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Dissociative Adsorption of CCl_4 on the $\text{Fe}_3\text{O}_4(111)-(2\times 2)$ Selvege of $\alpha\text{-Fe}_2\text{O}_3(0001)$

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Introduction: Recently the fundamental chemistry of environmentally important adsorbed molecules has been studied via the use of molecular specific surface probes, in conjunction with model mineralogical surfaces. These studies start with well-characterized single-crystal surfaces with the aim of developing a molecular-level understanding of the reactive chemistry. The surface and the surface chemistry is then progressively made more complex and, hence, realistic. This approach has the advantage of allowing probes such as synchrotron photoemission spectroscopy, low energy electron diffraction, and scanning tunneling microscopy to characterize the surface and its adsorbate chemistry.

Methods and Materials: We use ultrahigh vacuum for detailed studies of the chemistry of well-characterized surfaces formed on $\alpha\text{-Fe}_2\text{O}_3$ (hematite) single crystals. Natural single crystal samples of hematite were cut and polished along the (0001) orientation. They were processed in ultrahigh vacuum to produce a surface selvedge of $\text{Fe}_3\text{O}_4(111)-(2\times 2)$ and exposed at ~ 100 K to CCl_4 . The surface reactions were studied using Temperature-programmed desorption [1], Auger electron spectroscopy [2], synchrotron based X-ray photoelectron spectroscopy [3] and scanning tunneling microscopy [4].

Results: CCl_4 was found to dissociate on the Fe_3O_4 surface at 100 K producing chemisorbed Cl and adsorbed CCl_2 . TPD shows that the large majority of the dissociatively adsorbed CCl_2 fragments extract lattice oxygen and desorb as phosgene at >275 K. However, the XPS spectra show no evidence for the formation of surface-bound phosgene, at 100 K, indicating that its formation involves two steps. The first step, dissociation, is spontaneous at 100 K, whereas the second, oxygen atom abstraction to form phosgene, requires thermal excitation. Cl chemisorption yielded two separate species, the mono- and dichloride terminations of surface iron sites. The identification of these two surface terminations is based on the coverage dependence and the surface temperature history of their Cl $2p_{3/2}$ peak intensity. For example, heating to >450 K allows the monochloride to transform into iron dichloride, indicating Cl adatom mobility at these temperatures.

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References:

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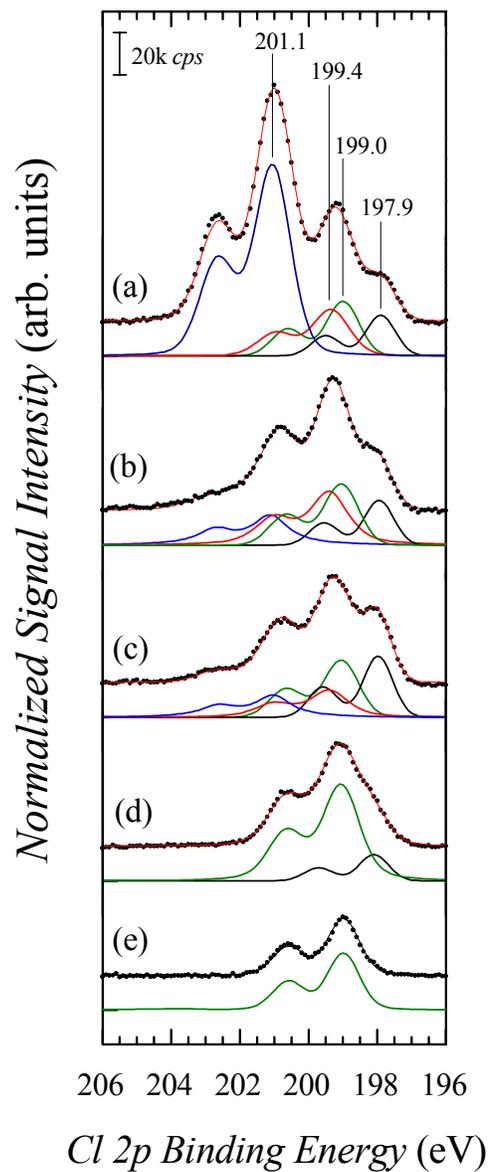


Figure 1. Cl 2p core level photoelectron spectra for a sample dosed with ~ 1 ML of CCl_4 at 100 K (a) and subsequently annealed to 180 K (b), 220 K (c), 600 K (d), and 850 K (e) at a heating rate of approximately 2.5 K/s. The different species are identified as chlorine adatoms (FeCl , FeCl_2), adsorbed CCl_2 and CCl_4 . After ref. [3].

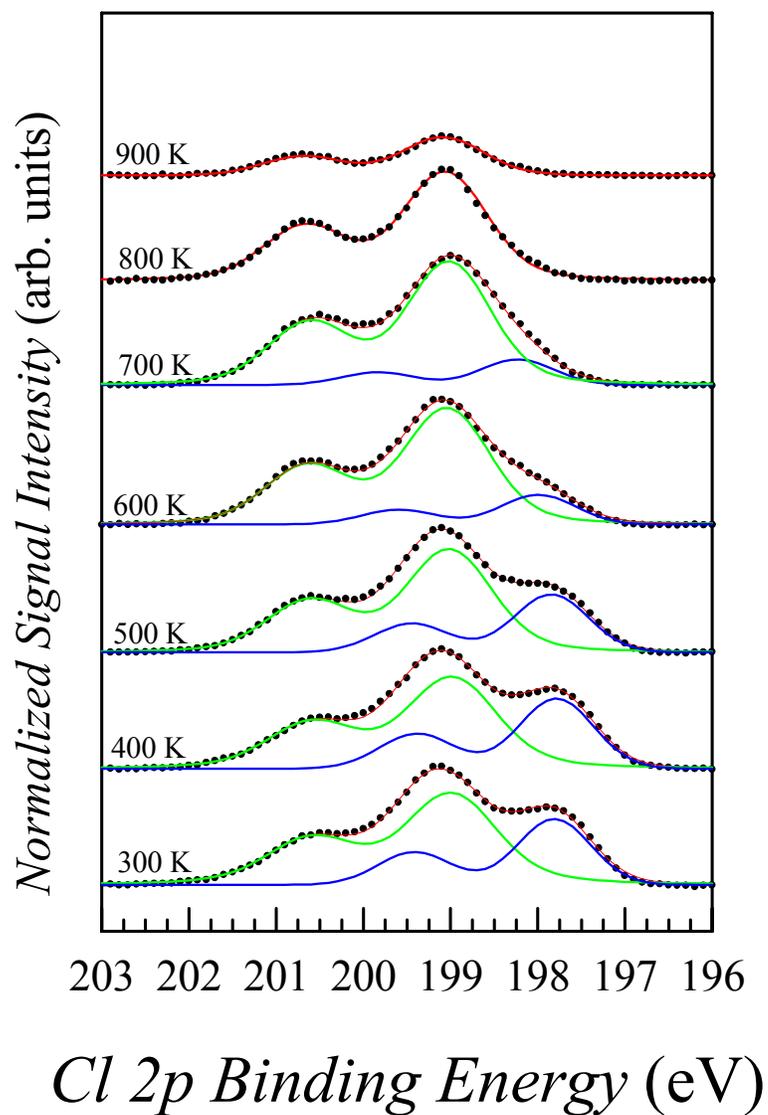


Figure 2. Cl 2p XPS spectra obtained immediately after exposing the Fe_3O_4 (111) surface to ~ 1 ML of CCl_4 at 300K and following heating the reacted surface to successively higher temperatures in 100 K increments. Due chlorine adatom mobility as a result of annealing FeCl species converts into FeCl_2 . After ref. [3].

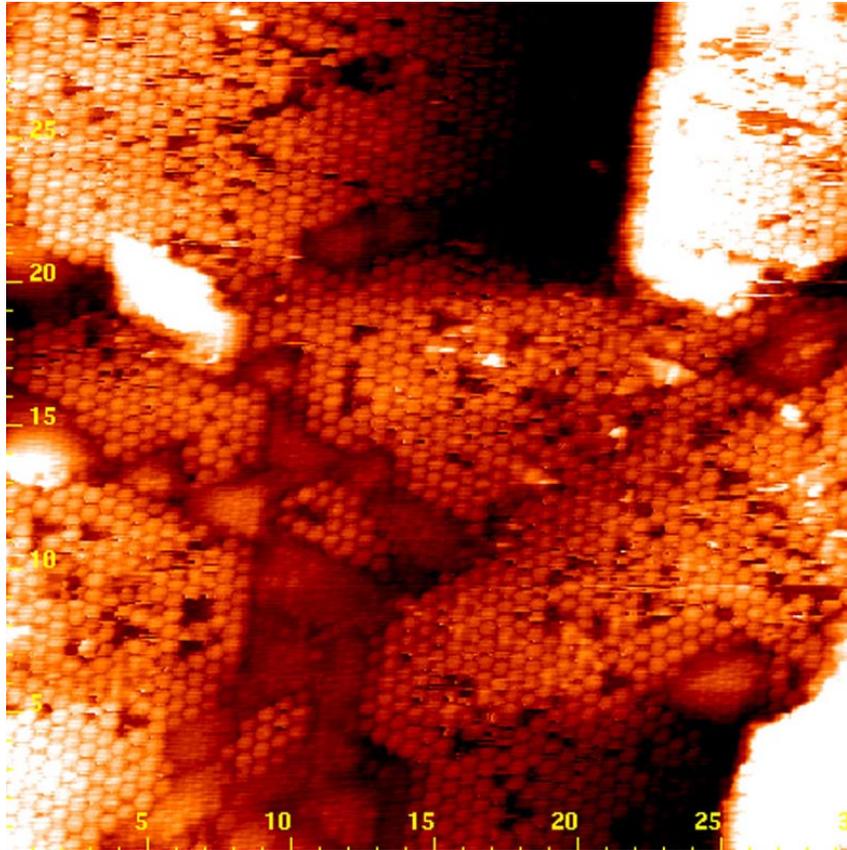


Figure 3. STM image of the $\text{Fe}_3\text{O}_4(111)$ selvedge formed on a sputtered and annealed $\alpha\text{-Fe}_2\text{O}_3(0001)$ natural single crystal surface displaying a complex surface termination commensurate with the rich surface chemistry observed. The Figure indicates the presence of the iron terminated $\text{Fe}_3\text{O}_4(111)$ surface (majority of the surface), a minority phase of unknown termination (lower center and left hand side) as well as surface defects (dark spots distributed throughout). The center-to-center distance of the iron sites in the $\text{Fe}_3\text{O}_4(111)$ area is approximately 6 Å. After ref. [4].