



# Reaction of sulfur dioxide with Ni(100) and Ni(100)-p(2 × 2)-O

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## Abstract

XPS, TPD, LEED and STM have been used to probe the interaction between sulfur dioxide and the Ni(100) and Ni(100)-p(2 × 2)-O surfaces. On Ni(100) at 300 K SO<sub>2</sub> disproportionates according to 2SO<sub>2</sub> → S(a) + SO<sub>3</sub>(a) + O(a). Sulfur and sulfite occupy sites in a p(2 × 2) arrangement, while oxygen adsorbs into c(2 × 2) domains amid Ni chains of (n√2 × 2√2)R45°/(2√2 × n√2)R45° (n = 7–12) periodicity that are presumed to be due to segregation of oxygen to the subsurface. On Ni(100)-p(2 × 2)-O at 300 K SO<sub>2</sub>(a) reacts with O(a) to form SO<sub>3</sub>(a). Sulfite adsorbs into p(2 × 2) islands encompassed by c(2 × 2)-O. TPD measurements with <sup>18</sup>O are suggestive of a monodentate sulfite binding configuration. © 2005 Published by Elsevier B.V.

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## 1. Introduction

Sulfur dioxide (SO<sub>2</sub>) is an environmental pollutant. It is a byproduct of the process used to generate electricity in coal-fired power plants [1]. SO<sub>2</sub> emissions can lead to adverse health and environmental effects. SO<sub>2</sub> is an irritant and a key component in the formation of sulfate aerosol particles [2], which act as cloud condensation nuclei in the

troposphere. Investigations of the interaction between SO<sub>2</sub> and various heterogeneous (metal and non-metal) surfaces will aid in the understanding of atmospheric phenomena, where an assessment of gas–surface interactions is required for accurate climate models.

Over the past twenty years the adsorption and reaction of SO<sub>2</sub>(g) has been investigated on a number of single crystal metal surfaces with an array of surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS) [3,4], near-edge X-ray absorption fine structure spectroscopy (NEXAFS) [5], temperature-programmed desorption (TPD)

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[3,4,6], reflection absorption infrared spectroscopy (RAIRS) [7,8], high-resolution electron energy loss vibrational spectroscopy (HREELS) [9] and scanning tunneling microscopy (STM) [4,6,10,11]. Depending on the surface temperature,  $\text{SO}_2$  adsorbs molecularly and dissociatively with the surfaces of Fe, Rh, W, Ni, Pd, Pt, Cu, and Zn to form  $\text{SO}_x$  ( $x = 1, 2, 3$ , or  $4$ ), whereas adsorption on Ag is only molecular [12,13]. Oxygen adsorbed on the Ag(110) surface affects the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  (sulfite) and  $\text{SO}_4$  (sulfate) [3,6].

Ohta et al. previously probed the reaction between  $\text{SO}_2(\text{g})$  and the Ni(100) and Ni(100)- $c(2 \times 2)$ -O surfaces using NEXAFS [5]. Their results indicate that below 300 K  $\text{SO}_2$  disproportionates on Ni(100) according to  $3\text{SO}_2(\text{a}) \rightarrow \text{S}(\text{a}) + 2\text{SO}_3(\text{a})$ . At room temperature a fraction of the sulfite decomposes into  $\text{SO}_2(\text{g})$  and  $\text{O}(\text{a})$ , leaving the surface partially covered with sulfur, sulfite and atomic oxygen, i.e.  $2\text{SO}_2(\text{a}) \rightarrow \text{S}(\text{a}) + \text{SO}_3(\text{a}) + \text{O}(\text{a})$ . On Ni(100)- $c(2 \times 2)$ -O at 300 K,  $\text{SO}_2(\text{a})$  reacts with oxygen to give  $\text{SO}_3$  and  $\text{SO}_4$  in approximately a 3:1 ratio.

In this paper we report XPS, TPD, LEED and STM studies of the reaction between  $\text{SO}_2(\text{g})$  with clean and the oxygen-covered Ni(100)- $p(2 \times 2)$ -O. STM has been used to elucidate the interaction between  $\text{SO}_2$  and the Ni(100) and Ni(100)- $p(2 \times 2)$ -O surfaces. Binding configurations and the distribution of structures produced by the reaction products are discussed.

## 2. Experimental

Experiments were performed in an ultrahigh vacuum chamber equipped with STM, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and a quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD) measurements. The chamber was equipped with a sputter ion gun and stainless steel gas dosers. The system exhibited a base pressure of  $4 \times 10^{-10}$  Torr which rose to approximately  $7 \times 10^{-10}$  Torr during experiments.

The homemade “Johnnie Walker” type STM (RHK STM 100) employed in this study utilized a Pt/Ir tip, which was conditioned via induced field

evaporation onto a gold foil ( $\sim 4 \mu\text{A}$ , 15 min) prior to imaging. Unless otherwise stated, all scans were taken in constant height mode.

The Ni(100) crystal used was aligned to within  $0.5^\circ$  of the (110) plane using Laue backscattering and was mechanically polished down to  $0.3 \mu\text{m}$  alumina paste. The crystal was cleaned in vacuum by three Ar ion sputter ( $2 \mu\text{A}$ , 500 eV, 15 min at 600 K) and anneal (800 K, 10 min) cycles, with the first anneal done in an oxygen atmosphere ( $1 \times 10^{-7}$  Torr) to cleanse the surface of impurities observed in STM images. Hydrogen treatment at 600 K followed by another sputter/anneal cycle removed residual oxygen. A sharp  $p(1 \times 1)$  LEED pattern and AES-spectra showed a well-order surface devoid of sulfur, carbon and oxygen impurities.

The crystal could be cooled to 120 K with liquid nitrogen and heated to 1100 K by electron bombardment to the back of the crystal. The temperature was monitored by a Chromel–Alumel thermocouple spot-welded to the back of the crystal. The STM ramp housing the crystal and the STM scan head were allowed to thermally equilibrate for 30 min prior to STM measurements.

Separate XPS measurements were made in a second UHV system consisting of interconnected preparation and analysis chambers. The analysis chamber exhibited a base pressure of  $2 \times 10^{-10}$  Torr and was equipped with LEED optics, a Perkin–Elmer 04-548 dual anode X-ray source, an EA-10-plus hemispherical energy analyzer from SPECS and a UTI 100c QMS used for TPD measurements. The ionizer of the QMS was enclosed in a glass cap with a small hole facing the crystal surface. A computer connected to the QMS was used to record TPD spectra. The preparation chamber reached a base pressure of  $8 \times 10^{-10}$  Torr and was equipped with a sputter ion gun and stainless steel gas dosers. The two chambers were isolated from each other during experiments.

In this system the crystal was supported by two W wires spot-welded to the back. The temperature was monitored by a Chromel–Alumel thermocouple spot welded to the back edge of the crystal. The surface was cleaned by three sputter-anneal cycles, with the first anneal (800 K) done in an  $\text{O}_2(\text{g})$

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