

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

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Work during the last year (August 1991 to July 1992) has concentrated on completing the previously initiated studies of the surface chemistry of C₁ oxygenates on SnO₂(110) and beginning studies of C₂ oxygenate surface chemistry. During the remaining six months of the second budget period, the C₂ studies will be continued.

Our work with the C₁ compounds (particularly methanol) has demonstrated that changing the defect (oxygen vacancy) density of the SnO₂(110) surface greatly effects the acid/base properties of this oxide surface. The stoichiometric surface with exposed five-coordinate Sn⁺⁴ cations and coordinately-unsaturated anions gives only a small (10-20%) conversion of methanol, but removal of the coordinately-unsaturated (bridging) anions to expose four-coordinate cations and coordinately-saturated anions increases the conversion to over 50%. In comparison to the basicity of adsorbed atomic oxygen on metal surfaces which is sufficiently basic to promote the dissociation and decomposition of alcohols, the coordinately-unsaturated anions should also be sufficiently basic to promote this reaction. Hence, it appears that the acidity of the four-coordinate cations controls the activity of the surface for the oxidation of methanol. In contrast, the conversion of the more acidic formic acid approaches 100% regardless of which of the two surface conditions described above is present.

In our previous annual report [1], we proposed investigating the relative acidity of the different surface cation sites by IRAS (infrared reflection-absorption spectroscopy) of adsorbed ammonia and pyridine. This work was outside the scope of the work originally proposed, and was dependent on the use of an infrared spectrometer obtained from another source. The FTIR has been purchased, but the technique is not yet functioning well enough to conduct these studies. We now hope to carry these measurements out in budget period 03. Such studies, potentially the first on a **well-defined** metal oxide surface, are still considered critical for understanding this system.

Additionally, a second type of oxygen vacancy can be introduced in the "in-plane" positions to give four- and three-coordinate cations. The activation energy for the selective, oxidative dehydrogenation of methanol to formaldehyde increases by about 6 kcal/mol at these sites, and the selectivity for formate decomposition (from formic acid) shifts from CO₂ to CO. The conversion

of both oxygenates, however, depends critically on the concentration of in-plane defects, and falls off to nearly zero at sufficiently high concentrations. The effects of such defects on the acid/base properties of the surface is not understood currently. We note also that we currently have no means for measuring the density of in-plane oxygen vacancies, either in an absolute or a relative sense. We are in the process of trying to find an appropriate probe molecule for such sites.

It was reported previously [1] that formaldehyde was formed as a reaction product from formic acid. At that earlier time, two possible explanations were given: (1) disproportionation of surface formate via a reaction directly analogous to the bimolecular ketonization of carboxylates reported by Kim and Barteau for TiO_2 surfaces [2] or (2) direct reduction of surface formate by surface hydrogen. The possibility that the bimolecular ketonization process might be operable led us to set our major focus, at the time, for budget period 02 as the study of C_2 and C_3 carboxylic acid surface chemistry. However, we have since determined that reduction of surface formate is the operable pathway, and so have continued with the more general study of the C_2 oxygenates instead. Professor Barteau has confirmed that such a reaction is also observed on highly defective TiO_2 surfaces [3], a condition similar to those found on SnO_2 when this reaction is observed.

The lack of bimolecular coupling reactions such as those observed over TiO_2 surfaces to form ketones from acids (or analogously, formaldehyde from formic acid) or ethers from alcohols [2] demonstrates a significant difference in the chemistry of TiO_2 and SnO_2 even though they have identical bulk crystal structures. Kim and Barteau [2] have postulated that the site requirements for these bimolecular reactions are the availability of two vacant coordination sites on the surface cations (i.e., four-coordinate Ti surface cations). Our $\text{SnO}_2(110)$ surface with bridging anions removed clearly fits this description when compared to the structure of the stoichiometric surface. However, the lack of such reactions on the SnO_2 surface does **not** invalidate the site requirements proposed by Barteau and coworkers. On TiO_2 , the four-coordinate cations are formed by surface reconstruction, and maintain the 4+ oxidation state. On $\text{SnO}_2(110)$, removal of the bridging anions to give four-coordinate cations is believed to result in the reduction of the adjacent cations to a 2+ oxidation state [4]. While such cations have two vacant coordination sites when compared

to the stoichiometric SnO₂(110) surface, the coordination chemistry of Sn²⁺ compounds generally gives rise to four- or five-coordinate metal centers [5]. Hence, in terms of the expected coordination chemistry of Sn⁺², there is reasonably only a single vacant coordination site associated with these cations.

REFERENCES

1. D.F. Cox, Annual Report for Budget Period 01, DOE/ER/14129-1.
2. K.S. Kim and M.A. Barteau, *Langmuir* **6**(1990)1485.
3. M.A. Barteau, Personal Communication, March 1992.
4. D.F. Cox, T.B. Fryberger and S. Semancik, *Phys. Rev. B* **38**(1988)2072.
5. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th Ed. (John Wiley & Sons, New York, 1980).

PUBLICATIONS

Two manuscripts are currently in preparation. The principle author will be the graduate student working on this project, Victoria A. Ralph.

1. "Formic Acid Decomposition on SnO₂(110)", **to be submitted** to *Surface Science*.
2. "Adsorption and Oxidation of Formaldehyde and Methanol over SnO₂(110): Effects of Oxygen Vacancies and Cation Coordination Number on Activity and Selectivity", **to be submitted** to *Surface Science*.

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