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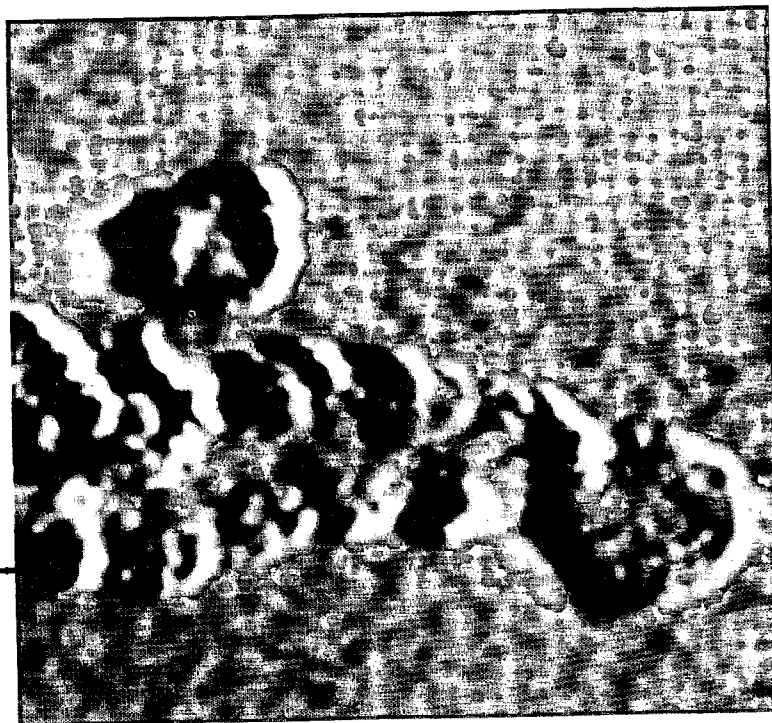
CAM

ANNUAL REPORT

1989

Surface Science and Catalysis

Catalyst Design, Characterization and Applications
Surface and Interface Compounds • Instrumentation for Surface Science



Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California

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Center for Advanced Materials

Annual Report • 1989

SURFACE SCIENCE AND CATALYSIS

G.A. Somorjai, Program leader
M.B. Salmeron, A.T. Bell, J. Clarke, Project leaders

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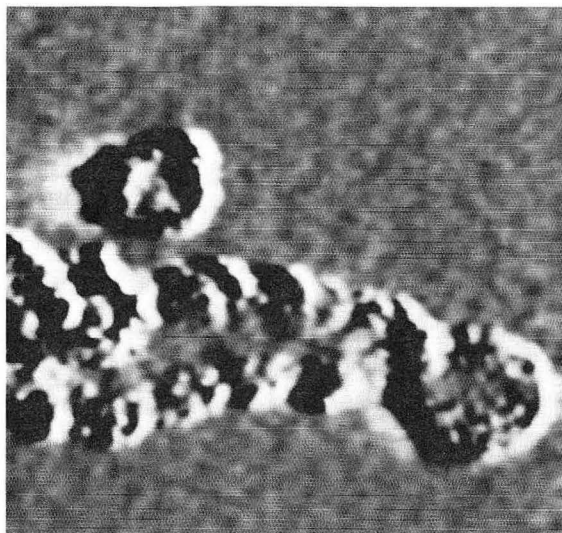
Cover and page 3: Strands of uncoated DNA deposited on graphite and imaged by the STM.

Surface Science and Catalysis

The CAM Surface Science and Catalysis program pursues interdisciplinary, basic research studies of surface and interface materials, phenomena, and processes at the molecular level. The research is focused on the chemical and mechanical properties of surfaces and on the development of new surface instrumentation to permit atomic level characterization of interfaces. Current research focuses on three areas.

The aim of the *CATALYST DESIGN, CHARACTERIZATION AND APPLICATIONS PROJECT* is to develop a fundamental understanding of the factors governing synthesis and performance of catalysts for a variety of processes. The focus is on the synthesis and characterization of novel microporous materials, including zeolites and transition metal nitrides, carbides, and oxides; the preparation and characterization of single-crystal, model catalysts; and the investigation of the fundamental aspects of the hydrogenation of CO and char gasification. Recent research results include several new findings:

- Cobalt-modified molybdenum surfaces have been found to be more reactive when stepped than when flat, showing structure sensitivity.
- A methodology has been discovered to prepare metal-oxide interfaces by deposition of crystalline monolayers of oxide on metal substrates.
- A powerful automated directed search method has been developed for surface structure determination by low-energy electron diffraction.
- Studies of Cu-containing catalysts have established that Cu^0 and Cu^+ sites are required for methanol synthesis and that Cu^+ sites are stabilized at the adlineation between metallic Cu and basic metal oxides.
- In collaboration with Mobil Research and Development Company, it was discovered that TPA^+ cations form silicate cages containing 22 Si atoms during the initial stages of Zsm-5 synthesis.
- In collaboration with Kodak Research Laboratories, it has been established that the BOC-MP approach provides a realistic description of the energetics of formic acid decomposition on Ag(111), Ni(111) and Fe/W(110) surfaces.



The *SURFACE STRUCTURE AND INTERFACE COMPOUNDS* project consists of three closely-linked efforts. The objective of the *Surface Structure and Bonding* group is the development of the molecular science of surface phenomena by means of the understanding of atomic-scale surface structure and chemical bonding of adsorbed monolayers and thin film coatings and their interfaces; the *Coatings* effort produces surface films that impart novel mechanical properties (scratch resistance, hardness) and chemical properties (protection against corrosion, diffusion barriers) to the substrate; the *Surface Compounds* effort involves studies on submonolayers of atomic and molecular adsorbates, as well as metal oxides (TiO_2 , Al_2O_3 and FeO), which can modify the chemical and mechanical properties of metal surfaces.

During the past year:

- STM images of native, uncoated collagen revealed a periodic structure with a 30Å repeat distance.
- The structure effect of repulsive close-range intermolecular interactions has been observed in densely adsorbed monolayers.
- It was found that the hardness of amorphous carbon films grown *in situ* from a plasma could be controlled by variation of the power supplied by the ions.

The *INSTRUMENTATION FOR SURFACE SCIENCE* project is concerned with the development of new techniques and instruments for the study of surfaces. These include the scanning tunneling (STM) and atomic force (AFM) microscopes, nonlinear optical techniques, laser and electron spectroscopies, and low energy electron (LEED) diffraction. A surface analysis facility that provides service for the entire division is also part of this project. During the past year:

- An atomic force microscope with a microfabricated cantilever spring and tip has demonstrated atomic resolution.
- Unenhanced surface Raman spectroscopy was used as a vibrational probe of physisorbed and chemisorbed molecules and films on a variety of surfaces from 14 K to well above room temperature.

CATALYST DESIGN, CHARACTERIZATION AND APPLICATIONS MICROPOROUS CRYSTALLINE MATERIALS

Zeolite Synthesis

A.T. BELL, C. CHANG*, D. M. GINTER, W. M. HENDRICKS, R. MORTLOCK

Zeolites are widely used in industry as catalysts for petroleum processing and chemical synthesis. The aim of this project is to understand the chemical and physical transformations occurring during the synthesis of zeolites from highly alkaline aqueous gels and the function of these processes in determining the structure and composition of the zeolites formed. These questions are being pursued through the use of such modern spectroscopic techniques as nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, x-ray diffraction, and electron microscopy, some of which were specifically modified for these studies at CAM.

In research supported in part by W.R. Grace and Company, studies were carried out to characterize the reactions of well defined silicate anions with aluminate anions. Aluminum wire was dissolved in a tetrapropyl ammonium silicate solution, and the resulting reactions between aluminate and silicate anions were followed by ^{29}Si and ^{27}Al NMR spectroscopy. The aluminate anions were found to react preferentially with low-molecular-weight silicate anions to form aluminosilicate anions. These reactions cause an imbalance in the equilibrium distribution of silicate anions and cause a depolymerization of higher-molecular-weight oligomers to replace the low-molecular-weight oligomers lost by reaction with aluminate anions. ^{27}Al NMR spectroscopy reveals that after reaction, most of the aluminum is present in aluminosilicate structures. The predominant structures are those in which an aluminum atom has one or two nearest neighbor silicon atoms. No evidence was found for isomorphic substitution of aluminum for silicon in preformed single- or double-ring silicate structures. These results indicate that larger aluminosilicate structures are built up by reaction of aluminate anions with small silicate anions.

In a collaborative study with C. Chang of Mobil Research and Development Corporation, the synthesis of ZSM-5 was investigated as a function of time using ^{29}Si NMR spectroscopy and other techniques. Immediately upon preparation, most of the silicon in the synthesis gel was found to be in Q_4 environments, with a smaller proportion present in Q_3 environments. As synthesis proceeded, the proportion of silicon in Q_3 environments declined and an x-ray diffraction pattern characteristic of ZSM-5 could be observed. Ion exchange experiments revealed that shortly after the onset of heating, a ratio of 22 silicon atoms per TPA^+ cation was established. This ratio was then maintained until all of the synthesis gel had been converted to crystalline zeolite. The observed Si/TPA^+ ratio can be attributed to the formation of silicate cage structures around each TPA^+ cation.

* CAM Industrial Fellow, Mobil Research and Development Corporation.

Transition Metal Nitrides and Carbides

P. A. ARMSTRONG, K. S. LEE, A.T. BELL, J. A. REIMER

Transition metal nitrides and carbides, such as Mo_2N , Mo_2C , W_2C , and WC , have been shown to be effective catalysts for a variety of reactions, including CO hydrogenation, olefin hydrogenation, hydrocarbon reforming, ammonia synthesis, and hydrodenitrogenation (HDN). The transition metals are cheaper and more abundant than the noble metals which are now used for the above reactions. Little is known about the reaction chemistry on these nitrides and carbides, however. The aim of this research is to study the surface chemistry of $\gamma\text{-Mo}_2\text{N}$ during representative hydrodenitrogenation reactions. The HDN reaction is important in the refining of petroleum to produce cleaner-burning fuels.

NMR spectroscopy has previously been shown by this group to be an effective technique for identifying surface species on $\gamma\text{-Mo}_2\text{N}$. In particular, adsorbed ammonia, carbon monoxide, hydrogen, and acetonitrile have been studied successfully by NMR spectroscopy. These investigations have laid the groundwork for continuing studies of adsorbed nitrogen heterocycles, such as pyridine and quinoline, and the species formed from these reactants during HDN. The selectivity of an HDN catalyst is determined by the ability of the catalyst to promote hydrogenation of only the heterocyclic rings of nitrogen heterocycles, and not other aromatic rings or olefinic groups. Experiments are currently in progress to observe per-deuterated quinoline adsorbed on $\gamma\text{-Mo}_2\text{N}$ to establish the mode of bonding and the motion of the adsorbate. These experiments will then be extended to observe the effects of hydrogenation. Model compound studies of HDN over high surface area $\gamma\text{-Mo}_2\text{N}$ have also been initiated recently.

Supported Vanadia

G. T. WENT, M. S. WENT, J. A. REIMER, A.T. BELL, S.T. OYAMA, K.B. LEWIS, G.A. SOMORJAI

Oxide catalysts are used for oxidation reactions that account for more than 25% by volume of the top 20 chemicals produced worldwide. Their use to catalyze NO_x and SO_x reductions will increase in the US in the next few years as more stringent air pollution laws are enacted. Until recently most of these oxide catalysts, consisting of transition metal oxides in bulk or supported on other oxides (i.e., $\text{V}_2\text{O}_5/\text{TiO}_2$), have been designed empirically. Many efforts have now been initiated to characterize the catalyst and to understand on an atomic scale the mechanisms by which they catalyze specific reactions. Specifically, spectroscopic studies have been aimed at understanding how surface geometry affects activity and selectivity, the structure of the catalyst on the support and how it is affected by dispersion, and the mechanism by which the support affects activity and selectivity.

Raman and NMR spectroscopy are being used to characterize the geometry and dynamics of several small molecules adsorbed on supported vanadia catalysts. ^1H , ^{15}N , and ^{17}O NMR spectroscopy are being used to study NH_3 and NO on $\text{V}_2\text{O}_5/\text{TiO}_2$ in an attempt to understand the catalytic chemistry of NO reduction. Raman spectroscopy complements these studies. One goal of this work is to observe reaction dynamics by detecting oxygen exchange between adsorbed species and oxygen in the catalyst.

Oxygen Chemisorption and Laser Raman Spectroscopy of Unsupported and Silica-Supported Vanadium Oxide Catalysts

S.T. OYAMA, G.T. WENT, K.B. LEWIS, A.T. BELL, G.A. SOMORJAI

An oxygen chemisorption method was developed for measuring the active surface area of supported and unsupported V_2O_5 following reduction in hydrogen. It is shown that to achieve complete reduction of the vanadia surface without reducing the bulk, reduction must be carried out at 640K. Oxygen uptakes of unsupported samples reduced at close to this temperature yield an oxygen atom site density of $3.2 \times 10^{18} \text{ m}^{-2}$, a value near that expected for a monolayer. The same oxygen-chemisorption technique is applied to silica-supported V_2O_5 . Laser Raman spectroscopy confirms that near 640K oxygen chemisorbs primarily at the surface of the dispersed vanadia, but does not exchange with the bulk of the oxide. For very low weight loadings, a limiting stoichiometry of one adsorbed oxygen atom per vanadium atom is obtained. This stoichiometry is used to calculate dispersions ranging from 93% to 50% for supported V_2O_5 samples of 0.3% to 9.8% weight loading.

CATALYTIC HYDROGENATION OF CO*

The purpose of this project is to develop an understanding of the fundamental processes involved in the catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors which limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. To meet these objectives, a variety of surface diagnostic techniques are used to characterize supported and unsupported catalysts before, during, and after reaction. The information is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation.

CO and CO₂ Hydrogenation Over LaMn_{1-x}Cu_xO_{3+λ} Perovskites and Related Catalysts

J. A. BROWN BOURZUTSCHKY, N. HOMS, A. T. BELL

CO hydrogenation was investigated over perovskites with the composition $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_{3+\lambda}$ ($x = 0, 0.2, 0.4, 0.5, 0.6, 1.0$); Cu supported on SiO_2 , unpromoted and promoted with La_2O_3 ; Cu supported on La_2O_3 and on $\text{MnO}_2/\text{La}_2\text{O}_3$; and unsupported Cu metal powder containing traces of sodium oxide (NaO/Cu). The $x = 0$ perovskite ($\text{LaMnO}_{3.24}$) is weakly active for CO hydrogenation, and produces only hydrocarbons, whereas all the other perovskites are more active and display > 90% selectivity to alcohols (80% methanol and 20% C_{2+} alcohols) (Figure 1). The C_{2+} alcohols follow a distribution characteristic of alkali-promoted copper catalysts. Cu/SiO_2 is > 80% selective to hydrocarbons, and < 5% selective to methanol. Introduction of La_2O_3 or NaO into the copper catalyst increases the CO hydrogenation activity and selectivity to alcohols. The activities and product distributions of the Cu-containing perovskites ($x > 0$) are similar to those of NaO/Cu and the La_2O_3 -containing catalysts, suggesting that the active sites in all of the catalysts are similar. It is proposed that

*This work was supported by the Division of Chemical Sciences.

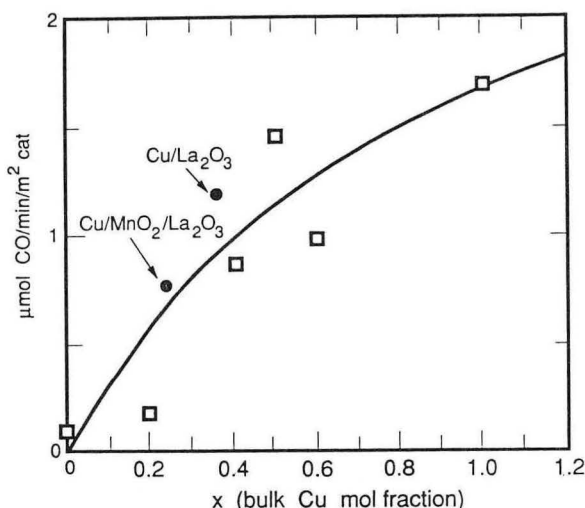


Figure 1
Correlation of CO hydrogenation activity with bulk Cu mole fraction, for perovskite (□) and lanthanum-supported (●) catalysts ($H_2/CO = 2$, $P = 10.6$ atm, $T = 573$ K). (XBL 901-332)

hydrocarbon synthesis occurs at Cu^0 sites, but that Cu^0 and Cu^+ sites are required for the synthesis of methanol and C_{2+} alcohols. It is also proposed that Cu^+ sites are stabilized at the adlineation between metallic copper and lanthana (or soda).

CO_2 hydrogenation was carried out over Cu/SiO_2 , $La_2O_3/Cu/SiO_2$, Cu/La_2O_3 , $Cu/MnO_2/La_2O_3$, and NaO/Cu powder. The major products are methanol and methane. Methyl formate was also produced at temperatures below 523K. In terms of oxygenate yield, the catalysts ranked in the order: $La_2O_3/Cu/SiO_2 > Cu/SiO_2 > Cu/La_2O_3 > Cu/MnO_2/La_2O_3 \gg NaO/Cu$. Lanthana promotion of Cu/SiO_2 increases the formation of methanol but not of the other products. The selectivity patterns of the lanthana-supported catalysts are similar to that of Cu/SiO_2 . Addition of Mn to Cu/La_2O_3 decreases the selectivity to methanol. Hydrogenation of CO_2/CO mixtures was studied over NaO/Cu , Cu/SiO_2 , and Cu/La_2O_3 (Figure 2). The NaO/Cu powder displayed higher selectivity to methanol in CO/H_2 than in CO_2/H_2 . The activity and selectivity to methanol decreased with increasing CO fraction over Cu/SiO_2 . Both activity and oxygenate selectivity increased with CO fraction over Cu/La_2O_3 . C_{2+} alcohols are produced in CO-rich atmospheres. The observed

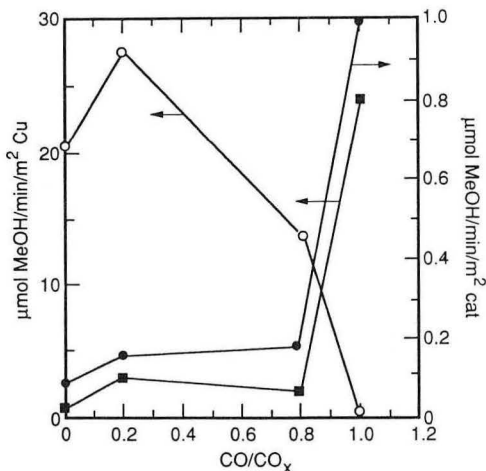


Figure 2
Hydrogenation of CO_2 and CO over copper catalysts: effects of CO/CO_x ratio on the methanol activity ($H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573$ K). (■) NaO_x/Cu , (○) Cu/SiO_2 , (●) Cu/La_2O_3 . (XBL 901-333)

effects of catalyst composition and feed composition on the activity and selectivity of Cu for methanol synthesis are attributable to the distribution of Cu^0 and Cu^+ sites.

SINGLE CRYSTAL CATALYSTS

Catalysis by Metals and Bimetallic Systems (Pt, Pt-Re, Fe, Mo, Mo-Co)

C. KNIGHT, M. VAN TOL, C. KIM, D. STRONGIN, G.A. SOMORJAI

Fundamental aspects of catalysis are investigated by the use of well-characterized single-crystal metal surfaces. Bimetallic surfaces are produced in ultra-high vacuum by deposition of a second metal. This procedure can generate a variety of bimetallic systems (Figure 3).

The *isomerization and hydrogenolysis of light alkanes* (ethane, n-hexane) were studied over platinum single crystal surfaces that were modified by the deposition of rhenium. The (111) face of platinum was used in most of these studies. The Pt-Re bimetallic system with one monolayer of ordered rhenium is a superior hydrogenolysis catalyst. The results suggest that a strong electronic interaction exists between the two metals that strongly influences the catalytic properties. The co-deposition of sulfur over the Pt-Re bimetallic system has been investigated in order to develop a Pt-Re-S model catalyst that was found to have superior activity and selectivity for dehydrocyclization in the petroleum refining technology. The sulfur surface coverage and hydrogenation rate have been determined over the bimetallic system in preparation for the catalytic hydrocarbon conversion studies.

The *reduction of NO by ammonia* has been studied over platinum as small area ($\sim 1\text{cm}^2$) foils and (111) orientation single crystals. Photo-ionization and gas chromatography were utilized to monitor the concentration of the reactants. The reaction occurs readily above 120°C . It is our aim to explore the activity of noble metal catalysts for this reaction, which has been usually carried out using vanadium oxide and titanium oxide, and to compare the rates and product distributions obtained for the metal and oxide systems.

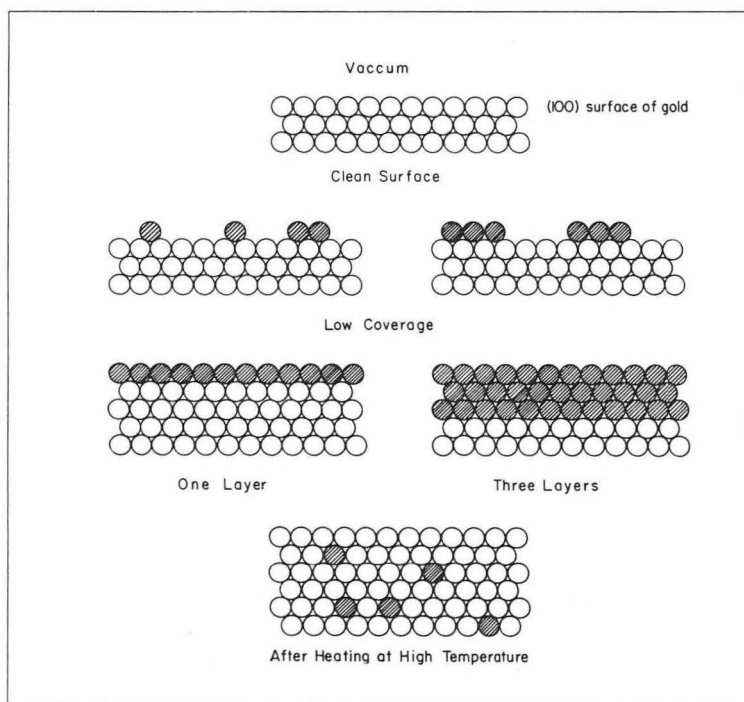
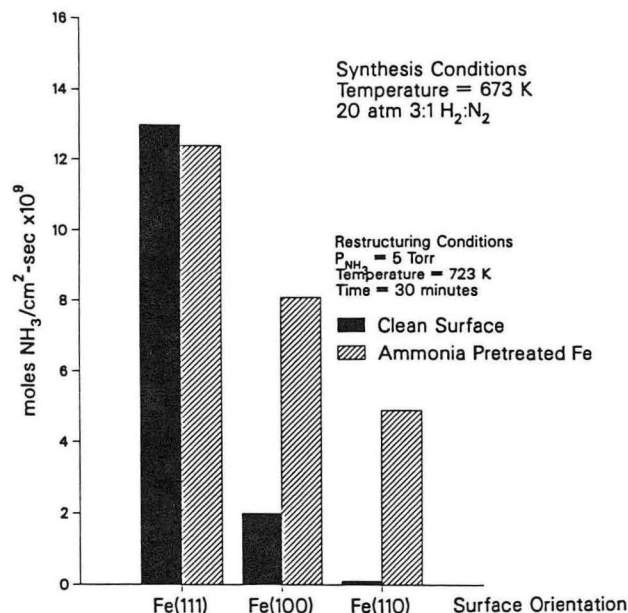


Figure 3
Different bimetallic growth modes are depicted, when one metal is deposited on a clean single-crystal substrate of another metal (shown on top panel). With increasing deposition, submonolayers become single and then multiple layers. At higher temperatures, an alloy may form. (XBL 7810-6070)

Figure 4

Comparison of ammonia synthesis over clean Fe single crystals and ones pretreated in ammonia prior to ammonia synthesis. Ammonia pretreatment restructures Fe(110) and Fe(100) to surfaces containing C_7 sites. Restructuring of Fe(111) has little change in ammonia synthesis activity. (XBL 8811-3901)



Molybdenum modified by the epitaxial deposition of cobalt was utilized for the hydrodesulfurization of thiophene to butenes and butane. Cobalt did not improve the reaction rate when it was deposited on the Mo(100) crystal face. However, when a stepped molybdenum single crystal was used, the deposition of less than a monolayer of cobalt increased the reaction rate over that of clean Mo. The formation of a Mo-Co compound at the stepped surface is indicated, which has superior catalytic activity. The roles of sulfur and carbon, which deposit during the reaction over the bimetallic interface, are being explored by pre-sulfiding or pre-carbiding the bimetallic system. We aim to prepare a Mo-Co-S catalyst to model one that has been found superior for the HDS reaction in petrochemical technology.

Effects of Ammonia Pretreatment on the Structure and Activity of Iron Single Crystal Surfaces for Ammonia Synthesis

D.R. STRONGIN, G.A. SOMORJAI

Treatment of the (110), (100), and (111) planes of iron with 5 Torr or 50 Torr of ammonia (at 723K for 30 minutes) causes surface restructuring, as evidenced by changes in ammonia synthesis activity (20 atm total pressure), temperature programmed desorption and the appearance of new surfaces as seen by scanning electron microscopy (Figure 4). The Fe(110) and Fe(100) surfaces are restructured to surfaces containing C_7 sites, such as Fe(111) and Fe(211). A stereographic analysis of the restructured Fe(111) surface, using scanning electron microscopy, taken together with the reaction rate measurements, suggest that (211) surface planes are formed upon ammonia treatment. The high concentrations of near-surface nitrogen that is deposited by the ammonia pretreatment does not block catalytic sites for the synthesis of ammonia. The presence of aluminum oxide on any of the iron single crystal surfaces inhibits the ammonia induced restructuring process, while the presence of potassium has no observable effect on the process. These results suggest a method of activating iron with both ammonia and water vapor restructuring in the presence of aluminum oxide and potassium to achieve a catalyst with optimal activity for ammonia synthesis.

CATALYSIS BY OXIDES AND METAL-OXIDE INTERFACES

Oxides are usually insulating materials and in many cases they are utilized in amorphous or polycrystalline form. To study the surfaces of such materials, and in particular, to study the structure and chemical properties of metal-oxide interfaces, we have developed a new methodology for sample preparation (Figure 5). In this method, single crystalline thin oxide films of Fe_2O_3 , V_2O_5 , Cu_xO , TiO_2 , Al_2O_3 and ZrO_x are deposited by the condensation and subsequent oxidation of a metal monolayer to build up the oxide thin film layer by layer. The substrate is usually a single crystal face of a noble metal, such as Rh, Pt, Au, etc. This method permits the control of the surface structure and composition of the growing oxide film.

This approach allows the use of electron spectroscopies that necessitate conductive substrates for their proper operation. It also enables one to change the physical properties of the oxide (crystalline structure, stoichiometry) and to study the interface with the metal substrate.

Preparation and Reactivity of Thin, Ordered Films of Iron Oxide on Platinum

G. VURENS, M. SALMERON, G.A. SOMORJAI

Iron oxide has been grown on Pt(111) and Pt(100) in a two-dimensional fashion, at least for the first atomic layer. A combination of auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD) was used to study these iron oxide overlayers. AES shows that the stoichiometry of the iron oxide is approximately $\text{Fe}:\text{O} = 1:1$, and XPS shows that the iron is in the Fe^{2+} oxidation state. However, the overlayer on Pt(100) contains less oxygen than the overlayer on Pt(111).

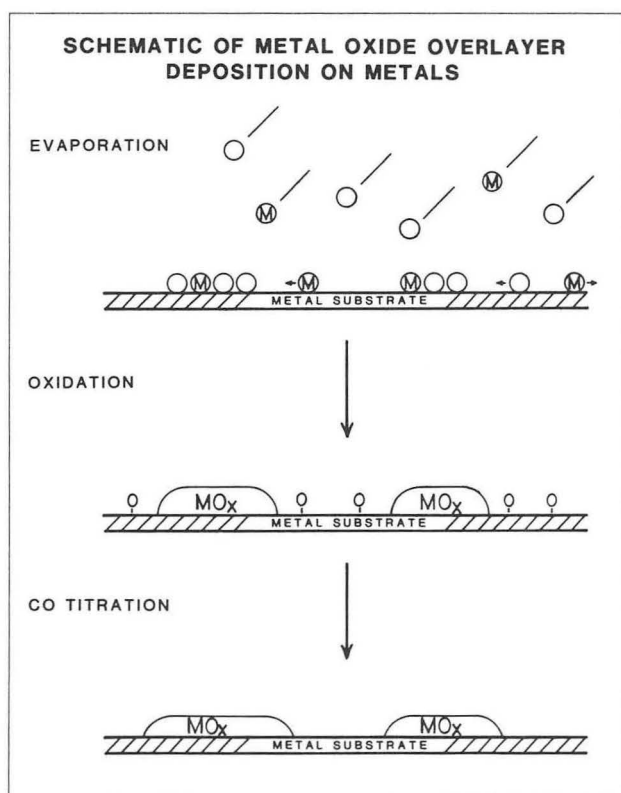
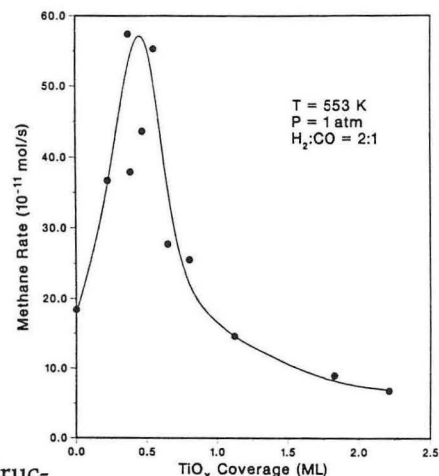


Figure 5
Thin metal oxide layers are grown on a metal substrate by deposition of evaporated metal, followed by oxidation and CO titration to remove excess oxygen. (XBL 8611-4263)

Figure 6
The rate of methane formation is shown on thin alumina layers deposited on a rhodium substrate, as a function of the oxide coverage on the surface.
(XBL 896-2171)



On both platinum surfaces the oxide overlayers form an ordered structure. An incommensurate overlayer is formed on the Pt(111) surface, while a $c(10 \times 2)$ structure is formed on the Pt(100) substrate.

The iron oxide overlayer on Pt(100) showed little reactivity towards water as determined with water TPD. Two desorption features were obtained, associated with a chemisorbed monolayer (190K) and a physisorbed multilayer (170K). The physisorbed multilayer shows zero order desorption kinetics, while the chemisorbed peak showed half order desorption kinetics. This is explained by desorption from the edges of two-dimensional water islands on the surface. The influence of sodium oxide overlayers on the iron oxide on Pt(111) and Pt(100) was studied. After heating to 850K, the two-dimensional overlayer on Pt(111) restructured (i.e., the overlayer formed three-dimensional crystallites), while on Pt(100) this restructuring did not occur.

Preparation and Reactivity of Thin, Ordered Films of Vanadium Oxide on Au(111)

K.B. LEWIS, S.T. OYAMA, G.A. SOMORJAI

Ordered vanadium oxide films can be grown on an Au(111) substrate. These films are formed when an evaporated layer of metallic vanadium is oxidized and annealed in UHV. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is observed for submonolayer to multilayer coverages of vanadium oxide on Au(111), and AES shows that the vanadium in the film is in the +3 oxidation state. Hydrogen, ethanol, and ethylene adsorption on the oxide films was studied with temperature-programmed desorption. Oxidized molecules (H_2O , CO, and CO_2) were the primary desorption products. Oxygen became more difficult to extract as the vanadium oxide film was reduced during successive TPD experiments.

Catalysis by Oxide-Metal Interface Systems ($Rh-TiO_2$, $Pt-Al_2O_3$, $Cu-ZnO$)

K. WILLIAMS, I. BÖSZÖRMENYI, S. FU, A.T. BELL, G.A. SOMORJAI

Oxide islands are deposited on single crystal surfaces or on polycrystalline foils of transition metals by depositing the metal from the vapor and subsequently oxidizing it. The surface coverage of the oxide is monitored by selective chemisorption, electron and ion spectroscopies (AES, ISS). The chemisorption and catalytic behavior of the oxide-metal systems is compared with that of the clean metal as a function of oxide coverage.

The hydrogenation of CO_2 to alkanes and the hydrogenation of acetone to isopropanol was studied over the $Rh-TiO_2$ system. A large enhancement in the reaction rate is observed at about one-half monolayer oxide coverage on the rhodium surface (Figure 6). The carbon-oxygen bond is being acti-

vated at the oxide-metal interface rather than the H-H bond, since hydrogenation of olefins and the hydrogenolysis of light alkanes are unaffected by the presence of the oxide. STM studies are being carried out to investigate the oxide-metal interface structure on the atomic scale. These studies explore the molecular ingredients of the so called strong metal-support interaction.

The isomerization of n-hexane and the ring opening of methyl-cyclopentane was investigated over the Pt-Al₂O₃ system. Enhanced isomerization activity has been detected in the presence of the oxide. The effect of chlorine as a reaction promoter when adsorbed on the oxide is being investigated. The purpose of these studies is to delineate the catalytic reactions that occur over the oxide and over the oxide metal interface as compared to the metal during petroleum refining to high-octane fuels.

The formation of methanol from CO and H₂ was explored over the Cu-ZnO system. The chemisorption properties of CO, H₂, CH₃OH, CO₂ and H₂O are markedly altered in the presence of zinc oxide. The existence of Cu_xZn_yO compounds at the interface could be detected. CO₂ only chemisorbs over the oxide while CO adsorbs on both Cu and ZnO. Our aim is to build a model catalyst that exhibits the same activity for methanol production as the Cu/ZnO system that is utilized in the chemical technology.

MODELING

Adsorbate-Induced Restructuring of Surfaces: Catalytic Implications

M.A. VAN HOVE, G.A. SOMORJAI

Chemisorbed atoms and molecules frequently restructure metal surfaces. Recent surface crystallography studies revealed the structural changes that occur on the atomic scale. The metal atoms relocate around the adsorbate accompanied by changes of bond distances and bond angles for both substrate and adsorbate. The restructuring may occur on the time scale of chemisorption ($\sim 10^{-3}$ seconds), of catalytic reactions (seconds) or by slower mass-transport (diffusion) controlled processes (days). Often, restructuring is necessary to create the catalytically active sites. Adsorbate-induced restructuring can explain the existence of classes of structure-sensitive and structure-insensitive reactions. Slow deactivation and regeneration processes observed and utilized in catalytic technologies can be interpreted as caused by adsorbate-induced restructuring.

*Analysis of Formic Acid Decomposition on Metal Surfaces by the BOC-MP Approach**

E. SHUSTOROVICH, A.T. BELL

The bond-order-conservation-Morse-potential (BOC-MP) approach, extended to treat the heat of chemisorption of bidentate species and of molecular radicals, has been used to analyze the energetics of formic acid decomposition at low coverages on Ag(111), Ni(111), and Fe/W(110) surfaces. These calculations project that on all three surfaces formate species are produced with a parallel formation of formyl plus hydroxyl species on Ni and Fe/W. Bidentate coordination of formate species is preferred over monodentate coordination, the energy difference increasing in the order Ag < Ni < Fe/W. The decomposition of formate species leads mainly to atomic hydrogen and CO₂ on Ag, whereas on Ni and especially on Fe/W, formate decomposition leads mainly to atomic oxygen and formyl species, the latter of which decomposes practically without activation to CO and atomic hydrogen. The findings of this study are in general agreement with experimental observation.

*This work was supported by the Division of Chemical Sciences.

Monte Carlo Simulation of Temperature-Programmed Desorption of Coadsorbed Species*

S. J. LOMBARDO, A.T. BELL

A Monte Carlo model has been developed for describing the temperature-programmed desorption of coadsorbed species from single-crystal surfaces. Interactions between the adsorbates and the metal surface as well as interactions between the adsorbates are taken into account using the bond-order-conservation-Morse-potential (BOC-MP) approach. The number, shape, and location of the peaks is found to be sensitive to the binding energy, coverage, and coordination of each coadsorbed species. The presence of a strongly bound coadsorbate on a bcc(100) surface is shown to shift the desorption spectrum for associative desorption of adsorbed atoms to lower temperatures. TPD spectra for the concurrent associative desorption of A atoms and the desorption of B molecules from a fcc(100) surface are of two types: in one case, both species exhibit new low-temperature features far removed from their pure component spectra (Figure 7); in the second case, only the species undergoing associative desorption display new spectral features. The simulated TPD spectra are in qualitative agreement with experimental results for H₂ coadsorbed with strongly bound atomic species on Mo(100) and Fe(100) surfaces as well as for CO and H₂ coadsorbed on Ni(100) and Rh(100) surfaces.

Directed Search Methods for Surface Structure Determination by LEED

P.J. ROUS, M.A. VAN HOVE, G.A. SOMORJAI

Conventional surface crystallography by low-energy electron diffraction (LEED) employs a trial-and-error search controlled at each step by a human being. This trial-and-error approach becomes very cumbersome and unreliable when it is applied to complex surfaces with a large number of unknown structural parameters. An automatic optimization procedure

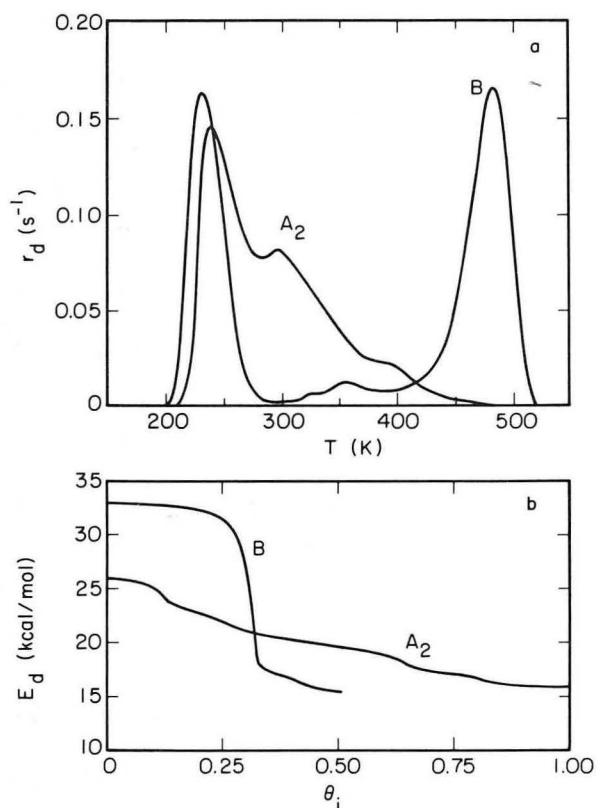


Figure 7
(a) Monte Carlo simulations of A₂ and B codesorption. (b) Variation of activation energy, E_d , as a function of adsorbate coverage. (XBL 897-2824)

*This work was supported by the Division of Chemical Sciences.

has been developed for LEED which combines the complementary techniques of Tensor LEED and a numerical search algorithm. This approach can reduce the computer time required for an entire structure determination by several orders of magnitude. It also allows all structural parameters to be found simultaneously; in particular, complex non-symmetric structures and adsorbate-induced substrate distortions can be readily determined. This method has been applied to the determination of the surface structures of clean Pd(111), and CO-covered Pd(111), as well as C- and S-covered Mo(100).

First-Principles Studies of Surface Structures and Properties

S.G. LOUIE, X.-W. WANG

First-principles studies are carried out to explain and predict the structures and properties of surfaces and chemisorption systems. Emphasis is on providing a microscopic understanding of the scanning tunneling microscopy (STM) images and the optical and photoemission spectra of systems of particular relevance to the experimental efforts in CAM. The theoretical methods employed include *ab initio* pseudopotential density functional calculations for ground-state properties and many-body quasiparticle calculations for excitation spectra. These methods allow accurate determination of solid state and surface properties from those of the atoms. Application to sulfur overlayers on Mo surfaces is reported under Surface Structure and Bonding.

Hydrogen Chemisorption on Diamond Surfaces

S.G. LOUIE, X.-W. WANG

We have initiated a project to investigate the properties of H chemisorption on the diamond (100) surface. The work is motivated by the observed differences in the behavior of this system from those of diamond (111) and other covalent semiconductor surfaces and by the current interest in the role of H in diamond film growth.

Hydrogen-Hydrogen Interactions in Palladium

S.G. LOUIE, X.-W. WANG, D. TOMANEK

The Pons-Fleischmann claim that cold fusion could occur in metal hydrides motivated our investigation of hydrogen interactions in and on palladium. Calculations have been carried out to evaluate the energetics and electronic structure of PdH_n where n is varied from 1 to 4. The interaction between a pair of hydrogen atoms in various locations in the Pd lattice was studied. This work was among the first to show that the separation between the hydrogens in Pd remained much larger than the value required for a significant fusion rate. The results, however, did indicate that, with a moderate chemical potential shift, a high density of hydrogen can be achieved inside the Pd crystal.

Dynamics of Deuterium Interstitials in Metals

K.B. WHALEY

Dynamics of atomic hydrogen and its isotopes in and on metals is dominated by quantum effects. Deuterium shows anomalous behavior in several instances, e.g., D/W(110) and D/Pd. We have developed a tight-binding theoretical approach to the coherent many-particle dynamics of strongly interacting tunneling particles, which is appropriate for analysis of deuterium dynamics at high concentrations. This model shows the marked effects of nuclear statistics in enhancing local site

density fluctuations for deuterium in small clusters of interstitial sites. This leads to a new type of screening of the deuteron-deuteron interaction, namely 'boson screening,' which has important consequences for deuterium dynamics at high concentrations. Application to the nuclear regime shows that finite temperature bosonic collective effects can enhance nuclear reaction rates involving deuterons in palladium deuterides. It is now being applied to the study of anomalous isotope effects for low temperature tunneling diffusion.

FUNDAMENTALS OF CATALYTIC GASIFICATION*

H. HEINEMANN, P. PEREIRA, G.A. SOMORJAI

It is the purpose of this project to achieve steam gasification of carbonaceous materials at temperatures below 1000K and to produce essentially only hydrogen and carbon dioxide and further to understand the reaction mechanism.

Earlier work in this laboratory had shown that catalysts of binary metal oxides such as alkali-transition metal oxides or alkali-earth alkali oxides can promote the gasification of graphite and of chars at temperatures of about 800-1000K and atmospheric pressure. It was also shown that for catalysts to be active at those conditions, they had to be able to dissociate water providing hydrogen and giving oxygen to the carbonaceous substrate. It had been concluded that the attack of a potassium-nickel oxide catalyst on the carbonaceous substrate proceeded by edge recession rather than by channeling. It was also found that potassium-nickel oxide catalysts are more subject to poisoning by ash components than alkali-earth alkali such as potassium-calcium oxide catalysts.

During 1989 it was demonstrated that poisoning of the potassium-nickel oxide catalysts was largely due to organic sulfur compounds in the ash. Against expectations pyrite was not a poison. Organic sulfur compounds did not appreciably poison potassium-calcium oxide catalysts. Additional electron microscopy work indicated that the mechanism of attack on the carbon is the same for potassium-calcium oxide as for potassium-nickel oxide catalysts. This work also demonstrated that each catalyst particle derived from impregnation of the carbonaceous substrate with nitrates of the metals followed by decomposition contains both potassium and calcium, regardless of the size of the particle.

The gasification work was extended to coals. It was found that coals impregnated with either of the catalysts could be gasified at much higher rates than the chars derived from the coals. The order of gasification rate for coals and chars was lignite > subbituminous > bituminous > graphitic.

Since catalysts of the alkali-alkali earth oxide type have previously been found to be active for oxidative coupling of methane, experiments were undertaken to carry out the gasification in the presence of steam, methane, and small amounts of oxygen. No conversion of methane to products other than carbon dioxide was observed until about 90% of the char had been gasified. At this point C₂ hydrocarbons were formed from methane and continued to be formed after 100% gasification of the char. Yields of about 10-15% of C₂ hydrocarbons were formed at temperatures which are about 200°C lower than those described in the literature for similar yields with other catalysts. This phenomenon is being further investigated.

*This work was supported by the Assistant Secretary of Fossil Energy.

SURFACE AND INTERFACE COMPOUNDS

SURFACE STRUCTURE AND BONDING

Structure of Disordered Molecular Adsorbates

G.S. BLACKMAN, P. DE ANDRES, R.Q. HWANG, D.F. OGLETREE, G.A. SOMORJAI,
M.A. VAN HOVE, A. WANDER, M.-L. XU

The use of low-energy electron diffraction (LEED) in determining bond distances and angles of adsorbates on surfaces has been greatly extended in this laboratory in recent years, both experimentally and theoretically. It is now possible to determine the surface structure of disordered monolayers on ordered substrates using a new digital-LEED apparatus and a new diffuse-LEED theory. For example, the disordered structures of benzene and carbon monoxide adsorbed on the Pt(111) single-crystal surface were determined. This involved the measurement and calculation of diffuse LEED intensities in order to determine the molecular adsorption sites, metal-carbon bond lengths and internal distortions of the molecules.

High-Density Molecular Monolayers on Metal Surfaces

G.S. BLACKMAN, C.-M. CHAN, C.-T. KAO, G.A. SOMORJAI, M.A. VAN HOVE

At high densities, close to saturation coverage, molecular monolayers exhibit strong adsorbate-adsorbate interactions. Such effects can involve charge transfer between inequivalent adsorbates, much studied in this laboratory in the past. Another type of interaction occurs with like adsorbates, as with a monolayer consisting of only NO molecules. Here non-ionic forces dominate which are repelling at close separations, defining Van der Waals radii. Structural analysis by LEED and high-resolution electron energy loss spectroscopy (HREELS) has exhibited this behavior

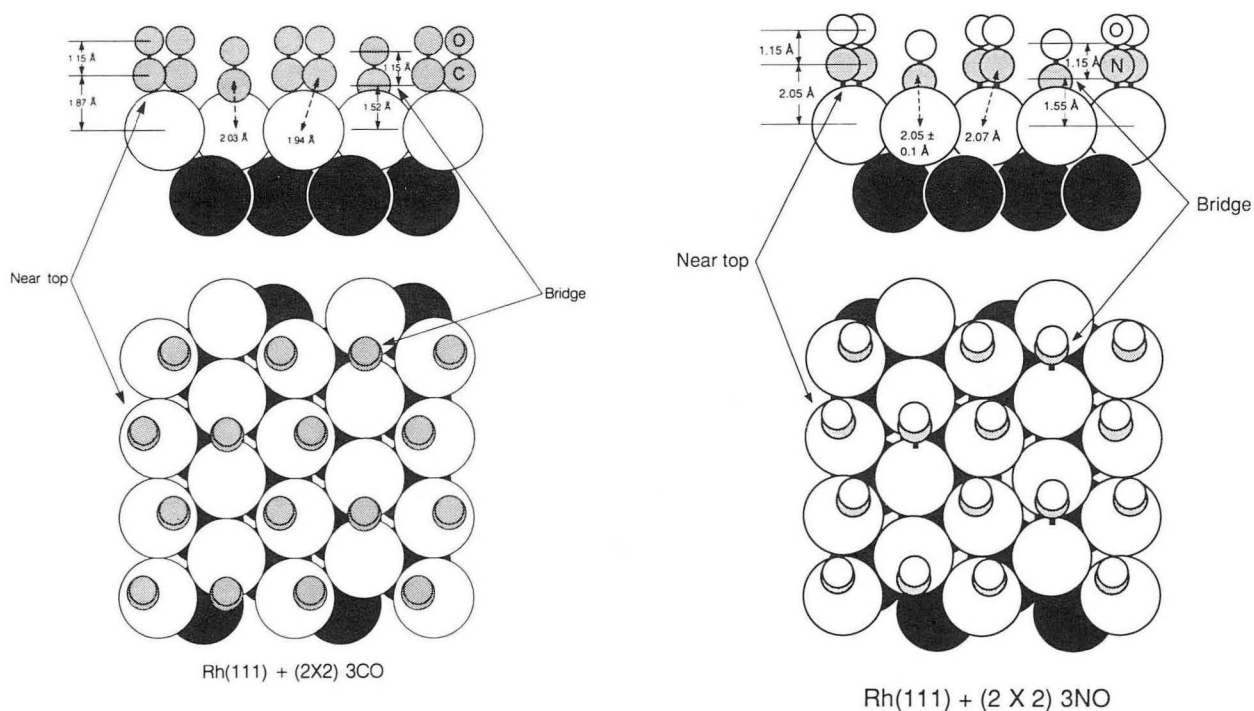


Figure 8
Side and near-perpendicular views of the best-fit models for dense structures of CO (left) and NO (right) on Rh(111).
(left: XBL 895-6910; right: XBL 888-8950)

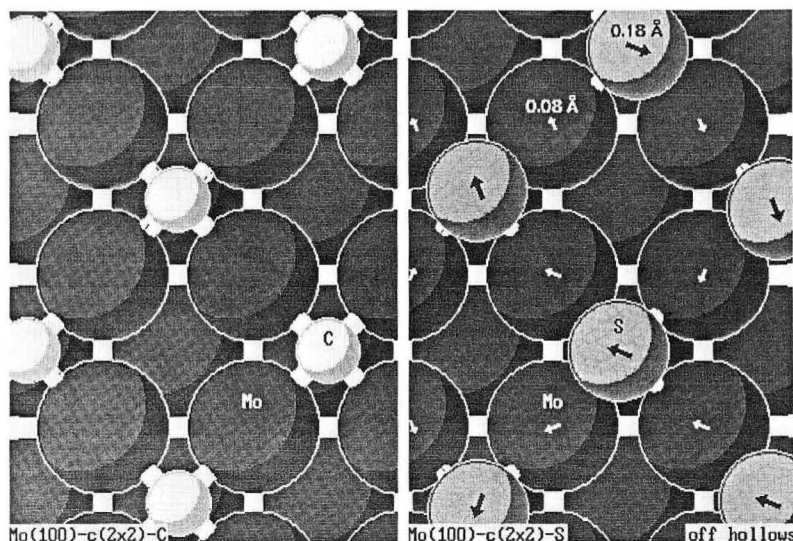


Figure 9
 At left: top view of a highly symmetric overlayer of carbon on Mo(100). At right: top view of $c(2 \times 2)$ sulfur overlayer on Mo(100) with asymmetric lateral shifts as shown by arrows. These shifts point in random directions. (XBB 895-4262)

for both a NO monolayer and a CO monolayer deposited on Rh(111). At saturation coverage a well-ordered (2×2) structure exists in both cases, with all molecules closely perpendicular to the surface. In each (2×2) unit cell, one molecule resides on a bridge site (two-fold coordination) (Figure 8) It pushes two neighboring molecules away from symmetrical top sites (one-fold coordination) by an amount closely related to the Van der Waals radii of the carbon atoms. This finding gives a direct measure of interactions between ad molecules and points to the validity of the conventional concept of Van der Waals radii when applied to adsorbed molecules.

Atomic Adsorption Structures on Metal Surfaces

D. JENTZ, D.G. KELLY, S.G. LOUIE, D.F. OGLETREE, C. OCAL, B. MARCHON, P.J. ROUS, M. SALMERON, G.A. SOMORJAI, M.A. VAN HOVE, X.-W. WANG

Structures of sulfur and carbon adsorbed on Mo(100) and Re(0001) were studied with LEED and STM as well as with total-energy calculations. Half-monolayer $c(2 \times 2)$ structures of sulfur or carbon atoms on Mo(100) have been investigated by LEED, allowing complete relaxation of the atoms in the first 3 layers (Figure 9). Whereas the carbon atoms nestle symmetrically at the center of the four-fold coordinated hollows of the substrate, the sulfur atoms are found to shift laterally and also induce marked lateral displacements in the topmost metal layer. With both C and S adsorption, significant changes in metal-metal interlayer spacings are observed, illustrating the phenomenon of adsorbate-induced restructuring. Corresponding total-energy calculations (keeping a rigid bulk-like substrate) predict no lateral shift of sulfur, and find S-Mo bond lengths closely similar to the LEED result. Calculations were also performed for the full-monolayer $p(2 \times 1)$ structure of S on Mo(100), to be compared with earlier STM images taken in this laboratory. The theory predicts a bridge-hollow chemisorption geometry as the most stable structure. This result is compatible with the STM data only if one assumes that STM is not sensitive to the difference in the heights of bridge-S and hollow-S above the metal. Further STM work has focused on sulfur layers on Re(0001), observed both in air and in ultra-high vacuum. A rich set of sulfur structures is obtained. For example, a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ sulfur overlayer chemisorbed on Re(0001) was prepared in UHV and then transferred through air to a scanning tunneling microscope (STM) operating at a vacuum of 10^{-7} Torr. This $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ sulfur overlayer passivates the

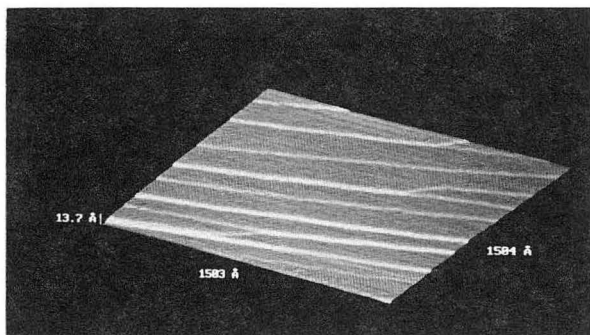


Figure 10
Steps of 2 atoms height and also 1 atom height are seen to separate terraces of (0001) orientation in this STM image of Re covered with a saturation layer of sulfur. Notice also the emergence of a screw dislocation in the lower right of the image giving rise to steps. (XBB 896-5072)

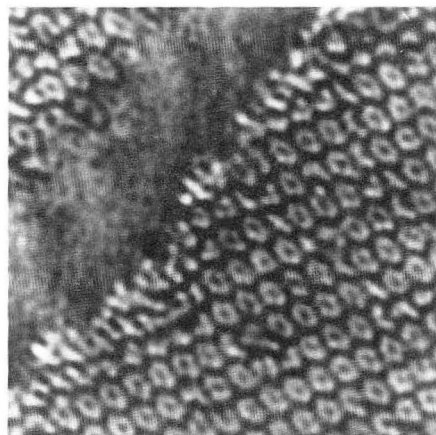


Figure 11
Scanning tunneling microscopy image of the $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ structure of sulfur on Re(0001). Sulfur forms rings of 6 atoms that cover the surface. The distance between ring centers is 9.5\AA . Two terraces are shown separated by a blurred region at the step. The size of this region is due to the finite tip radius. Notice also defects in the layer (broken rings, phase boundary crossing the middle part of the image perpendicular to the step). The corrugation height across sulfur rings (black to white) is about 2.4\AA . (XBB 888-8469)

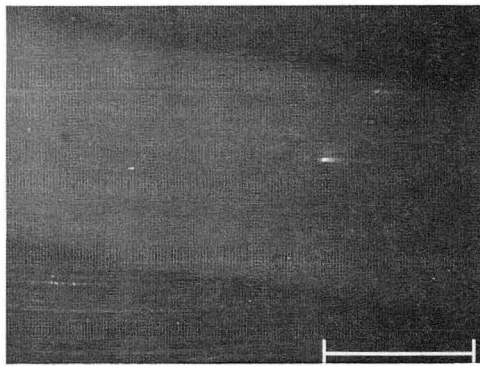
rhodium substrate in air. STM images show steps and dislocations on the metal surface (Figure 10). The atomic structure of the overlayer unit cell is shown to be a hexagonal ring of six sulfur atoms (Figure 11). Defect structures in the two-dimensional lattice of sulfur hexagons and overlayer domain boundaries can also be observed.

COATINGS AND INTERFACE COMPOUNDS: AMORPHOUS CARBON FILMS

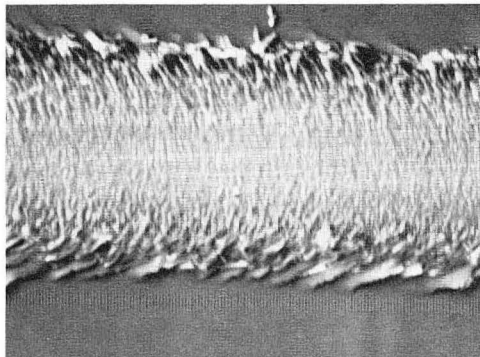
Formation of Hydrogenated Amorphous Carbon Films of Controlled Hardness from a Methane Plasma

G.J. VANDENTOP, M. KAWASAKI, R.M. NIX, I.G. BROWN, M. SALMERON, G.A. SOMORJAI

Studies of amorphous hydrogenated carbon ($\alpha\text{C:H}$) film deposition revealed that methyl radicals are the precursor species responsible for the bulk mass deposition of the films, while the ions act to improve the mechanical properties. The films were deposited on Si(100) substrates both on the powered (negatively self-biased) and on the grounded electrodes from a methane rf plasma (13.56 MHz) at 68 to 70 mTorr and 300 to 370K. The films produced on the powered electrode exhibited superior mechanical properties, such as high hardness and scratch resistance (Figure 12). A mass spectrometer was used to identify neutral species and positive ions incident on the electrodes from the plasma, and also to measure ion energies. Methyl radicals were incident on the electrode surface with an estimated flux of $10^{16}\text{cm}^{-2}\text{s}^{-1}$, for an rf power of 50 W. Methyl radicals appear to be the dominant intermediates in the growth of the soft carbon polymer, and there is a remarkable decrease in deposition rate due to the introduction of NO, a radical scavenger. A novel pulsed



powered electrode



grounded electrode

Figure 12
Secondary electron microscope images of scratch tracks made with a Rockwell C diamond tip at a load of 830g, for films formed on the powered and grounded electrodes. Little damage is apparent on the hard film formed on the powered electrode, while the soft film formed on the grounded electrode has suffered noticeable damage. (XBB 897-5454)

biasing technique was used so that the role of ions in the plasma could be studied separately. It was found that the hardness of the films depends on the power supplied by the ions to the growing film surface (the time averaged difference between the plasma potential and the electrode potential), but not on the energy of individual ions (Figure 13). The pulsed biasing technique offers an efficient method to adjust the film hardness by independent control of the neutral radical and ion fluxes to the surface.

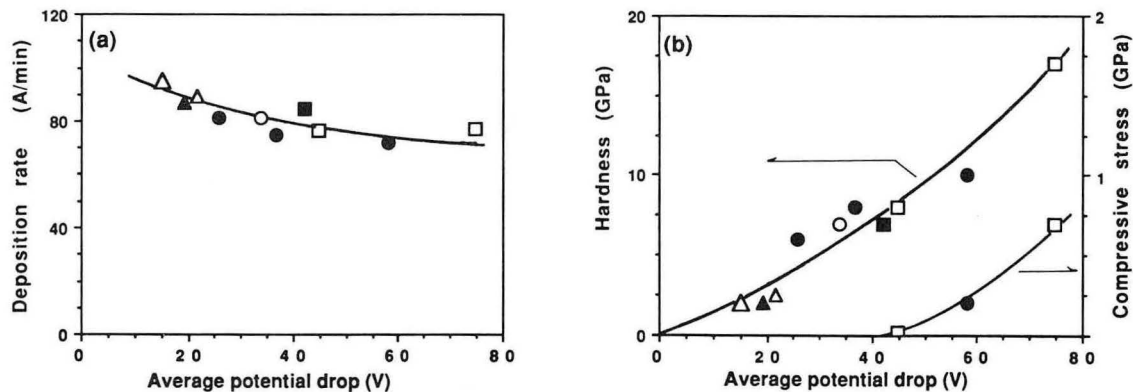


Figure 13
The dependence of hardness and compressive stress on the time averaged potential drop between the plasma bulk and the substrate. Hardness depends monotonically on the average potential drop between the plasma and the electrode; i.e., the power delivered to the film surface by ions as controlled by pulsed biasing. Deposition rate is independent of the average potential drop. The pulse frequencies are 25, 12.5, and 6.25 kHz for the -800 V pulses, 25 and 12.5 kHz for -1100 V, 25 kHz for -500 and -200 V, and 100 kHz for -20 and -800 V. (XBL 8911-4162)

Analysis of the Interface of Hydrogenated Amorphous Carbon Films on Silicon by Angle-Resolved X-Ray Photoelectron Spectroscopy

M. KAWASAKI, G.J. VANDENTOP, M. SALMERON, G.A. SOMORJAI

Thin amorphous hydrogenated carbon films were deposited from a methane rf plasma (13.56 MHz) at 68 mTorr on Si(100) substrates both on the powered (negatively self-biased) and on the nonpowered (grounded) electrode. The interface was analyzed with angle-resolved X-ray photoelectron spectroscopy. An approximately stoichiometric silicon carbide layer was found at the interface of a hard carbon film produced on the powered electrode. The thickness of the interfacial carbide as estimated from the angle resolved spectra was approximately 7\AA , which is much thinner than previously reported by other workers. There was no interfacial silicon carbide formation evident for a soft polymer-like film produced on the grounded electrode. Instead, a submonolayer amount of oxide which showed poor adhesion was detected at the interface of the soft carbon film. Our results indicate that the high energy ions incident on the powered electrode in the rf plasma are responsible for the production of the interfacial silicon carbide and are also likely responsible for the good adhesion of the film to the silicon substrate.

INSTRUMENTATION FOR SURFACE SCIENCE

OPTICAL SURFACE STUDIES

Determination of Surface pH Values by Optical Second Harmonic Generation

X.-D. XIAO, V. VOGEL, Y.R. SHEN

Optical second harmonic generation from protonable dye molecules at a lipid/water interface can be employed to determine the surface pH values (proton excess) at interfaces. This has been demonstrated on a stearic acid monolayer/water interfacial system. The surface proton concentration changes in response to variation of the bulk proton and salt concentration as shown in Figure 14 and can differ from the bulk proton concentration by 6 or 7 orders of magnitude. Probing the surface pH value by SHG provides the possibility for investigation of fast dynamic processes involving protons at interfaces.

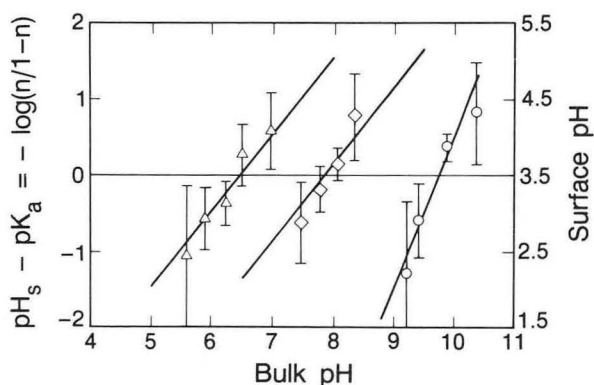
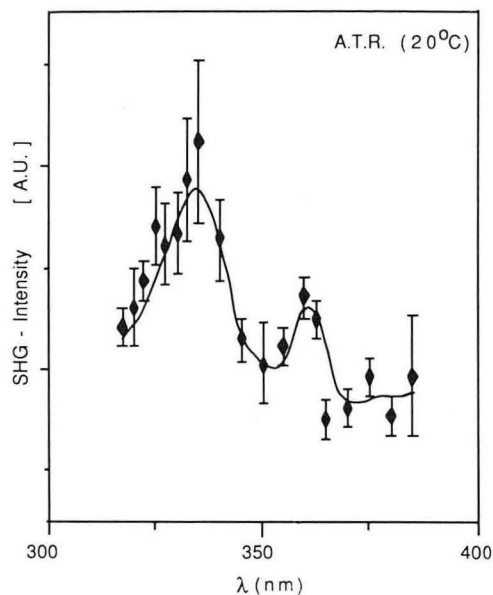


Figure 14

The effective molecular hyperpolarizability β of the hemicyanine dye deduced from the SHG results is plotted against pH_b for different salt concentrations. The hemicyanine dye is embedded into a negatively charged monolayer matrix of stearic acids in the molar ratio of 1/15. The symbols "O" and "Δ" represent the experimental data on 0, 5.6, and 100 mM NaCl solutions, respectively (200°C). The solid lines are theoretical curves. (XBL 895-5094)

Figure 15
SHG spectrum of all-trans retinal at an air-water interface.
(XBL 897-3927)



A New Vision on Vision

TH. RASING, J.Y., HUANG[†], A. LEWIS, T. STEHLIN, Y.R. SHEN

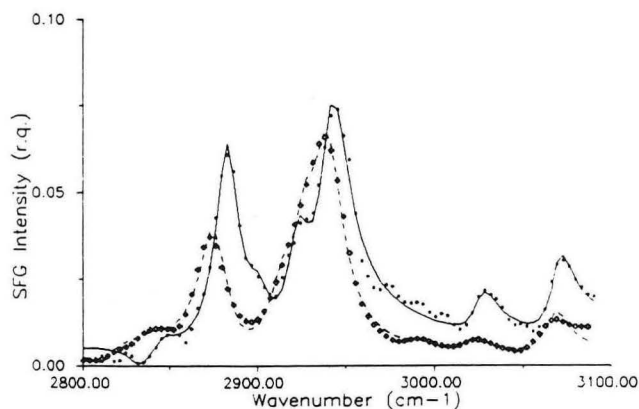
The orientation, hyperpolarizability, and spectrum of retinal chromophores were studied for monolayers of the pure chromophore and for the chromophore embedded in the purple membrane of *Halobacterium halobium* spread at the air-water interface using the technique of optical second harmonic generation. The hyperpolarizability in the membrane appears to be identical to that of the free chromophore. The spectrum of all-trans retinal monolayers exhibits a subsidiary one-photon forbidden peak in addition to the main absorption peak (Figure 15).

Study of Conformation, Orientation, and Interaction in Molecular Monolayers by IR-Visible Sum-Frequency Generation*

R. SUPERFINE, J.Y. HUANG[†], Y.R. SHEN

We have used sum-frequency generation to study the order in a silane monolayer. We observe an increase in the order of the chain of the silane molecule induced by the interpenetration of the liquid crystal molecules. By using SHG and SFG, we have studied the orientation and conformation of the liquid crystal molecule on clean and silane coated glass surfaces. On both surfaces, the biphenyl group is tilted by 70° with the alkyl chain end pointing away from the surface. The shift in the C-H stretch frequencies (Figure 16) in the coadsorbed system indicates a significant interaction between molecules.

Figure 16
SFG spectrum of 8CB monolayer on clean glass (solid curve) is compared to 8CP deposited on DMPOAP coated surface (dashed curve). (XBL 901-120)



* Supported by 3M Corporate Research Laboratories
† IBM Postdoctoral Fellow

Interference between Second Harmonic Generation from a Substrate and an Adsorbate Layer

G. BERKOVIC, Y.R. SHEN, G. MAROWSKY, R. STEINHOFF

Several experiments on surface second harmonic generation have been carried out to show how the contribution from a transparent substrate can interfere with that from an adsorbate monolayer. The interference depends on the relative phase of the two contributions, which varies with the molecular orientation, the laser frequency, the polarization, and the optical geometry.

Polymer Concentration Profile near a Liquid-Solid Interface: Evanescent Wave Ellipsometry Study

M.W. KIM, D.G. PEIFFER, W. CHEN, H. HSIUNG, TH. RASING, Y.R. SHEN

The phase retardation angle, $\Delta\Phi$, as a function of the incident angle was measured by evanescent wave ellipsometry technique to study adsorption and depletion of polymers near a solid substrate from a solution. A lightly sulfonated ionomer dissolved in a polar solvent displayed an appreciable interfacial adsorption layer, while the nonionic precursor in ethyl acetate exhibited a depleted concentration profile. The results are in good agreement with adsorption or depletion layer profiles obtained previously by other techniques, i.e., X-ray fluorescence for polymer adsorption and optical fluorescence wave technique for depletion.

Unenhanced Surface Raman Spectroscopy

J.W. AGER III, G.M. ROSENBLATT, D.K. VEIRS

Unenhanced surface Raman spectroscopy is used as a vibrational probe of physisorbed and chemisorbed molecules and films on a variety of surfaces from 14K to well above room temperature

Recent developments in two-dimensional single-photon sensitive detectors, as implemented in our laboratory, allow unenhanced surface Raman spectroscopy of physisorbed and chemisorbed adsorbates and of thin films. The sensitive Raman apparatus is coupled with an ultrahigh

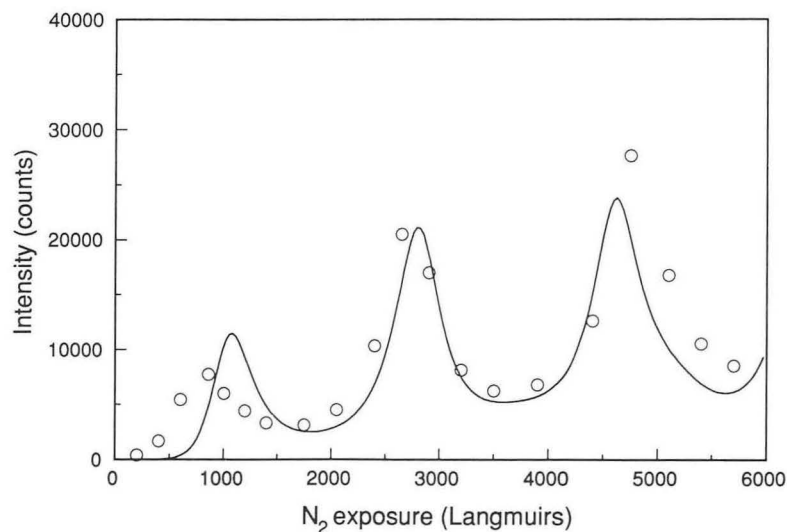


Figure 17

The Raman intensity at 2325 cm^{-1} of N_2 physisorbed on $\text{Ag}(111)$ at 14 K as a function of N_2 exposure. The intensity shows oscillations arising from interference effects. The experimental data are indicated by circles and the solid line is the theoretical prediction. The spacing between maxima is a measure of the film thickness and yields the sticking coefficient. (XBL 899-3324)

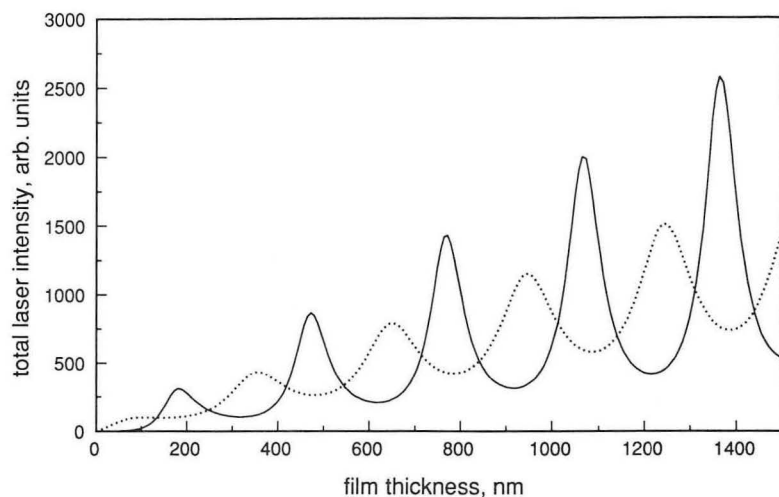


Figure 18
 The illumination intensity with an N₂ film on Ag as a function of coverage. The solid line is for 2-polarized incident light. For our experimental conditions the Raman intensity follows the illumination intensity. Note that at very low coverages, Raman scattering is produced only by p-polarized light and at higher coverages interference effects from s-polarized light dominate. (XBL 899-3322)

vacuum chamber capable of cooling samples to 14K and equipped with LEED/Auger surface characterization and ion bombardment and heating for surface cleaning to study the vibrational-rotational energy levels of low temperature adsorbates.

Following the first Raman measurements of a physisorbed system at low, near-monolayer coverages—N₂ adsorbed on Ag(111)—we have studied thicker adsorbed films of α -N₂ in order to examine optical polarization and film orientation. In contrast to near-monolayer films, where the Raman intensity varies linearly with coverage, large oscillations in the vibrational Raman intensity are observed as a function of film thickness (Figure 17). The observed oscillations are due to multiple beam interference caused by reflections at the vacuum-film and metal-film boundaries of the incident laser light and the Raman scattered light.

To describe the interference, we have extended the available theoretical development for Raman scattering in thin films to the general three-dimensional experimental geometry and have derived expressions for the total intensity as a function of film thickness, incident laser polarization and angle, and scattered light polarization and angle. As the film gets thicker, the theoretical development and the experimental observations show enhanced intensity from laser light polarized parallel to the surface (solid line in Figure 18), whereas scattering from laser light polarized perpendicular to the surface, which completely dominates at near monolayer coverages, is enhanced less by interference effects (dotted line in Figure 18). The calculated Raman intensities are in excellent agreement with the experimental results (solid line in Figure 17).

The observed period of the intensity oscillation relates the film thickness to the exposure allowing the sticking probability of N₂ on α -N₂ to be determined: 0.84 ± 0.2 at 14 ± 1 K (for α -N₂ one monolayer requires 3.3 L). In similar experiments, the sticking coefficient of O₂ on O₂ was found to be 0.82 ± 0.2 at 14 ± 1 K.

The unique Raman apparatus used in these studies was also applied to collaborative studies of crack propagation in zirconia (see R.H. Dauskardt and R.O. Ritchie's work in the Structural Materials Program) and of carbon films for Seagate Magnetics and IBM Corporation.

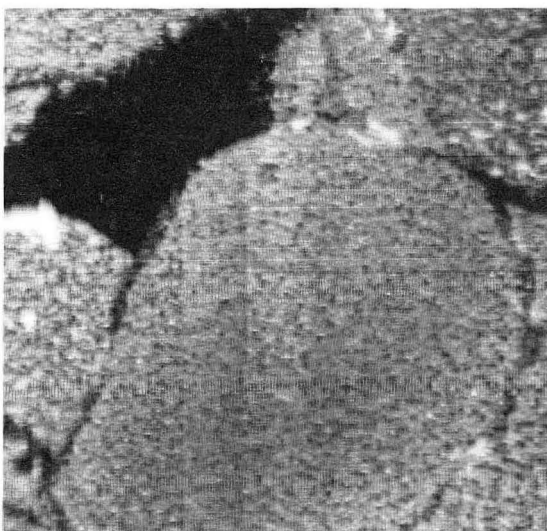


Figure 19
Top view of STM image of Pt-Ir-C coated purple membrane (PM). Large flat pieces of PM are visible as well as crevices between adjacent PM patches and areas without membrane. (XBB 890-10060)

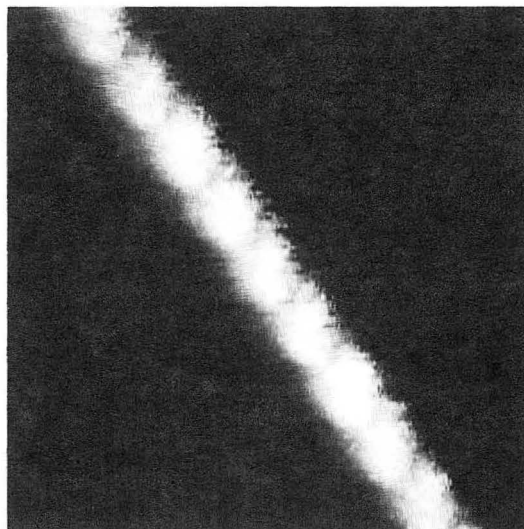


Figure 20
Top view of STM image of native uncoated collagen. The periodic repeat of the helix of the molecule is clearly resolved as well as other details of the molecule's morphology even though mobility and lack of conductivity are significant problems in STM of uncoated biological samples. (XBB 890-10040)

SCANNING TUNNELING MICROSCOPY

Application of STM to Studies of Organic and Bio-Organic Materials

J. CLARKE, M. SALMERON, T. BEEBE, J. ODRIOZOLA, T. WILSON, D.F. OGLETREE,
W. SIEKHAUS, K.A. FISHER*, M.B. SHATTUCK*, R. S. BHATNAGAU*, S. WHITFIELD, R.E. THOMSON

The ability of the scanning tunneling microscope (STM) to resolve the atomic structure and electronic properties of metal and semiconductor surfaces is now well established. More recently, the performance of the STM on various organic materials has been an area of intense interest. The use of STM on native biological materials has been limited by their inherent non-conductivity and relative mobility. Two approaches have been adopted in our laboratories. In one set of experiments, *we have performed investigations of membranes coated with thin conducting metal overlayers* as well as begun experiments on native uncoated collagen.

For this study, we used *Halobacterium halobium* purple membrane (PM) prepared by planar membrane monolayer techniques. These techniques produce large, optically flat areas of oriented membrane which can be coated with metals (usually Pt-Ir-C) for examination by both TEM and STM. STM top-view images (Figure 19) show membranes similar in size and shape to those imaged by TEM.

The exact height (or thickness) of the membrane is difficult to quantify with traditional techniques such as TEM. However, the STM is an ideal instrument for height measurements because the tunneling current is exponentially dependent on the tip-to-sample distance. After a careful calibration of the STM and determination of the effects of contamination-mediated surface deformation, we were able to measure the thickness of the PM both before and after a treatment with the proteolytic enzyme, papain. The apparent thickness of enzymatically modified PM increased after papain treatment from 46Å to 54Å on glass substrates and from 46Å to 48Å on mica substrates.

* University of California, San Francisco

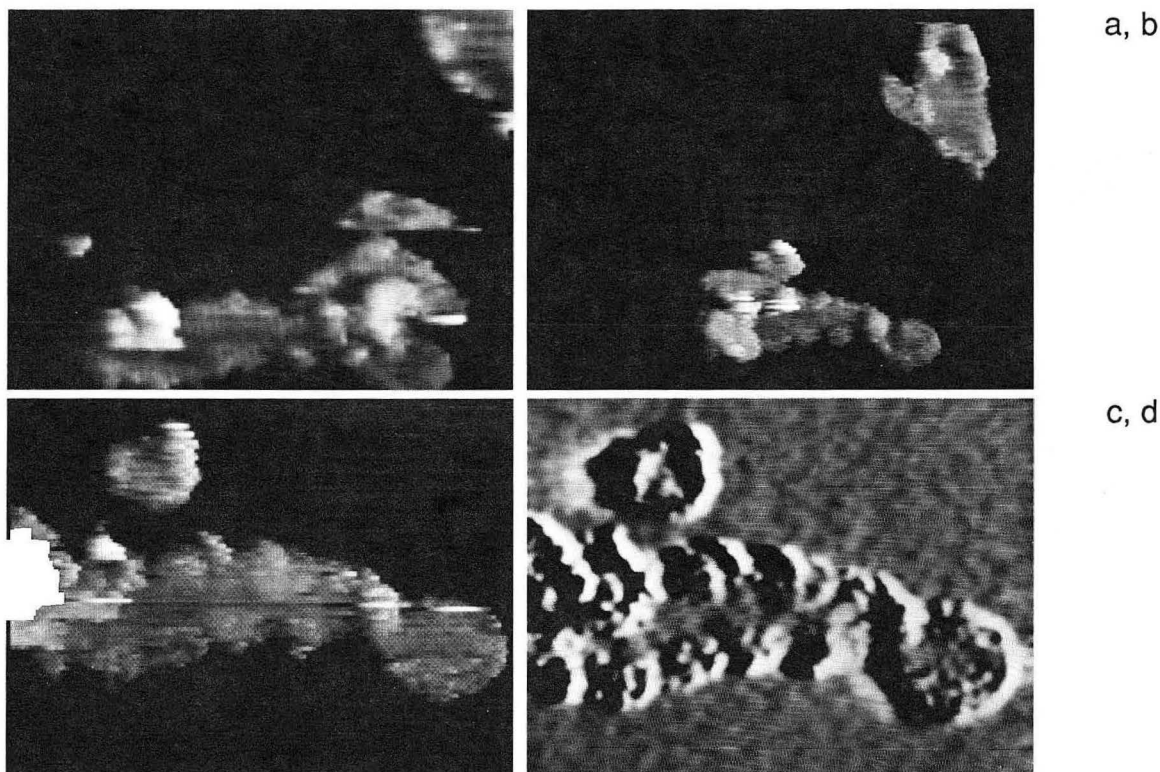


Figure 21

Strands of uncoated DNA deposited on graphite and imaged by the STM. Notice the displacement of material from image to image due to the forces exerted by the tip. These images are $400 \times 400 \text{ \AA}$ (a, c, d) and $600 \times 600 \text{ \AA}$ (b). Fig. 5d shows the processed image from Fig. 5c after smoothing and artificial light source illumination. (5a: BBC 893-1854; 5b: BBC 893-1852; 5c: BBC 893-1848; 5d: XBB 8810-9840)

In a different approach, we have also imaged native, uncoated molecules of collagen. Figure 20 shows a top view of an image of a single molecule of collagen taken in air at room temperature. The collagen molecule has a right-handed helical structure which, although it is somewhat variable, gives the molecule an average periodicity of 30 \AA . This periodicity is clearly resolved in our STM images. We are also able to see regions where the helix is nonuniform, regions where the helix is not present and regions where the collagen molecule appears to be flexible.

In a further set of experiments, we deposited DNA on graphite, and were able to image several isolated strands such as those shown in Figure 21. The resolution in some cases was such that the major and minor grooves in the DNA spiral could be distinguished. In order to make STM a routine technique for biological applications, however, methods of fixation of the biomolecules to the substrate must be developed to ensure that the non-negligible forces exerted by the tip do not displace the molecules during scanning. The example illustrates how DNA fragments are displaced by the forces exerted by the scanning tip.

INSTRUMENTAL DEVELOPMENT

Atomic Force Microscopy

J. CLARKE, M. SALMERON, W. KOLBE, M. GUSTAFSSON, K.A. FISHER*

The atomic force microscope (AFM) is an instrument similar to the STM, but with the ability to image insulating as well as conducting

* University of California, San Francisco

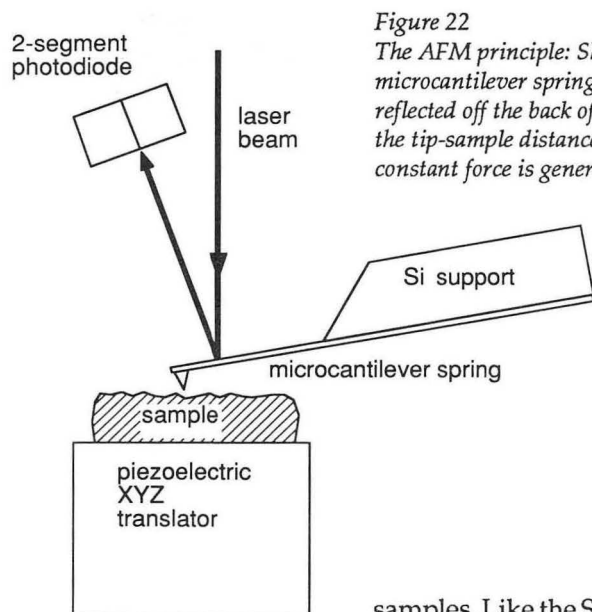


Figure 22

The AFM principle: Short range forces between the sample and a sharp tip deflect a microcantilever spring on which the tip is mounted. This deflects a laser beam which is reflected off the back of the spring. As the sample is scanned, a feedback loop regulates the tip-sample distance to keep the force constant. Thus an image of a surface of constant force is generated. (XBL 8911-4118)

samples. Like the STM, it generates atomic resolution images by scanning a sharp tip over the sample surface. Instead of sensing a tunneling current, the AFM senses the force between the tip and the sample, by detecting sub-Angstrom deflections of a cantilever spring on which the tip is mounted.

In one system under development in our laboratory, this spring motion is detected by measuring the angular deflection of a laser beam which is reflected off the back side of the spring (Figure 22). For high sensitivity and low noise, the AFM spring should have a low force constant and a high resonance frequency, which implies a low mass. We use microfabrication techniques to manufacture silicon nitride springs with masses below 10^{-11} kg, achieving resonance frequencies of 201kHz at a force constant of 1 N/m.

The sharpness of the tip is of great importance for high resolution AFM. Existing approaches to tip manufacturing involve attaching a fragment of a crushed diamond, or using etching techniques. The diamond, while quite sharp, seriously lowers the resonance frequency of the spring-tip system by its added mass. The etching methods, while adding only negligible mass, have not yet yielded tips sharper than 300 Å in radius. We have developed a simple method that attempts to combine negligible

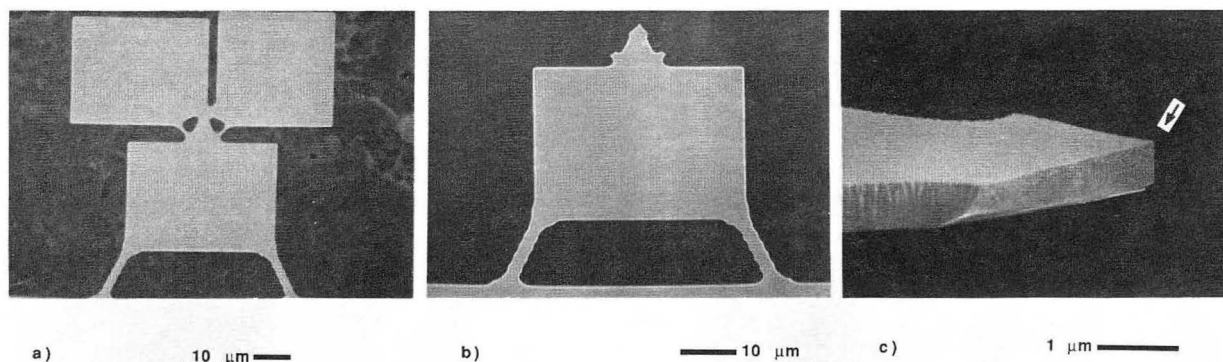
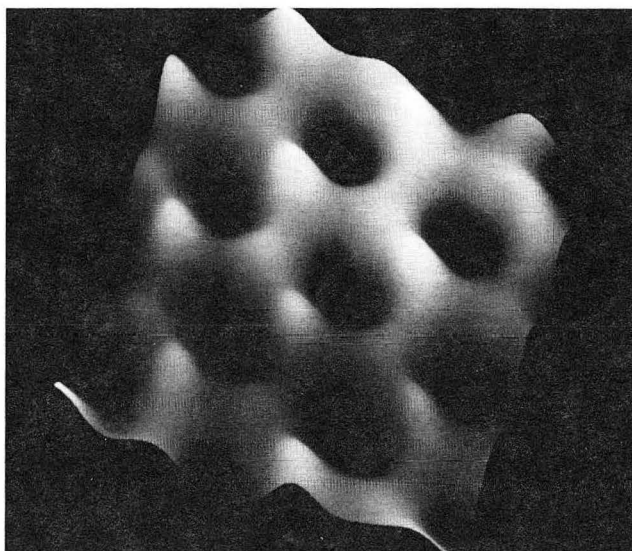


Figure 23

The micro springs are patterned from a $0.8\mu\text{m}$ thick Si_3N_4 film, supported at the base by a silicon chip. As the last processing step, the two plates shown in (a) are mechanically broken off (b). The sharp corner thus created is used as the AFM tip. Figure

Figure 24
AFM image of the surface of muscovite mica, showing the honeycomb lattice of SiO_4 tetrahedra. The spacing between holes is 5.2\AA . (XBB 8911-9921)



mass with the sharpness of intersecting fracture planes. The microcantilever springs are designed so that the spring material itself can be fractured in a controlled way (Figure 23 a, b), leaving a corner shaped tip (Figure 23 c). SEM images put an upper limit on the radius of this tip at below 100\AA .

Figure 24 is an image of the honeycomb-shaped atomic lattice of the surface of muscovite mica, acquired with this system.

A different AFM system, based on interferometry to measure the deflection of the cantilever spring, is also in its final stages of construction. This instrument will be used to study biological material that cannot be studied with the STM. It will also be used to study mechanical properties of surfaces by measuring the forces between tip and surface in the vertical direction (adhesion) and in the horizontal direction (friction).

DEVELOPMENT OF A COMBINED DIGITAL-LEED/STM INSTRUMENT

R.Q. HWANG, M. SALMERON, G.A. SOMORJAI

Recently it has been shown in our laboratory that measurements of diffuse LEED intensities can be used to extract structural information of disordered chemisorption systems. Our digital LEED system, with its high sensitivity pulse counting detector, is well suited for these measurements. However, initial guesses of the adsorbate geometry must come from other techniques. Scanning Tunneling Microscopy (STM) would allow us to directly image the adsorbate and hopefully the substrate simultaneously. This would give immediate information of adsorbate sites, and even crude estimates of bond lengths could be made. In addition, by imaging as a function of adsorbate coverage, short range order phenomena such as island formation can be studied and compared with the digital LEED information.

We are building and inserting an STM into the system that now contains the digital LEED apparatus. This will allow STM and digital LEED measurements to be made on the same surfaces. Modifications to the sample manipulator must be made to allow interchange of the sample between the two techniques. In addition, improved cooling capabilities are presently being added to the manipulator that will allow sample temperatures to reach approximately 100K . This will allow studies of molecular systems, such as ice grown on $\text{Pt}(111)$, that require low temperatures for adsorption.

Development of Instrumentation for Studies of Liquid-Phase Catalytic Reactions
M. QUINLAN, G.A. SOMORJAI

The techniques of surface science which have been successful in the elucidation of the mechanisms and adsorbed intermediates in the metal surface catalyzed hydrogenation of gaseous hydrocarbons will be applied to the study of hydrogenation reactions occurring at the liquid-solid interface. The added constraint of measuring meaningful specific catalytic reaction rates in the presence of the diffusional resistances commonly encountered in the liquid phase requires that a novel catalytic reactor geometry be used. Consequently, a rotating disk reactor employing a single crystal metal substrate is being designed and constructed. The impetus for the use of a rotating disk reactor to study liquid phase hydrogenation reactions arises from the formation of a well characterized one-dimensional, equiaccessible diffusion field to complement the well characterized atomic composition and geometry of the single crystal metal substrate. The thickness of the diffusion boundary layer varies inversely with the rotational rate of the disk, allowing the reaction kinetics to be determined under conditions free of mass transfer influences. The hydrogenation of liquid cyclohexane will be the initial reaction to be studied.

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AWARDS

Gabor Somorjai was awarded the Alexander von Humboldt Award for U.S. Senior Scientists.

Gabor Somorjai was awarded the E.W. Müller Award from the University of Wisconsin.

Stephen Louie was awarded a Guggenheim Fellowship.

John Clarke was elected a Visiting Fellow at Clare Hall, Cambridge, England.

INDUSTRY INTERACTIONS

Industrial Fellows

- David Denley of Shell Development Company joined the Surface and Interface Compounds group in a study of the design, construction, and use of the Scanning Tunneling Microscope and the Atomic Force Microscope
- Clarence D. Chang, Mobil Research and Development Corporation, worked with the Catalyst Design and Characterization Project on the use of MAS-NMR spectroscopy to characterize the composition of aluminosilicate gels used in the synthesis of zeolites.
- Bharat Bhushan of IBM Almaden Research Center is working with the Surface and Interface Compounds group studying plasma coatings and the tribological properties of surfaces.
- Mahn Won Kim worked with the Instrumentation for Surface Science Project on the application of second harmonic generation to the study of surfaces and monolayers.

Advisory Board

Roger Baetzold, Chairman	Eastman Kodak Company
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Kathleen Taylor	General Motors Technical Center
J.J. Wise	Mobil Research and Development Corporation
Jerry Meyer	Chevron Research Company

Gifts

- Gifts from Chevron Research Corporation and IBM were used to support the Surface Science and Catalysis Seminars.
- Gifts from E.I. DuPont de Nemours, Inc., provided support for research in nonlinear optics and microporous crystalline catalysts.
- A gift from Exxon was used to support studies of molecular diffusion in the 2-D and 3-D bioptical second harmonic generation (SHG).
- General Motors provided support for the International Conference on Structure of Surfaces.
- Grants from Harshaw/Filtrol, and W.R. Grace were used to support research on zeolite synthesis.
- A gift from Mobil Research and Development Corporation will be used for travel to scientific meetings.

* Retired in 1989.

† New member in 1989.

- A gift from Rhône Poulenc was used to perform experimental surface science studies of the catalytic oxidation of light alkanes.
- A gift from Shell Oil Development was used to support research on Atomic Force Microscope development and applications to zeolites.

Contracts

- 3M provided support for research on the development of the techniques of second harmonic generation and sum-frequency generation to study monolayers on surfaces.
- Dow Chemical Corporation provided support for studies of oxide surface structure using STM and AFM.
- E.I. DuPont de Nemours, Inc., provided support for research in electro-optics.

Collaborations

- In collaboration with Mobil Research and Development Company, it was discovered that TPA⁺ cations form silicate cages containing 22 Si atoms during the initial stages of Zsm-5 synthesis.
- In collaboration with Kodak Research Laboratories, was established that the BOC-MP approach provides a realistic description of the energetics of formic acid decomposition on Ag(111), Ni(111) and Fe/W(110) surfaces.

Technology Transfer

- Y. Ron Shen was awarded U.S. Patent No. 4,829,505 for Multiple Layer Optical Memory System using Second-Harmonic Generation Readout.

Surface Science and Catalysis Seminars

(Supported in part by gifts from Chevron Research Corporation and IBM)

- F.T. Wagner - GM Research, Warren, MI, "Modeling the Electrochemical Double Layer in UHV"
- U. Starke - University of Erlangen-Germany, "Reliability of Diffuse LEED Intensity Measurements"
- B.E. Bent - Dept. of Chem., Columbia Univ., NY, "Surface Reactions in the Chemical Vapor Deposition of Aluminum Using Triisobutylaluminum"
- M.P. Soriaga - Dept. of Chem., Texas A&M, TX, "Surface Chemical Studies of Noble-Metal Electrocatalysts"
- R.J. Koestner - Texas Instruments, Dallas, TX, "Molecular Beam Epitaxial Growth of HgCdTe Semiconductor Films"
- R. Szostak - Georgia Tech Research Institute, Atlanta, GA, "Non-aluminosilicate Molecular Sieves: New Compositions, Novel Applications"
- P.S. Bagus - IBM-Almaden, CA, "Core Level Binding Energy Shifts of Surface Atoms: A Theoretical Analysis"
- F. Zaera - UC-Riverside, CA, "Selectivity Between C-H Bond Breaking and Hydrogen Migration: C₂ Moieties on Pt (111) Surfaces"
- I. Horvath - Exxon Research Corporation-Annandale, NJ, "Mechanistic Studies of Hydroformylation Under Pressure With NMR and IR"
- H. Ibach - Jülich, Germany, "Surface Phonon Dispersion as a Measure of Surface Stress with Special Applications to Epitaxial Metal Overlayers"
- M. Halmann - Weizmann Institute, Israel, "Photosensitized Oxidation of Bromide Ion to Bromine in Aqueous Solution"
- Y. Murata - The Institute for Solid State Physics, Tokyo, Japan, "Dynamical Behavior of Hydrogen Adsorbed on W(110) Studied by Resonance Nuclear Reaction of ¹H(¹⁵N,αΓ)¹²C.
- S.M. Csicsery - retired from Chevron Research Corporation, "New Developments in Shape Selective Catalysts in Zeolites"
- J. Fripiat - University of Wisconsin, "Strange Coordination of Aluminum in Alumina and Silica-Alumina"

J.G. McCarty - SRI International, Menlo Park, CA, "Interaction of Homogeneous and Heterogeneous Reactions During Methane Dimerization"

J.B. Pendry - Imperial College, London, "Surface Structure and Catalysis"

H. Holleck - Kernforschungszentrum, Karlsruhe, Germany, "Advanced Concepts in PVD Hard Coatings"

C.-M. Chan - Raychem Corp., Menlo Park, CA, "Surface Oxidation of Nickel-Titanium Alloy"

P.W. Davies - Intel Corp., Santa Clara, CA, "Applications of Surface Science in Microelectronics"

T.N. Taylor - Los Alamos National Laboratory, "The Ag/Cu(110) Interface: Surface Properties and Their Correlation with Second Harmonic Generation"

Prof. Howard W. Pickering - Penn State, "A New Field Ion-Scanning Tunneling Microscope and Its Application For the Study of Semiconductor and Metal Surfaces"

S. Han - Mobil Research and Development Corporation, Princeton, NJ, "Direct Methane Conversion - Fame and Misfortune"

J. Blakely - Cornell Univ., Ithaca, "Composition and Ionic Transport at Sapphire Surfaces"

S. Topham - ICI, Bellingham, England, "Recent Developments in Syn-Gas Technology"

A. Kaldor - Exxon Research & Engineering Co., "Dissociative Chemisorption on Noble Metal Gas Phase Clusters: The Connection to Supported Cluster Materials"

P. Blau - Oak Ridge National Laboratory, "Tribology Research on Nickel Ni₃Al Alloys"

G. Pirug - Jülich, Germany, "The Coadsorption of CO and H₂O with Alkali Metals on Transition Metal Surfaces"

J.P. Biberian - Univ. of Marseille, France, "Field Emission Microtips: A New Technology in Microelectronics"

A. Vehanen - Helsinki Univ. of Technology, Finland, "Probing Solid Surfaces with Monoenergetic Positron Beams"

B. Tonner - University of Wisconsin, Milwaukee, "Photoelectron Microscopy of Reactions at Surfaces: Current Status and Future Prospects"

M. Wuttig - KFA, Jülich, Germany, "Structure, Dynamics, and Oxidation Behavior of Ni Alloys"

K. Trabelsi - French Institute of Petroleum, "Solid-Liquid Interactions In Oil Reservoir Rocks"

M. Folman - Technion I.I.T.-Haifa, Israel, "Some Aspects of I.R. Spectroscopy of Physically Adsorbed Molecules"

N. Roesch - Technical University, Munich, "CO+K Coadsorption on Transition Metal Surfaces: Insights from Computational Chemistry"

X.D. Zhu - UC Berkeley/UC Davis, "Surface Diffusion of CO on Ni(111)"

W. Ellis - Los Alamos National Laboratory, "Surface Stabilities of Fluoritic Oxides"

X.W. Wang - Center for Advanced Materials, Lawrence Berkeley Laboratory, "First-Principles Calculations of Sulfur on Mo(100)"

A. Gonis - Lawrence Livermore National Laboratory, "A New Method for the Determination of Electronic Structure for Surfaces and Interfaces"

O. Krause - Neste Co., Finland, "Components for the Unleaded Gasoline; Production and Properties"

A. Baiker - Federal Institute of Technology-Zurich, "New Perspectives in the Design of Solid Catalysts"

R. Kaplan - Naval Research Laboratory, "SiC Surface Structure and Composition and the Relation to Oxidation and Metallization"

S.M. Davis - Exxon, Baton Rouge, "Surface Science of Iron-Based Denitrogenation Catalysts"

R. Stulen - Sandia National Laboratory, Livermore, "Interaction of Hydrogen with Diamond(111) and (100) Surfaces"

N. Kruse - ETH-Zurich, "Kinetics of Surface Reactions on the Atomic Scale"

J.J. Barton - IBM-Yorktown Heights, "Photoelectron Holography"

C.S. Fadley - Univ. of Hawaii, "Recent Surface Structure Studies Using Photoelectron Diffraction"

M. Ishikawa - Hokkaido Univ., Sapporo, Japan, "Molecular Approaches in Heterogeneous Catalysis - Surface-Bound Metal Clusters, Their Structural Characterization and Catalysis"

K. Baberschke - Free University, Berlin, "Surface EXAFS: Local Bond Geometry, Debye-Waller Factor and Anharmonic Pair Potential"

S. Bernasek - Princeton University, "Small-Molecule Chemistry on Fe Surfaces"

L. Atanasoska - Univ. of Belgrade, Yugoslavia, "XPS Study of Chemical Bonding at Polyimide Interfaces with Metal and Semiconductor Overlayers"

P. Badziag - University of South Africa, "Atomic Cluster Calculations of Semiconductor Surface Structure"

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