

Organic Reactions at Well-Defined Oxide Surfaces

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Received November 1, 1995 (Revised Manuscript Received January 26, 1996)

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Mark Barteau was born and raised in the suburbs of St. Louis, MO. He received a B.S. in Chemical Engineering from Washington University in St. Louis in 1976, and M.S. (1977) and Ph.D. (1981) in Chemical Engineering (with a Chemistry Minor) from Stanford University under the direction of Professor Robert J. Madix. After a year of postdoctoral study in the Physics Department of The Technical University of Munich with Professor Dietrich Menzel, he joined the faculty of the University of Delaware in 1982. He is currently Robert L. Pigford Professor of Chemical Engineering and holds a joint appointment in the Department of Chemistry and Biochemistry. His research in surface science and catalysis has received wide recognition, including the Allan P. Colburn Award of the AIChE in 1991, the Paul H. Emmett Award in Fundamental Catalysis, awarded by The Catalysis Society in 1993, and the Ipatieff Prize of the ACS in 1995. His research interests include organic reactions on metal and metal oxide surfaces, self-assembly of oxide cluster monolayers, and the application of surface science to heterogeneous catalysis.

I. Introduction and Scope

The field of metal oxide surface science is young, even within the ~30-year history of ultrahigh-vacuum spectroscopic studies on single-crystal surfaces. The application of UHV surface science techniques to metal oxides has blossomed only within the last decade. An excellent and comprehensive compilation of work in this field may be found in the recent book by Henrich and Cox.¹ That book is a superb source for the physical and electronic properties of oxide surfaces and catalogs a number of examples of reactions on oxide surfaces as well. The focus of the current review is on the chemical properties of metal oxide surfaces, in particular on the principles, syntheses, and analogies to reactions in other media that one can develop from the growing body of research on reactions on well-defined oxide surfaces. As will be shown below, the key properties of oxide surfaces for this purpose are coordination environment, oxidation state, and redox properties, particularly of surface cations, and we shall focus on the connection of these, rather than surface composition and structure as such, in attempting to forge connections to surface organic reactions. Likewise, the application of various spectroscopies will be introduced as needed in the context of studies to probe surface chemical phenomena; the reader is referred to other sources for more technique-oriented information.^{2,3} The reason for this limited scope is to create greater recognition between disciplines, to provide surface scientists with examples of the ties between reactions on solid surfaces and other branches of chemistry, and to introduce the organic or organometallic chemist to familiar chemistry in unfamiliar surroundings without requiring an immersion in surface science.

II. What Is Different Between Metals and Oxides?

The most obvious difference between metals and oxides is one of conductivity. Oxides may be insulators, semiconductors, conductors, or even superconductors. Most of the simple oxides that have been examined in single-crystal surface science studies are insulators or semiconductors. That characteristic has probably been the single most important source of the lag in the growth of oxide surface science vs that of metals—causing greater difficulty in the application of charged particle spectroscopies that are the mainstays of the surface scientist's arsenal. The disruption of these spectroscopies by effects such as surface charging or band-bending turns out to have been much overrated (or at least less of a challenge to clever experimentalists than expected), and considerable progress is evident over the last decade in the application of a full complement of surface science techniques, including AES, LEED, XPS, UPS, ISS, and even HREELS, to single-crystal oxide surfaces. The range of these techniques can be extended even further by the use of model thin-film oxides on conductive substrates,^{4–6} although these require an additional level of effort in preparation and charac-

terization, and may not always be easy to prepare with adequate control of crystallinity or surface orientation. Nevertheless, it is clear that oxide surface science has come into its own over the last decade, and the monograph by Henrich and Cox¹ cites nearly 1000 references.

From the surface chemistry point of view, two characteristics of metal oxides distinguish them from metals, and perhaps lead to differences in the conceptual frameworks needed to describe reactions on these two classes of materials. The first is the absence of metal–metal bonds in the high-valent oxides that are nearly always the subject of such studies. The metal cations are thus isolated from each other by bridging oxygen anions. As such, they may resemble the metal centers in mononuclear metal complexes in solution more than they do metal atoms on an extended metal surface. Such analogies are not new, of course. The chemistry of olefin polymerization on other ionic solids such as TiCl_3 (Ziegler–Natta catalysis) is a textbook example of the application of concepts from coordination chemistry to reactions on ionic solids.⁷ We merely wish to point out that they may be particularly apt for oxide surfaces. A second characteristic of oxides reinforces this notion. The metal centers in an oxide are not in their zerovalent state, unlike the metal centers on a bulk metal surface. Once again this leads to the suggestion that one may find analogies in the chemistry of soluble metal complexes which also are often not zerovalent. Indeed, we have contended⁸ that metal oxides, rather than metals, are the most likely place to find strong analogies with organometallic chemistry and homogeneous catalysis by transition metal complexes.

Several other “materials” properties of oxides distinguish them from metals. From the experimental surface scientist’s point of view, oxides are more difficult to work with than metals for reasons beyond the problems of electrostatic charging and band bending noted above. “Simple” operations such as heating, cooling, and temperature measurement in vacuum are more taxing with materials that are difficult to maintain in good thermal contact with metals, e.g., by spot welding. Successful schemes for obtaining accurate measurements of the temperature of oxide single crystals include spring loading thermocouples against the sample,⁹ use of ceramic cements to attach the thermocouples to the sample,¹⁰ and use of low melting point metals such as indium to provide good thermal contact between the oxide sample and a metal holder to which the thermocouple is spot welded.¹¹ (Mounting the thermocouples on a metal sample holder without the indium layer in between the oxide sample and the holder can lead to large overestimates of the sample temperature as the mount is heated.) Perhaps a more important distinguishing characteristic is the difference in thermal stability of oxides and metals. While oxides are generally higher melting than the corresponding metals, they may undergo thermal fracture or phase transformations which limit the range of materials feasible to study in single-crystal form. More critical, from the point of view of the surface chemistry that they carry out, is the tendency of many oxide surfaces

to undergo thermally driven rearrangement, reconstruction, or faceting. This phenomenon arises from two characteristics of oxides. The first is the lower average coordination number of metal centers in oxides than in bulk metals, and the correspondingly greater relative free energy cost associated with creation of coordination vacancies, as at a surface. The second characteristic is the need for charge balancing at the surfaces of ionic solids. Together these effects tend to cause reconstruction to form structures which minimize surface polarity as well as the number of dangling bonds at the surface.

The tendency of oxide surfaces to reconstruct is a two-edged sword. While it makes it more difficult to vary surface structure for any given oxide than for most metals, it also permits one in some cases to examine the reactivity of different surface structures using only one single-crystal sample. A demonstration of such studies is included in the discussion of the site requirements for various surface reactions below. It is important to recognize, however, that one pays a price for such “versatility” of oxide surfaces. While the single-crystal oxide surfaces described below are certainly well defined with respect to composition and/or structure as compared to those one encounters in polycrystalline catalysts or ceramic materials, their structures are generally less well defined than those of metal single-crystal surfaces. This gap will undoubtedly narrow with increasing focus on oxide surfaces, and the reader should beware that there is considerable room for better definition of oxide surfaces that are today generously considered “well defined”.

III. Key Concepts To Describe Oxide Surfaces

Building on the analogies to the chemistry of transition metal complexes raised above, one can identify three key concepts applicable to the surface chemistry of metal oxides: (1) coordination environment of surface atoms; (2) redox properties of the oxide; and (3) oxidation state of the surface.

Each of these can be controlled, if not specified, by the experimentalist. Surface coordination environment can be controlled by the choice of crystal plane exposed and by the preparation procedure for materials which permit different metastable surface structures to be formed. Specification of redox properties is largely a matter of the choice of oxide. This can rarely be varied independent of the bulk or surface structure, owing to the much greater variation of crystal structures formed by even simple oxides than by pure metals. The more “idiosyncratic” structure of oxides thus leads one to search for characteristics, e.g., surface coordination environment, that can be used to compare the surfaces of different materials without the need to retain the details of different bulk structures. While such unifying concepts may on occasion produce oversimplifications or omissions, they clearly provide a more useful framework on which to build an understanding at this early stage of development of the field than would an attempt to maintain a “catalog” based on the detailed surface structures (which are not always known) of those materials that have been studied.

The redox properties of oxides are likewise decoupled from oxidation state in the framework utilized here. In realistic applications, e.g., catalysis, these are likely to be connected; oxides that are more difficult to reduce are more likely to function in a high valence state. In surface science experiments in vacuum, these properties may be effectively decoupled. Since the vacuum environment is intrinsically reducing, the stoichiometry of some oxide surfaces, especially the more easily reduced ones, can be varied by simple thermal treatment in vacuum. An elegant example is the work of Cox and coworkers varying the surface metal-to-oxygen ratio of the SnO_2 (110) surface.¹²⁻¹⁴ They were able to remove different, structurally discrete oxygen anions from the surface, to demonstrate by ISS and other techniques that this had been achieved, and to carry out selective isotopic labeling (with ^{18}O) of different sites to explore which surface oxygens participated in surface reactions. A less elegant approach, which nonetheless finds widespread use, is the use of ion bombardment techniques. Owing to the lower mass of oxygen atoms than of the metal atoms in all but a few oxides, the ballistic removal of material from oxide surfaces by sputtering with noble gas ions (usually argon) leads to preferential sputtering of oxygen from the near-surface region of the solid.¹⁵ As a result, even materials with high metal-oxygen bond strengths, e.g., TiO_2 , can be reduced to produce accessible lower oxidation states. For transition metal oxides where an assortment of lower oxidation states are usually feasible, sputtering may produce a mixture of these, as well as disrupting the crystallographic structure of the surface. For oxides of main group elements, the only lower oxidation state may be the zerovalent metal, and it is usually more difficult to build up or to maintain significant surface concentrations of it by sputtering.

Various other strategies for producing reduced surface sites on oxide single crystals have also been pursued. These include evaporation of the metal onto its oxide followed by thermal or oxidative treatments,¹⁶ electron beam stimulated reduction,¹⁷ laser irradiation,¹⁸ and chemical reduction.¹⁹ The efficacy of these different techniques is strongly material dependent, but systematic comparisons are, unfortunately, the exception, rather than the rule. The development of recipes and techniques for producing ordered, well-defined suboxide surfaces with controlled structure, composition, oxidation state distribution, and morphology remains an important challenge to researchers in this field. It is hoped that some of the chemistry described below and that yet to be discovered on reduced oxide surfaces will motivate this pursuit.

One of the advantages of surface reactivity studies in the UHV environment is that one can limit the exposure of the surface to reactant gases. Thus it is possible to create and to study the surface chemistry of reactive, reduced surfaces that would not "survive" more realistic ambient conditions.

A survey of the single-crystal surfaces of one important transition metal oxide, TiO_2 with the rutile bulk structure, which have been examined in the literature, serves to illustrate these concepts. It also

illustrates the wide variety of surfaces and their physical properties (and the characterization techniques needed to define these) that are accessible. TiO_2 has been one of the most popular oxide materials in surface science studies for a variety of reasons. It can be made conductive by slight reduction, and is thus a tractable material even for techniques that might be disrupted by charging effects, including STM. It finds application (or potential application) in a variety of technologies where surface chemistry is critical to success, including pigments and catalysts. In the latter area, it has been much explored as a support material for metals in so-called SMSI catalysts,²⁰ and it has been widely studied as a key component of potential photocatalysts for water splitting (photoreduction) and for degradation of organic contaminants in gas phase as well as aqueous streams (by photooxidation).²¹

The ideal structures of the (100), (110), and (001) planes formed by simple termination of the bulk rutile lattice are shown in Figure 1. It is immediately apparent that even these low-index planes exhibit a wide variety of surface coordination environments. The (110) plane of this material presents the least coordinatively unsaturated surface of the three and, not surprisingly, exhibits the greatest thermal stability. The ideal structure of this surface possesses both 5- and 6-fold coordinated surface cations; these are present in equal numbers on an ideal stoichiometric surface, as shown in Figure 1. The (100) plane would ideally expose five-coordinated cations and has been shown to reconstruct to generate several different surface structures.^{1,22} The structures proposed for the reconstruction on this and other oxide surfaces have been derived mainly from LEED results;¹ in recent years glancing angle XRD,²³ photoelectron diffraction,²⁴ and STM²⁵⁻³¹ have led to additional refinements. The $\text{TiO}_2(100)-(1 \times 3)$ structure in particular, has been associated with the formation of ordered arrays of oxygen vacancies in the topmost layer.^{29,30}

The (001) plane (which is not equivalent to the (100) in the rutile structure) is the least stable of all the low-index planes of TiO_2 . The ideal termination of the bulk structure in this direction exposes cations which are all four-coordinate. This high degree of coordinative unsaturation is thermodynamically undesirable, and cleaved surfaces which initially display this structure have been shown to undergo reconstruction upon quite mild annealing. The faceted structures formed on this surface give rise to different LEED patterns depending on the temperature at which one anneals; structures of these proposed by Firment³² to explain the LEED data are illustrated in Figure 2. The Firment model suggests that the reconstructed (001) surface is terminated by facets with different crystallographic structures; he has described the "low-temperature phase", produced by heating below ~ 850 K (the temperatures originally claimed are in error due to measurement difficulties³³), as "{011}-faceted", and the high-temperature phase, requiring temperatures of 950 K and above, as "{114}-faceted". The {011} facet planes lie 32.8° from the (001) plane toward the [100] direction. The unit mesh, depicted in Figure 2 is rectangular (5.46

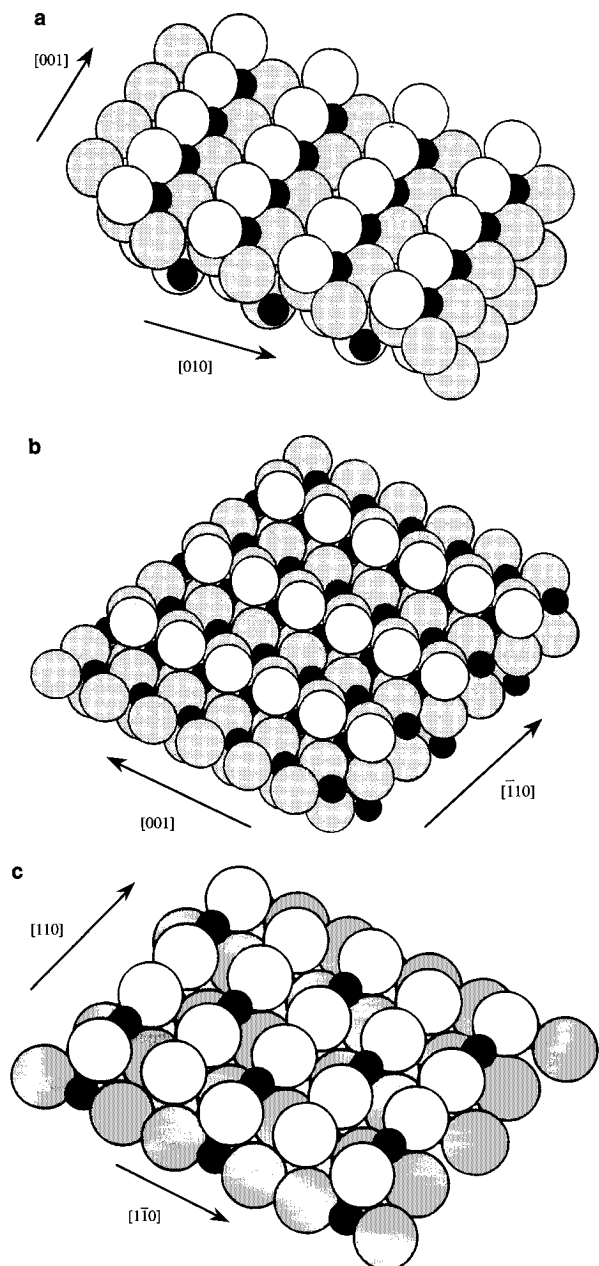


Figure 1. Ideal termination of (a) the $\text{TiO}_2(100)$, (b) the $\text{TiO}_2(110)$, and (c) the $\text{TiO}_2(001)$ surfaces: (open circles) top layer oxygen anions; (solid circles) titanium cations; (shaded circles) second (and deeper) layer oxygen anions. (From ref 1.)

$\times 9.18 \text{ \AA}$) and oriented in the directions illustrated in the figure.³² The $\{114\}$ facet planes lie 12.8° from the (001) in the $[110]$ direction, with a rectangular unit mesh of $6.49 \times 13.3 \text{ \AA}$ oriented as shown.³² Firment has suggested that the $\{114\}$ -faceted surface can be described as a stepped structure, with (001) terraces two unit cells wide linked by (111) steps. As pointed out by Henrich and Cox¹ these idealizations do not match the observed LEED patterns exactly, although additional refinements of the structure have not been suggested. Atomic resolution STM images of these structures are still lacking, but both STM³⁴ and RHEED³⁵ do show evidence for pronounced faceting of this surface.

The key point however is the distribution of coordination environments presented by these faceted structures. The $\{011\}$ -faceted (001) surface ideally

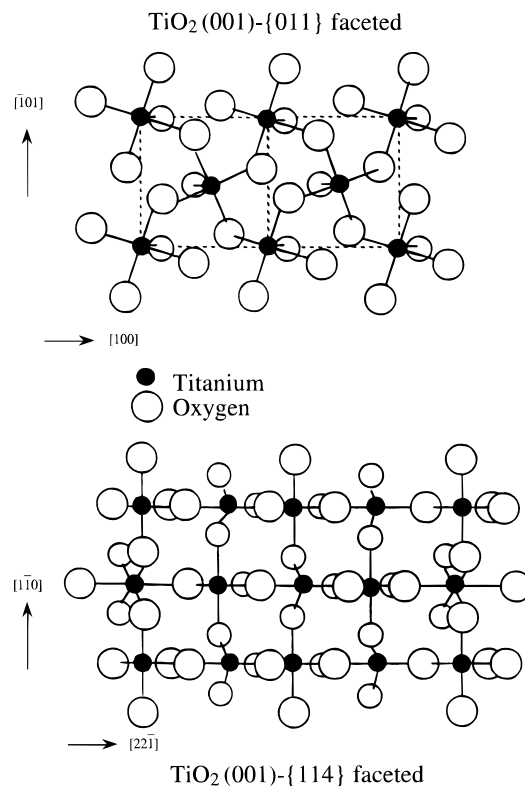


Figure 2. Individual facet structures proposed for reconstructed $\text{TiO}_2(001)$ surfaces. (From ref 32.)

contains only five-coordinated Ti cations, i.e., each surface cation possesses a single coordination vacancy. That such a structure should be more stable than the unreconstructed surface with two coordination vacancies per cation is not surprising. What is perhaps more surprising is the fact that this structure is not the most thermally stable version of this surface. The $\{114\}$ -faceted structure, formed at high temperature, ideally exposes equal numbers of cations with 4-, 5-, and 6-fold coordination.³² The average degree of coordinative unsaturation is thus the same as for the $\{011\}$ -faceted structure, but this surface now exposes cations with two coordination vacancies. Reactivity comparisons between the two surfaces permit one to deduce the chemical properties of singly vs doubly coordinatively unsaturated surface cations.

One can vary not only coordination environment, but also oxidation state. In continuing the example of titanium oxides, we shall treat these as essentially independent characteristics, which they clearly are not. Lowering the oxidation state may also reduce the maximum coordination number of the metal cations, and in some cases may decrease surface reactivity by producing reduced but coordinatively saturated surface cations (in contrast to the usual effect of reduction, increasing surface reactivity). The difficulty is that most of the reduction methods discussed above, especially bombardment techniques, introduce disorder, and it is often difficult to determine the coordination environment on reduced surfaces with any degree of reliability. STM may help to address this problem in future, but at present there are general techniques neither for producing nor for characterizing partially reduced oxide surfaces with well-defined structures. Indeed reactivity

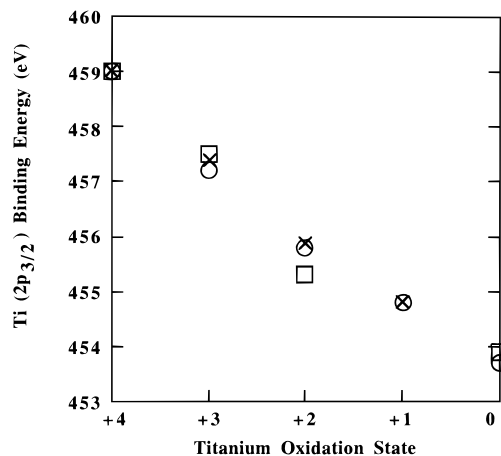


Figure 3. Variation of Ti(2p_{3/2}) binding energy with titanium oxidation state. (○, Rocker and Gopel;¹⁶ □, Carley et al.;³⁷ ×, Idriss and Barteau.³⁶)

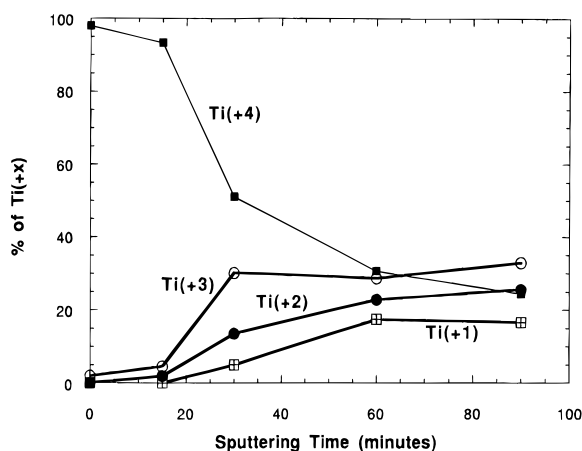


Figure 4. Population of Ti cations in different oxidation states on the TiO₂(001) surface as a function of sputtering time with Ar⁺ ions. Relative populations were determined from XPS spectra. (From ref 36.)

correlations of the sort discussed below might serve as important diagnostic tools for coordination environment and/or oxidation state of surface sites.

With that caveat, we note briefly the means for characterizing surface oxidation state. By far the most powerful and almost universally applicable is XPS. Shown in Figure 3 is a correlation of titanium 2p_{3/2} binding energy with oxidation state for titanium oxides. Such correlations, compiled from studies of bulk suboxides or of reduced high-valent oxide surfaces^{16,36,37} permit one to characterize the oxidation states of surface cations present in the near surface region of the solid sampled by XPS. Figure 4 illustrates the progressive increase in reduction of titanium cations at an ion-sputtered TiO₂ surface with sputtering time. Maps such as this provide a guide, both for preparation of surfaces with different average oxidation states, and for understanding the chemical reactivity of those surfaces in terms of average or specific oxidation states of such surfaces.

Recent studies by Chen and co-workers^{38,39} have advanced the application of near-edge X-ray absorption fine structure (NEXAFS) to determine the oxidation state of surface cations and to distinguish surface from bulk compositions in mixed oxides. The ability to probe composition differences arises from the very

different escape depths of electrons vs photons in electron yield vs. fluorescence measurements. While these techniques hold considerable promise for resolving questions of surface composition, oxidation states, surface geometry, and near-surface concentration gradients for complex oxide materials, they have not yet been applied to oxide single crystals or surfaces derived from them.

In the case of titanium oxides, UPS also provides a fingerprint to diagnose the presence of cations below the maximum, +4, oxidation state. As shown by Henrich and co-workers,⁴⁰ the presence of lower valent Ti centers at the surface gives rise to photoelectron emission from the bandgap region of TiO₂. These centers produce a peak about 1 eV below the Fermi level; the valence band maximum of stoichiometric TiO₂ is typically ~3 eV below the Fermi level. Emission from this state can be quenched by adsorption of species such as O₂ and SO₂⁴¹⁻⁴³ which oxidize the low-valent Ti centers. However no quantitative correlations with surface reactions of organics have been constructed from UPS data, unlike XPS.

It should be noted that the variations in surface composition and structure discussed above should be thought of primarily as local phenomena. Even changes detected by LEED and STM can be described in terms of alterations of local geometric structure, and do not necessarily propagate coherently over long (> 20 nm) length scales. AFM studies of reduced and various faceted, stoichiometric TiO₂(001) surfaces have shown little difference between them at length scales > 50 nm.⁴⁴

Finally, it should also be noted that there are at least two important issues in reactivity and catalysis by metal oxides where the still emerging field of oxide surface science has yet to rise to the challenge. The first is in the area of creating and characterizing the range of defects present on "real" oxide surfaces that may in fact dominate the chemistry of such materials. These include the usual menagerie of defects, e.g., F-centers, cation vacancies, anion vacancies, interstitials, trapped electrons or holes, that one can find in solid-state texts treating such materials. More effort is clearly needed, both in the creation of model systems which adequately reflect the properties of such centers, and in the development of surface science tools that can detect, fingerprint and count them, even in low concentration on low surface area, single crystal-derived samples. A start in this regard may be found in the work of Goodman et al., who have detected F-centers in MgO films using EELS and have correlated the concentration of these with activity for methane activation.⁴⁵ However, in the surface chemistry of oxide single-crystal surfaces discussed below, the various types of defects noted above, which might influence reactivity, are neglected. The reason is that one can rarely create or characterize reproducible populations of these. We shall therefore focus on those surface characteristics that are more amenable to control and characterization, in particular coordination environment and oxidation state. In some cases these characteristics may be surrogates for the properties and populations of different active surface sites, including defects. However, as we shall see below, such simplifications

can produce quite useful generalizations about the surface chemistry of metal oxides.

The second, and perhaps longer term challenge to oxide surface science is to address important issues in selectivity in catalytic oxidation, in particular the principle of "site isolation". There are a number of clear-cut examples in catalysis by mixed oxides, including the selective oxidation of propylene by Bi-Mo and U-Sb oxides⁴⁶ and the selective oxidation of butane to maleic anhydride with VPO catalysts,⁴⁷ where selectivity to the desired products (vs combustion products) relies on the limited availability of oxygen at site-isolated ensembles of the active metal oxide component. The validation of this principle by surface science studies of model oxide surfaces, and the development of quantitative ensemble size requirements and design principles from these, represent important but as yet unaddressed challenges to the field.

IV. Characteristic Reactions on Oxide Surfaces

As with all fields of chemistry, the question arises whether to organize reactions on surfaces by reactant or product classes, as some texts do, or to attempt classifications based on mechanism. The difficulty is that the former provides a greater degree of certainty, but the latter, even if not completely correct, permits a broader range of analogies and even qualitative prediction. Because of the importance of applying principles from surface science studies, even to the extent of catalyst "design", we therefore consider basic patterns of apparent mechanistic similarity in the reactions of organic molecules on oxide surfaces. In particular, if we can establish analogies to coordination chemistry in solution, then we can hope both to short cut some of the detail required to establish surface reaction mechanisms, as well as to provide a vehicle for connecting homogeneous catalysis to surface chemistry and then, perhaps, to new heterogeneous catalysts for hitherto homogeneously catalyzed processes.

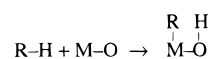
The simplest division of oxide surface reaction classes is into two groups: acid-base reactions and oxidation-reduction reactions. This is clearly a "broad brush" treatment; Henrich and Cox,¹ for example, distinguish five different types of surface-adsorbate interactions on oxides, even without considering the usual array of nucleophilic and electrophilic oxidation and reduction mechanisms from organic chemistry that undoubtedly occur to greater or lesser extents for organics on oxide surfaces. Nevertheless, the two broad reaction classes noted above provide a framework for comparing the behavior of widely different oxide materials and of sometimes apparently unrelated reactants.

A. Examples of Surface Acid-Base Reactions

The exposed cations and anions on oxide surfaces have long been described as acid-base site pairs.^{48,49} The oxygen anions can act as Brønsted or Lewis base sites; the metal cations are Lewis acid sites. Hydroxyl groups bound at certain oxide surfaces may exhibit considerable Brønsted acidity, but by and large we can neglect Brønsted acidity of oxide sur-

faces in surface science studies. There are a variety of reasons for this omission. First, in the UHV environment, it is fairly easy to create surfaces which are free of surface hydroxyls, but it is more difficult to create controlled hydroxyl populations. The vast majority of single crystal studies of oxide surface reactivity extant have therefore been performed on bare surfaces. Second, strong Brønsted acidity usually arises in mixed oxides rather than pure oxides, due to charge imbalances and/or coordination changes caused by incorporation of a second cation type.^{50,51} Since virtually all surface science studies to date have been conducted on single (cation) component oxides, such effects do not arise. Third, several emerging studies have addressed the influence of surface hydroxyls on materials such as TiO₂ upon the adsorption and reaction of Brønsted acids (mainly alcohols).⁵²⁻⁵⁴ Such species appear to have little effect; they are simply protonated and displaced from the surface by stronger acids.

Brønsted acids dissociate on a variety of oxide surfaces. The result of this process is the protonation of surface oxygen anions, and coordination of the conjugate base of the acid to surface cations. Such reactions are often depicted schematically⁵⁵ as



Dissociation reactions of Brønsted acids were among the first to be examined in detail on high surface area materials by infrared spectroscopy, and a substantial literature has grown up over the last four decades. Surface science studies of acid-base chemistry on single-crystal oxide surfaces are of more recent vintage. Henrich and Cox¹ have compiled a list of studies of organic molecules on single-crystal oxides through 1993 which includes examples on various crystal planes of MgO, ZnO, SnO₂, TiO₂, V₂O₅, NiO, MoO₃, and Cu₂O. Recent work has also been reported on ZrO₂.⁵⁶ This list represents approximately half of that of all single-crystal oxides on which adsorption studies have been carried out. Other oxides such as CaO, V₂O₃, Cr₂O₃, and FeO have been the target of studies of small molecule (H₂, O₂, H₂O, CO, SO₂, etc.) adsorption,¹ and are undoubtedly attractive subjects for future surface science studies of organic reactions on oxides.

The list of organics examined on oxide surfaces to date is already rich. Brønsted acids which have been shown to adsorb dissociatively on at least one of the oxides above include carboxylic acids (C₁-C₃ and aromatic), alcohols (C₁-C₃, aromatic and benzylic), alkynes (C₂, C₃, and aromatic), allene, acetaldehyde, acetone, and propylene. In most of these cases it has proven possible to obtain spectroscopic information by XPS, UPS, or HREELS about the stable conjugate base species produced by the initial dissociation reaction. Thus acid-base chemistry has provided an important set of standards for spectroscopic examination on oxide single crystals, just as it did for infrared spectroscopy on oxide powders in decades past.

What principles of surface reactivity can one derive from such studies? The principal one is an understanding of the surface site requirement for dissocia-

tion of Brønsted acids. The available oxide surface science literature, along with non-UHV studies of the influence of crystal habit of materials such as ZnO and MoO₃ on dissociation of reactants such as alcohols,^{57,58} suggests that the key requirement is one of coordination vacancies on the surface metal cations.⁸ Without available binding sites for the conjugate base ligands produced by Brønsted acid dissociation, this reaction is blocked. Surface base sites are also needed to abstract and to bind the protons originating from the adsorbate. One might also expect that coordinative unsaturation of the surface oxygens would also be required to accommodate protons, but experimental evidence, discussed below, suggests otherwise. Surface oxygen anions with the same coordination number as those in the bulk of the solid oxide appear to retain activity as base sites. Perhaps this lack of parallelism between the coordination requirements of surface cations and anions in generating surface reactivity should not be surprising. Oxygen can be found in a number of coordination environments in bulk oxides, even when its formal charge is invariant, and it is therefore perhaps less useful to attempt to apply the concept of coordinative saturation to it. One can also make steric arguments to account for the apparent coordination requirement difference between cations and anions. The oxide anions tend to have larger ionic radii than the metal cations,⁵⁹ thus neighboring cations in the lattice may obstruct access to oxide anions less than the anions obstruct the cations. On top of this, the two moieties produced by heterolytic dissociation of Brønsted acids are of vastly different sizes. The bare proton binds to the relatively unobstructed oxide anion; the bulky organic conjugate base anion must bind to the more hindered surface metal cation. Thus it is not surprising that the coordination environment of the surface cations is the critical surface characteristic.

The surface coordination vacancy requirement for surface cations in acid–base reactions is perhaps best illustrated by studies of Kung and co-workers^{60–64} and Vohs and Barteau^{65–70} on the polar planes of zinc oxide. The former group first demonstrated a significant difference in the reactivity of the two polar planes, the (0001)-Zn polar surface and the (000 $\bar{1}$)-O polar surface for dissociative adsorption and subsequent decomposition of methanol and formic acid. Subsequent studies by Jacobi,^{71,72} Campbell,⁷³ and by Vohs and Barteau^{65–70} of the adsorption of these molecules, higher alcohols and carboxylic acids, and other Brønsted acids suggested that this difference is an absolute one: the oxygen-polar surface exhibits no activity for Brønsted acid dissociation.

The relationship of these observations to the question of surface site requirements becomes apparent if one examines the structures of these two surfaces. The wurtzite structure of ZnO (Figure 5) is noncentrosymmetric (this material is piezoelectric) and termination of the lattice normal to the *c*-axis produces polar surfaces in which the zinc cations and oxygen anions do not occupy a common plane. Space-filling models of these polar surfaces are illustrated in Figure 6. The (0001) or zinc polar surface ideally exposes zinc cations at the outermost layer; each of these has a single coordination vacancy compared to

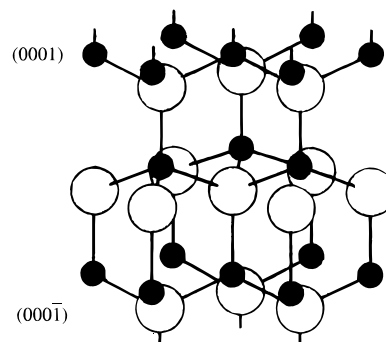


Figure 5. Bulk structure of ZnO (Wurtzite): (open circles) oxygen anions; (solid circles) zinc cations. (From ref 74.)

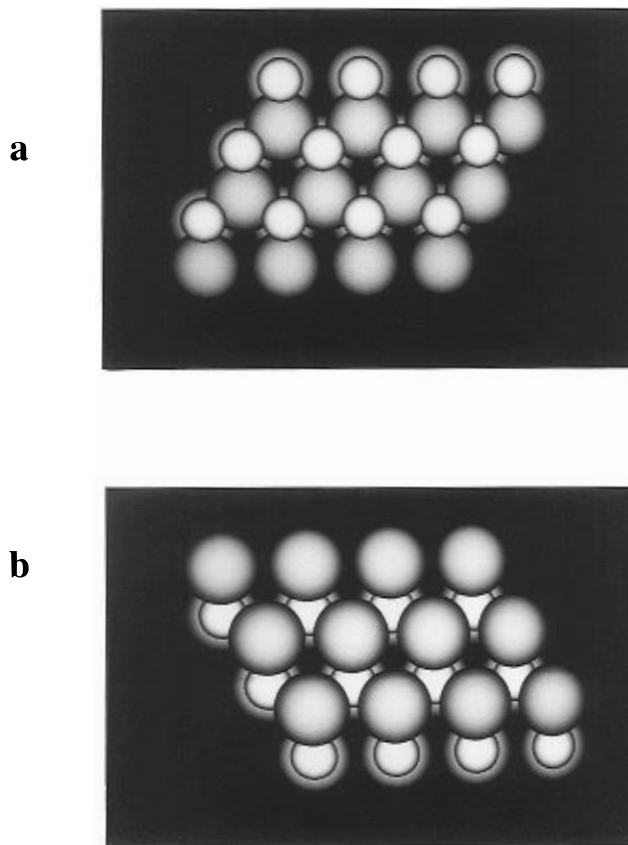


Figure 6. Space filling models of the (a) ZnO(0001)-Zn polar and (b) ZnO(000 $\bar{1}$)-O polar surfaces:⁶⁷ (smaller spheres) zinc cations; (larger spheres) oxygen anions.

the four-coordinate zinc cations in the bulk lattice. The oxygen anions are located in the plane immediately below; they are four-coordinate as are the bulk oxygens, but as noted above, they are not completely shielded by the cations in the outermost layer (see Figure 5). Various relaxations and reconstructions of this surface have been proposed;^{3,75–77} however, since these are not completely reproducible or unambiguous, since this material has yet to succumb to attempts at atomic resolution STM, and since these are unnecessary to account for the surface reactivity, we shall neglect them here. There is essentially universal agreement in the literature that the Zn polar surface, exposing three-coordinate zinc cations and four-coordinate oxygen anions, provides the acid–base sites necessary to dissociatively adsorb a wide variety of Brønsted acids.^{8,72}

The oxygen polar surface, in contrast, is essentially inert with respect to this chemistry. Once again the space-filling model of the surface makes it immediately apparent why. This surface is terminated by oxygen anions with a single coordination vacancy each; the Zn cations in the plane immediately below are both coordinatively saturated and are blocked by the bulky anions in the outermost layer. This surface does not do acid–base chemistry because it lacks the essential coordination sites at surface cations.

One of the beauties of ZnO for such studies is that it and related noncentrosymmetric materials can sustain polar surfaces which are not interconvertible. The zinc polar surface cannot be converted to an oxygen polar surface by removal of the outermost layer of zinc ions. Such an attempt would convert a surface with one dangling bond per surface cation into one with three dangling bonds per surface anion, a highly unstable situation. The same logic applies to the oxygen polar surface. This is in contrast to polar surfaces which might, hypothetically, be formed on centrosymmetric oxides. For example, cleavage of the rocksalt lattice of MgO along the (111) plane would ideally produce all-Mg and all-O surfaces on either side of the cleavage. However, in this case there is no coordination preference for individual ions on either side of the cleavage plane; the exposed ions will be three-coordinate (vs six in the bulk) whichever surface they find themselves attached to. As a result of this lack of coordination preference and of the requirements for surface charge balancing, the MgO-(111) cleavage plane will expose equal numbers of cations and anions; it will at best expose patches of both polar surfaces, and in fact will reconstruct to give more thermodynamically stable structures.¹ One cannot therefore utilize such materials as model systems to test surface cation coordination requirements.

There are a limited number of materials that one can use to test this site requirement hypothesis from a surface science perspective, although there are ample precedents in the catalysis literature. Layered materials such as MoO₃, MoS₂, and TiCl₃ which expose similar dense hexagonal anion arrays as the O polar surface on their basal planes typically exhibit catalytic activity only at edges and defects, not on their basal planes.⁷ Unfortunately these materials do not lend themselves to single-crystal surface science studies. One can indeed examine the basal planes, and to the extent to which this has been done in UHV, these materials have been shown to be unreactive.^{78,79} It is difficult, however to examine large edge planes of these materials as they tend to fragment when one attempts to cut across their natural cleavage (basal) planes. Supporting evidence has come from a surprising source, however. Cox et al.^{80–82} have shown that the SnO₂(110) surface, when highly reduced, is far less active than the stoichiometric surface for dissociation of Brønsted acids, including methanol, formic acid, and water. This result is in sharp contrast with those obtained on MoO₃,⁷⁸ MgO,⁸³ and TiO₂ surfaces (see below), where reduction by ion bombardment usually activates the surface. It is particularly surprising in that SnO₂ and TiO₂ have the same (rutile) bulk structures, and

might be expected to behave similarly as nonstoichiometric surfaces are created. In contrast to TiO₂, however, where reduction creates a broad distribution of cation oxidation states,^{3,36,37} reduction of SnO₂ produces Sn⁺².^{80–82} Although the coordination number of Sn²⁺ cations on heavily reduced SnO₂(110) surfaces is lower than that of the Sn⁴⁺ cations on stoichiometric surfaces, the *maximum* coordination number of Sn²⁺ is lower as well. Thus the dramatic activity decrease of the reduced surfaces may be explained in terms of the formation of four-coordinate (coordinatively saturated) Sn²⁺ cations on these surfaces. Cox et al.^{80–82} have also argued that the lower availability of surface oxide anions to serve as Brønsted base sites also contributes to the activity drop, and at this point the relative importance of the two characteristics of reduced surfaces—cation coordinative saturation and oxide anion availability—have yet to be unraveled.

Applications to Other Oxides. This simple picture of the coordination requirement of surface cations in surface acid-base site pairs can be applied to a host of other oxides. The low-index planes of the vast majority of oxides do, in fact, expose surface cations with at least one coordination vacancy, along with surface anions. Thus one may expect such surfaces to be active for the dissociative adsorption of Brønsted acids, and indeed this is the case. Clear-cut examples of Brønsted acid dissociation on single-crystal oxide surfaces with a single coordination vacancy per surface cation include ZnO(0001)^{60–72,84} and (1010),^{85,86} MgO(100),^{83,87–91} TiO₂(001)-{011} faceted,^{33,92–95} and ZrO₂(100) and (110)^{56,96} surfaces. Likewise surfaces where some fraction of the surface cations are coordinatively unsaturated also exhibit activity for carboxylic acid dissociation. Examples include SnO₂-(110),^{80–82} TiO₂(100),^{97–99} and (110).^{52,53,100–102}

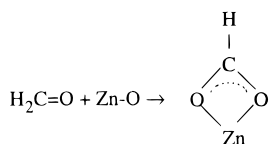
In most of the above cases, careful coverage calibrations have not been performed, and therefore one cannot say with certainty that the saturation coverage of dissociatively adsorbed Brønsted acid is of the order of one ligand per surface cation or initial cation coordination vacancy. Examples where the coverage calibrations have been performed and are consistent with this value include MgO(100).⁸⁷ Similar correlations of Brønsted acid dissociation capacity with the surface population of coordinatively unsaturated surface cations have been generated for polycrystalline samples of MoO₃¹⁰³ and TiO₂.⁵⁴

Some caution must be exercised in making the assumption that one and only one conjugate base ligand will be bound per surface cation coordination vacancy on oxide surfaces. First, this assumes that all such reactions are restricted to the surface. If the oxide is soluble in the acid, however, this will not necessarily be the case outside the vacuum environment. A simple example is provided by MgO. In UHV the uptake of carboxylic acid approaches one monolayer dissociatively adsorbed,⁸⁷ at higher pressures one can dissociate much larger amounts of acid.⁸ The reason is that the oxide is not impervious, and one can form bulk magnesium carboxylates by reaction of MgO with carboxylic acid vapors. The reaction is still of the acid–base type, but it no longer occurs only at the surface.

In some surface science studies, the deviation of the uptake of dissociatively adsorbed Brønsted acids may be in the opposite direction from the ideal value above, i.e., one may observe saturation uptakes that appear to be well below the number of acid–base sites that one would assume to be exposed on the basis of surface structure. Perhaps the clearest examples also come from oxides with the rocksalt structure, e.g., MgO and NiO. On the (100) surfaces of such materials, the maximum uptakes of dissociatively adsorbed alcohols, water, alkynes, etc. are well below one per surface cation.^{87,89} Similar effects are observed on polycrystalline materials at higher pressures;^{104–106} they are usually interpreted in terms of the acid and base strength of the adsorbate and the surface. From the examples above it is apparent that weaker acids may not be able to populate the surface sites with the lowest extent of coordinative unsaturation, and these sites are therefore presumed to be the weakest acid–base sites on polycrystalline surfaces. Sites which exhibit a greater degree of coordinative unsaturation may be able to dissociate weaker acids, and correlations of adsorbate acidity with the degree of coordinative unsaturation required for dissociation have been produced for polycrystalline MgO and other materials.^{104–106} In UHV experiments, one must also consider that the limitations to complete population of surface acid–base sites may be kinetic rather than thermodynamic. If the rate of dissociation of adsorbing acid molecules on sites with the lowest degree of coordinative unsaturation is low, and if diffusion from other more reactive sites is also slow, then not all sites capable of binding conjugate base ligands may be populated by the limited gas exposures usually employed in such experiments. Definitive evidence for such kinetic barriers to surface saturation in acid–base reactions on oxides is still lacking, although such effects have been invoked to explain limitations to water dissociation on single crystal surfaces of MgO^{83,87} and may help to explain some of the conflicting observations noted¹ on TiO₂(110) as well.

B. Oxidation and Reduction Reactions

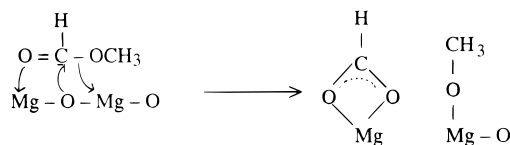
Oxygen anions on metal oxide surfaces can act as Lewis as well as Brønsted bases. As such, they may oxidize adsorbed organics. The most common examples of such reactions in the metal oxide surface science literature are nucleophilic oxidations of carbonyl compounds. Aldehydes are oxidized to the corresponding carboxylates on a number of oxide surfaces. Examples include the oxidation of formaldehyde to adsorbed formate intermediates on ZnO(0001):^{65,107}



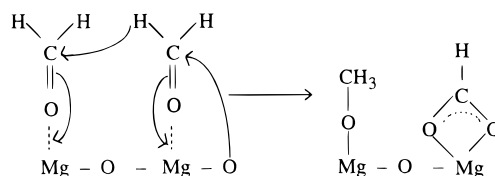
Higher alcohols and aldehydes also form carboxylate intermediates on ZnO^{67,107–110} and Cu₂O.^{111,112} Other related species such as esters exhibit similar chemistry; oxidation of methyl formate on the ZnO(0001)

surface,¹⁰⁷ for example, yields formates, although the methoxide ligands that would be expected to result from nucleophilic attack of oxygen at the carbonyl carbon were not isolated, presumably because they, too, were oxidized further.

Although this chemistry has straightforward analogies to the chemistry of bases in aqueous solution, as well as to the chemistry of oxygen atoms adsorbed on late transition metal surfaces, there are several “twists” to surface oxide chemistry that are worth noting. First, such reactions may occur even on nonreducible oxides. For example, adsorption of formaldehyde (H₂CO) or methyl formate (HCOOCH₃) on the MgO(100) surface produces in each case roughly equal surface coverages of formate (HCOO) and methoxy(CH₃O) intermediates,¹¹³ both of which were identified on the basis of their characteristic C(1s) binding energies in XPS. The C:O ratio of an adsorbate layer consisting of equal amounts of formates and methoxies is 1:1.5, whereas the C:O ratio for either of the reactants, formaldehyde or methyl formate, is 1:1. This implies that surface lattice oxygen atoms are incorporated into the organic intermediates. In the case of formate plus methoxy formation from methyl formate, the reaction would involve nucleophilic attack of lattice oxygen at the carbonyl carbon of the ester; elimination of the methoxy ligand would produce the pair of surface intermediates observed:



Isotopic labeling studies to examine the incorporation of surface lattice oxygen into adsorbed intermediates and volatile products would provide an important test of this proposed mechanism, however, these have not been performed. In the case of formaldehyde the surface chemistry has been explained in terms of the Cannizzaro reaction: nucleophilic attack of surface oxygen at the carbonyl carbon accompanied by hydride transfer to a second adsorbed formaldehyde molecule to produce the methoxy:¹¹³



In both cases, however, the surface apparently only “lends” its oxygen to the adsorbate; thermal decomposition of the adsorbed layer in both cases yields CO as the only carbon-containing product, thus the C:O ratio of the reactants is preserved in the desorbing products, as is the surface stoichiometry.

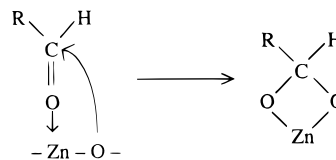
The second “twist” concerns the nucleophilicity of adsorbed hydroxyls vs lattice oxygen anions on metal oxide surfaces. In considering surface acid–base reactions above, we dismissed surface hydroxyls as inconsequential, largely because they are protonated and displaced by adsorbing Brønsted acids. The net

result is population of the surface with adsorbed conjugate base ligands and oxide-bound protons, just as for Brønsted acid adsorption on a bare oxide surface. Such displacements are, of course, equilibrium processes, but in the absence of one of the acids (H_2O) in UHV, they are generally fast and complete at modest exposures of the organic acid. Indeed, on some oxides, titration of surface hydroxyls may be more facile than dissociations of Brønsted acids on the bare surface.¹¹⁴ One cannot dismiss surface hydroxyls quite as blithely in surface oxidation processes. Available evidence from the literature of both surface science and catalysis of metal oxides suggests that hydroxyl groups on oxide surfaces are much weaker nucleophiles than are lattice oxide anions. This assertion is not surprising if one considers it from the perspective of the expected higher coordination and lower electron density of oxygen centers in hydroxyl species compared to oxide anions. Indeed the charge issue has been addressed directly by surface science studies; surface hydroxyl groups typically exhibit O(1s) binding energies ~ 2 eV higher than those of lattice oxide anions (typical values on MgO, for example are 533 for OH vs 531 eV for the oxide),^{83,115,116} consistent with a lower valence electron density on the hydroxyls. The effect on the surface chemistry is, however, surprising viewed from the perspective of the minimal consequences of surface OH population on Brønsted acid–base chemistry.

The evidence for lower nucleophilicity of adsorbed OH comes once again from XPS studies of formaldehyde adsorption on MgO. As noted above, adsorption of formaldehyde on a bare MgO surface produces equal amounts of formate and methoxy intermediates via the Cannizzaro reaction.^{89,113} Adsorption of water or methanol to saturation coverages at room temperature is sufficient to block the Cannizzaro reaction upon subsequent exposure of the surface to formaldehyde, although formaldehyde adsorption is not blocked.⁸⁹ In effect, protonation of the lattice oxide anions renders them less nucleophilic, and adsorbed formaldehyde on such a surface desorbs intact at higher temperature. This phenomenon may also have important consequences for commercial catalytic processes employing oxide catalysts, in particular the selective oxidation of methanol to formaldehyde with molybdate-based catalysts. Sleight and co-workers have shown that the undesired reaction in this process—readsorption and further oxidation of formaldehyde—is inhibited by both the reactant methanol and the byproduct of methanol oxidative dehydrogenation, water.¹¹⁷ Since both the reactant and the byproduct inhibit overoxidation of the desired product, formaldehyde, the process can be operated at high selectivity even at high conversion. The reason is that at high conversion the product water takes over the role of methanol in inhibiting formaldehyde oxidation; it presumably does so by adsorbing preferentially on the surface to form hydroxyl species, inhibiting the nucleophilic attack on the formaldehyde. Thus this represents an example in which one can identify in the functioning of relevant catalytic processes the operation of principles deduced from surface science studies on oxides. One

of the challenges to the field is to make such connections to not yet known processes, i.e., to invent new catalysis starting from surface science-derived principles.

The final “twist” in nucleophilic oxidations studied on single-crystal oxide surfaces is the unusual selectivity observed for ligand displacement for aldehyde oxidation on the ZnO(0001) surface. Nucleophilic attack of surface oxide anions at the carbonyl carbon of aldehydes would produce a dioxyalkylidene complex (RCHO):



Spectroscopic evidence for such species has been offered from studies of both oxide single crystals and high surface area oxide catalysts.^{108,109,118–120} The usual reaction path in such nucleophilic substitutions, whether in solution or on surfaces, is the elimination of the hydrogen originally bound at the carbonyl carbon, yielding a carboxylate of the same carbon number as the aldehyde reactant. On ZnO(0001), however, it was shown that the alkyl group was eliminated preferentially following adsorption at low temperatures, yielding instead adsorbed formates and surface-bound alkyl groups. These alkyl groups decompose unselectively to deposit carbon and oxygen atoms on the surface (both of which may be oxidized by subsequent extraction of additional oxygen from the lattice), but they can still be identified as stable intermediates below their decomposition temperatures by quite characteristic fingerprints in X-ray and ultraviolet photoelectron spectra.^{109,121} The extent to which this chemistry may occur on other oxides is uncertain, although it has been suggested as a possible product loss route on molybdate-based allylic oxidation catalysts.¹⁰⁸ However, it serves as a useful reminder of the potential limitations to analogies drawn between surface and fluid-phase phenomena.

Just as oxide surfaces may donate oxygen to adsorbed organics, they may also abstract it. The number of examples from the surface science literature of net reduction of organics (necessarily accompanied by oxidation of the solid surface) is rather small compared to the number of oxidations, at least on oxide surfaces. The reason is, as noted before, that it is difficult to prepare single-crystal surfaces of oxides below their maximum oxidation state with well-defined structure and stoichiometry. Typical approaches involve production of less oxidized surfaces by ion bombardment, electron bombardment, or thermal treatment of stoichiometric samples in the highest oxidation state. The success of these methods depends on the oxide; ion bombardment tends to produce the greatest extent of reduction, owing to preferential sputtering of oxygen relative to the invariably more massive metal component. However, ion bombardment also causes the greatest disruption in the structure of the surface and near-surface region of the solid. In any case, studies of partially reduced surfaces of materials such as TiO_2 have

demonstrated that such surfaces exhibit considerable capacity for oxygen abstraction from adsorbates, leading to at least partial restoration of the surface cations to higher oxidation states. From the perspective of the organic adsorbate, the result may be either unselective fragmentation, depositing additional carbon- and hydrogen-containing fragments on the surface, or in some cases, rather surprising selective reductions. In the latter category, the selective (>70%) reductive coupling of aldehydes and ketones on reduced TiO₂(001) surfaces, forming olefins with twice the carbon number of the reactant,¹²² is perhaps the most surprising (and unprecedented as a surface reaction). This chemistry is discussed in greater detail below.

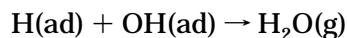
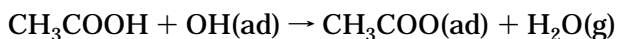
C. Reactions of Adsorbates and Relationship to Surface Characteristics

The adsorption, whether dissociative or otherwise, of molecules on the surface is usually but the first in a sequence of reactions that may be of interest. Indeed, for a catalytic process, subsequent steps which regenerate the active surface sites must occur. The menu of feasible reactions for an adsorbate, e.g., the conjugate base of a Brønsted acid, will depend not only upon its own structure, but also upon the availability of potential reaction partners. These may be fluid-phase species impinging on the surface layer, other adsorbates at the surface, or constituents of the solid surface itself. Examples of the latter two reaction types include bimolecular reactions with other organic adsorbates and oxidation of the adsorbate by surface lattice oxygen atoms. We shall neglect the fluid phase as unimportant in UHV and consider only examples of bimolecular processes which involve adsorbed or lattice species. Clearly in the absence of suitable targets for bimolecular reaction, e.g., in the absence of other adsorbates in the vicinity or in the absence of labile oxygen atoms, other, most typically unimolecular, reaction pathways will likely be preferred. We consider here the competition between unimolecular and bimolecular reaction pathways of conjugate base ligands adsorbed on oxide surfaces and, in particular, the role of surface cation coordination environment in determining the selectivity between these.

In the case of adsorbed carboxylates, a variety of reaction types have been observed. If one restricts attention to the most studied member of this family, formate, the principal reaction channels observed on oxide surfaces are dehydrogenation to CO₂ plus H₂, and dehydration to CO plus H₂O.¹²³ The parent acid is usually regenerated to some extent by recombination of adsorbed carboxylates with hydrogen atoms liberated by these decomposition reactions. Additional reaction pathways reported include net reduction to yield formaldehyde^{81,93,99,124} and, in a few isolated examples, acetylene^{56,124} (by reaction paths as yet unknown). For higher carboxylates, the product slate is even richer. Net dehydration yields ketenes with carbon number equal to that of the reactant, decarboxylation produces CO₂ plus unselective decomposition products of the original alkyl group, and ketonization leads to ketones containing $2n - 1$ carbon atoms, where n is the carbon number

of the reactant.⁸ The selectivity to these various reaction channels depends on the nature of the surface, and nicely illustrates the influence of the three principal characteristics noted above: coordination environment of surface cations, oxidation state of surface cations, and redox properties of the solid.

The surface chemistry of carboxylates on single-crystal surfaces of TiO₂ illustrates these concepts and provides a basis for comparison with other oxides. Surfaces which expose surface cations with a single coordination vacancy, including the (110)-, (100)-, and {011}-faceted (001) surfaces, are quite selective for carboxylic acid dehydration in adsorption and temperature-programmed desorption experiments in UHV.^{93,99,100,124} Formate decomposition selectivities of 60–74% to CO (not including the formic acid regenerated) on these three surfaces have been reported.^{93,100} The activation barriers to formate decomposition are also insensitive to surface structure; typical peak temperatures in TPD experiments on all three surfaces are ca. 560 ± 10 K.^{93,99,100,124} Higher carboxylates have been less frequently examined, but they provide important clues to help unravel the surface-state dependence of the chemistry of their C₁ homologues. On the {011}-faceted (001) surface, adsorbed acetate intermediates react with high (>70%) selectivity to produce ketene.^{8,33,95} The overall reaction with respect to the original reactant, acetic acid, is net dehydration: one molecule of acetic acid forms one molecule of ketene (H₂CCO) and one molecule of water. The sequence of reactions has been shown³³ to involve protonation of surface oxide anions (designated as O(/) in the reaction sequences below) by dissociative adsorption, with restoration of oxygen to the surface by reaction of surface acetates (CH₃COO) to form ketene (H₂C=C=O):



The principal side reaction is the unselective decarboxylation of the acetate, liberating CO₂ which desorbs from the surface and depositing hydrocarbon fragments which decompose further.

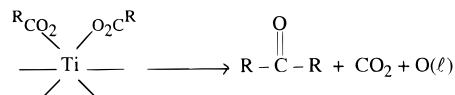
Both the dehydration and decarboxylation of adsorbed carboxylates represent unimolecular reaction channels; they involve bond-scission processes of individual carboxylate intermediates on the surface. These unimolecular channels are, in fact, the principal reactions observed for carboxylates on the large majority of single-crystal oxide surfaces examined to date. They are characteristic of the chemistry of oxide surfaces with singly coordinatively unsaturated surface cations, as will be discussed below. Selectivity comparisons between different oxides do help to resolve the origin of the preference for dehydration vs. dehydrogenation on different oxides, at least under UHV conditions. For acetic acid decomposition on the ZnO(0001),⁶⁷ TiO₂(001)-{011} faceted,³³ and

MgO(100)⁸⁸ surfaces, all of which expose only singly coordinatively unsaturated surface cations, the selectivity for dehydration increases across this series, reaching essentially 100% on MgO(100). A similar trend is found in the CO/CO₂ ratio produced by formate decomposition on these oxide single-crystal surfaces which expose cations with equivalent degrees of coordinative unsaturation.^{33,65,88} This trend suggests that the availability of oxygen from the lattice influences the selectivity for unimolecular decomposition: the less reducible the oxide, the higher the dehydration selectivity. As pointed out previously,⁸ this correlation can be explained in terms of the oxygen consumption of each of these reaction channels. If water is produced by the titration of surface oxygen anions, oxygen must be removed from the carboxylate ligand to restore the stoichiometry of the surface. Acetate decomposition to ketene leaves oxygen behind; decarboxylation to CO₂ does not. Thus the decarboxylation reaction, if accompanied by water formation, is a net consumer of surface oxygen, and is favored on more easily reduced surfaces. That decarboxylation of carboxylic acids does indeed reduce the surface can be easily demonstrated on ZnO. In that case, zinc metal results from reactions which remove oxygen from the surface, and desorption of zinc atoms accompanies the release of CO₂ from all carboxylates examined on this oxide.^{65,67}

Other products of carboxylate decomposition result if one changes either the oxidation state or coordination environment of surface cations. Carboxylate chemistry on reduced oxide surfaces involves reduction of the organic and oxidation of the surface, as expected.^{56,81,95,124} On reduced TiO₂ surfaces, for example, formates are reduced to formaldehyde,¹²⁴ acetates to acetaldehyde,⁹⁵ and acrylates to acrolein.⁹⁵ On the heterogeneous surfaces produced by ion bombardment, these reactions are not very selective; they compete with complete decomposition which presumably occurs at the most reactive (reduced, coordinatively unsaturated) sites on the surface.^{33,95} It would be most interesting to examine this chemistry on well-ordered suboxide surfaces to determine whether it and related reductions can be carried out more selectively, but this has not been done to date.

The effect of decreasing the coordination of fully oxidized surface cations leads to chemistry with century-old precedents in preparative organic chemistry,¹²⁵ but no precedent in surface science prior to 1990. The new reaction that occurs on multiply coordinatively unsaturated surface cations is ketonization. The formation of ketones with $2n - 1$ carbon atoms from carboxylates with n carbons clearly requires the coupling of a pair of carboxylates, and we therefore refer to it as a bimolecular reaction. On single-crystal oxide surfaces in UHV, carboxylate ketonization has only been reported to date on the TiO₂(001)-{114} faceted surface.^{8,33,95} As noted above, this structure places a portion (ideally one-third) of the surface Ti⁴⁺ cations in a four-coordinate environment, i.e., these cations each have two coordination vacancies on the bare surface. The unique activity of this surface for ketonization of higher carboxylates has therefore been ascribed to these sites. Apparently in order to couple a pair of carboxylate ligands

(liberating CO₂ in the process) the carboxylates must be bound to the same surface cation:



In the absence of such sites, one of the unimolecular decomposition channels is followed.

Additional examples of higher carboxylate ketonization on single-crystal oxide surfaces are lacking, beyond those noted on TiO₂(001)-{114} faceted surfaces. However, several other observations support the assignment of this reaction on oxide surfaces to multiply coordinatively unsaturated sites that can accommodate the pair of carboxylate ligands to be coupled. First, the analogous reaction of formates has been observed, not only on this surface but on the TiO₂(100)-(1×3) surface which exposes Ti³⁺ cations that are also multiply coordinatively unsaturated.⁹⁹ The association of formaldehyde with bimolecular carboxylate coupling is not as clear-cut, since this product can also result from reduction of surface formates. Indeed, we have shown that formaldehyde can be produced on both reduced TiO₂ surfaces and stoichiometric (001) surfaces with {114} facets, but not on the {011} faceted structure of this plane.^{93,124} Thus to produce formaldehyde from formates one needs either a reduced surface or multiply coordinatively unsaturated surface cations. In the case of higher carboxylates the products of these two surfaces are distinguishable: aldehydes of carbon number n on reduced surfaces and ketones of carbon number $2n - 1$ on oxidized surfaces with multiply coordinatively unsaturated surface cations.

This surface site requirement is directly related to the classical production route for symmetric ketones. Pyrolysis of bulk carboxylate salts of divalent and higher valent cations produces ketones with carbon number $2n - 1$.^{125,126} Such salts provide coordination of multiple carboxylates to each cation, while those of monovalent cations do not. The same coordination requirement thus appears to be operative on metal oxide surfaces.

The chemistry of alkoxide ligands on oxide surfaces is analogous to that of carboxylates. The principal unimolecular reactions of higher alkoxides are dehydrogenation (to the corresponding aldehyde or ketone for primary and secondary alcohols, respectively) and dehydration (to the corresponding olefin).^{53,64,69,71,94,127,128} The limited single-crystal studies to date suggest that the selectivity between these two is also influenced by the reducibility of the oxide; more easily reduced oxides like ZnO⁶⁹ produce more aldehyde than does TiO₂.⁹⁴ In the light of the discussion of carboxylate chemistry on oxide surfaces above, this trend is not surprising; however, it does suggest that considerable caution is in order in using alcohol dehydration/dehydrogenation selectivities as a measure of surface acid-base properties, as is often done in the catalysis literature.

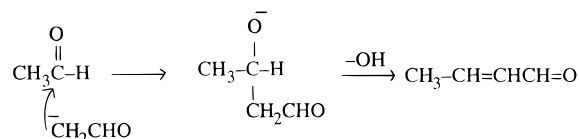
Just as carboxylates may couple on surfaces which provide the opportunity to coordinate two ligands on individual surface cations, alcohols can also be coupled to ethers on such surfaces. The TiO₂(001)-{114}-

faceted surface couples adsorbed methoxy intermediates to form dimethyl ether.⁹² TiO₂ surfaces without such sites, including the {011}-faceted (001) and (110) surfaces, produce no ethers.^{92,129} Likewise no ether formation has been observed on ZnO(0001), MgO(100), or SnO₂(110) surfaces, all of which are characterized by singly coordinatively unsaturated surface cations.

The chemistry of alcohols and carboxylic acids on oxide surfaces illustrates the roles that may be played by two of the three key surface properties noted above: the coordinative unsaturation of surface cations and the redox properties of the oxide. Interestingly, the chemistry of the class of oxygenates in between these two with respect to their degree of oxidation—aldehydes and ketones—exhibits an important dependence on the third key surface property—the oxidation state of the surface. The chemistry of these compounds has been most extensively studied on stoichiometric and reduced surfaces of TiO₂. Some of the reactions observed on that material likely also can occur on certain other oxides, but others may be more limited in their generalizability to other materials. The chemistry of organic molecules on well-defined oxide surfaces below their maximum oxidation state is, as yet, relatively untouched. However if the chemistry of carbonyl compounds on titanium oxides is any indication, this will be a fertile field indeed.

Let us begin with the chemistry of aldehydes on stoichiometric TiO₂ surfaces. On the basis of the discussion above, one might expect that the principal reaction pathway would involve oxidation to form surface carboxylates, as in the examples discussed on ZnO surfaces. In the presence of gas-phase oxygen, aldehyde oxidation to carboxylates will occur on titania, as demonstrated by infrared spectroscopy studies on TiO₂ powders.¹³⁰ However in the UHV environment, the relatively strong Ti—O bond (154 kcal/mol for TiO₂¹³¹) makes this oxide a rather poor oxygen donor. Photoexcitation of the surface may lead to oxidation of adsorbates by adsorbed oxygen,¹³² but the extent of thermally driven oxidation of organics by titania in single-crystal studies is minimal. To formaldehyde, for example, the stoichiometric faceted (001) surfaces appear to be nonreducible, and the principal reaction observed is the Cannizzaro reaction to produce adsorbed methoxides and formates,¹³³ as on completely nonreducible oxides like MgO.¹¹³ Higher aldehydes, however, have alternative acid–base reaction pathways accessible and may follow these with high selectivity. Acetaldehyde is relatively acidic, exhibiting a gas-phase acidity between those of CHF₂CH₂OH and CF₃CH₂OH,¹³⁴ and can dissociate on surface acid–base sites. The adsorbed conjugate base that would result from this reaction, an enolate intermediate CH₂CHO, has not yet been isolated in spectroscopic studies on oxide single crystals. There is some spectroscopic evidence for stable enolate formation from acetone on ZnO and Cu₂O surfaces,^{70,112} and the chemistry of acetaldehyde on TiO₂ overwhelmingly implicates the formation of enolates on that oxide as well.¹³⁵ The reason is that stoichiometric TiO₂ surfaces, even without multiply coordinatively unsaturated surface cations, can couple

acetaldehyde to form products of higher carbon number. In the case of acetaldehyde on the {011} and {114} faceted (001) surfaces of TiO₂, those coupling products are crotonaldehyde, CH₃CH=CHCHO, and crotyl alcohol, CH₃CH=CHCH₂OH. These are the products of the aldol condensation reaction, the base-catalyzed version of which is well known both in solution and on basic surfaces.¹³⁶ Aldol condensation involves the nucleophilic attack of the enolate formed by the initial proton abstraction step at the carbonyl carbon of a second aldehyde molecule:



Dehydration of the primary aldol product leads to an α, β unsaturated aldehyde product and is usually quite favorable. In the case of acetaldehyde, crotonaldehyde is the α, β -unsaturated product of aldol condensation plus dehydration, and crotyl alcohol production presumably involves further hydrogenation of this product by hydrogen atoms on the surface.

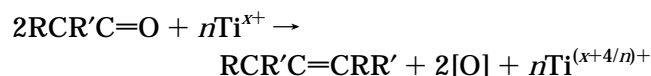
Several aspects of this reaction on TiO₂ surfaces are rather striking. First, in spite of the fact that one is producing products of higher molecular weight in UHV, the conversion of the adsorbed layer and the selectivity of its transformation to coupling products are quite high, 61 and 96%, respectively on the TiO₂(001)-{114} faceted surface.¹³⁵ This is less mysterious than it appears at first glance, however, as the net reaction



conserves the number of molecules between reactants and products and is thus not strongly disfavored on entropic grounds at low pressures, unlike simple assembly processes. Perhaps more surprising in the context of the bimolecular reactions of carboxylates and alkoxides discussed above is the fact that, unlike those examples, aldol condensation of aldehydes to form higher carbon number products does NOT require surfaces with multiply coordinatively unsaturated surface cations. Although somewhat less selective than the {114} faceted surface, the {011} faceted TiO₂(001) surface yields significant quantities of aldol condensation products from acetaldehyde.^{135,137} The explanation advanced in the original report is that aldol condensation involves the reaction of an adsorbed conjugate base anion with an adsorbed molecule, whereas carboxylate ketonization and alkoxide etherification involve the coupling of a pair of conjugate bases. Thus the former may be thought of as an ion–molecule reaction, the latter two as ion–ion reactions. From this limited set of examples, it therefore appears that surface ion–molecule condensation reactions do not exhibit a requirement for multiply coordinatively unsaturated surface cation sites. In effect, the aldol condensation is an “outer-sphere” process; carboxylate ketonization may be thought of as an “inner-sphere” reaction as those terms are used in inorganic chemistry.

From the perspective of those attempting to bridge the gap between single-crystal surface science and practical catalysis, one of the striking aspects of the aldol condensation reaction is the close parallel between the energetics and selectivity of this reaction in a UHV environment and those observed on high surface area titania catalysts. For example TPD experiments with acetaldehyde on faceted $\text{TiO}_2(001)$ single-crystal surfaces produced the high yields of aldol condensation products noted above, with the principal desorption channel for these products occurring at 400–450 K. Similar experiments on high surface area TiO_2 powders generated a 75% yield of aldol products over the same temperature range.¹³⁵ These results are in excellent agreement with the high activity of titania for aldol condensation reported in the patent literature.¹³⁸ For example, 80% conversion of C_3 and C_4 aldehydes to α,β -unsaturated C_6 and C_8 aldehydes with 90% selectivity has been reported on titania catalysts at 400–500 K.¹³⁸ The close correspondence between the energetics and selectivity in TPD experiments on single crystals in UHV and steady-state experiments on titania catalysts at much higher pressures suggests that this reaction is not very sensitive to surface characteristics, as deduced from the surface science experiments and that the results obtained in such studies are directly applicable to the catalytic reaction. Other such examples on oxides will undoubtedly emerge as the range of organic reactants examined on well-defined oxide surfaces continues to grow.

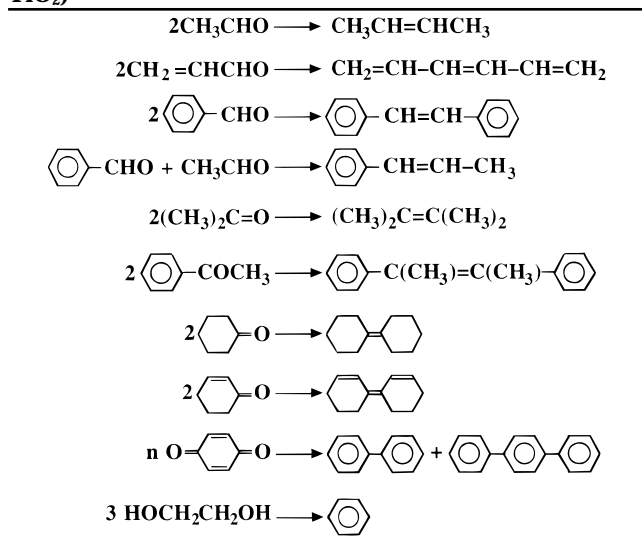
As facile as the aldol condensation reaction is on stoichiometric TiO_2 surfaces, it is overtaken dramatically by other coupling chemistry on surfaces containing Ti cations in lower oxidation states. On reduced surfaces, the preferred reaction channel for carbonyl compounds switches over with high selectivity to reductive coupling to form symmetric olefins with twice the carbon number of the reactants.¹³⁷ This reaction is a net four-electron reduction of the organics involved and thus must oxidize the surface by depositing on it the oxygen atoms eliminated from the carbonyl groups. It is not surprising therefore that this chemistry, which may be written as



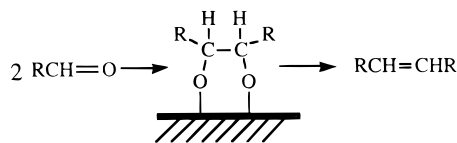
requires reduced surface sites capable of undergoing the required four-electron oxidation.¹³⁹ It is also obvious that this represents a necessary but not sufficient condition. The reaction is clearly driven by the strength of the metal oxygen bonds formed (~ 154 kcal/mol in the case of oxidation of TiO to TiO_2 ¹³¹), to overcome the high cost of $\text{C}=\text{O}$ scission (~ 175 kcal/mol¹⁴⁰).

Reductive carbonyl coupling on reduced TiO_2 single-crystal surfaces, first reported by Idriss et al., in 1991,¹⁴¹ has now been the subject of study by different laboratories,^{122,137,141–146} and has even begun to be employed as a characterization tool to probe the oxidation state and nuclearity of discrete clusters of early transition metals on oxide supports.¹⁴⁷ Examples reported to date as gas–solid reactions on reduced titania surfaces are shown in Table 1. This

Table 1. Examples of Reductive Coupling Demonstrated (Gas–Solid Reactions on Reduced TiO_2)^{122,137,141–143,145}



chemistry is essentially the well-known “McMurry reaction”, commonly carried out in liquid–solid slurries of low-valent titanium in the presence of a strong reducing agent.¹³⁹ Prior to the work of Idriss, it had not previously been demonstrated to occur as a gas–solid reaction, in UHV or otherwise. The parallels between the liquid–solid and gas–solid versions of carbonyl coupling are quite striking, however, and lead one to the conclusion that these are indeed the same reaction. In both cases the reaction occurs with high selectivity and yield at modest temperatures (~ 100 °C or less^{122,139,148}) and is applicable to a wide variety of carbonyl compounds (although aromatic aldehydes and ketones produce the highest yields in both cases^{122,139}). The mechanism of this reaction in the classic slurry case is thought to involve an initial two-electron reductive coupling of a pair of carbonyls to produce a pinacolate (a.k.a. diolate) intermediate bound to the surface of the solid reduced-titanium-containing reagent.¹³⁹ Subsequent scission of both $\text{C}-\text{O}$ bonds (and concomitant formation of the $\text{C}=\text{C}$ bond) yields the olefin product and leaves the oxygen behind, bound to surface titanium centers:



Pinacol intermediates and products can be observed spectroscopically at low temperature in these slurries (e.g., by in situ infrared spectroscopy¹⁴⁸), and the product pinacols can also be isolated by quenching the reaction of the slurry at low temperature. A recent study by Pierce of the reductive coupling of acetophenone on reduced TiO_2 single-crystal surfaces has, for the first time, produced a pinacol product by this route in UHV,¹⁴⁵ confirming the participation of pinacols in gas–solid reductive carbonyl coupling as well.

The key feature of the single-crystal studies, however, is that they permit the examination of the impact of surface oxidation state on this chemistry

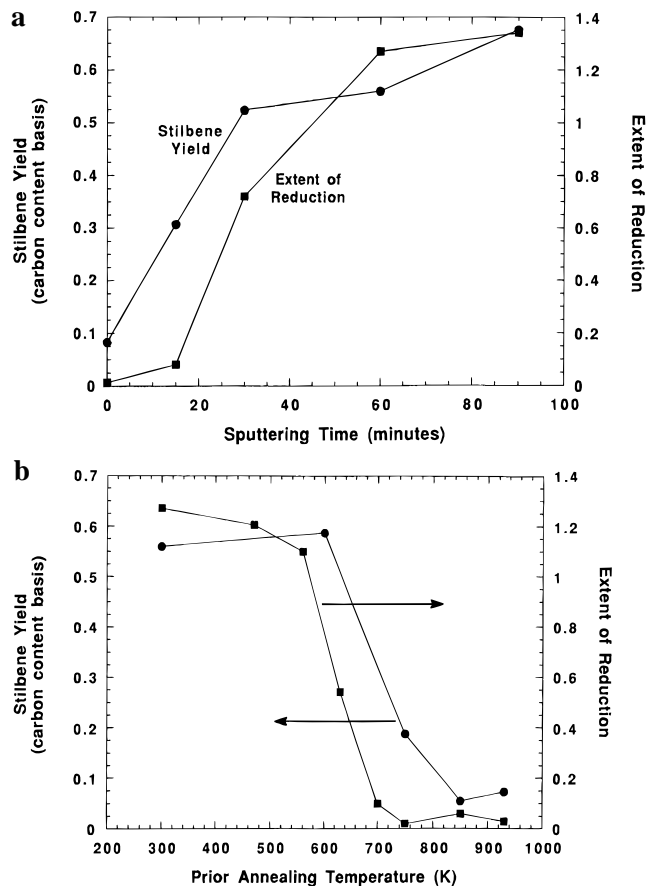


Figure 7. Stilbene yield from reductive coupling of benzaldehyde on reduced TiO_2 surfaces. (From ref 122.) The extent of reduction is given by

$$\sum_{n=0}^4 X_{\text{Ti}^{n+}}(4-n)$$

where $X_{\text{Ti}^{n+}}$ is the fraction of Ti species in the $+n$ oxidation state (determined by XPS).

in a way that slurry phase studies cannot. In UHV, the oxidation states of Ti cations in the surface and near surface regions of the solid are accessible for determination of their oxidation states by XPS. The results of Idriss et al., illustrated in Figure 7, demonstrate that on surfaces reduced to different extents by ion bombardment and annealing of a TiO_2 sample, the activity for reductive coupling of carbonyl compounds clearly tracks the extent of reduction of the surface below the Ti^{4+} state.¹²² Since no Ti^0 was detected,³⁶ these results clearly implicate Ti cations in the $+1$, $+2$, and $+3$ oxidation states. Since none of these is capable of carrying out this four-electron reduction individually, the participation of an ensemble of low valent cations collectively able to undergo a four-electron oxidation is required.^{122,137} Presumably such ensembles consist of neighboring cations in oxidation states below $+4$. Beyond the requirement of such surface ensembles, however, there is no clear connection to any particular oxidation state; the reaction can still occur, albeit with lower yields, on surfaces containing only Ti^{3+} and Ti^{4+} cations.¹²² Likewise, the high yields of coupling products observed on the most reduced surfaces (>0.5 monolayers¹²²) argue against the requirement of any specific surface structural defect. The yield of the reductive coupling reaction essentially follows the

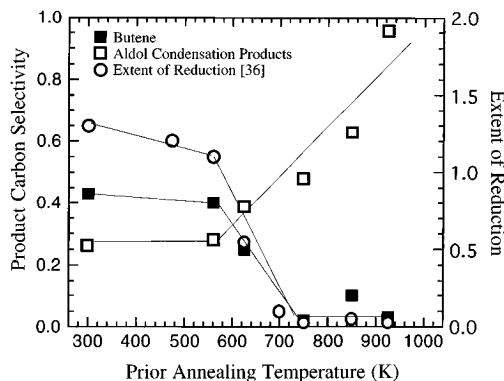


Figure 8. Dependence of the selectivity of C–C bond-forming reactions of acetaldehyde on the extent of surface reduction of the $\text{TiO}_2(001)$ surface.¹⁴⁹

capacity of the surface to take up oxygen, rather than requiring any specific oxidation state or defect site.

A recent report from Yates et al.¹⁴⁶ has added to the understanding of the chemistry of carbonyl compounds on reduced titania surfaces. These workers carried out thermal reductions of the $\text{TiO}_2(110)$ surface, producing a less heavily damaged surface than one obtained by ion bombardment and containing Ti cations in only the $+3$ and $+4$ states. These surfaces still show activity for carbonyl coupling. Yates et al. have reported reductive coupling of formaldehyde to form ethylene on these surfaces,¹⁴⁶ a reaction not previously recognized in studies of formaldehyde on ion-sputtered $\text{TiO}_2(001)$ surfaces. Nevertheless, this and previous studies by Idriss clearly demonstrate that one does not need zerovalent titanium to carry out reductive carbonyl coupling (in spite of claims to the contrary in the slurry phase literature) and that even ensembles of Ti^{3+} cations at the surface can effect this reaction.

In the case of carbonyl compounds, such as acetaldehyde, which contain α -hydrogens and are therefore capable of aldol condensation, one observes a clear changeover in selectivity from reductive coupling to aldol condensation products as the titanium oxide surface is progressively oxidized. This changeover of coupling mechanism is illustrated in Figure 8 for the case of acetaldehyde, for which the principal coupling product switches from 2-butene to crotonaldehyde as the sputtered $\text{TiO}_2(001)$ surface is oxidized by annealing.

Thus we see that relatively simple C_2 oxygenates such as acetic acid and acetaldehyde exhibit at least three different pathways for the formation of higher carbon number products by C–C bond formation on various titanium oxide surfaces, even under UHV conditions. Each of these reactions requires something different of the surface, but those site requirements can be interpreted in terms of local properties of the surface cations—their coordination number and oxidation state—without considering the longer range geometric or electronic properties of the different surfaces examined. Carboxylate coupling requires surface cations with pairs of coordination vacancies to accommodate the pair of ligands to be coupled; aldol condensation, which involves the coupling of dissociatively and molecularly adsorbed surface species, does not. Reductive carbonyl coupling requires the presence of reduced cations on the surface in

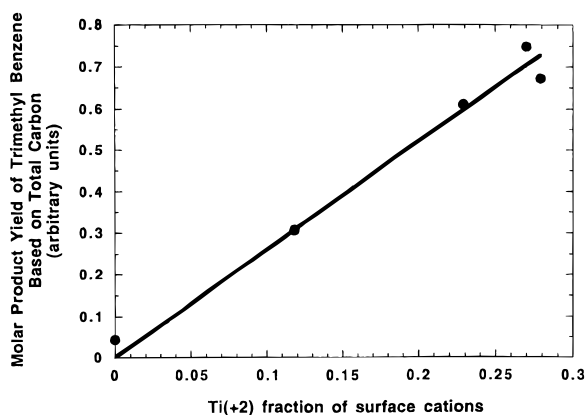


Figure 9. Yield of trimethylbenzene from cyclotrimerization of methylacetylene on reduced TiO_2 surfaces, as a function of the population of $\text{Ti}(+2)$ cations.¹⁵¹

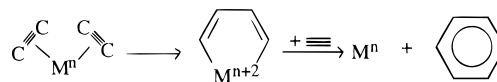
order to carry out this four-electron reduction, but this requirement can be met by a variety of ensembles of lower valent cations at the surface.

The crucial tests of these concepts and the local site requirements deduced from single crystal studies on oxides is their generalizability. At present, we are unaware of any published studies on other oxide surfaces that contradict these assignments and, as noted above, those studies of simple oxygenates such as HCOOH and H_2CO that have been carried out on other oxides/other titania surfaces are consistent with the concepts advanced above. Provided that a sufficient body of consistent observations can be accumulated, it may even be possible to use these reaction classes as diagnostics for the presence of different site types on the surfaces of other oxide materials with unknown or incompletely defined surface characteristics.

It should be noted however that these coupling reactions from titania single crystal surfaces in UHV can be connected to the chemistry of these reagents on polycrystalline titania powder catalysts at higher pressures. All three, carboxylate ketonization,¹⁵⁰ aldol condensation,¹³⁵ and reductive carbonyl coupling,¹³⁷ have been demonstrated on such materials, and the titania-catalyzed aldol condensation is a patented process for production of higher α,β -unsaturated aldehydes and alcohols.¹³⁸

This review would not be complete without the mention of yet another class of C–C bond-forming reaction observed on oxide surfaces recently. This reaction, the cyclotrimerization of alkynes to form aromatics, also occurs with high conversion and selectivity (up to 86% for hexamethyl benzene from 2-butyne) on reduced $\text{TiO}_2(001)$ surfaces. However, unlike reductive carbonyl coupling, this reaction requires cations in a specific oxidation state, +2 in the case of reduced titania. Thus this reaction is much more sensitive to the distribution of cation oxidation states on the surface than is carbonyl coupling and shows a quantitative correlation with the surface Ti^{2+} population from XPS^{151,152} (Figure 9). The reason for this site requirement can be easily understood in terms of the mechanism of catalytic alkyne cyclotrimerization by low oxidation state transition metal complexes in solution, demonstrating yet another analogy between the surface chem-

istry of oxides and that of organometallic complexes in solution. The homogeneously catalyzed version of this reaction involves coordination and coupling of a pair of alkynes to form a metallacyclopentadiene intermediate; insertion of a third alkyne molecule and elimination of the aromatic product restores the initial complex:¹⁵³



The initial formation of the metallacyclopentadiene requires the formal two electron oxidation of the metal center, and thus requires that this site have an accessible oxidation state two units higher. This requirement translates directly to titanium oxide surfaces active for alkyne cyclotrimerization: the activity of the surface for this reaction correlates with the population of Ti^{2+} centers on the surface, as only this and sites of lower oxidation state are capable of undergoing a two electron oxidation. Thus, although spectroscopic verification of the metallacyclopentadiene intermediates in this oxide surface reaction has yet to be developed, the surface chemistry observed is completely consistent with the mechanism borrowed from homogeneous catalysis. Interestingly, Ti^{2+} centers on oxide surfaces appear to be more active for this reaction than are the homogeneous Ti(II) complexes which carry out this chemistry. The latter tend to form stable metallacyclopentadiene complexes and exhibit low conversion of these to the aromatic cyclotrimerization product.¹⁵⁴ In contrast, on reduced TiO_2 surfaces, as much as 60% of the adsorbed alkyne molecules are converted to the cyclotrimerization product at very modest temperatures (~ 400 K).

V. Conclusions and Challenges

We have discussed above three key concepts for interpretation of the surface reactivity of metal oxides and have attempted to draw analogies to organometallic chemistry wherever possible. We conclude with a list of questions that the field of oxide surface science, emerging over the last decade, might address in the next decade:

(1) Do the concepts above regarding the importance of local coordination environment, oxidation state and redox properties stand up across the wide range of oxides and surface structures (as well as those of other compounds, e.g., sulfides, halides, etc.) that have yet to be examined? Can they be utilized as diagnostic tests for the surface chemical properties or structural characteristics of “unknowns”?

(2) Can these concepts and principles be applied to the specification and “design” of new catalytic materials and processes? Can we invent new oxide catalysis from surface science discoveries?

(3) What are the limitations to the analogies drawn between the surface chemistry of oxides and that of organometallic complexes in other environments? Can such analogies, which permit one to “transfer” the chemistry without reproducing the organometallic complex on a surface, provide a more effective

vehicle for "heterogenizing homogeneous catalysis" than those attempted to date?

Much remains to be done (indeed, to be begun) at a less philosophical level. There is a continuing need to develop better model surfaces, particularly of suboxides, and to characterize the detailed structures of these and of the specific defects which occur on them. The range of surface organic chemistry explored on oxide single crystals to date is still relatively limited. Important connections remain to be made from oxide surface science to demonstrated catalytic processes utilizing oxide-based catalysts, including examples such as alkane oxidation, methanol synthesis, and hydrocarbon cracking. Oxide surface science has barely begun to address the reactivity of ensemble sites and the involvement of specific combinations of cations in catalytic processes, especially selective oxidation. Of particular technological importance are mixed and supported oxide catalysts, where such surface ensembles may incorporate cations of more than one metal. The questions and challenges presented here will, it is to be hoped, stimulate the continuing growth of oxide surface science. We believe that they contain the seeds for increasing technological impact of this field over the next decade and beyond.

VI. Acknowledgments

The continuing support of the National Science Foundation (currently Grant CTS 9410965) for our work on oxide surface science over the last decade is gratefully acknowledged. Support from industrial sources, E. I. du Pont de Nemours & Co., Inc., and Hercules, Incorporated, along with the Delaware Research Partnership Program, has permitted us to explore the applications of this research to heterogeneous catalysis. I also thank the talented co-workers whose names appear throughout the Bibliography for many contributions to the development of the principles of oxide surface chemistry advanced in this article.

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