DOE/ER/14129-Final

DOE/ER/14129--T1

INFLUENCE OF SURFACE DEFECTS AND LOCAL STRUCTURE ON ACID/BASE
PROPERTIES AND OXIDATION PATHWAYS OVER METAL OXIDE SURFACES

Final Report

David F. Cox

Department of Chemical Engineering

Virginia Polytechnic Institute & State University

Blacksburg, Virginia 24061-0211

RECEIVED

SEP 01 1998

OSTI

June 1990 - January 1997

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG05-90ER14129

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This final report covers work done during Project Period One and Project Period Two under grant number DE-FG05-90ER14129. All the work in project period one was focused on the selective oxidation of oxygenated hydrocarbons over the $\text{SnO}_2(110)$ single crystal surface. In project period two, the emphasis was on the acid/base properties of $\text{SnO}_2(110)$ as well as two different Cu_2O single crystal surfaces. Prior to the summary of results, a description of these different surfaces is given as background information.

1. Oxide Single-Crystal Surfaces of Interest

2.1 $\text{SnO}_2(110)$

SnO_2 has the cassiterite (rutile) structure. The ideal, stoichiometric $\text{SnO}_2(110)$ surface is illustrated in Figure 1. This ideal surface is nonpolar and exposes five-coordinate Sn^{4+} cations in the second atomic layer (one coordination vacancy). All second layer "in-plane" O^{2-} anions are fully (three) coordinate. The outer atomic layer is composed of two-coordinate anions (one coordination vacancy) which occupy bridging positions between otherwise inaccessible, fully (six) coordinate, second layer Sn^{4+} cations. It has been shown previously that a well-oxidized, nearly-stoichiometric (110) surface can be reproducibly prepared from an oriented crystal by oxidation at 700 K in 1 Torr of O_2 or 0.1 Torr of N_2O [1,2].

Heating the stoichiometric surface in vacuum to temperatures up to 700 K removes only the top-layer, bridging oxygen anions as illustrated in Figure 2. The coordination of the newly exposed tin cations associated with the "bridging oxygen vacancies" drops from six to four, with an apparent change in oxidation state from Sn^{4+} to Sn^{2+} [1,3,4]. Tight-binding, total-energy calculations of the relaxed surface structure suggest that removal of the bridging oxygen anions is accompanied by a small "rumple" of the surface layer with the surface tin cations remaining in approximately their bulk positions [5]. The predicted relaxation is small because the surface topology forbids bond-length-conserving motions of the surface atoms [5]. For notational convenience this surface condition will be referred to as the "reduced surface" as in Ref.5.

Further heating to temperatures above 700 K removes some in-plane oxygen anions from what was initially the second atomic layer as illustrated in Figure 3 [1]. This reduces the coordination of the neighboring cations from five and four

Figure 1 Ideal, stoichiometric, $\text{SnO}_2(110)$ surface. The small solid circles represent Sn cations while the large open circles represent O^{2-} anions.

Figure 2 "Reduced" $\text{SnO}_2(110)$ Surface. (Assumes no relaxation.)

coordinate to four and three coordinate, respectively. This condition will be referred to as the "defective surface" for notational convenience. [Note that the "reduced" and "defective" designations for the different surface conditions are inexact since the two surface conditions are, in fact, both reduced and defective in comparison to the

stoichiometric surface.] The concentration of in-plane vacancies is strongly dependent on the immediate sample history. Oxidation prior to high-temperature (e.g., 950 K) annealing produces a less-defective surface with an estimated 20% in-plane oxygen vacancies [2,6]. Ion bombardment and high-temperature annealing with no intermediate oxidation step produces a surface with an estimated 50% in-plane oxygen vacancies [2,6]. This highly defective surface has a composition approaching that of SnO , and the concentration of in-plane vacancies is sufficient to effect the coordination of nearly every surface cation.

All the compositional changes described above occur with no change in the surface periodicity from the (1×1) LEED pattern expected and observed for the stoichiometric surface. Also, no evidence of metallic tin (Sn^0) is seen in XPS for any of the surface preparations. Full details of the surface characterization are given elsewhere [1].

1.2 $\text{Cu}_2\text{O}(111)$

The $\text{Cu}_2\text{O}(111)$ surface may be prepared in two forms that differ in the availability of surface lattice oxygen and the local Cu^+ site configuration. The ideal, stoichiometric $\text{Cu}_2\text{O}(111)$ surface is illustrated in Figure 4. As with other cubic crystals, the (111) surface possesses hexagonal symmetry. The stoichiometric surface is nonpolar. No single atomic layer parallel to the (111) surface contains both copper cations and oxygen anions, and a three-plane repeat unit perpendicular to the surface is required to satisfy stoichiometry and charge neutrality. The stoichiometric termination of the $\text{Cu}_2\text{O}(111)$ is composed of an outer atomic layer of triply-coordinate oxygen anions (bulk coordination is four), the second atomic layer being composed of Cu^+ cations and the third atomic layer of oxygen anions. In the second atomic layer, copper cations can be either singly- or doubly-coordinate in the ratio of 1 to 3, respectively. The bulk Cu^+ coordination is two. As shown previously [7], a nearly stoichiometric surface can be prepared by ion bombardment followed by annealing to 1000 K.

Formation of oxygen vacancies in the outer atomic layer has been observed following repeated exposures of the $\text{Cu}_2\text{O}(111)$ surface to reducing gases [8]. The (1×1) LEED periodicity of the stoichiometric surface is replaced by a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity associated with a third of an atomic layer of oxygen vacancies [7]. Each

Figure 3 "Defective" $\text{SnO}_2(110)$ Surface. (Assumes no relaxation.)

Figure 4 Ideal, Stoichiometric $\text{Cu}_2\text{O}(111)$ Surface. (Assumes no relaxation.)

oxygen vacancy gives rise to a threefold site of singly-coordinate Cu^+ cations in the second atomic layer. No metallic copper is observed at the surface following this reduction, indicating that the charge is delocalized in this p-type semiconductor. Hence, the coordinately-unsaturated cation sites on the stoichiometric and oxygen-deficient $\text{Cu}_2\text{O}(111)$ surfaces are geometrically and compositionally different, while maintaining the same cation oxidation state and coordination number (one anion nearest neighbor). A ball model illustration of the oxygen-deficient $\text{Cu}_2\text{O}(111)$ - $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface is shown in Figure 5.

Figure 5 Oxygen-Deficient, $\text{Cu}_2\text{O}(111)$ - $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ Surface. (Assumes no relaxation.)

2. Overview of Results from Project Period One

2.1. Dissociation and Reaction of Brønsted Acids

2.1.1 Methanol. Our results for the study of different Brønsted acids indicate that the reactivity with SnO_2 surfaces can be alternately controlled by either the acidity of the molecules or the surface conditions. The oxidation of methanol over the different $\text{SnO}_2(110)$ surfaces is 100% selective; formaldehyde is the only carbon-containing product. For this weak Brønsted acid, the stoichiometric surface (Fig. 1a) is nearly inert for dissociative adsorption. A minor amount of formaldehyde is formed, but only at temperatures sufficiently high to remove part of the terminating layer of bridging oxygen anions. As the initial concentration of bridging oxygen on the surface is decreased, the number of exposed four-coordinate Sn^{2+} cations increases, and the conversion to formaldehyde increases. The conversion to formaldehyde is a maximum in TPD (temperature programmed desorption) for the reduced surface (Figure 1b) then decreases with the introduction of in-plane oxygen anion vacancies. Photoemission measurements demonstrate that the changes in methanol conversion track the ability of the surface to promote the heterolytic dissociation reaction (i.e., loss of the acidic proton to form methoxide, CH_3O^-). Similar effects of the surface stoichiometry on dissociation probability are observed for water and isopropanol.

These results demonstrate that the dissociation of methanol occurs preferentially at four-coordinate Sn^{2+} sites, and that the dissociation probability at five-coordinate Sn^{4+} sites on the stoichiometric surface is low. The unimolecular decomposition of surface methoxide to formaldehyde at four-coordinate Sn^{2+} sites is observed at 450 K. The introduction of in-plane oxygen vacancies with the creation of the defective surface introduces an additional methoxide decomposition channel at 540 K associated with the presence of the in-plane vacancies. Hence, while the introduction of in-plane oxygen vacancies decreases the extent of methanol dissociation and conversion, methoxide is stabilized significantly, by nearly 6 kcal/mol, at the low-coordination cations associated with these defects.

The most surprising result is that the highly-defective surface is the most nearly inert for methanol oxidation in TPD (conversion < 5%). Since all the

surfaces investigated expose a significant concentration of surface cations and anions (i.e., potential acid/base site pairs) it is apparent that the site requirements for methanol dissociation involve more than just the availability of such cation/anion pairs. Clearly, the local composition and cation coordination environments play a major role in defining the surface ensemble for the dissociation reaction and the methoxide decomposition kinetics.

2.1.2 Formic Acid. For this stronger Brønsted acid, the differences observed for methanol between the stoichiometric and reduced surfaces (Fig. 1a and 1b) are not apparent. Submonolayer coverages of formic acid on either surface give nearly 100% conversion to CO and CO₂. Hence, the site requirements for dissociation are less stringent due to the higher molecular acidity. However, introduction of in-plane oxygen vacancies decreases the conversion significantly (to about 50%) while a large contribution from molecularly adsorbed formic acid becomes apparent in TPD (desorption temperature 200 K). Hence, the dissociation probability for the highly-defective surface condition is significantly lower even for this strong Brønsted acid, indicating that the surface condition again controls the chemistry. Based on best estimates of in-plane oxygen vacancies as the surface changes from the reduced to the defective condition, the decreases in the extent of dissociation and conversion of formic acid tracks the initial fraction of in-plane anions remaining intact following a given surface preparation.

For formic acid, CO and CO₂ are the primary carbon containing products that are formed. Both products result from formate decomposition, but the relative selectivities are strongly dependent on the initial surface condition. For a stoichiometric surface, the CO₂:CO product ratio (dehydrogenation to dehydration ratio) is about 3.5, but decreases as the initial surface condition becomes more oxygen deficient. For highly defective surfaces, CO and CO₂ are produced in about a 1:1 ratio. The less-oxygenated product distribution reflects the less oxygenated initial condition of the surface. Trace formaldehyde production is also observed on the highly-defective surface, a result of formate reduction by surface hydrogen.

The kinetics of formate decomposition are also effected by the initial surface condition. While the rate-limiting step for CO₂ production is relative insensitive to surface condition, a lower-temperature decomposition channel primarily to CO is observed in the presence of vacancies. The activation energy for formate decomposition in the presence of bridging oxygen vacancies is higher than that observed in the presence of in-plane oxygen vacancies. Hence, formate is more readily deoxygenated around sites with the lowest cation coordination numbers.

Because of the variations observed in the extent of dissociation and reaction of Brønsted acids with surface condition and the implications regarding surface acid/base properties, the adsorption and reaction of isopropanol was investigated. The selectivity for dehydration to propene and dehydrogenation to acetone have traditionally been used as a characterization of surface acidity and basicity [9]. Given the apparent changes in the acid/base properties (i.e., Brønsted acid dissociation probability) of the SnO₂(110) surface with initial condition, any variations in dehydration/dehydrogenation selectivity may be directly relatable to local site configurations. We note that there have been several investigations of

metal oxide surface chemistry which demonstrate that both dehydration and dehydrogenation of alcohols proceed through a common surface alkoxide intermediate [10-14]. Hence, it is clear that the selectivity is not necessarily an indication the presence of different acid and base surface sites, but an indication of different reaction channels for surface isopropoxides.

The overall conversion in TPD for isopropanol follows a similar trend as that observed for methanol: an increase in conversion as the surface condition changes from stoichiometric to reduced, and a subsequent decrease in conversion as the reduced surface becomes more highly defective (i.e., as in-plane oxygen vacancies are introduced). As with methanol, the changes in overall conversion are related to the changing fraction of alcohol dissociated to alkoxide upon adsorption.

Acetone and propene are the only two carbon-containing reaction products formed, and both are produced through an isopropoxide surface intermediate. Acetone is produced via a typical unimolecular hydride elimination from the carbon α to oxygen. As observed for methoxide decomposition, isopropoxide decomposition to acetone occurs in two temperature ranges with the higher-temperature channel associated with the presence of in-plane oxygen vacancies. Unlike the case for methoxide, however, this higher-temperature reaction channel is only slightly populated, suggesting a steric constraint for the interaction of isopropoxide with in-plane vacancies. Propene is formed by deoxygenation and α -hydride elimination. The activation energy for propene formation is about 7 kcal/mol higher than for acetone production.

The dehydration/dehydrogenation selectivity is dramatically effected by surface condition. Following isopropanol adsorption on the stoichiometric surface, propene and acetone are produced in ratio of 2:3. For changing surface conditions, the acetone yield tracks the total conversion and hence the amount of isopropoxide formed by dissociative adsorption. A maximum in acetone production is observed for the reduced surface. For propene, however, the yield is a maximum from the stoichiometric surface, and decreases as the surface becomes more oxygen deficient. For a highly-defective surface, no propene production is observed, a surprising result considering that deoxygenation is required for propene production. This trend in the observed dehydration/dehydrogenation selectivity with surface stoichiometry is the opposite of that observed for formic acid. As of yet we can offer no explanation for this observation.

2.2 Other Molecules

The remainder of the molecules investigated (H_2O , formaldehyde, acetone, propene, acetic acid and carbon monoxide) provide useful comparisons and information regarding the TPD studies of molecules described above. As with methanol and isopropanol, the heterolytic dissociation of H_2O is affected by the initial surface condition. Water dissociation is promoted on the reduced surface, but the stoichiometric and defective surfaces are much less reactive. The H_2O TPD results also allow us to assign rate-limiting steps for water formation in the reaction of hydrocarbon oxygenates. Dehydrogenation reactions of hydrocarbon surface intermediates can be identified by H_2O desorption when the temperature is greater

than that observed for molecular water desorption and OH disproportionation.

Formaldehyde and acetone both adsorb molecularly on all preparations of the $\text{SnO}_2(110)$ surface. No reaction products are observed. The desorption temperatures are, however, sensitive to the initial surface condition, and also confirm that the formaldehyde and acetone reaction products from methanol and isopropanol, respectively, are reaction limited. Our preliminary thermal desorption studies with propene confirm that propene production from isopropanol is also reaction limited. Preliminary acetic acid TPD studies were pursued only to the point of looking for acetone as a product from a bimolecular ketonization reaction; none was observed.

The one real disappointment from our previous work was the investigation of CO adsorption. It was hoped that CO would be sensitive to cations in the various coordination environments associated with bridging and in-plane oxygen vacancies, possibly providing a convenient measure of defect densities obtainable from thermal desorption measurements. While CO is known to be an extremely useful probe molecule for metal surfaces, it was so weakly adsorbed and the uptake was so low at the 170 K adsorption temperature accessible to all the different surface preparations that essentially no useful information was obtained.

2.3 Related Accomplishments

A probe molecule has not yet been found which can quantitatively probe the in-plane oxygen vacancy concentrations via thermal desorption. An upper-limit estimate of the concentration of in-plane defects has been made, however, using the methanol oxidation reaction to introduce defects chemically and relying on the reaction stoichiometry to indicate the amount of lattice oxygen consumed. It appears that the most dramatic effects on reactivity (loss of dissociation ability) occurs for average in-plane defect densities approaching one per surface unit cell (i.e., loss of approximately half of the in-plane oxygen anions). Simple charge counting arguments indicate that this high concentration of defects is equal to that required to reduce all surface cations to a 2+ oxidation state.

A new oxidation procedure has also been found which is much more UHV-friendly than using O_2 at 1.0 Torr as in earlier studies. The sub ppm levels of water in research grade O_2 amount to greater than a 300 L dose of water during a typical (1.0 Torr O_2 over a 5 to 10 minute time period) oxidation treatment. Using N_2O as an oxidant allows us to use an order of magnitude lower pressure (0.1 Torr). Also, the contaminants in N_2O (N_2 , O_2 , CO , CO_2 and CH_4) are much more easily pumped to regain the UHV environment, and are typically much less reactive with oxide surfaces (at low pressure and temperature) than H_2O . Our procedures should be of significant utility to other investigators studying oxide surfaces that require demanding oxidation conditions for sample preparation.

2.4 Comparison to Relevant Literature

Recent studies of the reactions of Brønsted acids on oriented metal oxide single crystals have allowed the testing of previously existing ideas regarding site requirements for reactions on oxide surfaces, and have led also to a number of

interesting new discoveries. The site requirements for the dissociation of Brønsted acids have long been described as involving acid/base (i.e., cation/anion) site pairs. This principle is convincingly demonstrated by the reactivity differences of a variety of Brønsted acids on the Zn-terminated and O-terminated (0001) polar surfaces of ZnO [11,15-21]. These studies on ZnO single crystal surfaces have helped define the coordination requirements for surface cations and anions in the heterolytic dissociation of acids [22]. The critical requirements are coordinatively-unsaturated surface cations, while the coordination environment of the participating oxygen anions apparently is much less critical [22]. These requirements are also consistent with the available data for MoO₃ (010) [23,24], MgO(100) [25,26] and TiO₂ (001) surfaces [27-29].

The observed variations in the extent of dissociation of Brønsted acids on SnO₂(110) indicate a clear structure/composition dependence for the heterolytic dissociation reaction. Since all the surfaces investigated expose a significant concentration of surface anions and coordinately-unsaturated cations, it is clear that the site requirements for methanol dissociation involve more than just the availability of cation/anion pairs. Our work on SnO₂(110) indicates that cation/anion site pairs, while necessary, cannot be considered a sufficient condition for the dissociation of Brønsted acids. Clearly, the local structure plays a major role in defining the surface ensemble for the acid/base dissociation reaction on SnO₂ surfaces.

Similar observations are available in the literature concerning the interaction of H₂O with a variety of titanium oxide surfaces. Molecular H₂O adsorption has been reported on the stoichiometric TiO₂(100)-1x3 surface, but dissociative adsorption occurs in the presence of Ti³⁺ defects sites [30]. The cation oxidation state is not the only controlling factor because molecular adsorption is observed on the stoichiometric Ti₂O₃ (047) surface [31]. For the stoichiometric TiO₂(110) surface, dissociative adsorption is observed [32] in contrast to the (100) surface. As with the SnO₂ surfaces we have studied, all these titanium oxide surfaces expose cation/anion pairs with coordinately-unsaturated cations. As suggested by Kurtz and Henrich [31], local structure and composition appears to be responsible for the observed effects.

An interesting comparison can also be made between the observed reaction products on the SnO₂(110) surface and those reported previously by Kim and Barteau for the TiO₂(001) surface [17-19,33]. The bimolecular coupling of surface methoxide to dimethyl ether was observed on the {114}-faceted TiO₂(001) surface which exposes four-coordinate Ti⁴⁺ cations [18]. The site requirement for this reaction is two coordination vacancies on a single cation capable of binding the two methoxides [18]. The same site requirements were also demonstrated for bimolecular ketonization reactions on this surface between carboxylate surface intermediates [19,33]. On the reduced SnO₂(110) surface, four-coordinate Sn²⁺ cations are available, but no bimolecular coupling of methoxide to dimethyl ether is observed. Also, no carboxylate coupling to acetone was observed from surface acetates in acetic acid thermal desorption studies. The one clear difference between these two cases is the oxidation state of the available four-coordinate

cations. On $\text{TiO}_2(001)$, the four-coordinate cations remain in a 4+ oxidation state, and are exposed as the result of surface faceting [18,34,35]. On $\text{SnO}_2(110)$, the removal of bridging oxygen anions to expose four-coordinate cations is accompanied by the requisite reduction of the cations from a 4+ to a 2+ oxidation state. If one examines the coordination chemistry of Sn^{2+} compounds, coordination numbers of three and four are typical. In the common blue-black form of SnO , each Sn^{2+} cation has a bulk coordination number of four (four O nearest neighbors) in a square-based pyramidal configuration with a natural apparent coordination vacancy occupied by a stereochemically-active lone pair [36]. Hence, while the four-coordinate cations on the reduced surface appear to have two coordination vacancies relative to Sn^{4+} cations at the stoichiometric surface, they are probably best thought of as having a single coordination vacancy, more in line with the expectations for Sn^{2+} compounds.

3. Overview of Results from Project Period Two

3.1 $\text{SnO}_2(110)$

3.1.1 NH_3 Adsorption. Our studies of the interaction of alcohols (i.e., weak Brønsted acids) with different preparations of the $\text{SnO}_2(110)$ surface have shown that the probability for alcohol dissociation to surface alkoxides is strongly dependent on the nature of the exposed surface cation [2,37]. This dissociation process is normally considered a simple acid/base reaction, with the alkoxide ion bonding to a surface cation (Lewis acid site), and the proton binding at surface lattice oxygen anion (basic site) to form a surface hydroxyl. The generally accepted site requirement for the dissociation of Brønsted acids is the availability of cation/anion (acid/base) site pairs on the surface [38]. However, unlike the previous well-documented case of $\text{ZnO}(0001)$ surfaces [21,36,41-46], the differences on $\text{SnO}_2(110)$ are not simply related to the accessibility of cation/anion (acid/base) surface pairs. On the different SnO_2 surfaces, cation/anion pairs are always accessible, but specific surface features are required to promote the alcohol dissociation reactions. For example, the stoichiometric and highly-defective surfaces are nearly inert for methanol dissociation [2]. The highest extent of dissociation and oxidation is observed on the reduced surface in the presence of a maximum concentration of bridging oxygen vacancies but a minimum concentration of in-plane vacancies. Hence, the ability of the surface to promote the acid/base dissociation reaction depends critically on the details of local composition and structure.

Since the dissociation behavior of alcohols on $\text{SnO}_2(110)$ is strongly dependent on the nature of the exposed surface cations [2,37], ammonia adsorption was employed as a probe of the Lewis acidity of surface cations as a function of surface preparation. One goal of the investigation was to determine if there is a connection between the Lewis acidity of the different cations and the ability of a site to dissociate alcohols. Also, since few well-defined defective oxide surfaces have been studied by NH_3 adsorption, this investigation was viewed as a opportunity to test what ammonia probes (particularly in terms of ionic and

covalent contributions to the chemisorption bond) in a situation where reasonably well-defined surface defect sites are available.

NH_3 thermal desorption studies from the nearly-stoichiometric surface give only one coverage-dependent, low-temperature thermal desorption feature indicating that five-coordinate Sn^{4+} cations take up ammonia with a coverage dependent heat of adsorption (ΔH_a) between 15 and 18 kcal/mol. The reduced surface exposes four-coordinate Sn^{2+} cations as well as the five-coordinate Sn^{4+} cations found on the stoichiometric surface. In addition to the low temperature desorption feature observed on the stoichiometric surface, the reduced surface exhibits an additional high temperature feature ($\Delta H_a \approx 30$ kcal/mol) attributable to four-coordinate Sn^{2+} cations at bridging oxygen vacancies. These results indicate that four-coordinate Sn^{2+} cations are stronger Lewis acid sites than five-coordinate Sn^{4+} cations on $\text{SnO}_2(110)$, at least as probed by the NH_3 heat of adsorption. Similarly, changes in the surface dipole and band bending on adsorption (as measured by He I UPS) indicate a larger extent of charge transfer to the surface from ammonia chemisorbed at four-coordinate Sn^{2+} cations. If the alcohol dissociation process is viewed in acid/base terms, promotion of the dissociation reaction by four-coordinate Sn^{2+} cations associated with bridging oxygen vacancies can be described simply as dissociation of a weak Brønsted acid at the surface acid/base site pair with the highest acidity. This view is generally in agreement with suggestions by Barteau [38] that the coordination environment of oxygen anions are much less critical than those of surface cations for the heterolytic dissociation of Brønsted acids on oxide surfaces.

Given that cations in higher oxidation states are generally considered to be more acidic than those in lower oxidation states, the ammonia thermal desorption results demonstrate that the covalent interaction of ammonia with cations on SnO_2 is significantly more important in the chemisorption bond than the ionic (ion-dipole) interaction. This suggestion is verified by UPS measurements which show a 1 eV greater relaxation of the NH_3 $3a_1$ lone-pair MO on the reduced surface than on the stoichiometric surface. The $3a_1$ stabilization energy provides an electronic measure of an increased covalent contribution to the chemisorption bond, as long as the d character of the cations involved is similar [47], a situation that is reasonably met with Sn^{2+} and Sn^{4+} where the filled 3d levels reside ~ 25 eV below the Fermi level.

Chemisorption behavior similar to that observed for ammonia is also seen for formaldehyde, $\text{H}_2\text{C}=\text{O}$ [39]. A higher heat of adsorption is observed in the presence of four-coordinate Sn^{2+} cations associated with bridging oxygen vacancies than for the five-coordinate Sn^{4+} cations on the stoichiometric surface. Given that ammonia, formaldehyde and methoxide ion are all anticipated to interact with surface cations through lone-pair-like MOs, it is suggested that orbital overlap is maximized at the four-coordinate Sn^{2+} sites, by analogy to the criterion of Stair [40] for the description of surface Lewis acids and bases. Using density functional theory, Gillan and coworkers [41] have recently shown that the charge density associated with Sn^{2+} cations on the reduced surface is highly asymmetric and occupies the space "in the immediate neighborhood of the removed bridging oxygen" [41]. The DFT calculations suggest a picture similar to the coordination

chemistry description normally used to describe Sn^{2+} in the blue-black form of SnO . In SnO , five oxygen atoms coordinate Sn^{2+} in a nearly octahedral fashion, with the sixth position occupied by a stereochemically active lone pair [49]. In comparison to the stoichiometric surface, the four-coordinate Sn^{2+} cations on the reduced $\text{SnO}_2(110)$ surface appear to have *two* coordination vacancies. However, from a simple charge counting perspective, one can imagine four anions, a lone pair, and a *single* coordination vacancy in the octahedron surrounding these surface Sn^{2+} sites. We anticipate testing the idea of overlap between lone-pair-like states at Sn^{2+} cations computationally (see below) for ammonia chemisorption.

Further reduction to a defective surface by the introduction of in-plane oxygen vacancies reduces the heat of adsorption of ammonia at both sites. Thermal desorption experiments on a highly-defective surface where the concentration of in-plane oxygen vacancies is sufficient to effect the local coordination environment of nearly every surface cation demonstrate that lowering the coordination of the Sn^{2+} sites decreases the ΔH_a by 7 kcal/mol (i.e., from 30 to ~ 23 kcal/mol). We view this as an inductive effect due to the electron density left behind in the in-plane oxygen vacancy, but we currently lack any experimental evidence to substantiate this view. We hope to address this point by using BF_3 or a similar Lewis acid molecule to probe the charge density associated with in-plane vacancies (see below).

3.1.2 Carbon Dioxide Adsorption. Little is known about the surface properties of oxides that lead to "basicity". Surface base sites are typically considered to be electron-rich surface oxygen anions ("oxide" ions) which can donate electronic charge or bind acidic protons to form surface hydroxyl groups [40,42]. Attempts to study surface basicity typically employ CO_2 as a probe molecule [43-45] since it has been found to poison reactions thought to proceed over basic surface sites [43]. CO_2 adsorption was investigated on SnO_2 to compliment the ammonia chemisorption studies described above.

The adsorption of CO_2 on an oxide surface to form a surface carbonate can be naively viewed as an interaction with a basic surface lattice oxygen anion. However, the interaction is more complex. Both monodentate and bidentate surface carbonates have been identified by IR over a number of different metal oxides [43,46]. For example, one monodentate carbonate and two energetically different bidentate carbonates have been observed over Cr_2O_3 surfaces. The formation of the weaker bidentate carbonate and the monodentate carbonate are believed to occur at cation sites with one coordination vacancy, while the stronger bidentate carbonates are postulated to involve surface cations initially with two coordination vacancies [43,47]. Similar suggestions regarding the role of coordinately unsaturated cations in CO_2 adsorption have been made regarding alumina and magnesia surfaces [43]. Hence, CO_2 appears to probe not just the basic oxygen anions, but the local acid/base site pairs (i.e., cation/anion site pairs) associated with "basic" surface sites. We have attempted CO_2 adsorption studies on the $\text{SnO}_2(110)$ surface, both as a tool for characterizing the surface, and also in

an attempt to characterize how the CO_2 probe molecule interacts with cation/anion pairs of different local geometry and electronic structure on these well-defined surfaces.

CO_2 exposures at LN_2 temperatures in UHV show evidence only for weakly adsorbed molecular CO_2 . Expecting that the carbonate formation process is activated, exposures were also done at room temperature (RT) in UHV, as well as from RT up to 100°C (for all but the stoichiometric surface) in one atmosphere of CO_2 in a high pressure cell attached to the vacuum system. *No evidence of any CO_2 uptake was observed* by XPS or thermal desorption experiments for a room-temperature surface following these treatment conditions.

Because our exposure conditions are much more severe than the 0.1 atmosphere RT exposures required to produce vacuum-stable unidentate carbonates on SnO_2 powders [48], it does not appear that the lack of CO_2 uptake or carbonate formation is due to a failure to surmount an activation barrier to the process. There are two other reasonable explanations for these results: (1) either the sites for carbonate formation on tin oxide powders are not present in detectable concentrations on the low-index (110) surface in all its stoichiometric and defective forms, or (2) the carbonates formed on this low-index surface are weakly bound species which are not stable in UHV at room temperature. Weakly bound carbonates which desorb at RT in vacuum are also observed on SnO_2 powders [48], hence the second explanation appears to be the most likely. Given these results, our $\text{SnO}_2(110)$ surfaces contain at best only "weakly basic" sites based on the standard CO_2 probe molecule used for such determinations.

3.1.3 Propene Adsorption and Oxidation. The adsorption and oxidation of propene over $\text{SnO}_2(110)$ has been investigated as a model for the allylic oxidation of olefins. Propene adsorption at low temperature in UHV does not produce any oxidation products, selective or nonselective. The interaction of propene with five-coordinate Sn^{4+} cations on the stoichiometric surface is weak, and molecular propene desorbs around 200 K. The removal of bridging oxygen anions to expose four-coordinate Sn^{2+} sites gives rise to an additional, less-intense, desorption state at 280 K. Introduction of in-plane oxygen vacancies broadens the high temperature feature (280 K-300 K), but does not give rise to any additional well-defined desorption features. The appearance of a small $\text{C}_3\text{H}_5\text{D}$ desorption feature near 300 K from a D-predosed surface suggest the high temperature desorption state is associated with the recombination of surface allyl and hydrogen at in-plane oxygen vacancy sites. Similar behavior has been observed on $\text{Cu}_2\text{O}(110)$ where propene dissociation is observed at oxygen vacancies in UHV [8].

The adsorption of propene at 1 atmosphere and room temperature was investigated using a flow cell attached to the UHV system in an attempt to activate the selective oxidation to acrolein ($\text{CH}_2=\text{CHCHO}$). Trace amounts of acrolein were observed from the stoichiometric surface in thermal desorption experiments following atmospheric pressure exposures at room temperature. However, the apparent yields of acrolein were always less than 0.1%. Also, because of the high pressure exposures used in this procedure, significant desorption signals for propene and carbon oxides from sample holder hardware (i.e., non sample

surfaces), were observed, even when utilizing a skimmer on the front end of the mass spectrometer. The small size of our SnO_2 single crystal contributed significantly to these problems. While the initial observation of trace acrolein was encouraging, these difficulties made it impossible to close a material balance and determine how the oxidation selectivity varies with surface condition.

3.2 $\text{Cu}_2\text{O}(111)$

Complimentary work beyond that originally proposed was undertaken to study the chemistry of surface oxygen vacancies on single-crystal $\text{Cu}_2\text{O}(111)$. The cuprous oxide studies were initially pursued when the work on $\text{SnO}_2(110)$ was delayed by a broken sample. A replacement for the broken SnO_2 sample was subsequently oriented, polished, and used to continue the work originally proposed.

3.2.1 Acid/Base Probes of $\text{Cu}_2\text{O}(111)$: NH_3 and CO_2 Adsorption. CO_2 adsorption was investigated on stoichiometric and oxygen-deficient $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surfaces to compare cation/anion site pairs of different composition and geometric structure. CO_2 adsorption at pressures and temperatures ranging from UHV and 100 K to 1 atmosphere and 200°C was investigated. The exposure conditions at elevated temperature and pressure are more stringent than those reported for CO_2 adsorption on copper oxide powders [49,50]. As with SnO_2 , no stable surface species at 300 K were observed by XPS or thermal desorption following CO_2 exposure. These results are consistent with one IR study on powders that suggests CO_2 is only weakly bound to copper oxides [50], although another study reports carbonate formation over copper oxide powders [49]. Regardless of the true situation for copper oxide powders, it is clear that CO_2 fails to exhibit any significant difference in the interaction between various cation/anion site pairs on $\text{Cu}_2\text{O}(111)$ surfaces.

Because oxygen vacancies on $\text{Cu}_2\text{O}(111)$ are known to dissociate propene under UHV conditions, NH_3 thermal desorption experiments were done to probe any apparent differences in the Lewis acidity of the cation sites on stoichiometric and oxygen-deficient surfaces. In contrast to the site-dependent heat of adsorption observed on $\text{SnO}_2(110)$, the thermal desorption traces are essentially indistinguishable from the stoichiometric and oxygen-deficient $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ $\text{Cu}_2\text{O}(111)$ surface. No higher-temperature desorption features are observed due to the presence of cations associated with surface oxygen vacancies. Hence, these different sites show no increased Lewis acidity as measured by the NH_3 heat of adsorption. Unlike the case with SnO_2 where cation coordination and oxidation state changes are observed for bridging oxygen vacancies, the cation coordination numbers and oxidation states on $\text{Cu}_2\text{O}(111)$ are the same in the presence of an oxygen vacancies as for coordinately unsaturated cations on the stoichiometric surface.

3.2.2 Investigations with other Probe Molecules: CO and H_2O . CO is a standard surface science probe molecule for metal surfaces [51]. Also, because hydroxylation of metal oxides is a generally observed phenomenon, water is one of the most studied adsorbates on well-defined oxide surfaces. We have investigated the interaction of these two molecules with different cation sites on $\text{Cu}_2\text{O}(111)$.

These chemisorption studies on stoichiometric and oxygen-deficient $\text{Cu}_2\text{O}(111)$ have shown that three-fold hollow Cu^{+1} sites associated with oxygen vacancies are (as seen for NH_3 adsorption above) remarkably uninteresting as chemical centers except for their noted ability to dissociate propene [8]. There is no preferential dissociation of H_2O at these oxygen vacancies, and the heat of adsorption of CO is weak compared to sites on the stoichiometric surface. From the literature on well-defined metal oxide surfaces [52], the conclusion is easily drawn that surface oxygen vacancies are sites of high reactivity. However, a variety of our results on $\text{SnO}_2(110)$ and $\text{Cu}_2\text{O}(111)$ indicate that such a conclusion can be misleading.

Despite the lack of interesting chemistry at oxygen vacancies on $\text{Cu}_2\text{O}(111)$ however, an effect of local surface structure on CO adsorption is observed by comparing the low coverage heat of adsorption on the stoichiometric surface to that observed previously on the Cu^{+} -terminated $\text{Cu}_2\text{O}(100)$ surface [53]. Cations at sites of C_{3v} symmetry on the stoichiometric (111) surface have coordination vacancies perpendicular to the surface. These sites bind CO nearly 6 kcal/mol more strongly than cations on the (100) surface with coordination vacancies that are not perpendicular to the surface. The 22 kcal/mol low-coverage heat of adsorption observed for the C_{3v} site geometry on the stoichiometric (111) surface matches the 21 kcal/mol value reported by Solomon and coworkers for Cu^{+} cations of proposed C_{3v} symmetry on ZnO single-crystal surfaces [54]. XPS indicates that a small π backbonding contribution not observed on the (100) surface is enabled by the local site geometry of the (111) surface.

3.3 STM Investigations

While the presence of bridging and in-plane oxygen vacancies on the $\text{SnO}_2(110)$ surface have been demonstrated experimentally [1,2,6], the details of the local geometric structure (extent of relaxation around the vacancies) and electronic structure in the neighborhood of these defects are not known. STM and STS (tunneling spectroscopy) are currently being used in an attempt to investigate these details.

After encountering recurring start up problems which delayed the full commissioning our UHV STM, this instrument finally came on line in December 1995. Atomic resolution is easily obtained on the usual array of test samples such as $\text{Si}(111)-(7\times7)$ and highly-oriented pyrolytic graphite, as well as on mineral samples such as PbS and FeS_2 . Since December, we have made a number of modifications to the sample manipulation system to allow us to heat to the temperatures required to produce flat terraces on $\text{SnO}_2(110)$.

As of yet, atomic resolution of the $\text{SnO}_2(110)$ surface has not been achieved. We initially encountered problems tunneling to a high-temperature annealed sample. For annealing temperatures where the ion-bombarded surface begins to form terraces, the conductivity drops, and it is difficult to establish a tunneling current. [Note that unlike the case for TiO_2 , SnO_2 does not undergo any significant bulk reduction by heating in vacuum. Hence, most of the changes in conductivity are associated with changes in surface properties.] We have recently had success

establishing tunneling currents by illuminating the sample with UV light from a Hg vapor lamp to excite charge carriers. However, we have still not obtained atomic resolution. Another strategy we will pursue is Sb doping of our SnO_2 single crystal to increase the conductivity.

3.4 Computational Work Directly Related to the Current DOE Project

We are currently involved in computational work directed at understanding the geometric and electronic structure of defective oxide surfaces using local density functional (LDF) calculations. The focus of this research is problem solving, not code development. While no funds from DOE are used in this effort, the computational work is directly aimed at providing insight into the work we are pursuing experimentally through our BES project. Theoretical expertise is provided through a collaboration with Andrew Gibson (formerly of the Environmental Molecular Sciences Laboratory at Battelle Pacific Northwest Laboratories) and John LaFemina (EMSL, Battelle PNL). The PI's primary role is problem definition and running the code. Computation time is provided free of charge by the VPI&SU Computing Center. Work is currently in progress to predict the relaxed structures of $\text{SnO}_2(110)$ surfaces similar to those we are examining experimentally. This work is intended to complement our STM investigations by providing insight into what relaxed surface structures might be expected, and what electronic properties might be associated with particular sites in STS investigations.

To date, we have predicted a relaxed surface structure for the nonpolar, stoichiometric $\text{SnO}_2(110)$ surface which is similar to that predicted in an earlier tight-binding calculation [5], and in a recent LDF calculation by Gillan and coworkers [55]. These results for the stoichiometric surface provide confidence that the code is working correctly and predicting reasonable structures. A relaxed surface structure has also been obtained for the defective surface with no bridging oxygen anions and an in-plane oxygen anion vacancy concentration corresponding to a (2×1) LEED periodicity. We are currently running the reduced surface with no bridging oxygen anions but an intact layer of in-plane anions.

Our calculations for the defective surface are the first ever done for a SnO_2 surface with this extent of oxygen deficiency; in-plane oxygen vacancies have not been examined in the previous computational studies. The ions in the outer two atomic layers exhibit relaxations perpendicular to the surface with magnitudes up to about $0.4 \text{ \AA}$ which decrease the surface dipole induced on the bulk-terminated surface by the oxygen deficiency. The largest relaxations perpendicular to the surface are for anion bordering the in-plane vacancy and anions coordinated to the low-coordination cation associated with the vacancy. Relaxation parallel to the surface plane are small, even in the vicinity of in-plane oxygen vacancies. While some relaxation is clearly apparent, the in-plane oxygen vacancies still appear as "holes" in the surface structure similar to the ball model diagrams based on the bulk-terminated surface (Figure 3). Two different occupied electronic states appear in the band gap, in agreement with earlier photoemission measurements [1]. Details of the local electronic charge densities associated with particular sites are under investigation.

Following completion of the calculations for the relaxation of the reduced surface, we plan to continue by investigating the heat of adsorption of NH_3 at different cation sites on the relaxed stoichiometric, reduced and defective surfaces. It is hoped these calculations will provide insight into the experimentally observed variation in the NH_3 heat of adsorption with surface condition.

4. Publications Resulting from this Grant

1. V.A. Gercher, D.F. Cox and J.-M. Themlin, Oxygen-Vacancy-Controlled Chemistry on a Metal Oxide Surface: Methanol Dissociation and Oxidation on $\text{SnO}_2(110)$, *Surface Science*, **306**(1994)279.
2. V.A. Gercher and D.F. Cox, Formic Acid Decomposition on $\text{SnO}_2(110)$, *Surface Science*, **312**(1994)106.
3. V.A. Gercher and D.F. Cox, Water Adsorption on Stoichiometric and Defective $\text{SnO}_2(110)$ Surfaces, *Surface Science*, **322**(1995)177.
4. A.-C. Christiaen and D.F. Cox, Stoichiometric and Non-Stoichiometric $\text{SnO}_2(110)$ Single Crystal Surfaces, *Surface Science Spectra*, **4**(1996)220. (invited contribution for a special issue on oxide surfaces).
5. A.-C. Christiaen, M.A. Abee and D.F. Cox, Stoichiometric and Non-Stoichiometric $\text{Cu}_2\text{O}(111)$ Single Crystal Surfaces, *Surface Science Spectra*, **4**(1996)279. (invited contribution for a special issue on oxide surfaces).

5. Presentations of Work Performed under this Grant ([†] Invited)

- 1.[†] "Reduced-Coordination Cation Sites at Surface Oxygen Vacancies on $\text{SnO}_2(110)$ ", D.F. Cox, 43rd National Symposium of the American Vacuum Society; Philadelphia, PA, October 1996.
- 2.[†] "Properties of Reduced-Coordination Sites at Surface Oxygen Vacancies on $\text{SnO}_2(110)$ ", D.F. Cox, Tenth DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conference; Montgomery, Texas, May 1996.
3. "Characterization of $\alpha\text{-Mo}_2\text{C}(0001)$ ", T.P. St.Clair, D.F. Cox and S.T. Oyama, 1996 Tri-State Catalysis Club Spring Symposium; Charleston, WV, May 1996.
4. "Acidic Properties of $\text{SnO}_2(110)$ Surfaces", M.W. Abee and D.F. Cox, 1996 Tri-State Catalysis Club Spring Symposium; Charleston, WV, May 1996.
- 5.[†] "Site Specificity for Acid-Base Reactions on SnO_2 Single Crystal Surfaces"; D.F. Cox, Materials and Interfaces Group, Batelle Pacific Northwest Laboratories, Richland, WA, Feb. 1995.
6. "Reaction of Isopropanol Over Stoichiometric and Defective $\text{SnO}_2(110)$ Surfaces"; D.F. Cox and V.A. Gercher; 1994 Annual Meeting of the AIChE; San Francisco, CA; Nov. 1994.
- 7.[†] "Compositionally-Induced Variations in $\text{SnO}_2(110)$ Surface Acid-Base Properties"; D.F. Cox; Highlands in Chemistry Seminar Series, Chemistry

Department, Virginia Polytechnic Institute & State University; Blacksburg, VA; October 1994.

- 8.[†] "Site Specificity for Acid-Base Reactions on SnO₂ Single Crystal Surfaces"; Chemical Engineering Department, University of Pennsylvania; Philadelphia, PA; October 1994.
9. "Influence of Surface Composition and Defects on Oxygenate Reactions over SnO₂(110)"; D.F. Cox; Ninth DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conference; Oconomowoc, Wisconsin; May 1994.
- 10.[†] "Compositionally-Induced Variations in SnO₂(110) Surface Acid-Base Properties"; D.F. Cox and V.A. Ralph; 13th North American Meeting of the Catalysis Society; Pittsburgh, PA; May 1993.
11. "Methanol Oxidation on SnO₂(110)"; V.A. Ralph and D.F. Cox; 1992 Annual Meeting of the AIChE; Miami Beach, FL; November 1992.
- 12.[†] "Influence of Surface Composition and Defects on Oxygenate Reactions over SnO₂(110)"; D.F. Cox; Eight DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conference; Santa Monica, CA; March 1992.
13. "Preferential Isotopic Labeling of Lattice Oxygen Positions on the SnO₂(110) Surface"; D.F. Cox, T.B. Fryberger and V.A. Gercher; 1991 Annual Meeting of the AIChE; Los Angeles, CA; November 1991.
14. "Preferential Isotopic Labeling of Lattice Oxygen Positions on the SnO₂(110) Surface"; D.F. Cox and T.B. Fryberger; 37th National Symposium of the American Vacuum Society; Toronto, Canada; October 1990.

6. References

1. D.F. Cox, T.B. Fryberger and S. Semancik, *Phys. Rev. B*, **38**(1988)2072.
2. V.A. Gercher, D.F. Cox and J.-M. Themlin, *Surf. Sci.*, **306**(1994)279.
3. P.A. Cox, R.G. Egdell, C. Harding, W.R. Patterson and P.J. Tavener, *Surf. Sci.*, **123**(1982)179.
4. J.M. Temlin, R. Sporken, J. Darville, R. Caudano, J.M. Gilles and R.L. Johnson, *Phys. Rev. B*, **42**(1990)11914.
5. T.J. Godin and J.P. LaFemina, *Phys. Rev. B*, **47**(1993)6518.
6. V.A. Gercher and D.F. Cox, *Surf. Sci.*, **312**(1994)106.
7. K.H. Schulz and D.F. Cox, *Phys. Rev. B*, **43**(1991)1610.
8. K.H. Schulz and D.F. Cox, *Surf. Sci.*, **262**(1992)318.
9. M. Ai, *Bull. Chem. Soc. Jpn.*, **50**(1977)2579.
10. M. Bowker, E. Houghton, K.C. Waugh, *J. Chem. Soc., Faraday Trans. 1*, **78**(1982)2573.
11. J.M. Vohs and M.A. Barteau, *J. Chem. Phys.*, **95**(1991)297.
12. S.L. Parrott, J.W. Rogers Jr. and J.M. White, *Appl. Surf. Sci.*, **1**(1978)443.
13. K.S. Kim and M.A. Barteau, *J. Mol. Catal.*, **63**(1990)103.
14. K.S. Kim, M.A. Barteau and W.E. Farneth, *Langmuir*, **4**(1988)533.
15. S. Akhter, K. Lui and H.H. Kung, *J. Phys. Chem.*, **89**(1984)1958.

16. G. Zwicker, K. Jacobi and J. Cunningham, *Intern. J. Mass Spectrosc. Ion Processes* , **60**(1984)213.
17. J.M. Vohs and M.A. Barteau, *Surf. Sci.* , **176**(1986)91.
18. J.M. Vohs and M.A. Barteau, *J. Phys. Chem.* , **91**(1987)4766.
19. J.M. Vohs and M.A. Barteau, *Surf. Sci.* , **201**(1988)481.
20. M.A. Barteau and J.M. Vohs, in Successful Design of Catalysts; Ed., T. Inui (Elsevier, Amsterdam, 1988) p. 89.
21. J.M. Vohs and M.A. Barteau, *Surf. Sci.* , **221** (1989)590.
22. M.A. Barteau, *J. Vac. Sci. Technol. A* , July/August 1993, IN PRESS .
23. C.J. Michaels, W.H. Cheng, U. Chowdhry, W.E. Farneth, F. Hong, E.M. McCarron and A.W. Sleight, *Appl. Catal.* , **25**(1986)249.
24. W.E. Farneth, R.H. Staley and A.W. Sleight, *J. Am. Chem. Soc.* , **108**(1986)2327.
25. X.D. Peng and M.A. Barteau, *Langmuir* , **7**(1991)1426.
26. X.D. Peng and M.A. Barteau, *Catal. Lett.* , **7**(1990)395.
27. K.S. Kim and M.A. Barteau, *J. Catalysis* , **125**(1990)353.
28. K.S. Kim and M.A. Barteau, *Surf. Sci.* , **223**(1989)13.
29. H. Idriss, K.S. Kim and M.A. Barteau, in Structure-Activity and Selectivity Relationships in Heterogeneous Catalysis; Eds., R.K. Grasselli and A.W. Sleight (Elsevier, Amsterdam, 1991) p. 327.
30. W.J. Lo, Y.W. Chung and G.A. Somorjai, *Surf. Sci.* **71**(1978)199.
31. R.L. Kurtz and V.E. Henrich, *Phys. Rev. B* **26**(1982)6682.
32. V.E. Henrich, G. Dresselhaus and H.J. Zeiger, *Solid State Commun.* **24**(1977)623.
33. K.S. Kim and M.A. Barteau, *Langmuir* , **6**(1990)1485.
34. L.E. Firment, *Surf. Sci.* , **116**(1982)205.
35. R.L. Kurtz, *Surf. Sci.* , **177**(1986)526.
36. P.G. Harrison, in Comprehensive Coordination Chemistry , Vol. 3; Ed. G. Wilkinson (Pergamon Press, Oxford, 1987) p. 186-188.
37. V.A. Gercher and D.F. Cox, *J. Phys. Chem.*, in review.
38. M.A. Barteau, *J. Vac. Sci. Tech. A*, **11**(1993)2162.
39. V.A. Gercher and D.F. Cox, unpublished data.
40. P.C. Stair, *J. Am. Chem. Soc.*, **104**(1982)4044.
41. I. Manassidis, J. Goniakowski, L.N. Kantorovich and M.J. Gillan, *Surf. Sci.*, **339**(1995)258.
42. K. Tanabe, Solid Acids and Bases (Academic Press, New York, 1970).
43. H. Knözinger, *Adv. Catal.*, **25**(1976)184.
44. N. Cardona-Martinez and J.A. Dumesic, *Adv. Catal.*, **38**(1992)149.
45. A. Auroux and A. Gervasini, *J. Phys. Chem.*, **94**(1990)6371.
46. G. Busca and V. Lorenzelli, *Mat. Chem.*, **7**(1982)89.
47. A. Zecchina, S. Coluccia, E. Guglielminotti and G. Ghiotti, *J. Phys. Chem.*, **75**(1971)2790.
48. E.W. Thornton and P.G. Harrison, *J. Chem. Soc. Faraday Trans. I*, **71**(1975)461.

49. V.G. Amerikov and L.A. Kasatkina, *Kinet. Katal.*, **12**(1971)165.
50. J.W. London and A.T. Bell, *J. Catal.*, **31**(1973)32.
51. J.T. Yates, Jr., *Surf. Sci.*, **299/300**(1994)731.
52. V.E. Henrich and P.A. Cox, *The Surface Science of Metal Oxides*, (Cambridge University Press, Cambridge, 1994).
53. D.F. Cox and K.H. Schulz, *Surf. Sci.*, **249**(1991)138.
54. S.V. Didziulis, K.D. Butcher, S.L. Cohen and E.I. Solomon, *J. Am. Chem. Soc.*, **111**(1989)7110.
55. I. Manassidis, J. Foniakowski, L.N. Kantorvich and M.J. Gillan, *Surf. Sci.*, **339**(1995)258.