

Reactions of ethyl groups on a model chromia surface: Ethyl chloride on stoichiometric α -Cr₂O₃ (10 $\bar{1}2$)

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ABSTRACT

The reaction of CH₃CH₂Cl over the nearly-stoichiometric α -Cr₂O₃ (10 $\bar{1}2$) surface yields gas phase CH₂=CH₂, CH₃CH₃, H₂ and surface chlorine adatoms. The decomposition reaction is initiated via C–Cl bond cleavage to give a surface ethyl (CH₃CH₂–) intermediate. A rate-limiting β -hydride elimination from the surface ethyl species produces gas phase CH₂=CH₂ and surface hydrogen atoms. Two parallel competing reactions form CH₃CH₃, via α -hydride addition to remaining surface ethyl species (reductive elimination), and H₂, via the combination of two surface hydrogen atoms. The chlorine freed from the dissociation of CH₃CH₂Cl binds at the five-coordinate surface Cr³⁺ sites on the stoichiometric surface and inhibits the surface chemistry via simple site blocking. No surface carbon deposition is observed from the thermal reaction of ethyl chloride, suggesting that ethyl intermediates are not primary coke forming intermediates in the dehydrogenation of ethane over (10 $\bar{1}2$) facets of α -Cr₂O₃.

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1. Introduction

Catalytic routes for ethane (CH₃CH₃) dehydrogenation to ethylene (CH₂=CH₂) are desired to improve selectivity compared to traditional steam cracking processes which are driven by a nonselective, homogeneous, free-radical chain reaction mechanism [1]. Since the dehydrogenation reaction is highly endothermic it requires high temperature to give significant ethylene yields [2], and these high temperatures lead to additional cracking reactions and coke formation [3]. While the kinetics of ethane dehydrogenation are controlled by the initial C–H bond activation [4], it seems likely that the catalytic selectivity will be controlled by the characteristics of the catalytic reaction site and the chemistry of different reaction intermediates formed from ethane or by reactions of the ethylene product.

Supported chromia catalysts are used industrially in the catalytic dehydrogenation of C₃ and C₄ alkanes [3], and a number of studies have examined the applicability of chromia catalysts to the dehydrogenation and oxidative dehydrogenation of ethane [5–9]. In this study, the reactions of ethyl fragments are examined over a model chromia single crystal surface, α -Cr₂O₃ (10 $\bar{1}2$). Ethyl species are of interest because they are the primary C₂ reaction intermediate expected from ethane by cleavage of a single C–H bond. For this study, surface ethyl species are generated via the thermal dissociation of ethyl chloride.

The elementary reaction steps of ethyl species on metal surfaces have been examined because of their relevance to the catalytic

dehydrogenation of ethane to ethylene [10–26]. Typically, the absorbed ethyl species are formed from the dissociative adsorption of halogenated molecules (ex., ethyl iodide, ethyl chloride, ethyl bromide) [10,12–20,22,23,25], while some groups have managed to form ethyl species by other methods such as UV-illumination [12] and coadsorption of di- σ -bonded CH₂=CH₂ and H atoms from a hot tungsten filament [21]. The ethyl moieties react via three primary pathways: β -hydride elimination to CH₂=CH₂, reductive elimination with hydrogen to CH₃CH₃ (α -addition) and reductive elimination with ethyl moieties to produce n-butane (C–C coupling).

2. α -Cr₂O₃ (10 $\bar{1}2$)

The α -Cr₂O₃ (10 $\bar{1}2$) single crystal surface has been previously characterized [27]. A ball model illustration of the ideal, stoichiometric surface is displayed in Fig. 1. The (10 $\bar{1}2$) facet of α -Cr₂O₃ has the lowest energy of all low-index surfaces [28], and has a rectangular (almost square) periodicity with a ratio of sides $a/b = 0.94$, as shown in Fig. 1 [27]. Energetic considerations indicate that the (10 $\bar{1}2$) surface should be terminated in a non-polar fashion [29], where one stoichiometric repeating unit includes the top five layers of atoms arranged as [O, Cr, O, Cr, O]. The O²⁻ anions comprising the top atomic layer are 3-coordinate with a pyramidal local coordination and the Cr³⁺ cations in the second atomic layer are 5-coordinate leaving one degree of coordinative unsaturation relative to their bulk counterparts [30]. The nearly-stoichiometric surface can be prepared by Ar⁺ sputtering and annealing to 900 K [27].

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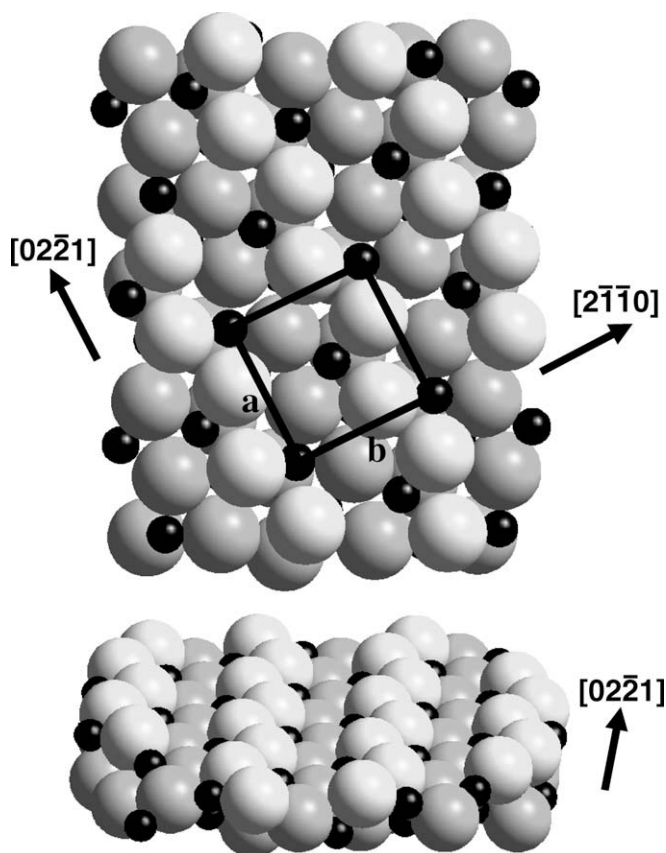


Fig. 1. Ball model illustration of the ideal nearly-stoichiometric $\alpha\text{-Cr}_2\text{O}_3$ ($10\bar{1}2$) surface. The top view shows the surface periodicity ($a:b = 0.94$) looking down the $[10\bar{1}2]$ surface normal. The bottom view gives a perspective across the surface down $[02\bar{2}1]$ for a cross-section of one stoichiometric repeating layer. In both top and bottom views the small black spheres represent Cr^{3+} cations and the large gray spheres represent O^{2-} anions with increasing shading representing increasing depth into the bulk.

Oxygen exposure caps surface cations with terminal chromyl oxygen ($\text{Cr}=\text{O}$) [27]. The oxygen-terminated surface exposes 3-coordinate O^{2-} anions and terminal chromyl oxygen ($\text{Cr}=\text{O}$), leaving no coordination vacancies on the surface Cr cations [27]. In reaction studies of hydrocarbon fragments on $\alpha\text{-Cr}_2\text{O}_3$ ($10\bar{1}2$), oxygenated gas phase products are only observed in the presence of terminal $\text{Cr}=\text{O}$ species [31]. No combustion products (CO , CO_2 and H_2O) and no oxygenates are seen in reaction studies of hydrocarbon fragments on the nearly-stoichiometric surface [31,32].

3. Experimental Methods

The reaction of ethyl chloride ($\text{CH}_3\text{CH}_2\text{Cl}$) over the nearly-stoichiometric $\alpha\text{-Cr}_2\text{O}_3$ ($10\bar{1}2$) surface was investigated using thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Thermal desorption and AES experiments were conducted in an ion-pumped UHV chamber equipped with a Physical Electronics Model 15-155 single-pass CMA for AES and an Inficon Quadrex 200 mass spectrometer for TDS. The base operating pressure for this study was 1×10^{-10} Torr. A broad-beam ion gun was used for sample cleaning.

The $\alpha\text{-Cr}_2\text{O}_3$ crystal was oriented to within 1° of the $(10\bar{1}2)$ surface using Laue backreflection and polished to a final mirror finish with $0.25 \mu\text{m}$ diamond paste. The sample was mechanically clamped onto a tantalum stage that was fastened to LN_2 -cooled copper electrical conductors. A Type K thermocouple was attached

through a hole in the stage to the back of the single crystal using Aremco #569 ceramic cement. This arrangement allowed direct measurement of the sample temperature.

AES data were collected using a primary electron beam energy of 5 keV. Spectra were collected in EN(E) mode and differentiated numerically. All AES measurements were collected at 800 K to avoid sample charging. Because of overlap between the primary oxygen and chromium AES peaks, the surface chromium concentration was followed by measuring the Cr $L_{2,3}M_{2,3}M_{2,3}$ (490 eV) peak-to-peak height [27]. Atomic Cl/Cr ratios were estimated with AES using appropriate sensitivity factors for Cl KLL [33] and Cr $L_{2,3}M_{2,3}M_{2,3}$ [27]. Electron stimulated reduction of the surface (i.e., lattice oxygen removal) was not observed during AES experiments, consistent with other observations (see below and Ref. [27]) that the surface is quite nonreducible.

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. Photoemission spectra are referenced to a Cr $2p_{3/2}$ binding energy of 576.9 eV [27,34].¹ Compensation for surface charging during synchrotron-based 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.

Sigma-Aldrich 99.7% ethyl chloride ($\text{CH}_3\text{CH}_2\text{Cl}$), Sigma-Aldrich >99.99% hydrogen (H_2), Specialty Gas Group 99.9% ethylene ($\text{CH}_2=\text{CH}_2$) and Sigma-Aldrich 99.99% ethane (CH_3CH_3) were used as received. Gas dosing was accomplished by backfilling the chamber through a variable leak valve. For TDS experiments, the sample surface was exposed to the dosed gas at 90 K and heated to 700 K using a linear temperature ramp of 2.5 K/s. 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

A nearly-stoichiometric (1×1) surface was prepared by ion-bombardment and annealing to 900 K. Following preparation, AES was used to check for surface cleanliness prior to TPD experiments.

4. Results

A combination of TDS and AES results reveals that $\text{CH}_3\text{CH}_2\text{Cl}$ decomposes into ethylene ($\text{CH}_2=\text{CH}_{2(g)}$), ethane ($\text{CH}_3\text{CH}_{3(g)}$), dihydrogen ($\text{H}_{2(g)}$) and absorbed chlorine. Gas phase products were identified by comparison of mass spectrometer fragmentation patterns to thermal desorption peak intensities. The relative intensities of four m/z signals were used to identify $\text{CH}_3\text{CH}_2\text{Cl}$ (66, 64, 29, 27), $\text{CH}_2=\text{CH}_2$ (27, 26, 25, 24) and CH_3CH_3 (30, 29, 27, 26). Overlap of mass signals from ethyl chloride, ethane and ethylene was accounted for by subtracting overlapping contributions out of the raw mass spectrometer signal. Following these subtractions, the relative intensities of m/z fragments for all hydrocarbon products formed were found to be in good agreement with mass spectrometer cracking patterns of hydrocarbon standards. Other products were excluded by a search that included m/z values ranging from 2 to 200. Specifically, no CO , CO_2 , HCl , Cl_2 , butane or any other oxygenated molecules, halogenated compounds or coupling products were produced from the reaction of ethyl chloride over

¹ For XPS 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.

² An ion gauge sensitivity of 4.0 was used for ethyl chloride [35]. Relative mass spectrometer sensitivity factors of 0.06 for ethyl chloride (m/z 64), 0.27 for ethylene (m/z 27), 0.15 for ethane (m/z 30), and 1.23 for H_2 (m/z 2) were determined experimentally.

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