and P. B. Kenen, Eds. (Elsevier, Amsterdam, 1985), vol. 2, pp. 859–916]. For a model with rational expectations, see M. Obstfeld ["Floating exchange rates: Experience and prospects," *Brookings Papers in Economic Activity*, no. 2 (Brookings Institution, Washington, DC, 1985)].

5. In technical terms, the set of (linear) differential equations used to describe the movements of the exchange rate and other economic variables has a saddle point solution, whereby one path to equilibrium is stable while the others are not. In forward-looking markets the exchange rate will jump onto the stable path. This process gives rise to the exchange rate "overshooting" its new long-run equilibrium value in order to maintain momentary equilibrium by compensating for the sluggishness or inflexibility of other prices in the economy. This phenomenon illustrates Le Chatelier's principle in physics as applied to an economic system. In Fig. 2, the cumulative surplus achieved between t_0 and t_1 will result in new claims on the rest of the world, hence new earnings on those claims. To restore a situation in which net claims are no longer changing therefore requires some appreciation of the home currency in real terms, for example, a trade deficit offset by the net earnings from abroad. Thus in the long run, the e schedule drops below the P schedule (Fig. 2).
6. J. Tobin and J. B. de Macedo, in *Flexible Exchange Rates and the Balance of Payments*, J. S. Chipman and C. P. Kindleberger, Eds. (North-Holland, Amsterdam, 1980), pp. 5–28.
7. For a summary of empirical work on open economies, see J. Helliwell and T. Padmore [in *Handbook in International Economics*, R. W. Jones and P. B. Kenen, Eds. (Elsevier, Amsterdam, 1985), vol. 2, pp. 1107–1151; and the references therein]. For a quantitative model of the United States that allows explicitly for disequilibrium in some markets, see R. Fair [*Specification, Estimation, and Analysis of Macroeconomic Models* (Harvard Univ. Press, Cambridge, 1984)].
8. For summaries of and references to the work in this area, see K. Rogoff [*J. Monetary Econ.* **14**, 133 (1984); and (*9*)].
9. J. Frankel, in *How Open is the U.S. Economy?*, R. W. Hafer, Ed. (Lexington Books, Lexington, MA, 1986), pp. 33–67.
10. R. Dornbusch, "Purchasing power parity," in *The New Palgraves Dictionary of Economics* (Macmillan, London, 1986).
11. The slope of the GG schedule would be altered by a move from a closed to an open economy, with the GG schedule becoming steeper because some part of any additional expenditure will be used for the purchase of imports and thus will not increase domestic output.
12. The ratio of imports to the U.S. gross national product has more than doubled since the mid-1960's. The share of foreign ownership of securities in the United States and the ratio of foreign to total loans by U.S. banks have roughly trebled. See R. Cooper, in *How Open is the U.S. Economy?*, R. W. Hafer, Ed. (Lexington Books, Lexington, MA, 1986), pp. 3–24.

Molecular Transformations on Single Crystal Metal Surfaces

R. J. MADIX

One of the primary objectives of modern surface chemistry of transition metals is the synthesis of surface compounds and complexes and the understanding of their reactivity, structure, and bonding. Such considerations are paramount for advancing understanding of catalysis, adhesion, organic thin-film growth, and electrocatalysis. On selected metals, particularly copper, silver, and gold, selective scission of X–H bonds (where X is oxygen, carbon, nitrogen, or sulfur) by surface-bound atomic oxygen occurs to form moderately stable species that can be isolated for further study. Selective oxidation reactions may occur heterogeneously by means of this novel oxygen-activated route. Furthermore, this selective chemistry offers a paradigm for synthesis of a wide variety of surface organometallic complexes, whose formation can be predicted from acid-base principles. These subjects are discussed in this article with emphasis on their role in catalytic oxidation cycles.

IDEALLY, A CHEMICAL CATALYST OR CATALYTIC AGENT increases the rate of a chemical reaction without itself being consumed in the reaction. For example, without chemical intervention carbon monoxide (CO) and nitric oxide (NO), formed in the combustion process, exhaust from an automobile without reacting further and contribute to atmospheric pollution. In the presence of a catalytic converter, these gases react to form harmless carbon dioxide (CO_2) and N_2. The relative rate at which a reaction transpires on a given catalyst is known as the catalyst activity; the degree to which the catalyst directs the course of the chemical conversion toward one product is known as its selectivity. Normally, one desires a maximum rate along with a high selectivity, since this combination maximizes production. For specialty products, however, selectivity considerations may dominate.

Often, catalytic materials interact with the reactant molecules to form intermediate compounds or complexes that undergo further reaction easily. For example, in the conversion of N_2 and H_2 to ammonia (NH_3), if the catalyst is to be of any utility, it must provide a more facile path than that available in the gas phase. This conversion is accomplished catalytically by N–N and H–H bond scission on the surface of the metal catalyst to produce atoms of nitrogen and hydrogen bound to the metal (*1*). A reaction sequence then occurs on the surface with energetic barriers for each step that are lower than the barrier would be in the absence of the catalyst.

This mechanistic principle of catalysis also applies to complex cycles of reactions in living systems (*2*). However, even for simple reaction schemes, a number of reaction paths can be accessible to the reactants; the selective formation of a single product depends on the relative rates of the possible reaction channels. Thus, an understanding of the kinetics of these conversions is important for progress in the field, and manipulation of the state of the surface may enhance or suppress certain reactions. Furthermore, specific identification of the intermediates formed and a detailed understanding of the available reaction channels is crucial. It may be possible to guide the reaction in more desirable directions by intercepting it at specific stages. The methods of surface science offer the opportunity to dissect such processes on the molecular scale and to predict reaction

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behavior over a wide range of operating conditions. Recent studies of oxidation on metals in groups IB and VIII in the periodic table illustrate these points.

Catalytic oxidation is the basis for the synthesis of a large number of important chemicals, since air is inexpensive and reactions of readily available hydrocarbons with oxygen over heterogeneous catalysts produce a variety of useful species. Metals and metal oxides are used as catalysts in these processes (*3*). Complete oxidation of a hydrocarbon to CO_2 and H_2O is desirable in circumstances such as the control of emissions from internal combustion engines. Usually more subtle partial oxidations are designed to form molecules of greater utility, such as the oxidation of ethylene to ethylene oxide (*4*), butane to maleic anhydride (*5*), or methanol to formaldehyde (*6*).

Metals Used in Heterogeneous Oxidation Catalysis

Transition metals can be qualitatively divided into those that form stable oxides and those that do not. In a similar fashion these metals, respectively, do or do not reversibly activate O_2; that is, they do or do not cleave the O–O bond to form oxygen atoms bound to the metal surface and subsequently regenerate O_2 via recombination of the atoms on the surface. Iron and molybdenum form stable oxides (*7*), whereas the elemental metals to the lower right in the periodic table reversibly activate O_2 (*8*). There is a strong correspondence between the relative stabilities of the bulk oxides and the strength of the metal-oxygen surface bond. As expected from their general passivity to chemical reaction, silver and gold bond with oxygen most weakly. Several other metals recombine with oxygen atoms well below their melting points. Of these, platinum, palladium, and silver are widely used as oxidation catalysts (*9*). Iron and molybdenum oxides are also found in some oxidation catalysts (*10*), but they are typically used at temperatures sufficiently high to involve substantial amounts of oxygen from the crystal lattice itself and will not be discussed further in this article. Platinum and palladium typically produce complete oxidation, whereas silver is used in selective partial oxidations (*9*).

The Ultimate Goal and the Idealization

To study the basic chemistry and physics of catalytic reactions, it is necessary to idealize the real catalyst substantially. For this purpose the battery of surface science tools initially developed for the study of surface physics has been extensively used in the study of reactions on metallic single crystals. The ultimate goal of such work is to determine the identity of the intermediates formed on the surface along the reaction path from reactants to products, to characterize their structure and bonding, and to determine the activation energy and entropy for their reactions on the surface. From such studies a

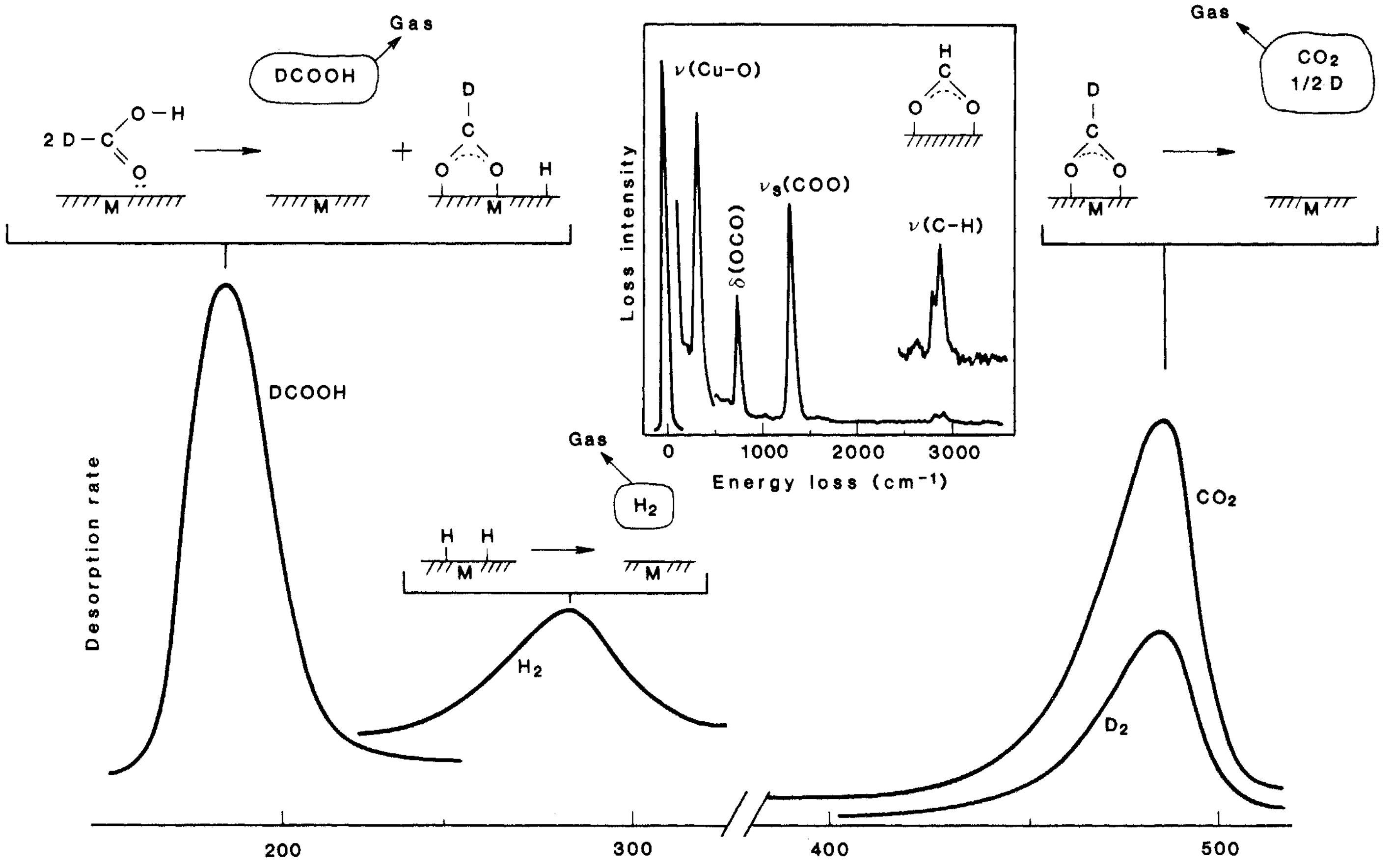

Fig. 1. Temperature-programmed reaction spectrum (TPRS) for formic acid reaction with Cu(110). Each step in the reaction DCOOH = $H_{(a)}$ + $D_{(a)}$ + CO_2 is revealed by product evolution into the evacuated gas phase as the surface complex is heated. Simultaneous formation of CO_2 and D_2 at 480 K is clear indication of the $DCOO_{(a)}$ intermediate. The vibrational spectrum for the formate existing between 300 to 480 K is shown in the inset. The absence of the asymmetric O–C–O stretch indicates bidentate or chelating bonding to the copper atoms on the surface. The combination of these spectroscopies makes it possible to determine both chemical and structural identity.

molecular basis for the rational design of chemical catalysts may emerge. Marked progress has already been made on some reactions (see below). Two of the fundamental quantities for the study of surface reactivity, the structure and composition of the surface, are determined by a combination of low-energy electron diffraction (LEED) (*11*), Auger electron spectroscopy (*12*), and x-ray photoelectron spectroscopy (XPS) (*13*). These tools have been outlined in some detail (*14, 15*).

The reaction paths and the identities of the intermediates for selected reactions are determined by a combination of thermochemical and molecular spectroscopic techniques. Illustrated in Fig. 1 is the combined use of temperature-programmed reaction spectroscopy (TPRS) and high-resolution electron energy loss vibrational spectroscopy (EELS). With TPRS reactant molecules are adsorbed below the temperatures at which reactions occur, and the surface temperature is then increased linearly with time. Reaction channels open at temperatures characteristic of the activation barriers, and products leave the surface to be detected in vacuo. As a reaction proceeds, the rate first increases as a result of the exponential dependence of the rate constant on temperature and then decreases to zero as the concentration of the reactive intermediate is depleted, giving rise to a peak. By contrasting the temperatures at which product species are evolved as a result of the surface reaction of a given reactant with the temperatures at which they appear when adsorbed separately, one can identify surface intermediates.

In Fig. 1 several elementary reaction steps are thus identified. From the shape of the curve of rate versus temperature thus generated, both the activation energy and preexponential factor for the elementary steps can be determined. The effects of crystallographic orientation or of ordered layers of adsorbed species, such as sulfur, carbon, alkali metals, or alloyed metallic species on surface reactivity, can thus be elucidated. Two extreme effects that can be expected from the surface additive are (i) simple blocking of reaction sites, such as high coordination centers between metal atoms, or (ii) perturbations in the electronic states, which extend well beyond the radius of the modifier. Indeed, evidence for both types of behavior has been cited (*16, 17*). This subject is highly relevant to the actual practice of catalysis. In general, for a given metal, modification of surface composition leads to more dramatic changes in surface reactivity than changes in the crystallographic symmetry of the surface (*18*).

Oxygen Activation on Silver: A Paradigm for Synthesis of Surface Compounds

It may seem paradoxical that silver, which is passive to reaction with organic molecules, forms an almost limitless number of surface compounds with otherwise unreactive organic species, if appropriately treated. The direct consequence of this unique property is that silver catalytically oxidizes molecules with high selectivity. Let us first consider two extreme mechanisms for catalytic oxidation (Fig. 2). In both cases the extended surfaces, here schematically depicted by $Pt_{(s)}$ and $Ag_{(s)}$, activate O_2, producing oxygen atoms bound to the metal surface. In case (a) the surface is also sufficiently reactive to cleave bonds in the molecule to be oxidized (BH) such that fragments of this molecule also bind to the surface. These fragments can further react on the surface, independent of the presence of the oxygen. Ultimately the surface is covered with a mixture of molecular fragments and adsorbed atomic oxygen, and the fragments can then be scavenged by the oxygen, forming gaseous products. This extreme example, which ignores interaction of the reaction partners before formation of the product of oxidation, is termed the scavenger mechanism. At the other extreme, the surface-bound oxygen participates from the outset. Thus, in case (b) the molecule is not activated by the metal in the absence of oxygen, but it requires surface oxygen for the initial bond-breaking step. Products are formed solely on the basis of the reactivity patterns of the fragment thus formed. This mode of oxidation is known as the oxygen-activated mechanism.

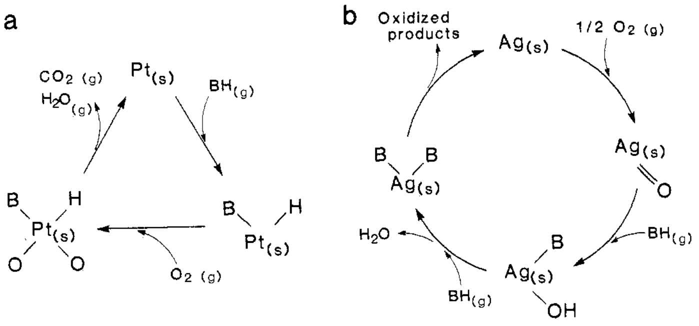

Fig. 2. Schematic illustration of catalytic cycles for (a) the scavenger and (b) oxygen-activated mechanisms for heterogeneous oxidation of substrate BH on extended platinum and silver surfaces, denoted by (s), respectively. In (a) the reactants interact independently with the surface, whereas in (b) adsorbed oxygen activates the substrate BH directly. Bonding is shown schematically and does not occur to a single metal atom center.

In reality, stability of the fragments bound to the surface can be affected by the surface oxygen in both cases, and, certainly, for a given metal it could be expected that a combination of both mechanistic routes exists for a given reaction. However, in the case of metallic silver the oxygen-activated mechanism predominates (*19*), and studies on silver single crystals have led to the discovery of this pathway (*20*). The use of oxygen activation combined with the relative unreactivity of silver allows the synthesis of a host of surface species near room temperature in near monolayer concentrations, providing abundant opportunity for the detailed study of surface structure and bonding. Similar species exist on surfaces of other metals that are intrinsically more reactive, the basic difference being that they must be isolated at lower temperatures to prevent further reaction. These general observations have contributed to the emergence of the field of the organometallic chemistry of transition metal surfaces, a discipline that impacts many of the problems of catalysis.

Selective Oxidation by Oxygen Activation

To appreciate the manner in which deductions can be made from studies of surface reactivity that are relevant to heterogeneous oxidation, it is fruitful to consider the selective oxidation of methanol (CH_3OH) to formaldehyde (H_2CO) on copper and silver. The overall reaction is

$$CH_3OH \rightarrow H_2CO + H_2$$

which in principle could proceed in the absence of oxygen. Indeed, on platinum, palladium, nickel, and ruthenium total dehydrogenation to CO and H_2 occurs (*21*). Studies of the reaction of CH_3OH on Ni(100) with vibrational spectroscopy illustrate that CH_3O is first formed on the surface, but that total dehydrogenation to CO occurs rapidly because of the ease of C–H bond cleavage and the relative stability of adsorbed CO (*22*). Similarly, on copper single crystal surfaces the O–H bond is also cleaved, leading to the formation of both CH_3O and hydrogen atoms bound to the surface (*23*). The C–H bond scission is more difficult on copper than on nickel however, and, if the hydrogen atoms recombined readily on copper to evolve H_2, the reaction would proceed directly to the

Table 1. Relative stabilities of surface intermediates as determined by the displacement reaction $B_{(a)} + B'H_{(g)} \rightarrow BH_{(g)} + B'_{(a)}$ following formation of $B_{(a)}$ by quantitative titration of $O_{(a)}$ by $BH_{(g)}$; pK_a, negative logarithm of the acidity constant.

Order of stability of $B_{(a)}$ on Ag(110)	$B_{(a)}$	$BH_{(g)}$	ΔH°_{acid} (gas phase) (kcal/mol)	pK_a	D° (B–H) (kcal/mol)	Identifying product in TPRS (characteristic temperature, K)
1, 2	HCOO	HCOOH	345.2	3.7	112	CO_2 (420)
	CH_3COO	CH_3COOH	348.5	4.8	112	CO_2 (650)
3	C_2H_5O	C_2H_5OH	376.1	17	104	CH_3CHO (275)
4	C_2H	C_2H_2	375.4	26	120	C_2H_2 (270)
5	CH_3O	CH_3OH	379.2	15.5	104	H_2CO (300)
6, 7	C_3H_5	C_3H_6	390.8	35	89	
	OH	H_2O	390.8	15.7	119	H_2O (320)

formation of H_2CO via subsequent cleavage of the C–H bond. However, copper is a very poor metal for the recombination of adsorbed hydrogen atoms (*24*). Thus, although the binding energy of the hydrogen atoms to the copper surface is low compared to that on nickel, platinum, palladium, and iron surfaces (*25*), the anomalous recombination kinetics to form H_2 causes the hydrogen atoms and the CH_3O groups to recombine to reform CH_3OH, and further reaction to H_2CO does not occur (*23*). In the presence of adsorbed oxygen, this reaction sequence is dramatically altered, however.

Dioxygen is readily dissociated on copper surfaces to form oxygen atoms bound to sites of high symmetry (*26*). In the presence of this adsorbed oxygen, the hydroxyl hydrogen in CH_3OH is transferred directly to the surface oxygen to form surface-bound OH groups, which, in turn, accept a second hydrogen to form water, which desorbs (*23*). This low-energy pathway for the disposal of the hydrogen leaves the CH_3O group intact. Subsequently, the cleavage of the C–H bond proceeds by transfer of the methyl hydrogen to the surface to form H_2CO with high selectivity. Indeed, some of the hydrogen atoms released to the surface during this dehydrogenation step recombine with CH_3O groups to reform CH_3OH in direct competition with H_2CO formation, thus reducing the overall efficiency of the oxidation process (*27*). Furthermore, in the presence of excess adsorbed oxygen, H_2CO undergoes further reaction (*28*). The adsorbed oxygen attacks the aldehyde at the electron-deficient carbon to form a strongly bound H_2CO_2 intermediate, which dehydrogenates quickly to the surface formate HCO_2. The result of this secondary step is the production by HCO_2 of CO_2 (Fig. 3). Since the surface formate is more stable than the methoxyl group (*27, 29*), it may build up on the surface in appreciable quantity, blocking the surface for further reaction unless the surface temperature is maintained at sufficiently high values to prevent its accumulation. Information of this nature can be used in the design of operational schemes for the optimal conversion of reactants to the desired products, as the elements of the reaction network describing the overall conversion and the side reactions are known.

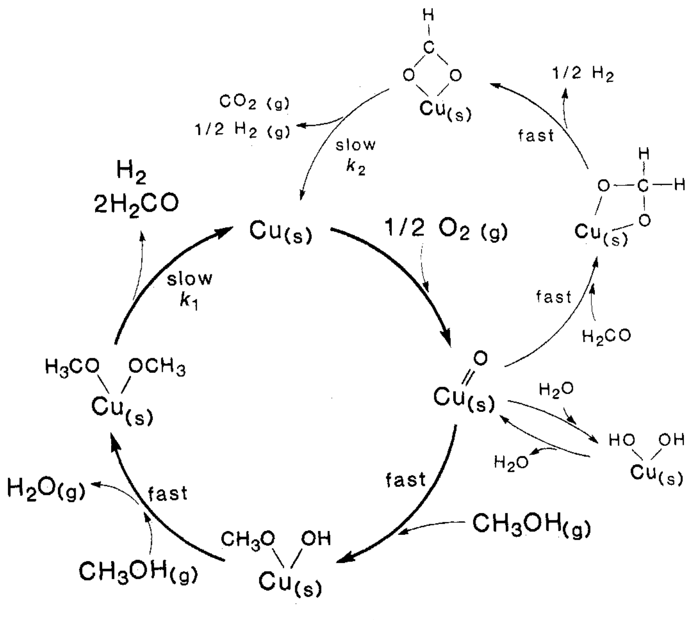

Fig. 3. Catalytic cycle for the oxidation of methanol on copper in lean oxygen conditions, showing competing side reactions. The extended copper surface is schematically designated by $Cu_{(s)}$, and reactions do not occur on a single copper atom. The first-order rate constants for the surface dehydrogenation reactions of the methoxyl and formate species on Cu(110), determined by TPRS, are $k_1 = 5 \times 10^{12} \exp(-22{,}100 \text{ cal mol}^{-1}/RT)$ and $k_2 = 9 \times 10^{13} \exp(-31{,}900 \text{ cal mol}^{-1}/RT)$, respectively (where R is the Boltzmann constant and T is absolute temperature). The cycle for oxidation of methanol on silver is similar with an additional side reaction of H_2CO and $CH_3O_{(a)}$ to produce methyl formate and the reversible reaction of CO_2 and $O_{(a)}$ to yield $CO_{3(a)}$.

Similar reactions occur on silver, but the role of activation by surface oxygen is more dramatic. On silver single crystals alcohols do not dissociatively adsorb. In fact, the presence of oxygen adatoms is required for the facile activation of alcohols as well as a variety of other molecules including carboxylic acids and unsaturated hydrocarbons, some of which are listed in Table 1 (*30–35*). In addition, CH_3CN, $C_2H_5NH_2$, NH_3, and $NH_2CH_2CH_2OH$ are activated by adsorbed oxygen, whereas H_2, C_2H_4, and C_2H_6 are not. All these reactions proceed by means of hydrogen transfer directly to the surface oxygen with simultaneous formation of a bond between the remaining molecular fragment and the surface. In the case of CH_3OH the reactions observed on Ag(110) are identical to those on copper described above. An interesting side reaction between CH_3O and the H_2CO on the surface is the formation of methyl formate (*36*). Furthermore, on silver nucleophilic attack of $HCOOCH_3$, RCHO, CO_2, SO_2, and NO_2 to selectively form adsorbed HCOO and CH_3, $RCHO_2$, CO_3, SO_3, and NO_3, respectively, occurs. The patterns of reactivity observed on silver can be understood in terms of general acid-base terms. This generalization leads to predictions that can provide the basis for understanding selective oxidation reactions and for the synthesis of a nearly limitless number of surface compounds. The surface-bound oxygen acts as a chemical switch that selectively opens certain reaction channels to the reactant molecule.

Oxygen exhibits three distinct behaviors on the surface. The negative charge on the oxygen bound to the surface of silver is sufficient to cause the oxygen to interact strongly with electron-deficient centers in molecules. (i) Consequently, the oxygen acts as a Bronsted base; that is, it abstracts hydrogen from a variety of molecules (*30–32*). (ii) It also attacks carbon in aldehydes and esters, exhibiting rather strong nucleophilicity (*33, 36*). (iii) Since the oxygen draws negative charge away from surrounding metal atoms on the surface, it creates sites that are partially electron-deficient, leading to the stabilization of donor-acceptor bonding at those locations; that is, it creates Lewis acid sites in its immediate vicinity (*37*). This induced Lewis acidity has been demonstrated recently for the bonding of CO to Cu(100) resulting from the presence of adsorbed formate groups (*38*). Reactions exemplifying each of these properties can be found in the literature. The use of isotopic labeling with deuterium in several alcohols and carboxylic acids shows that O–H bond activation by surface oxygen on silver is a general property (*30*). Similarly, work with NH_3 and ethylamine indicates that N–H bonds are easily activated (*39*). Reactions of acetylene and propylene demonstrate that C–H bonds can be split by adsorbed oxygen (*31*). Although I know of no studies yet published concerning reactions of S–H-containing molecules with surface oxygen, it seems certain that analogous reactions will be reported.

One interesting example of C–H bond activation by adsorbed oxygen occurs with acetylene. This gas (C_2H_2) exhibits a variety of reactivities on group VIII metals, such as platinum, iron, and nickel, dehydrogenating to hydrogen and surface carbon subsequent to formation of the surface-acetylene complex. On platinum, for example, the reaction is believed to proceed through partially dehydrogenated fragments on the initially clean surface (*40*).

In contrast, on palladium (*41*) and copper (*42*) a rather unique cyclization reaction to benzene occurs; on silver the interaction between C_2H_2 and the clean surface is weak, and no reaction takes place (*43*). In the presence of oxygen on silver, however, a single hydrogen is selectively removed from C_2H_2; this hydrogen titrates the surface oxygen and leaves C_2H fragments. The concentration of these species is quantitatively determined by the initial concentration of adsorbed oxygen, since the reaction is stoichiometric. Near room temperature these C_2H fragments disproportionate to emit C_2H_2 into the gas phase, leaving intact C_2 groups on the surface. Differing two-dimensional structures are formed by these C_2 entities with different initial oxygen coverages. Upon further heating, this acetylide dissociates to surface carbon atoms.

Each step in the process can be followed by a variety of spectroscopies (Fig. 4). The chemical composition of the intermediates was determined directly by titration of the C_2H and C_2 species with deuterated acetic acid, which yielded C_2HD and C_2D_2, as expected. XPS showed the titration between the two species to be quantitative, according to the general scheme (subscript a denotes an adsorbed species and g a gaseous species)

$$BH_{(g)} + B'_{(a)} = B_{(a)} + B'H_{(g)}$$

where this notation designates a molecular fragment B bound to hydrogen, such as CH_3O–H or HCC–H. This displacement can be readily identified by TPRS (*44*). The products to be expected from specific intermediates and the temperatures at which they are evolved are listed in Table 1. Running these displacement reactions in both directions established that the relative stabilities of the intermediates on silver follow their relative gas-phase acidities (*45*), and the surface displacements are ordered according to the enthalpies ΔH for the gas-phase reaction

$$BH_{(g)} + B'^{-}_{(g)} = B^{-}_{(g)} + B'H_{(g)}$$

The close correlation between the energetics for this gas-phase exchange reaction and the surface displacement reactions follows if the enthalpies of adsorption of the gas-phase negative ions are similar. This result would be expected for a homologous series such as methanol, ethanol, propanol, and so forth, and has been shown to be the case on copper for this extended series (*46*). In comparing O–H, C–H, S–H, and N–H acids, deviations from the strict ordering imposed by the gas-phase acidities may occur, since bond strengths of the fragment B with the surface will vary for oxygen, carbon, sulfur, and nitrogen. The degree to which this difference complicates the relative stability scale is under study (*47*). These results demonstrate that oxygen activation on the group IB metals affords a synthesis route for a limitless number of surface compounds that have carbon, oxygen, nitrogen, or sulfur linkages to the surface. As a result, the systematics of the molecular chemistry of these surfaces can be explored. This field of organometallic surface chemistry is now extremely fertile. In the next few years we should expect an explosion in the generic understanding of the bonding and reactions of more complex molecules at surfaces with considerable relevance to the fields of catalysis, adhesion, coatings, and electrochemistry.

The enthalpy of the displacement reaction can be related to the gas-phase acidity. Contributions to ΔH_{acid} for the reaction

$$BH_{(g)} \rightarrow B^{-}_{(g)} + H^{+}_{(g)}$$

can be broken down into three terms according to

$$\Delta H_{acid} = D_o - EA + IP$$

where D_o is the homolytic bond dissociation energy, EA the electron affinity of the radical species B, and IP is the ionization potential of the hydrogen atom (*45*). With reference to Table 1, which shows that the ordering does not follow the relative values of D_o, the order of stabilities of the surface species is related to the electron affinities, which suggests that there is appreciable charge transfer from the metal to the adsorbed species. Measurements of the change in work function of the metal due to these species generally confirm this expectation.

These observations permit a more complete description of the initial reaction between surface oxygen and the molecule. In the case of the activation of CH_3OH on Cu(110) by adsorbed oxygen there appears to be hydrogen-bond formation between the O–H hydro-

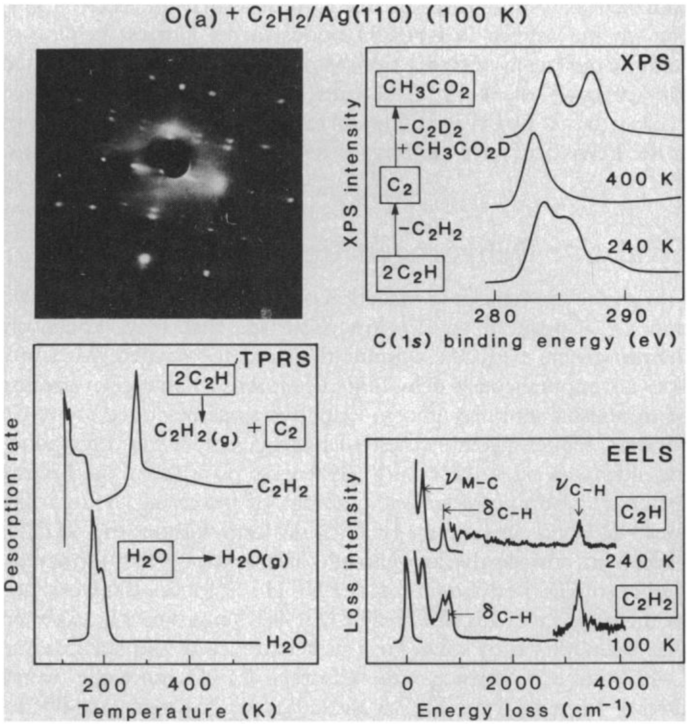

Fig. 4. Spectroscopic evidence for C–H bond activation in C_2H_2 by adsorbed oxygen. (bottom left) TPRS of water and acetylene formed by the disproportionation of adsorbed C_2H. Reactions are indicated, and the product detected is shown on each curve (surface-bound species are boxed). (lower right) The electron energy loss vibrational spectrum at different annealing temperatures showing adsorbed C_2H_2 at 100 K and the C_2H intermediate at 240 K. (upper right) The x-ray photoelectron spectrum after the formation of $C_{2(a)}$ from C_2H and its subsequent titration with acetic acid to form the surface acetate. The multiple peak structure in the C_2H spectrum is due to the two inequivalent carbons and an intramolecular relaxation peak. The two peaks in the acetate spectrum derive from the two inequivalent carbons in the acetate. (upper left) The low-energy electron diffraction pattern derived from reaction of acetylene with 0.25 monolayer of adsorbed oxygen to form a structured C_2 overlayer.

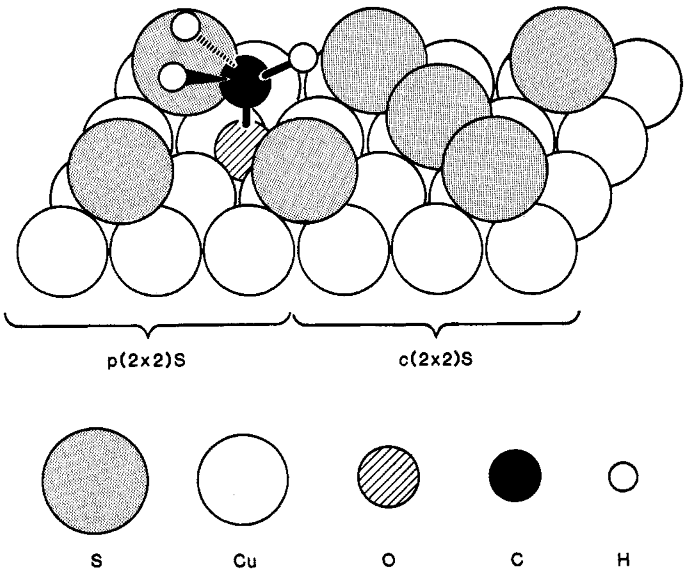

Fig. 5. Schematic drawing of the active site for selective oxidative dehydrogenation of methanol on Ni(100) covered with 0.38 monolayer of adsorbed sulfur. Note the partial coverage of sulfur by the combination of the $p(2\times2)$ and $c(2\times2)$ structures. The central atom of sulfur in the $c(2\times2)$ structure adds additional stability to the adsorbed CH_3O.

gen in CH_3OH and surface oxygen before the transfer reaction. Given the existence of oxygen-induced Lewis acid sites next to the adsorbed oxygen, it is reasonable to believe that the electron lone pair on the oxygen in CH_3OH bonds to the surface, helping to stabilize this precusor to reaction. Similar models can be constructed for activation of N–H, S–H, and C–H bonds (in unsaturated hydrocarbons) by oxygen. They all can form donor-acceptor bonds at the Lewis acid sites, utilizing either nonbonding or π electrons.

Oxidative Dehydrogenation

With the mechanism of oxidation of CH_3OH understood, we are now in a position to develop a surface that may oxidatively dehydrogenate CH_3OH without the need for oxygen. Methanol does not spontaneously dehydrogenate to H_2CO on copper because of an unusual interplay of competing reactions described above. In contrast, higher alkoxyls readily dehydrogenate to the corresponding aldehydes on Cu(110) (*48*). If it were possible to stabilize the methoxyl group on nickel, for example, by increasing the difficulty for C–H bond activation, H_2CO could form without the need for oxygen to provide the low-energy pathways for water formation. Earlier studies have shown that the Ni–H surface bond is weakened by the presence of adsorbed sulfur (*17, 49*). Thus it may be expected that the addition of sulfur to a nickel surface would stabilize the C–H bond and, consequently, adsorbed CH_3O, since the overall driving force to form H_2CO and adsorbed hydrogen would decrease. This indeed proves to be the case, and the dehydrogenation of CH_3OH can be selectively limited to H_2CO formation on Ni(100) with the addition of 0.38 monolayer of sulfur (*50*). This concentration forms a structure that is intermediate between $p(2\times2)$ and $c(2\times2)$ (Fig. 5), optimizing the C–H bond stability with the number of available fourfold hollow sites for the reaction. Basically, the increase in activation energy for C–H bond scission caused by adsorbed sulfur stabilizes the methoxyl group and, upon loss of a single hydrogen, greatly enhances the desorption of H_2CO prior to further dehydrogenation to CO and H_2. The active site for this process is the open fourfold hollow on this surface sulfide (*51*) (Fig. 5).

Generalization to Other Metals

The degree to which activation by oxygen extends to other metals may be a general principle in the mechanism of oxidation reactions. Recent studies (*52*) on Au(110) show that adsorbed oxygen activates HCOOH, CH_3OH, and C_2H_2 by hydrogen transfer, but not C_2H_4. Furthermore, nucleophilic attack of H_2CO to form $HCOO_{(a)}$ occurs. These patterns are strictly analogous to those observed on copper and silver, illustrating the analogous behavior for group IB metals.

There is less clear-cut information on group VII metals. Studies of the bonding and structure of water (*53*) and NH_3 (*54*) at metal surfaces reveal that ordered overlayers of oxygen on nickel, copper, and ruthenium strongly influence the arrangement of these molecules as a result of hydrogen bonding, implying strong chemical forces due to surface oxygen. On the metals that reversibly activate O_2, namely, platinum and palladium, hydrogen transfer from H_2O to adsorbed oxygen to form surface hydroxyl groups takes place, whereas the clean surfaces do not activate water (*55*). Similarly, it appears that oxygen on palladium exhibits both Bronsted basicity and strong nucleophilicity, although studies to date are limited (*56*).

The Structure of Surface Species

The determination of the structure of surface species is the most vexing problem in surface chemistry. This difficulty contrasts with that of mononuclear complexes or cluster compounds whose structures are regularly determined by a combination of nuclear magnetic resonance, infrared spectroscopies, and x-ray diffraction. For surface species the primary tools for structure determination have been LEED and EELS (*57*). The most notable success with these methods has been the identification of alkylidyne species on Pt(111); these species bind with one carbon in sites of threefold coordination with the alkyl group away from the surface (*15*). Structural determinations by LEED are difficult, however, and other methods are sorely needed. Recently, use of the fine structure in the x-ray absorption edge of core levels of carbon, oxygen, and sulfur has shown promise (*58*). With polarized synchrotron radiation, in favorable cases, bond lengths and bond angles can be determined (except bonds with hydrogen). To date only a few studies have been completed; the structure of formate on Cu(110) and Cu(100), respectively, offers an interesting comparative use of the technique, which reveals unusual bonding (*59*).

The two structures formed on these surfaces differ dramatically as a result of the availability of sites of differing local coordination (Fig. 6). The unit cell structure of Cu(110) possesses rectangular symmetry in contrast to the square symmetry of the (100) surface. Vibrational spectroscopy of $HCOO_{(a)}$ on Cu(100) indicates that the bond orders are nearly identical to those of bulk sodium formate (*60*), so that the surface species cannot be seriously distorted from that geometry. The polarization dependence of the x-ray absorption due to electronic excitation near the absorption edge shows that the plane of the formate is normal to the surface on both copper surfaces and that the C–O bond length is the same as that of bulk formate. The extended fine structure on the (100) surface indicates that the formate bridges adjacent fourfold hollow sites with a Cu–O bond length of 2.38 Å, an unusually long value for a metal-oxygen bond. In contrast, on the (110) surface the formate group aligns the oxygens along the close-packed direction on the surface and exhibits a normal oxygen-metal bond distance. The extraordinary Cu–O bond distance on the (100) surface is due to the repulsive interaction of the carbon atom in the formate with the copper atoms on the surface. To bring the oxygen atoms closer to the surface would require that the carbon move to within a bonding distance of the copper, reducing the C–O bond order normally found in the formate. This configuration is apparently energetically unfavorable. This example illustrates that the structure of surface species may differ significantly on surfaces of differing symmetry, particularly when two or more points of attachment are involved. Structural determinations are important for the theoretical treatment of bonding at surfaces and for the calculation of potential energy surfaces for reactions of surface species.

High-Pressure Environments

The question has often been asked how studies of surface reactivity, conducted in ultrahigh vacuum with the use of spectroscopies that demand ultralow pressures, can be related to the real problems of catalytic chemistry. (This question is distinct from the related issue of whether studies of reaction kinetics and catalysis on metallic single crystals carried out under conditions close to the actual temperature and pressure of the real process impact directly on the understanding of real catalytic materials.) The question is often asked with emphasis on the difference (many orders of magnitude) between the pressures of ultrahigh vacuum and those of catalytic operations and is referred to as the "pressure gap." This framework is, however, quite imprecise.

The issue addresses the scientific dilemma of extrapolation from idealized to practical conditions. On the one hand, idealized conditions afford fundamental insight into the molecular details of surface reactivity under conditions that do not exactly duplicate actual process conditions; on the other hand, studies under process conditions yield little mechanistic information. Several studies of catalytic reactions have been carried out on single crystals near atmospheric pressure; these experiments successfully simulate process conditions and have yielded basic information on the nature of the catalyst. Notably, in the case of the synthesis of CH_4 from CO and H_2 over metallic nickel, the reaction has been shown to proceed in the same fashion over single crystals as over supported nickel catalysts (*61, 62*). These studies revealed that the crystallographic symmetry of the surface has little effect on the rate of the conversion. In a similar way, it has been shown that the rate of conversion of N_2 and H_2 to NH_3 proceeds most rapidly on the (111) plane of iron (*63*). These results exemplify how modern materials and surface science can be coupled to shed light on classic problems. The question remains, however, how to relate low-pressure studies to heterogeneous catalysis. The key issue to this connection is that catalytic reactions proceed on surfaces of well-defined composition, determined by the gas-phase pressure and composition and the system temperature, via intermediates of a specific nature. Thus, by working at lower temperatures and using surfaces of predetermined structure and composition, one can stabilize intermediates, derived from specified reactants, that are transitory under high pressure–high temperature conditions. The chemical reactivity of the surface intermediates and their surface concentration are the important features in the surface reactions, not the pressure at which one studies their existence. The problem of simulating the practical conditions by idealization is illustrated in the following example, which is related to undesired side reactions in the partial oxidation of ethylene.

Ethylene oxide, the essential intermediate in the manufacture of antifreeze, is formed by partial oxidation of ethylene over a silver catalyst. Although the overall reaction appears simple, the exact chemical state of the oxygen that reacts with ethylene to form ethylene oxide is not yet positively established (*64*). Moreover, the source of undesired total combustion products is uncertain. It has been proposed that acetaldehyde, an isomer of ethylene oxide, is formed in the steady-state reaction and is further oxidized to CO_2 and H_2O (*65*). However, acetaldehyde is readily oxidized by nucleophilic attack of surface oxygen to form surface acetate on silver, and the acetate is stable to temperatures greatly exceeding that at which the ethylene oxidation is conducted (*66*). On the basis of this finding, the acetate groups should accumulate on the surface and shut down the reaction. This stability, however, was determined for the surface covered with acetate groups in the absence of other surface species. On the other hand, when these acetate groups are exposed to gaseous O_2 at higher pressure or when atomic oxygen is coadsorbed, they are dramatically destabilized, which renders them unstable at temperatures used in actual ethylene oxide production (*67*). This destabilization occurs via attack of the methyl carbon of the acetate by surface-bound oxygen atoms, leading to decarboxylation of the acetate and oxidation of the methyl group to a formate species. The formate is even further destabilized by the presence of the surface oxygen, attributable to inductive effects produced by coadsorbed oxygen. Thus, in this case the key connecting factor between the practical conditions and the idealization is the relative concentration of reactants on the surface. Reactions that involve surface species that can be isolated at temperatures sufficiently high to permit examination of their reactivity can be idealized and studied, whereas reactions involving populations of very weakly held species that can only be trapped on the surface at very low temperatures will be hard to simulate under low-pressure conditions at temperatures sufficiently high to clear the activation barriers present.

One alternative way to conduct a reaction at a low surface temperature, hence with an appreciable population of a desired, weakly bound intermediate, and yet supply sufficient energy for passage over energetic barriers is to use molecular beams of reactant molecules with energy in the reaction coordinate that greatly

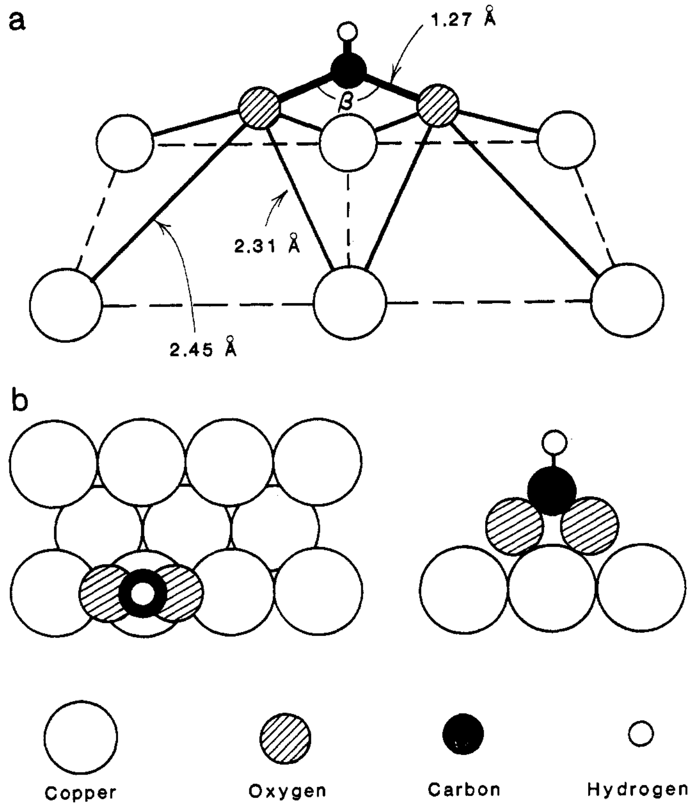

Fig. 6. Schematic drawing of the structures of surface formate on (a) Cu(100) and (b) Cu(110), respectively.

exceeds the characteristic thermal energy of the surface (*68*). Although studies of exactly this type have not yet been conducted, work to date concerning the activated adsorption of small molecules indicates that this route is a possibility. Thus it has been shown that translational energy provides the activation of H_2, N_2, CO, and hydrocarbons on metals for which dissociation possesses an energy barrier, and that channels of reactivity not normally accessible in ultrahigh vacuum can be accessed with translationally excited beams (*69*). Essentially, one varies the energy of the molecules to scan the Boltzmann tail of the velocity distribution. Furthermore, the dynamics of these collisional events can be examined in great detail to yield information on the reactive potential surface (*70*).

The Future

It is intriguing to ask how the fundamental understanding of surface organometallic chemistry as defined above may impact on a variety of practical areas of interest. It is clear from studies to date that the study of molecular interactions with surfaces will yield an abundantly rich chemistry. Though this article was focused on oxidation chemistry, there are numerous studies of the reactions and bonding of hydrocarbons and heterocycles on clean surfaces of group VIII metals, most notably on nickel, platinum, and palladium (*71*). Regioselectivity for C–H bond activation has been demonstrated for dehydrogenation of toluene on nickel single crystals, and strong evidence exists for α-pyridyl intermediates in the coordination of pyridines to nickel (*72, 73*). Recent studies show the formation of a metallocycle in the desulfurization of thiophene on platinum (*74*). A subset of the observations expected to evolve from future work will undoubtedly show ready analogy to existing concepts in organometallic chemistry, with appropriate adjustments for the bulk nature of the metal; other observations are certain to demand extensions of our present understanding of the chemistry of metals. In any event, our knowledge of the molecular processes governing chemical phenomena at surfaces is set for rapid development, given the necessary resources.

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