

sulfur,^{7b,69} one has yet to establish the need for invoking a pentacoordinated intermediate with any degree of certainty. In large measure, the same may be said for reactions of arsenic and antimony derivatives. In these cases competing processes,⁵ dissociation and fission mechanisms, formation of hexacoordinated species, and

(68) A case in point involves the inversion of configuration obtained for base hydrolysis of *cis*- and *trans*-1-ethoxy-3-methylthietanium ions: Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 5644. This is analogous to inversion of configuration of $C(CH_3)_2C(CH_3)C(CH_3)_2PCl$ (Smith, D. J. H.; Trippett, S. *Chem. Commun.* **1969**, 855), which also may proceed via a diequatorially placed ring system.⁴

(69) (a) Trost, B. M. *Top. Curr. Chem.* **1973**, *41*, 1. (b) Kaiser, E. T.; Zaborsky, O. R. *J. Am. Chem. Soc.* **1968**, *90*, 462. (c) Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders Co.: Philadelphia, 1977, p 441.

polymerization processes, take over to a large extent in determining product formation.

Future studies in this area are expected to provide greater definition of similarities and differences in structural preferences among pentacoordinated main-group elements. It should then be possible to decide the role of postulated pentacoordinated species in reaction mechanisms with increased certainty, regarding both their existence and relative nonrigidity.

Grateful appreciation is expressed to the National Institutes of Health and the National Science Foundation for support of much of the work of the author and his collaborators presented here. I am also deeply indebted to the valuable contributions of my colleagues, past and present, in these studies, particularly those of Professors Roberta O. Day and Joan A. Deiters.

Surface Reactivity: Heterogeneous Reactions on Single Crystal Surfaces

ROBERT J. MADIX

Department of Chemical Engineering, Stanford University, Stanford, California 94305

Received August 29, 1977 (Revised Manuscript Received February 23, 1979)

With the advent of modern instruments for characterizing the structure and composition of solid surfaces, it has become possible to understand the mechanisms of molecular rearrangements on solid surfaces. Previously, for reactions in both the gas and liquid phases, a refined understanding of kinetics and mechanism had been obtained for a variety of reactions, but similar advances for heterogeneous reactions lagged due largely to the difficulty in characterizing the surface species and their concentrations.

There are numerous intriguing and challenging surface-chemical problems relating to such important fields as heterogeneous catalysis, fuel cells, and electrocatalysis. Recent studies in my laboratory illustrate how basic questions of surface reactivity can be approached by study of chemical reactions on well-defined single-crystal surfaces.

Five major categories of problems are: (a) the structure sensitivity of surface reactions; (b) the effects of structured surface layers of "foreign" atoms (adlayers) on reaction pathways and rates; (c) the detection of interactions between adsorbed species and the identification of reaction intermediates; (d) the mechanism of surface reactions; and (e) the determination of rate constants for elementary reaction steps.

The first category relates to the effect of the local coordination of adsorbed species by the surface atoms. These effects have been discussed thoroughly elsewhere and will not be presented here.^{1,2} Our recent work has largely concerned problems in categories b-e. The

results of these studies conclusively show that the presence of carbon, oxygen, or sulfur on metal surfaces can alter totally the reaction mechanism and/or change the rate constant for a given reaction by orders of magnitude. Additionally, kinetic effects similar to ligand effects in transition-metal chemistry have been observed.

Experimental Considerations

Currently the experimentalist has at his or her disposal a battery of powerful tools to approach these problems of surface chemical physics. Surface structures can be observed with low-energy electron diffraction (LEED); composition can be measured with Auger electron spectroscopy (AES); binding and composition can be probed with photoelectron spectroscopy (PES), using either ultraviolet (UPS) or X-ray (XPS) sources. Other inelastic scattering processes such as inelastic electron-loss spectroscopy are also useful for observing the surface binding of adsorbed species.

With LEED an incident beam of low-energy electrons (20-150 V) is directed at the surface and the elastically back-scattered electrons are observed.³ The presence of a two-dimensional structure is easily recognized by the diffraction pattern produced on the display screen, and the degree of surface disorder can be judged by the pattern contrast and definition; the sharper are the spots, the less is the disorder.⁴ Surface structural changes produced by adlayers are also easily observed. Though the exact lattice position of this layer may be difficult to determine, the presence of new periodic

Robert J. Madix was born in Indiana in 1938. He obtained his B.S. in chemical engineering from the University of Illinois and, forsaking baseball for science, he obtained his Ph.D. at the University of California, Berkeley, with Michel Boudart. He then did a year of postdoctoral work with Carl Wagner at the Max Planck Institute for Physical Chemistry in Göttingen, Germany, and in 1965 joined the faculty of Stanford University, where he is now Professor of Chemical Engineering.

(1) M. Boudart, *J. Vac. Sci. Technol.*, **12**, 1 (1975).

(2) G. A. Somorjai, *Catal. Rev.*, **7**, 87 (1972).

(3) G. Ertl and J. Kuppers, "Low Energy Electrons and Surface Chemistry", Verlag Chemie, Weinheim, Germany, 1974.

(4) R. L. Park and J. E. Houston, *Surf. Sci.*, **18**, 213 (1969).

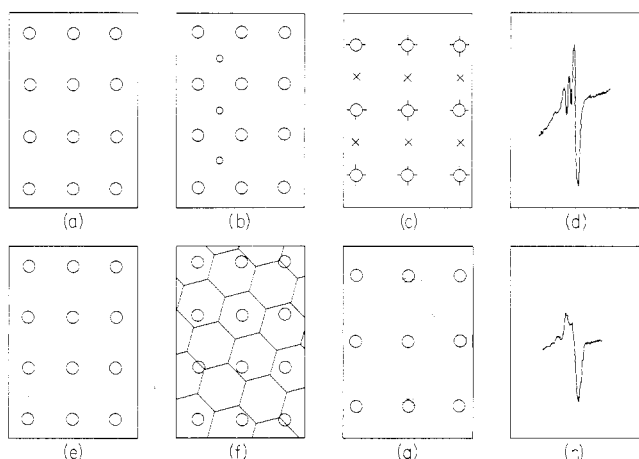


Figure 1. LEED and Auger characteristics of carbon chemilayer structures on Ni(110). (a) Clean Ni(110) surface structure; (b) Ni(110) (2×1)C; (c) Ni(110) (2×1)C LEED pattern; (d) Ni(110) (2×1)C AES fine structure for the carbon 272-V peak showing carbide carbon; (e) clean Ni(110) surface structure; (f) Ni(110) + graphite overlayer surface structure; (g) Ni(110) + graphite overlayer LEED pattern; (h) Ni(110) + graphite overlayer AES fine structure for the carbon 272V peak showing graphitic carbon.

arrays due to adlayer formation is evident, as are structural transformations occurring as the surface concentration of adsorbed species is changed.

In conjunction with LEED, AES is used to determine surface composition and, in some cases, surface binding. In AES high-energy electrons are employed to generate Auger electrons emergent from the surface.⁵ Analysis of the energy spectrum of these Auger electrons presents a set of compositional fingerprints for the surface. The fine structure for a given Auger transition may in certain cases reveal much about the surface bond.⁶

As an example of the application of these techniques to surface chemical physics, consider the changes observed on a Ni surface oriented parallel to the (110) plane following exposure of the clean surface to ethylene at elevated temperatures.^{7,8} The clean surface exposes nickel atoms in the regular, rectangular two-dimensional lattice shown in Figure 1e. When ethylene was cracked below 500 K on this surface to form surface carbon, the diffraction pattern shown in Figure 1c was observed. This structure is referred to as the Ni(110) (2×1)C structure due to the 2×1 periodicity of the overlayer with respect to the (110) lattice. The AES fine structure shown in Figure 1d was indicative of carbide carbon, similar to that observed in transition-metal carbides.⁹ Above 700 K the LEED and AES patterns in Figure 1g,h were observed, indicative of a monolayer "skin" of graphitic-like carbon blanketing the surface.¹⁰ A quantitative comparison of the carbon coverages of these two surfaces revealed the possible presence below 500 K of C₂ fragments bridging the furrows on the (110) surface, as shown schematically in Figure 2. When the Ni(110)(2×1)C surface was heated to 700 K this (2×1) structure converted to the more dense two-dimensional

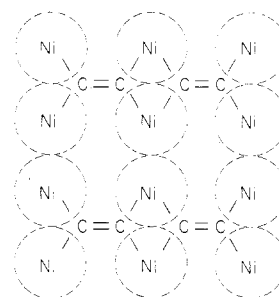


Figure 2. Schematic drawing of the carbidic chemilayer on Ni(110).

graphitic phase, producing patches of bare metal among the graphitic islands. The combined use of AES and LEED was essential for this understanding.

Since we are interested in the relationship between surface properties and their chemical behavior, a "chemical probe" is most useful for examining the surface. The study of gas adsorption/desorption behavior provides this link between studies of surface composition and structure and the kinetics and mechanism of surface reactions. The quantitative study of these phenomena is accomplished with high-resolution flash desorption spectroscopy (FDS).¹¹

With FDS a surface is pre dosed with a desired quantity of gas. The adsorbed species are then evolved into the evacuated region when the surface is progressively heated in ultrahigh vacuum. Roughly speaking, desorption into the gas phase occurs at a temperature, T_p , which is proportional to the activation energy ($E_a \sim T_p/16$ kcal/mol). Provided the rate of removal of the desorbing species from the gas phase is sufficiently high, the partial pressure pulse formed during the product evolution yields directly the rate of surface reaction as a function of temperature. The information contained in this flash desorption peak characterizes the reaction order, n , activation energy, E , and preexponential factor, ν , for the surface reactions occurring during the heating process.¹²

Several analytical approaches are available for the accurate evaluation of n , E , and ν . For isolated peaks resulting from a single reaction channel, the activation energy can best be measured by plotting $\ln \beta/T_p^2$ vs. $1/T_p$, where β is the linear heating rate and T_p is the temperature of the flash peak. The slope of such a plot equals (E/R) . With the activation energy and reaction order determined, the value of ν can be calculated from the peak temperature or peak width at half-maximum. Figures 3 and 4 illustrate this method for the simple desorption of CO from Ni(110). The shift of T_p to lower temperatures with increasing β is shown in Figure 3. The activation energy given by the slope of the plot in Figure 4 for this first-order reaction was 32.2 kcal/mol. The preexponential factor was $8.5 \times 10^{15} \text{ s}^{-1}$; this value is significantly larger than 10^{13} s^{-1} due to the increased entropy of the transition state. Such large preexponential factors are typical of these unimolecular processes which do not form cyclic transition states. This effect is highly reminiscent of the "abnormally" high preexponential factors observed for gas-phase unimolecular reactions which are, of course, now viewed as normal.

(5) E. N. Sickafus, *J. Vac. Sci. Technol.*, **11**, 299 (1974).

(6) J. T. Grant and T. W. Haas, *Surf. Sci.*, **24**, 332 (1971).

(7) J. P. Coad and J. C. Riviere, *Surf. Sci.*, **25**, 609 (1971).

(8) R. C. Pitkethly, "Chemisorption and Catalysis", Institute of Petroleum, London, 1970, 00 107-108.

(9) T. W. Haas, J. T. Grant, and G. J. Dooley in "Adsorption Desorption Phenomena", F. Ricca, Ed., Academic Press, New York, 1972, p 359.

(10) J. G. McCarty and R. J. Madix, *J. Catal.*, **48**, 422 (1977).

(11) D. Menzel, *Top. Appl. Phys.*, **4**, 1 (1975).

(12) J. Falconer and R. J. Madix, *Surf. Sci.*, **48**, 393 (1975).

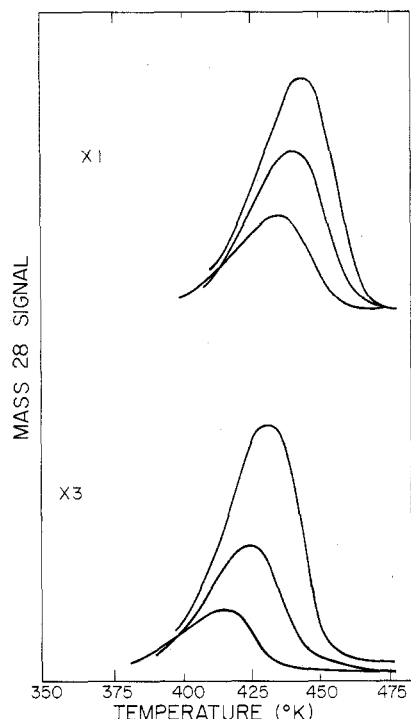


Figure 3. Flash desorption curves for CO/CO from Ni(110) at various heating rates β . The peak temperature moves to lower values with decreasing β .

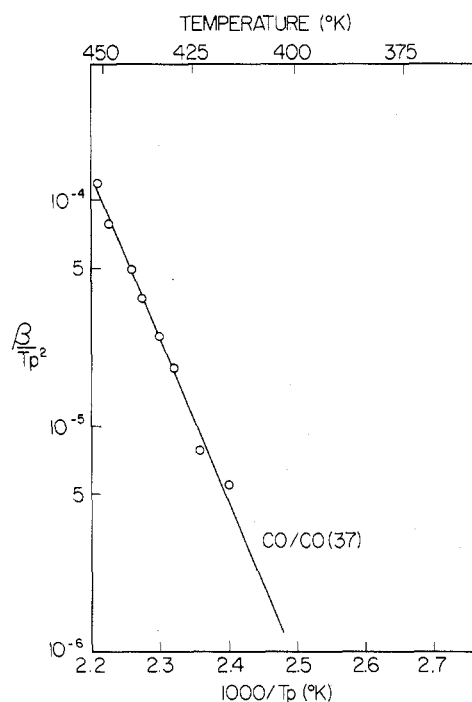


Figure 4. Plot of $\ln \beta/T_p^2$ for the curves of Figure 5. The slope of the straight line is E/R .

With these methods for study of the effects of surface composition and structure on surface reactivity at hand, we have been able to investigate the effects of surface structure and composition on a wide variety of reactions. A few illustrative examples are now presented.

Adlayer Effects

The addition of "foreign atoms" to the surface of a metal may have profound effects on the chemical nature of the surface. Qualitatively speaking, the adlayer may (a) act to form a new compound with characteristics

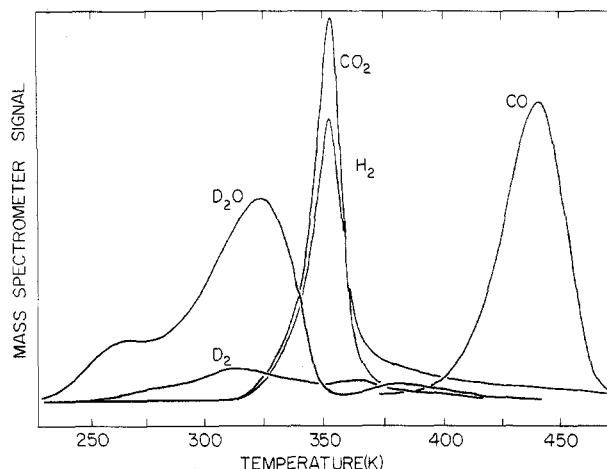


Figure 5. The temperature-programmed reaction spectrum for products resulting from HCOOH adsorption and decomposition on clean Ni(110).

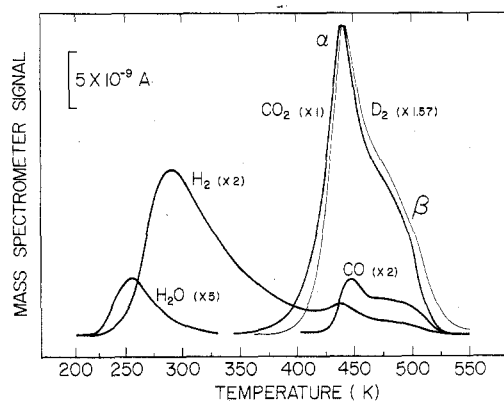
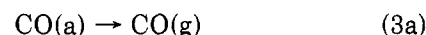
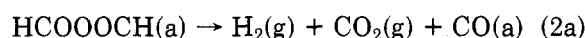


Figure 6. The temperature-programmed reaction spectrum for products resulting from DCOOH adsorption and decomposition on Ni(110) (2x1)C.

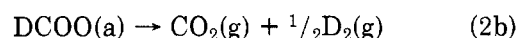
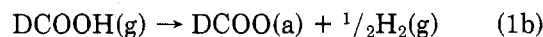
distinctly different from the metallic surface, (b) act as a ligand to the metal, causing only minor changes in chemical behavior of the metal, or (c) affect surface bonding by blocking or otherwise altering the accessibility of binding sites. These effects are now discussed with special attention to the adsorption and decomposition of formic acid.

The effects of adding carbon to the (110) surface of nickel on the decomposition of adsorbed formic acid are summarized in Figures 5 and 6 and in Table I. These figures show the rate of product evolution as the surface was heated for the Ni(110) and Ni(110) (2x1)C surfaces, respectively. This molecule, when adsorbed, decomposed via the competing pathways¹³⁻¹⁶ of mechanisms A and B.

Mechanism A



Mechanism B



(13) J. G. McCarty, J. Falconer, and R. J. Madix, *J. Catal.*, **30**, 235 (1973).

(14) J. G. McCarty and R. J. Madix, *J. Catal.*, **38**, 402 (1975).

(15) S. W. Johnson and R. J. Madix, *Surf. Sci.*, **66**, 189 (1977).

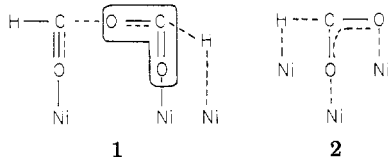
(16) D. H. S. Ying and R. J. Madix, to be published in *J. Catal.*

Table I
Kinetic Parameters for CO₂/HCOOH from
Different Surfaces

surface	E_{app} , kcal/ mol	A_{app} , s ⁻¹	T_p , K	intermediate
Ni(110) (clean)	26.6	2×10^{15}	~370	anhydride
Ni(110) (2 × 1)C	25.5	5×10^{12}	~430	HCOO
Ni(110)O	N.D.	N.D.	~440	HCOO
Cu/Ni(110)- (65/35)	27.6	N.D.	~400	HCOO
Cu(110)	31.9	1×10^{14}	~475	HCOO

The evolution of only D₂O (with no H₂O) at low temperatures subsequent to HCOOH adsorption on Ni(110) at 200 K (notation: D₂O/HCOOH(200)) shown in Figure 5 clearly indicated the occurrence of reaction 1a of mechanism A on this surface. The simultaneous formation of H₂ and CO₂ at 375 K resulted from reaction 2a, and CO was evolved by the sequence of steps 2a and 3a, with 3a rate determining. On the Ni(110) (2×1)C surface, however, reaction 1a occurred only to a minor extent, and reaction path B predominated, as shown by the formulation of H₂ and D₂ at 300 and 450 K from DCOOH (Figure 6). The presence of carbon effected a total change in the stable intermediate formed upon adsorption.

Of further significance is that the value of T_p increased by 60 K on the carbide surface, indicating a much less active surface. From Table I this decrease in reactivity can be seen to be due to a decrease in the preexponential factor of 10² on Ni(110) (2×1)C relative to the clean surface. The large value of A_{app} for the Ni(110) surface probably stemmed from a large gain in the entropy of the transition state in the formation of CO₂, since the cyclic transition state 1 splits out a nearly



free CO₂ molecule with considerable rotational entropy. For reaction 2b, however, the transition state probably involves a cyclic intermediate with bonding of both oxygen atoms to the surface, as in structure 2, resulting in appreciably lower values of the activation entropy.

The effect of a chemilayer of oxygen was dramatically different from that of carbon for oxygen coverages below a monolayer, exhibiting true ligand effects. As shown in Figure 7 the fractional oxygen coverage on the surface was varied from zero in curve a to 0.5 in curve b. Corresponding to curve b a (2×1) LEED pattern identical with the (2×1) carbide structure in Figure 1c was observed. The effect of oxygen was initially to *perturb* the clean surface behavior (shift the major peak) while simultaneously introducing a new reaction pathway, evidenced by the broad shoulder growing in at moderate oxygen coverages. The presence of this sharp peak was very structure sensitive.¹⁷ Since this peak shifted gradually with oxygen coverage, it appears that adsorbed oxygen acted as a ligand to the binding sites for the adsorbed intermediate to modify the re-

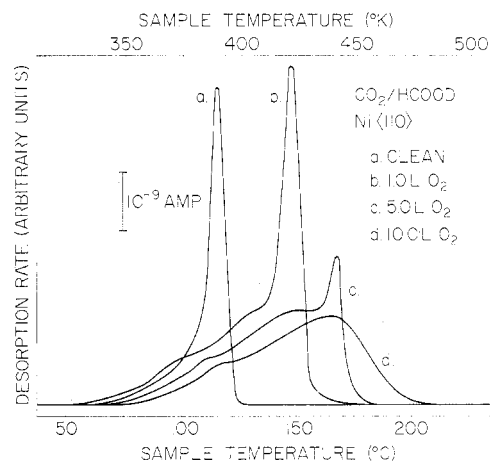


Figure 7. The temperature-programmed reaction spectrum for CO₂ resulting from HCOOH adsorption and decomposition on Ni(110)O with varying amounts of oxygen.

activity of the Ni(110) surface for reaction 1 above. Evidence due to Brundle¹⁸ and Norton¹⁹ from XPS indicating two forms of surface oxygen, one of which appears NiO-like, supports this view. Presumably the broad CO₂ peak was the result of decomposition on the true oxide, as it predominated at high oxygen coverages.

The behavior of these "compound surfaces" is somewhat analogous to the effects we have observed with bimetallic alloys. In this respect it is interesting to compare the chemical behavior of the Ni(110) and Ni(110) (2×1)C surfaces to the behavior of Cu(110) and surface alloys of copper and nickel. As shown in Table I, the formate intermediate forms on Cu(110) and on a Cu/Ni alloy surface of 65% copper composition. Since the temperature at the maximum of the flash peak roughly characterizes the relative rates, R , of decomposition on the various surfaces (lower temperature implies a faster reaction), it is immediately apparent from Table I for Ni(110) that $R_{clean} > R_{Cu/Ni} > R_{carbide}$. The surface composition of the alloy was 65% Cu/35% Ni.

Further studies revealed that the rate of decomposition on Cu(110) was similar though somewhat slower than that on Ni(110) (2×1)C.¹⁶ There is then a clear progression from the properties of clean nickel toward that of copper, as copper or *carbon* was added to the nickel surface. The incorporation of these atoms into the surface stabilized the adsorbed HCOO intermediate at the expense of a formic anhydride intermediate on the Ni(110) surface.²⁰ The decrease in the relative rate of CO₂ formation from HCOO on Cu/Ni(110), Ni(110) (2×1)C, and Cu(110) probably reflected a decrease in the strength of hydrogen bonding of the formate intermediate to the surface in traversing the series, causing a weaker perturbation of the bonds within the adsorbed intermediate and an increase in the activation as the surface became more copper-like. The difference in intermediates formed on these surfaces was also reflected in the CO₂/CO ratio evolved from each surface due to the respective decomposition steps 1a–2b above.

Since copper and nickel form a homogeneous solution and the Cu/Ni surface composition is easily varied, the number of nickel atoms in a cluster necessary to sta-

(17) J. Falconer and R. J. Madix, *Surf. Sci.*, **46**, 473 (1974).

(18) C. R. Brundle and A. F. Carley, *Chem. Phys. Lett.*, **31**, 423 (1975).

(19) P. Norton et al., *Surf. Sci.*, **65**, 13 (1977).

(20) D. H. S. Ying and R. J. Madix, *Inorg. Chem.*, **17**, 1103 (1978).

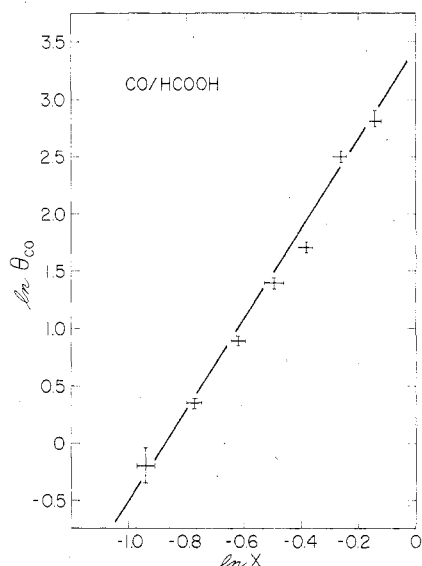


Figure 8. A plot of the amount of CO formed via the HCOOOCH intermediate on Cu/Ni alloy surfaces as a function of the alloy surface composition.

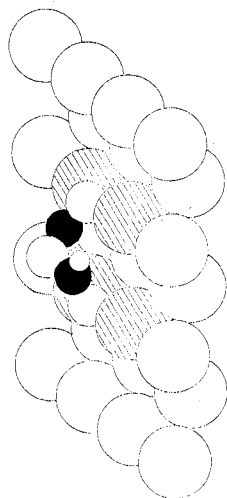


Figure 9. Schematic drawing of adsorbed HCOOOCH on Cu/Ni(110). Large open circles, copper atoms; medium open circles, oxygen atoms; small open circles, hydrogen atoms; shaded circles, nickel atoms; dark circles, carbon atoms.

bilize the formic anhydride could be measured. This conclusion follows from the consideration that the chance of forming a cluster or ensemble of n nickel atoms on the surface varies as x_{Ni}^n , where x_{Ni} is the surface nickel atom fraction. By varying the annealing temperature of a 90% Ni bulk alloy following ion bombardment of the surface, we obtained surfaces of varying Cu/Ni ratio.²¹ The CO/CO₂ product ratio decreased smoothly from unity to zero as the surface nickel concentration decreased. Since Cu(110) did not stabilize the anhydride nor produce CO, CO was formed from the anhydride adsorbed on nickel sites only by reaction 2a.

The log-log plot of the amount of CO formed against the surface nickel concentration (determined by AES), shown in Figure 8, has slope 3.9 ± 0.1 , indicating that four nickel atoms were necessary to stabilize the anhydride. This intermediate is believed to sit as shown in Figure 9. Rotation of the anhydride about the

Table II
Adsorption Characteristics of Different Surfaces
for Simple Gases^a

surface	active adsorption, $S_0 > 0.1, N_{sat} > 10^{14} \text{ cm}^{-2}$
Ni(110)	CO, H ₂ O*, H ₂ , CO ₂ , HCOOH
Ni(110) (2 × 1)C	CO, H ₂ O*, HCOOH
Ni(110) (2 × 1)O	CO, H ₂ O*, HCOOH
Cu/Ni(65/35)(110)	CO*, H ₂ O*, HCOOH, H ₂ , CO ₂
Cu(110)	CO*, H ₂ O*, HCOOH
Ni(110) graphite	HCOOH*

^a * indicates a very weakly bound state.

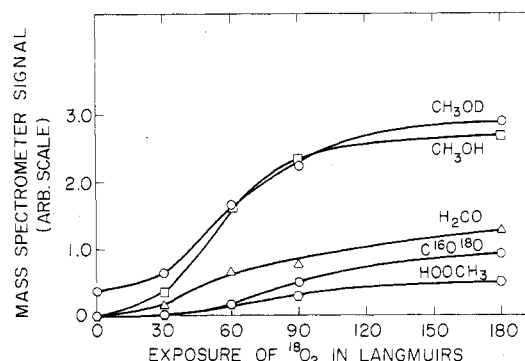


Figure 10. The dependence of the amount of CH₃OD adsorbed and oxidation products H₂CO and C¹⁶O¹⁸O on the surface oxygen concentration on Cu(110).

C-O-C single bond places the carboxylic oxygen directly above the bridging positions along the (10) directions. These are the sites calculated from LEED intensity measurements by Demuth et al. which are preferentially occupied by adsorbed oxygen atoms.²²

Shortening the distance between adjacent close-packed rows would severely strain this intermediate. Indeed more cracking of the anhydride intermediate to produce surface oxygen was observed on the Ni(100) surface.^{23,24} The detailed interpretation of the complex geometry may need further refinement, but there can be no doubt that a small cluster of nickel atoms is necessary to stabilize this intermediate. It should be apparent that a wide variety of alloy systems and reactions are subject to this type of study.

The ability of these surfaces to adsorb molecular species from the gas phase is illustrated in Table II. The surfaces were grouped qualitatively into "active" and "inactive". Those surfaces which exhibited an adsorption probability of 0.1 or greater and saturation coverages of greater than one molecular species per 10 metal atoms were termed active for that particular gas, and conversely. The dissociative adsorption of both H₂ and CO₂ was very sensitive to surface composition. The presence of surface oxygen or carbon completely removed the reactivity of the surface for dissociative adsorption. It is evident that the adlayers often effected changes in the chemical reactivity of the surface by orders of magnitude.²⁵

As a final example of an effect that an adlayer can have on the chemical reactivity of surfaces, we consider the effect of oxygen on the dissociative adsorption of

(22) P. M. Marcus, J. E. Demuth, and D. W. Jepsen, *Sur. Sci.*, **53**, 501 (1975).

(23) Recent unpublished work by Lee and Aldag has revealed a difference in the surface reaction for Ni(100).

(24) J. B. Benziger and R. J. Madix, *Surf. Sci.*, **79**, 394 (1979).

(25) J. G. McCarty and R. J. Madix, *Surf. Sci.*, **54**, 121 (1976).

methanol on a silver single-crystal surface.²⁶ On the clean surface, methanol, in the form of CH₃OD, adsorbed nondissociatively with a binding energy of about 12 kcal/mol; no bond-breaking occurred. With the preadsorption of isotopic oxygen, on the other hand, dissociative adsorption to form a surface methoxide and D₂¹⁸O occurred. The development of the amount of each product with increasing preexposure to ¹⁸O₂ is shown in Figure 10 (1 langmuir = 10⁻⁶ torr/s). Clearly surface oxygen was *necessary* for product formation, even though most of the products did not contain isotopic oxygen. The adsorbed surface oxygen induced the dissociative adsorption, acting as a chemical switch. This induced chemical reactivity may be due to the energy gained in forming the ¹⁸O-H bond with the surface oxygen which is a much stronger bond than the hydrogen silver bond. This effect is a dramatic one in which an adsorbed species provides a reaction pathway inaccessible and disfavored by the clean surface. In this case the surface methoxide determines the chemistry of alcohol oxidation.

Concluding Remarks

The effect of adsorbed layers on the surface reactivity of metals is pronounced and varied. Commonly, structured overlayers may reduce the dissociative adsorption probabilities of simple gases such as H₂ and CO₂ by several orders of magnitude. Except in a few

(26) I. E. Wachs and R. J. Madix, *J. Surf. Sci.*, **76**, 531 (1978).

cases^{27,28,29} the effect of surface composition on reactivity is much larger than reported effects of surface structure, particularly for hydrogen adsorption.³⁰ Adsorbed overlayers can manifest chemical changes by (a) preferentially stabilizing certain intermediates, (b) acting as ligands to surface complexes, (c) changing surface distributions of active clusters which stabilize reactive intermediates, (d) providing greatly different accessible reaction pathways which actually switch on reactive behavior on otherwise passive surfaces and (e) selectively inhibiting the dissociative adsorption of simple molecules. Examples of each case have been presented above.

The simple conclusion must be drawn that the surface is a dynamic participant in heterogeneous processes. Its composition plays a determining role in the chemistry observed.

I wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF-MRL Program through the Center for Materials Research at Stanford University for support of this work. I also thank my collaborators for their many invaluable contributions to the development of this subject and Tina Bellandi for help with the manuscript preparation.

(27) S. P. Singh-Boparai, M. Bowker, and D. A. King, *Surf. Sci.*, **53**, 55 (1975).

(28) C. R. Helms, H. P. Bonzel, and S. Keleman *J. Chem. Phys.*, **65**, 1773 (1976).

(29) W. Erley and H. Wagner, to be published.

(30) K. E. Lu and R. R. Rye, *Surf. Sci.*, **45**, 677 (1974).