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INFLUENCE OF SURFACE DEFECTS AND LOCAL STRUCTURE ON
OXYGENATE REACTION PATHWAYS OVER METAL OXIDE SURFACES

Progress Report

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Introduction

Our efforts in the first 2½ budget periods have been directed at studying the effects of local surface site variations on the adsorption and reaction of hydrocarbon oxygenates over well-defined, but highly variable $\text{SnO}_2(110)$ surfaces. Model $\text{SnO}_2(110)$ surfaces have been investigated because they allow one to examine the effects of cation and anion coordination number by selectively introducing two different types of surface lattice oxygen vacancies using combinations of high-pressure (1.0 Torr) oxidation treatments, vacuum annealing and ion bombardment [1]. To date, complete thermal desorption and photoemission studies of seven molecules (methanol, formaldehyde, formic acid, isopropanol, acetone, water and carbon monoxide) have been completed on four different $\text{SnO}_2(110)$ surfaces (stoichiometric, reduced, slightly-defective and highly-defective - see descriptions below). Initial thermal desorption studies of acetic acid and propene have also been done. Our results indicate that the different initial surface conditions can dramatically effect: (1) the probability for heterolytic dissociation of Brønsted acids, (2) reaction kinetics for the unimolecular decomposition of oxygenated surface intermediates, and (3) product selectivity.

SnO_2 has the cassiterite (rutile) structure. The ideal, stoichiometric $\text{SnO}_2(110)$ 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 [1].

Heating the stoichiometric surface in vacuum to temperatures up to 700 K removes only the top-layer, bridging oxygen anions. 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]. 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 [4]. The predicted relaxation is small because the surface topology forbids bond-length-conserving motions of the surface atoms [4]. For notational convenience this surface condition will be referred to as the "reduced surface" as in Ref.4.

Further heating to temperatures above 700 K removes some in-plane oxygen anions from what was initially the second atomic layer [1]. This reduces the coordination of the neighboring cations from five and four 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 oxygen-deficient surface than ion bombardment and high-temperature annealing alone as demonstrated clearly in a previous ion scattering spectroscopy (ISS) study [5].

All the compositional changes described above occur with no change in the surface periodicity from the (1x1) 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].

Dissociation and Reaction of Brønsted Acids

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 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 TDS for the reduced surface 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. 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 most highly-defective surface is the most nearly inert for methanol oxidation in TDS. 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.

Formic Acid

For this stronger Brønsted acid, the differences observed for methanol between the stoichiometric and reduced surfaces 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 TDS (desorption temperature $\approx$ 200 K). Hence, the highly-defective surface condition decreases the dissociation probability even for this strong Brønsted acid, indicating that the surface condition again controls the surface 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 in tact 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.

Isopropanol

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 [6]. Given the apparent changes in the acid/base properties (i.e., Brønsted acid dissociation probability) of the $\text{SnO}_2(110)$ 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 [7-11]. 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 TDS 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 proceed 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, propoxide 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 β -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 acetic acid. As of yet we can offer no explanation for this observation.

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 TDS 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 TDS results also allow us to assign rate-limiting steps for water formation in the reaction of other hydrocarbon oxygenates to

dehydrogenation reactions of hydrocarbon surface intermediates 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 TDS studies were pursued only to the point of looking for acetone as a product from a bimolecular ketonization reaction; none was observed. Work on propene and acetic acid adsorption is still in progress.

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.

Related Accomplishments

A probe molecule has not yet been found which can quantitatively probe 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.

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PUBLICATIONS

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*, **Submitted**.
2. V.A. Gercher and D.F. Cox, "Formic Acid Decomposition on $\text{SnO}_2(110)$ ", *Surface Science*, **Submitted**.

MANUSCRIPTS CURRENTLY IN PREPARATION

1. V.A. Gercher and D.F. Cox, "Site requirements for H_2O Dissociation on $\text{SnO}_2(110)$ Surfaces", in preparation.
2. V.A. Gercher and D.F. Cox, "Isopropanol Dehydration and Dehydrogenation on $\text{SnO}_2(110)$: A Thermal Desorption Study of the Effects of Local Surface Composition on Activity and Selectivity", in preparation.

PRESENTATIONS (* Invited)

1. * "Compositionally-Induced Variations in $\text{SnO}_2(110)$ Surface Acid-Base Properties"; D.F. Cox and V.A. Ralph; 13th North American Meeting of the Catalysis Society; Pittsburg, PA; May 1993.
2. "Methanol Oxidation on $\text{SnO}_2(110)$ "; V.A. Ralph and D.F. Cox; 1992 Annual Meeting of the AIChE; Miami Beach, FL; November 1992.
3. "Methanol Oxidation on $\text{SnO}_2(110)$ "; V.A. Ralph and D.F. Cox; 39th National Symposium of the American Vacuum Society; Chicago, IL; November 1992.
4. "Influence of Surface Composition and Defects on Oxygenate Reactions over $\text{SnO}_2(110)$ "; D.F. Cox; Eight DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conference; Santa Monica, CA; March 1992.
5. "Preferential Isotopic Labeling of Lattice Oxygen Positions on the $\text{SnO}_2(110)$ Surface"; D.F. Cox, T.B. Fryberger and V.A. Gercher; 1991 Annual Meeting of the AIChE; Los Angeles, CA; November 1991.

Outline of Plans for the Upcoming Year

For the remainder of budget period 03 (Through 1/31/94)

- I. Complete TDS investigation of propene adsorption in UHV.
- II. Complete photoemission and remaining TDS work on acetic acid adsorption.

For the pending 3-year renewal

Full details given in enclosed renewal proposal.

Remaining Funds From Budget Period 03

It is anticipated that the balance in research funds from Budget Period 03 (2/1/93 to 1/31/94) will be less than \$500.

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