

INTRODUCTION

The original proposal for research consisted exclusively of determining the local electronic and geometric structures of defective SnO₂ surfaces. Scanning tunneling microscopy can be used to determine the local electronic structure of any conducting solid. The use of scanning tunneling microscopy and atomic force microscopy (AFM) on metal oxide surfaces initially centered around the imaging of steps which often represent centers of catalytic activity. One current area of interest with using STM to atomically image metal oxide surfaces lies in the potential to identify point defects (e.g. oxygen vacancies are the most commonly encountered type), and relating these defects to catalytic reactivity. The surface characterization techniques available previously, including low-energy electron diffraction (LEED) and ion scattering spectroscopy (ISS), are useful primarily in indicating long range order and are not always effective in identifying the number and type of point defects. STM, and to a lesser extent AFM, provide the opportunity for the first time to diagram in real-space individual atom positions.

Work proceeded in this area for nine months until it was discontinued due to the slow pace of progress. Progress was slowed due to the high demand for time on the STM system, which limited experimental time to one week per month. A review of the STM work completed on natural and synthetic SnO₂ samples is presented in Chapter 1.

Adsorption of water on the clean, nearly stoichiometric Cr₂O₃ (10 $\bar{1}$ 2) surface was studied. This work was undertaken to provide experience with standard surface science techniques including thermal desorption spectroscopy (TDS) and Auger electron

spectroscopy (AES). Additionally there is a great deal of interest in the mechanisms of water adsorption as water is one of the most studied adsorbates on well-defined metal oxide surfaces.

Water adsorption on surfaces is very important in heterogeneous catalysis where even trace amounts of water can alter the selectivity of a reaction. Well-ordered stoichiometric oxide single crystal surfaces have frequently been found to be unreactive towards H₂O adsorption, while powdered surfaces are easily hydroxylated. However, molecular and dissociative adsorption of water have been observed on several single crystal oxide surfaces. The Dissociative adsorption of water is often observed at steps and local defects. The study of water adsorption on the clean, nearly stoichiometric Cr₂O₃ (10 $\bar{1}$ 2) surface is presented in Chapter 2.

The exchange of halogen and oxygen on Cr₂O₃ (10 $\bar{1}$ 2) surfaces was studied to compliment previous work completed in the laboratory in the areas of oxidation and CFC chemistry on Cr₂O₃ (10 $\bar{1}$ 2). Several key CFC alternatives have been produced using chromium(III) oxide based catalysts. Chromia catalysts have proven effective in a variety of halocarbon reactions, including halogen exchange, isomerization, and disproportionation. The reversible creation of active sites on chromia is believed to proceed through a series of oxidative reduction and halogenation steps. The study of halogen-oxygen exchange on Cr₂O₃ (10 $\bar{1}$ 2) surfaces is presented in Chapter 3.