces show that the most common reaction pathways of methyl are hydrogenation to produce methane and decomposition to surface carbon [4]. C–C bond formation to produce ethane is seen on silver and gold surfaces [5–7], while ethylene is produced on copper surfaces by methylene ($=CH_2$) formed from the dehydrogenation of methyl. Two routes to ethylene production have been observed: (1) direct coupling of two methylenes, and (2) the migration and insertion of methylene into methyl, with β-H elimination of the resulting ethyl species [8–10].

Henderson has examined the thermal and photochemical interaction of methyl bromide with α-Cr_2O_3(0001) [11]. CH_3Br is thermally unreactive on most surfaces [11] and adsorbs and desorbs molecularly with no thermal decomposition on α-Cr_2O_3(0001). Irradiation with a Hg arc lamp causes photodesorption and photodecomposition of methyl bromide. Photodecomposition leads to CH_3 group ejection with little or no retention on the surface. Similarly, studies of methyl on well-defined Fe_3O_4(111) shows methyl radical ejection at all coverages, but also coupling to ethane at high coverages [12].

A few studies of methyl reactions on oxygen-covered metal surfaces have also been done. Studies by Bol et al. show that methyl radicals form methoxy and desorb as gas-phase methyl radicals from O-covered Mo(110) [13], while methyls directly add to surface oxygen [14], producing CO_2, CO, and formaldehyde on the O-covered Rh(111) surface [15]. Kim et al. observed a migratory insertion route for higher alkene production by methylene formed by the dehydrogenation of methyls on Mo(100) with near monolayer coverages of atomic oxygen in 4-fold hollow sites, but also saw this reaction route suppressed at higher oxygen coverages leading to terminal ($Mo = O$) surface species [16]. A related HREELS study shows that methyl binds to surface Mo sites [17].

In this study, the dehydrogenation of methyl fragments and migration of the resulting methylene have been observed on a non-reducible, well-defined metal-oxide surface, α-Cr_2O_3(0001). Methyl intermediates have been generated through the thermal dissociation of iodomethane (CH_3I) and studied experimentally with temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). First-principles DFT calculations have been used to examine the methyl adsorption on α-Cr_2O_3(0001).

2. α-Cr_2O_3

α-Cr_2O_3 has a corundum bulk structure and is an insulator with a band gap of 3.2 eV [18–21]. 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 [22]. Along the [0001] direction, three atomic planes provide a stoichiometric repeating unit with compositions of [Cr, 3O, Cr]. Cleavage

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between the planes of closely lying Cr layers yields a hexagonal, nonpolar, 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 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 [23]. 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 $h\nu = 700$ eV. Compensation for surface charging during 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 was 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.

α-Cr_2O_3(0001) surfaces described in the literature have been prepared by the direct oxidation of Cr(110) with 10–20 L of oxygen at 625 K followed by annealing in vacuum at 925 K [24] and by molecular beam epitaxy on α-Al_2O_3 substrates [25]. For the epitaxial thin films, Henderson and Chambers [25] 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 [25,26] and gives a characteristic fingerprint for water desorption from the stoichiometric surface.

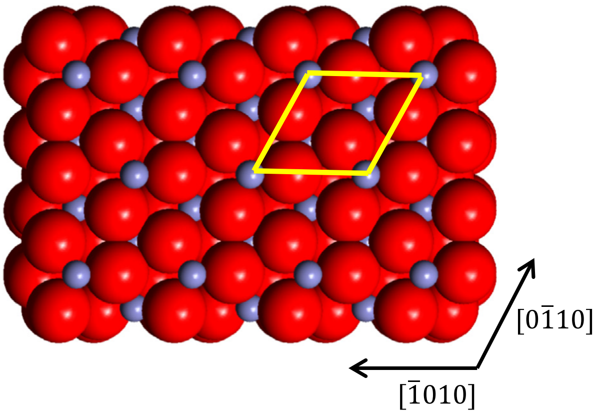

Fig. 1. Ball model illustration of the ideal nearly stoichiometric α-Cr_2O_3 (0001) surface. Small grey spheres represent Cr^{3+} cations and the large red spheres represent the O^{2-} anions.

The studies reported here were conducted on a (0001)-terminated bulk single crystal of α-Cr_2O_3. We use a simple 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 [25], 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 [27]. 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 is used to check for surface cleanliness, and LEED is used to confirm the hexagonal (1 × 1) 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 iodomethane (CH_3I) 99.5%, iodomethane-d_3 (CD_3I) 99.5 atom% D, Sigma-Aldrich dichloromethane (CH_2Cl_2), anhydrous ≥ 99.8%, and Matheson CP grade 99.7% deuterium (D_2) 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. Additionally, TPD runs to specifically sample desorption from the sample holder were made for comparison to ensure that the reported desorption traces originate from the sample surface. 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 [29,30] within the Vienna Ab-initio Simulation Package (VASP) [31–33]. The Perdue-Burke-Ernzerhof (PBE) approximation was used to treat exchange and correlation utilizing a standard generalized gradient approximation (GGA) [34]. As in our earlier study [35], an 80-atom slab with a vacuum gap of 20 Å was used for all 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 Cr^{3+} cations (d^3) were set following the known antiferromagnetic ordering in α-Cr_2O_3 [36], which is also found to be the ground-state magnetic order using DFT calculations within the GGA [37]. For all geometry-optimized structures, the forces on the individual atoms are less than 0.01 eV/Å.

DFT calculations are known to have difficulties in predicting the electronic properties of strongly correlated transition metal oxide materials [37]. It has been suggested that this problem can be overcome with the inclusion of an on-site Coulomb repulsion (DFT + U) [38,39]. A DFT + U study of α-Cr_2O_3 [37] 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_2O_3. In the current study, results for both DFT and DFT + U are presented for comparison.

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[1] An ion gauge sensitivity of 9.5 was used for CD_3I using a correlation by S. George as reported by Brainard and Madix [28]. Relative mass spectrometer sensitivity factors of 0.05 for CD_3I (m/z = 145), 0.23 for $CD_2 = CD_2$ (m/z = 32), and 0.66 for methane (m/z = 20 and 19) were determined experimentally.