

# Chloromethane surface chemistry on $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$ : A thermal desorption spectrometry comparison of $\text{CCl}_4$ , $\text{CBr}_2\text{Cl}_2$ , and $\text{CH}_2\text{Cl}_2$

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## Abstract

The surface chemistry of  $\text{CBr}_2\text{Cl}_2$  on the  $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$  seldedge of single-crystal  $\alpha\text{-Fe}_2\text{O}_3(0001)$  has been investigated using temperature programmed reaction and desorption (TPR/D) measurements. The spectra obtained in this case show that strong chemisorption occurs and that a series of adsorbed halogenated reaction products are present. By comparison, studies of the adsorbed phase of  $\text{CH}_2\text{Cl}_2$  show that only physisorption occurs. The TPR/D spectra of  $\text{CBr}_2\text{Cl}_2$  show that dissociative formation of  $\text{CCl}_2$  followed by its reaction with lattice oxygen is central to the monolayer reaction chemistry in this chloromethane. The branching ratios of the various desorbed products are compared with those obtained from  $\text{CCl}_4$  adsorbed on the same  $(2 \times 2)$  surface.

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## 1. Introduction

Chemistry at iron-oxide surfaces plays an important role in the environment; this is in large part due to the natural abundance and relatively high molecular reactivity of iron oxides in soils. One of the most abundant oxides,  $\alpha\text{-Fe}_2\text{O}_3$  (hematite), contains  $\text{Fe}^{3+}$  in 2/3 of its octahedral interstitial sites within the oxygen lattice of its corundum structure. Another common iron oxide,  $\text{Fe}_3\text{O}_4$  (magnetite), contains  $\text{Fe}^{2+}$ , distributed in the octahedral sites, and  $\text{Fe}^{3+}$ , distributed equally between octahedral and tetrahedral sites, within the oxygen lattice of its inverse spinel structure. Because of their abundance and reactivity, there is a growing interest in understanding the reaction paths and reactive sites of iron-oxide surfaces at the molecular level within the context of environmental applications. Chlorome-

thanes, such as carbon tetrachloride ( $\text{CCl}_4$ ), are of particular interest for environmental chemistry studies on iron-oxide surfaces because they are common environmental pollutants of many commercial processes.

In order to develop a more precise understanding of the surface reactivity, recent experimental and theoretical papers have considered the study of model single-crystal iron-oxide surfaces [1–5]. It is interesting that even the basic structure of these solids continues to be an active area of research [6]. For the reasons mentioned above, a particularly important case is that of  $\alpha\text{-Fe}_2\text{O}_3$ . Several crystal planes of this mineral are important; however, the  $(0001)$  plane has received the most theoretical and experimental attention. In fact, several groups have shown the interrelationship of structure and reactivity on  $\alpha\text{-Fe}_2\text{O}_3(0001)$  surfaces [7–9]. This  $(0001)$  plane exhibits at least three important ordered surface phases [9–12]. These are commonly referred to as the  $(1 \times 1)$ , biphasic, and  $(2 \times 2)$  (or magnetite seldedge) structures; we will focus on the  $(2 \times 2)$  surface in this paper.

These different phases can be readily prepared on the surface of a  $\text{Fe}_2\text{O}_3$  surface using different schedules of sput-

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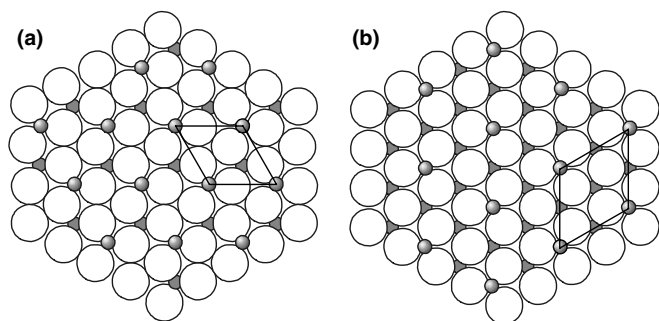


Fig. 1. (a) The top three layers of the  $\alpha$ - $\text{Fe}_2\text{O}_3(0001)-(1 \times 1)$  surface. Oxygen atoms (larger circles) form a close-packed layer parallel to the (0001) surface. Iron cations (smaller circles) occupy octahedral interstitial sites. (b) Top three layers of the  $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$  surface. Iron cations (smaller circles) are distributed in the octahedral and tetrahedral interstitial sites. The  $\text{Fe}_3\text{O}_4(111)$  surface is crystallographically similar to the  $\alpha$ - $\text{Fe}_2\text{O}_3(0001)$  making it easy to form the selvedge of  $\text{Fe}_3\text{O}_4$  on  $\text{Fe}_2\text{O}_3$ . The surface unit meshes are indicated. The Fe–Fe separations indicated are 5.03 Å for  $\text{Fe}_2\text{O}_3$  and 5.92 Å for  $\text{Fe}_3\text{O}_4$ .

tering and annealing in an oxygen atmosphere [9,10,13–15]. For example, at relatively low annealing temperatures ( $\approx 1000$  K), a selvedge region of  $\text{Fe}_3\text{O}_4(111)$  forms on the surface [12,16,17]. Conventionally, this is referred to as the  $(2 \times 2)$  reconstruction [18–20] because the LEED pattern shows a periodicity that is simply twice that of the close-packed oxygen sublattice of (111)-oriented  $\text{Fe}_3\text{O}_4$  (see Fig. 1). Conceptually, reference to the oxygen lattice is useful because the  $\text{Fe}_3\text{O}_4(111)$  and  $\alpha$ - $\text{Fe}_2\text{O}_3(0001)$  oxygen planes are crystallographically similar. For example, with reference to the hexagonally-packed  $\text{Fe}_3\text{O}_4(111)$  oxygen sublattice, the surface lattice of the  $\text{Fe}_3\text{O}_4(111)$  selvedge is simply  $(2 \times 2)$ , while the  $\alpha$ - $\text{Fe}_2\text{O}_3(0001)-(1 \times 1)$  lattice, ignoring slight deviations from ideal hexagonal packing in  $\alpha$ - $\text{Fe}_2\text{O}_3$ , corresponds to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  reconstruction, with a  $\sim 2\%$  larger lattice constant [19]. This crystallographic similarity facilitates the formation of the  $\text{Fe}_3\text{O}_4(111)$  selvedge on  $\text{Fe}_2\text{O}_3(0001)$ . The  $(2 \times 2)$  surface is the subject of this study and the details of its preparation will be presented in Section 2.

Site-specific reactions of this model single-crystal  $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$  surface have been studied in a recent series of papers by several groups [21–29]. For example, temperature programmed desorption was used by Weiss and coworkers [21] to study water adsorption/reactions on synthetically grown  $\text{Fe}_3\text{O}_4$  single-crystal thin films. More recently our laboratory has used temperature programmed reaction and desorption (TPR/D) to study the interactions between  $\text{CCl}_4$  and the  $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$  surface formed on a natural hematite crystal using reducing conditions in an UHV environment [25]. This study revealed a complex surface chemistry with rich site dependence; six separate desorption features were clearly observed from four desorbing species:  $\text{CCl}_4$ ,  $\text{OCCl}_2$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{FeCl}_2$ . Based on this observation, we suggested that  $\text{CCl}_4$  dissociatively adsorbs, at temperatures no greater than 250 K, on  $\text{Fe}_3\text{O}_4(111)$  to form  $\text{CCl}_2$  and Cl. These results indicated that dichlorocar-

bene plays a key role in this surface chemistry and that several surface mechanisms compete for this same reaction precursor at a limited number of reaction sites. Subsequent STM (scanning tunneling microscopy) [28,29] and SXPS [26] (synchrotron X-ray photoelectron spectroscopy) studies further indicated the importance of dichlorocarbene in the  $(2 \times 2)$  surface chemistry and helped to sharpen the details of the surface-site and activation-barrier pictures.

In this paper, we describe a set of experiments, which have the general goal of investigating the reactions and intermediates of molecular adsorbates on iron-oxide surfaces. Our specific goal is to further probe the role of dichlorocarbene in the surface chemistry of halocarbons, in general, and of halomethanes, in particular, on the  $(2 \times 2)$  reconstructed surface of hematite. Our primary surface instrumentation is TPR/D spectrometry in an UHV environment. The experiments described below first use  $\text{CBr}_2\text{Cl}_2$  to examine the changes in surface reactions (compared to those seen in the case of  $\text{CCl}_4$ ) observed in the presence of a mixed halogenated species. The importance of a relatively low molecular binding energy for the surface chemistry of chloromethanes is shown by the behavior of a closely related partially chlorinated methane  $\text{CH}_2\text{Cl}_2$ , which only appears in a physisorbed state. Our observations with  $\text{CBr}_2\text{Cl}_2$  are then discussed and compared with those seen for  $\text{CCl}_4$ .

## 2. Experiment

The experiments were performed in a turbo-pumped ultrahigh vacuum (UHV) surface analysis system with a typical base pressure below  $3 \times 10^{-10}$  Torr. The system is equipped with a quadrupole mass spectrometer (QMS), rear-view low energy electron diffraction (LEED) optics, an Auger-electron spectroscopy (AES) system, a retractable pinhole doser, and an ion-sputtering gun. A more detailed description of the apparatus has been reported previously [30,31].

Our  $10 \times 10 \times 1$  mm  $\alpha$ - $\text{Fe}_2\text{O}_3(0001)$  “wafer” samples (Commercial Crystal Laboratories, Inc.) were sliced from a naturally occurring single crystal, mechanically polished to a mirror finish and cleaned by ultrasonication in ethanol, prior to insertion into the UHV system. The crystal was mounted on a 0.025 mm-thick Mo foil, which was in thermal contact with the liquid- $\text{N}_2$  reservoir of the manipulator, and could be cooled to  $\sim 100$  K and resistively heated to  $\sim 1200$  K by passing current through the foil. All temperature-programmed measurements in this study were performed on the  $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$  selvedge surface with a heating rate of 2.5 K/s. The surface temperature was measured with a thermocouple held against the surface of the crystal sample by a Ta clip, see Ref. [25,27]. The surface was prepared in vacuo by cycles of sputtering ( $\text{Ar}^+$  ion bombardment at 2 keV for 30 min at room temperature with current through the sample measured to be  $\sim 5 \mu\text{A}$ ) and multiple 30-s annealing cycles at 1100 K. Further comments on surface preparation are provided in Section 3. It should be noted that for a given surface preparation meth-

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