

Abstract

Metal oxides offer a diversity of structures and compositions that make them excellent candidates as catalysts for reactions involving organic compounds. In this context, magnetite, Fe_3O_4 , appears as an attractive material due to its naturally abundance and its electronic properties that make it a material widely used in several catalytic process. Its catalytic activity is related to the presence of both, Fe^{2+} and Fe^{3+} cations, in its inverse spinel structure. Moreover, the presence of these cations together with oxygen anions represent an important aspect in its acid-base chemistry.

The present thesis presents a surface science study with the aim to understand the reactivity of the $\text{Fe}_3\text{O}_4(001)$ surface toward small organic molecules such as methanol (CH_3OH) and formic acid (HCOOH), as well as its role in the water gas shift reaction. The surface chemistry was investigated using an array of surface science techniques including scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), temperature programmed desorption (TPD), and infrared reflection absorption spectroscopy (IRRAS) (in collaboration with another group).

The $\text{Fe}_3\text{O}_4(001)$ surface undergoes a $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ reconstruction associated with a cation rearrangement in the subsurface layers, involving two subsurface Fe vacancies and one interstitial Fe atom per unit cell. A major part of the work presented here was devoted to the identification of the most common surface defects, and determining their effect on adsorption. It was discovered that surface defects can be classified in two groups. The first group, line defects include step edges and anti-phase domain boundaries (APDBs). The latter arise because the $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ reconstruction is lifted during annealing cycles, and then renucleates on cooling through 723 K with one of two distinct registries with respect to the underlying bulk. The second group, point defects, include surface hydroxyl groups and a defect related with Fe atoms incorporated in the subsurface. In this thesis

this defect is identified, and purposely created by the deposition of Fe onto the clean surface at room temperature. This process also leads to Fe adatoms, and, at high coverage, the so called Fe-dimer surface. Here the Fe atoms of the "dimer" are fourfold coordinated to surface oxygen atoms, filling two of the four octahedral interstitial sites per unit cell. XPS indicates that the Fe-dimer surface contains Fe^{2+} .

The $\text{Fe}_3\text{O}_4(001)$ surface adsorbs HCOOH and CH_3OH at room temperature, yielding adsorbed formate (HCOO^-) and methoxy (CH_3O^-) species, respectively. Formate adsorbs in a bridging bidentate configuration at regular iron surface lattice sites locally producing two different periodicities, one with (1×1) symmetry and a second one with (2×1) symmetry. The adsorbed formate decomposes to produce CO , H_2O , CO_2 , and H_2CO , and the reactivity is linked with the presence of surface defects. Methanol adsorbs dissociatively on the $\text{Fe}_3\text{O}_4(001)$ surface at defect sites that were identified as step edges, antiphase domain boundaries (APDB), iron adatoms and incorporated-Fe defects. The adsorption at the steps and Fe adatoms can be explained in terms of coordinative unsaturation, while the reactivity at the APDBs and incorporated Fe defects is linked to the local electronic structure; specifically to the presence of Fe^{2+} cations in the surface layers. The adsorption of multiple methoxy species at the latter two defects promotes a disproportionation reaction to form methanol and formaldehyde.

The implications of $\text{Fe}_3\text{O}_4(001)$ surface chemistry on catalytic processes was studied using the water gas shift reaction as an example. The co-adsorption of CO and H_2O generates the presence of four carbon surface species that are stable at room temperature. Three of them were identified as formate, iron carbide, and carbon in the form of graphite or CH_x hydrocarbon fragment respectively. The other species was postulated to be HOCO or HCO groups, but test experiments on formaldehyde adsorption did not confirm this hypothesis. Theoretical studies would be necessary for complete identification.