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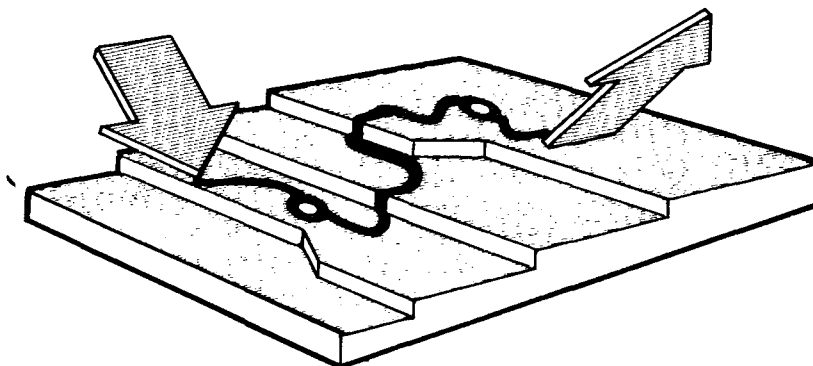
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Second Berkeley CATALYSIS AND SURFACE SCIENCE CONFERENCE

January 1984



Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California

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Second Berkeley
CATALYSIS AND
SURFACE SCIENCE
CONFERENCE

January 1984

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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PROGRAM

SECOND BERKELEY CATALYSIS AND SURFACE SCIENCE CONFERENCE

January 11-13, 1984

Bldg. 50 Auditorium

Lawrence Berkeley Laboratory
Berkeley, California

Wednesday, January 11

8:00 a.m. Bus pickup at Claremont and Durant Hotels
8:30-9:00 Registration at LBL Auditorium
9:00-9:10 G.A. Somorjai—Greetings

CHEMICALS FROM METHANOL

Chairman: H. Heinemann

9:10-9:55 I. Wender (University of Pittsburgh)
*Mechanistic Pathways for the Production of
Chemicals from Methanol*

9:55-10:10 Coffee break

10:10-10:55 C.D. Chang (Mobil Research & Development Corporation)
Methanol Conversion to Light Olefins

10:55-11:40 W.H. Calkins (E.I. DuPont)
Commercial Chemicals from Methanol

11:40-1:00 Lunch

HYDROTREATING OF HYDROCARBONS

Chairman: E.E. Petersen

1:00-1:45 p.m. R.R. Chianelli (Exxon Research and Engineering Company)
Heterogeneous Catalysis by Transition Metal Sulfides

1:45-2:30 H. Topsoe, B.S. Clausen, R. Candia,
O. Sorenson, and N-Y Topsoe (Haldor Topsoe A/S)
*The Role of Cobalt and Molybdenum in
Hydrodesulfurization Catalysts*

2:30-2:45 Coffee break

2:45-3:45 F.M. Dautzenberg and J. De Deken
(Catalytica Associates, Incorporated)
*Reactor Developments in Hydrotreating
and Conversion of Residues*

3:45 Bus returns to hotels

6:00 Bus pickup at Claremont and Durant Hotels
6:30 Cocktails
7:30 Banquet and Lawrence Hall of Science
Speaker: Prof. Alan Dundes
(University of California, Berkeley)

Thursday, January 12

8:15 a.m. Bus pickup at Claremont and Durant Hotels

CATALYST PREPARATION

Chairman: G.A. Somorjai

8:45-9:30 E.M. Flanigen (Union Carbide Corporation)
*Molecular Sieve Materials: Their Synthesis,
Properties, and Characterizations*

9:30-10:00 W.M. Keely, P. Jerus, E.K. Dienes, and A.L. Hausberger
(United Catalysts Incorporated)
*Preparation Techniques of Hydrotreating Catalysts and
Their Influence on the Location of the Metal Oxides
and Performance*

10:00-10:20 Coffee break

10:20-11:05 C.J. Pereira, G. Kim, and L.L. Hegedus
(W.R. Grace and Company)
A Novel Catalyst Geometry for Automobile Exhaust Control

11:05-11:50 J.M. Maselli and A.W. Peters (W.R. Grace and Company)
*Preparation and Properties of Fluid Cracking Catalysts
for Residual Oil Conversion*

11:50-1:30 Lunch

MONOMERS AND POLYMERS

Chairman: A.T. Bell

1:30-2:15 p.m. F.J. Karol (Union Carbide Corporation)
Studies with High-Activity Catalysts for Olefin Polymerization

2:15-3:00 W.W. Kaeding (Mobil Chemical Company)
Zeolite Catalysts for Production of Monomers and Polymers

3:00-3:15 Coffee break

3:15-4:00 J.C.W. Chien (University of Massachusetts)
*Fundamental Studies on High-Activity Catalysts
for Olefin Polymerization*

4:00-4:45 H.L. Hsieh (Phillips Petroleum Company)
Olefin Polymerization Catalyst Technology

4:45 Bus returns to hotels

6:00 Bus pickup at Claremont Hotel only
(walking distance from Durant Hotel)
6:15 Wine and cheese party at Faculty Club
7:30 Bus returns to Claremont Hotel

Friday, January 13

8:30 a.m. Bus pickup at Claremont and Durant Hotels

PHOTOCATALYSIS AND PHOTOVOLTAICS

Chairman: H. Heinemann

9:00–9:45 a.m. A. Heller (Bell Laboratories)
*Photoelectrolysis with Catalyst-Activated
Semiconductor Electrodes*

9:45–10:05 Coffee break

10:05–10:50 G.A. Somorjai (LBL/UC Berkeley)
The Catalyzed Photodissociation of Water

10:50–11:25 F.V. Wald (Mobil Solar Energy Corporation)
*The Present Status of Industrial Production and
Use of Photovoltaic and Photocatalytic Solar
Energy Conversion Devices*

11:25 Concluding remarks

MECHANISTIC PATHWAYS FOR THE PRODUCTION OF
CHEMICALS FROM METHANOL

Irving Wender

University of Pittsburgh

Methanol and formaldehyde (the chief chemical made from methanol) are presently the commercial source of a number of chemicals. In the future, it is possible that methanol, perhaps driven by its large potential consumption as a fuel, will be the source of chemicals that are now produced from other raw materials or feedstocks. Included in some of these are ethanol, methyl acetate, acetic anhydride, methyl formate, acetaldehyde, ethyl acetate, vinyl acetate, glycolic acid, ethylene glycol, and oxalic acid and its esters, oxamide, styrene, and terephthalic acid.

The physical and chemical properties of methanol and the mechanisms involved in the syntheses of some of these chemicals will be discussed.

METHANOL CONVERSION TO LIGHT OLEFINS

Clarence D. Chang

Mobil Research and Development Corporation

Light olefins will play a dominant role in any future methanol-based chemicals economy. The current state of the art of olefin synthesis from methanol is surveyed. Recent results from studies of the zeolite-catalyzed reaction are presented. Included is a kinetic analysis of the influence of reaction and catalyst parameters on selectivity. The interdependence of temperature, pressure, contact time, and catalyst Bronsted acidity in controlling olefin selectivity is detailed. It is shown how olefin formation can be decoupled from aromatization.

Olefin distributions are discussed. Thermodynamic equilibrium is approached at low conversions. With increasing conversion, olefin distributions become kinetically controlled due to autocatalysis.

COMMERCIAL CHEMICALS FROM METHANOL

W. H. Calkins

E. I. DuPont de Nemours and Company

While most of the industrial organic chemicals and polymeric materials produced in the United States today are derived from either petroleum, natural gas liquids, or natural gas, a significant number of important chemicals (formaldehyde, chloromethanes, methyl amines, and acetic acid) are produced from methanol. Methanol itself, while currently produced mainly from natural gas, either has been or is being produced from coal or petroleum fractions and is derivable from any carbonaceous raw material. Products derived from methanol are therefore at least potentially independent of the increasingly expensive and limited supplies of petroleum and natural gas.

Most of the processes for these methanol-derived products have been operating for many years. However, new chemistry uncovered in the past twenty years, particularly in the field of homogeneous catalysis, is now being commercialized. Acetic acid from methanol has been commercial since 1975, displacing the ethylene-based process. A plant for producing acetic anhydride from coal-based methanol is now being completed by Tennessee Eastman. Other methanol-based processes for vinyl acetate, ethanol, and many others are likely to be commercialized in coming years.

The chemistry and processes for both the old and the new commercial products based on methanol will be briefly described in this paper.

HETEROGENEOUS CATALYSIS BY TRANSITION METAL SULFIDES

R. R. Chianelli

Exxon Research and Engineering Company

As supplies of clean petroleum feedstocks dwindle, industry will be called upon to process and upgrade "dirtier" feedstocks (petroleum residua, shale oil, and coal liquids). Feedstocks of this type contain large amounts of sulfur and nitrogen which must be removed for utilization and further processing. Catalysts based on transition metal sulfides are currently used for such processes but fall considerably short of requirements for future use. In spite of the importance of these catalysts, little is understood regarding the general fundamental basis for and origin of their catalytic activity. This paper reports some of our recent studies of the fundamental properties of transition metal sulfide catalysts. The primary effect in the hydrodesulfurization (HDS) of dibenzothiophene by transition metal sulfides is "electronic," i.e., it is related to the position the metal occupies in the periodic table. This effect, which determines the ability of the transition metal sulfides to catalyze the HDS reaction, varies over three orders of magnitude across the periodic table. The first row transition metal sulfides are relatively inactive, but the second and third row transition metals show maximum activity with Ru and Os. Over the years numerous examples of "periodic effects" have appeared in the catalyst literature, and because of their characteristic shape they are called "volcano" plots. The origin of such plots has in the past been explained by noting correlations between such quantities as the heat of formation of a compound or Pauling percent d character and catalytic activity. Recently, using SCF- $X\alpha$ calculations on cluster models of transition metal sulfides, we have been able to identify electronic factors related to catalytic activity. Calculated quantities are combined to form an activity parameter which shows a direct correlation between electronic structure and catalytic activity of the sulfides.

A secondary effect in HDS catalysis by transition metal sulfides is "geometric" in origin. MoS_2 catalysts which have a highly anisotropic layered structure exhibit a poor correlation between total surface area and HDS activity. However, a linear relationship emerges when activities are plotted against O_2 chemisorption. We believe that this arises because the O_2 adsorbs preferentially on the edge planes and not on the basal planes of MoS_2 . Promotion of MoS_2 by Co can be understood by combining geometric and electronic effects. Co is located at the edge planes of MoS_2 . Although the structure of the cobalt-promoted edge plane is unknown, we can postulate that the structure contains a sulfur shared between a Co and a Mo. This sulfur behaves in an "average" way, giving rise to "pseudobinary behavior" and electronic promotion.

THE ROLE OF COBALT AND MOLYBDENUM IN HYDRODESULFURIZATION CATALYSTS

Henrik Topsoe, Bjerne S. Clausen, Roberto Candia,
Ole Sorenson, and Nan-Yu Topsoe

Haldor Topsoe A/S

The industrial developments which have occurred in hydrotreating catalysts (e.g., Co-Mo/Al₂O₃ or Ni-Mo/Al₂O₃) have to a large extent been based on trial-and-error type experiments rather than on an understanding of the nature of the active phase and the factors governing its formation. This is undoubtedly due to the fact that it has not even been possible to arrive at a structural description of the active state of such catalysts, although these have been some of the most studied. However, a detailed understanding of both the structural and the catalytic aspects of such catalysts has recently been obtained. This progress has to a large extent been attributed to the introduction of novel in situ techniques such as Moessbauer emission spectroscopy and EXAFS (extended x-ray absorption fine structure), but it has also been attributed to the application of more conventional techniques (IR, HREM, XPS, etc.) which have been essential in arriving at our present understanding. These new developments will be discussed, and special attention will be given to a description of the catalytically active phase--the so-called CO-MO-S "phase."

REACTOR DEVELOPMENTS IN HYDROTREATING AND CONVERSION OF RESIDUES

Fritz M. Dautzenberg and Jacques De Deken

Catalytica Associates, Incorporated

Selection of the most appropriate residue upgrading technology is a complex, multiparameter problem for many refineries. This paper provides relevant technological information, emphasizing reactor engineering challenges and solutions developed so far. Catalyst deactivation phenomena, hydrodemetallization, and fluid dynamics are discussed for some of the promising catalytic hydrogen-addition technologies. Fixed-bed "trickle-bed" reactor applications and ebullated-bed reactor technology are compared. Slurry-phase reactors are also examined. These emerging technologies offer advantages over well-known commercially available reactor systems, although further developments are required.

MOLECULAR SIEVE MATERIALS: THEIR SYNTHESIS,
PROPERTIES, AND CHARACTERIZATIONS

Edith M. Flanigen

Union Carbide Corporation

An overview of the history and development of molecular sieve materials since their discovery and commercialization will be presented. The evolutionary changes in their composition, sorptive and catalytic properties, surface selectivity, and stability characteristics will be emphasized.

The hydrothermal methods developed for synthesizing molecular sieves by crystallization of reactive hydrous oxide gels will be reviewed, highlighting the innovations in synthesis chemistry and structural and mechanistic concepts which resulted in the discovery of new materials.

The importance of complete characterization of molecular sieve materials as it affects their catalytic properties and applications will be illustrated. Physical, chemical, and spectroscopic methods developed to characterize the structure, composition, purity, and adsorptive and catalytic properties will be reviewed.

PREPARATION TECHNIQUES OF HYDROTREATING CATALYSTS AND THEIR
INFLUENCE ON THE LOCATION OF THE METAL OXIDES AND PERFORMANCE

W. M. Keely, P. Jerus, E. K. Dienes, and A. L. Hausberger

United Catalysts Incorporated

A series of alumina-supported cobalt molybdenum oxide catalysts were prepared by different procedures and tested for hydrodesulfurization of a light cycle oil. The different catalyst preparation procedures involved various salts of cobalt and molybdenum and variations in the order of addition of these salts. Surface study methods, ESCA, SEM, and TEM were used to characterize the catalysts in addition to the conventional bulk chemical and physical analyses. The activities of the catalysts were found to vary with the preparation technique, and these results are compared to the corresponding bulk and surface properties of the catalysts.

The various catalyst preparation procedures demonstrated the importance of the type of cobalt and molybdenum salts and the influence of order of addition as compared to simultaneous addition and dry compounding. Surface enrichment was studied by SEM and ESCA and correlated to preparation type and performance. X-ray diffraction studies, surface area, pore volume, and pore volume distribution were related to surface information, preparation type, and performance. X-ray fluorescence documentation indicated major and minor components and all trace impurities in the carrier and active ingredients.

A NOVEL CATALYST GEOMETRY FOR AUTOMOBILE EXHAUST CONTROL

C. J. Pereira, G. Kim, and L. L. Hegedus

W. R. Grace and Company

There are two catalyst support systems in current commercial use in automobile exhaust converters. Converters containing catalyst pellets are characterized by excellent heat and mass transfer properties but often possess significant thermal inertia. Monolithic converters, while having favorable thermal characteristics, are limited by laminar-flow transport properties.

A new catalyst geometry has been developed which attempts to combine the favorable characteristics of the above two systems. The support consists of high-porosity alumina, extruded to the shape of very small monoliths.

The paper will discuss the performance characteristics of this new catalyst in simulated automobile exhaust.

PREPARATION AND PROPERTIES OF FLUID CRACKING CATALYSTS
FOR RESIDUAL OIL CONVERSION

James M. Maselli and Alan W. Peters

W. R. Grace and Company

Increasing numbers of refiners are cracking residual oil to gasoline and other higher value products in fluid bed units. The catalysts used are significantly different from catalysts that would be designed to process gas oil distillates. They must be able to maintain activity and selectivity in the presence of large amounts of nickel and vanadium contaminants, and must have increased hydrothermal stability as a result of generally higher regenerator temperatures. There must also be a pore structure and a surface activity within the pore capable of cracking very large resid-type molecules. At the same time the catalyst is converting these residual molecules to gasoline and other liquid products, the amount of coke produced must be minimized. In addition, in order to be retained in the unit, the catalyst must be hard and have a certain optimum density for fluidization.

No single prescription can fill all of the requirements. Qualitative reaction engineering principles suggest that low surface area or the wrong type of surface can result in excessive metals deactivation, while too high a surface area and small pores may cause excessive amounts of gas or coke. The optimum catalyst is bifunctional, containing an optimum mix of zeolitic and amorphous matrix activity.

STUDIES WITH HIGH-ACTIVITY CATALYSTS FOR OLEFIN POLYMERIZATION

F. J. Karol

Union Carbide Corporation

Olefin polymerization catalysis is an area of great technological importance forming the basis of several large-scale processes for production of high- and low-density polyethylene, polypropylene, and ethylene-propylene and diene rubbers. Significant progress in research and development continues to be made through worldwide studies in catalysis.

Reactions of specific magnesium, titanium, and aluminum compounds have provided a major impetus in the development of high-activity Ziegler-Natta catalysts. Operational methods to these catalysts have included: (1) chemical anchoring to the surface of substrates, (2) formation of bimetallic complexes, (3) insertion into defects of a substrate, (4) formation of high-surface-area sponges, and (5) precipitation to form solid solutions containing magnesium halides. The presence of magnesium in high-activity catalysts for ethylene polymerization provides high productivity, stability from deactivation processes, an increase in chain transfer response, and leads to polyethylenes with a narrow molecular weight distribution.

X-ray diffraction studies have been carried out to monitor the effect of different degrees of activation of $MgCl_2$ on its crystal structure. Scanning electron microscopy has been widely used in the study of catalyst morphology and the replication of this morphology in the resultant polymer particles. Electron spin resonance studies have helped to probe the valence state and ligand environment in highly active Ziegler-Natta catalysts. Numerous analytical techniques have been used to study reactions between aluminum alkyls and electron donor modifiers in $MgCl_2$ -supported propylene polymerization catalysts. Recent views of the origin of stereospecificity in the synthesis of isotactic polymers connect this origin with the ability of the catalyst-growing polymer system to distinguish between the two prochiral faces of the α -olefin.

Results of experiments to determine the number of active centers (C^*) have indicated that for first generation Ziegler-Natta catalysts only a small fraction of the total amount of transition metal compound is catalytically active at any time. Catalysts of higher productivity often show higher (C^*) values.

The direct use of organometallic compounds of transition metals for preparation of solid catalysts has been well documented, and active research continues in this area. Catalyst research with transition metal oxides on refractory metal oxides, e.g., CrO_3/SiO_2 , remains an area of continuing study, with emphasis on factors involved in chemical anchoring of CrO_3 to the silica surface, and to the effect of silica surface modifications on the nature and behavior of active sites.

After nearly a half century of preparation of low-density polyethylenes at pressures up to 50,000 psi and polymerization temperatures near 300°C, radical new technology capable of operating at less than 300 psi and near 100°C has emerged (LLDPE). Key to the new developments is families of catalysts that trigger the polymerization reaction at the much lower pressures and temperatures.

ZEOLITE CATALYSTS FOR PRODUCTION OF MONOMERS AND POLYMERS

Warren W. Kaeding

Mobil Chemical Company

New, synthetic, high-silica zeolite catalysts have been discovered and developed for alkylation and disproportionation reactions. The eventual large-volume end products for commerce are monomers and polymers. The first process applications at Mobil, which are now firmly established in the marketplace, are the alkylation of benzene with ethylene to produce ethylbenzene for subsequent conversion to styrene and isomerization of ortho/meta xylene raffinate mixtures to the para isomer for purification and oxidation to monomer grade terephthalic acid. Direct preparation of p-xylene by selective toluene disproportionation and selective alkylation of toluene with methanol over modified ZSM-5 catalysts have been reported.

More recently, p-methylstyrene (PMS) monomer has been produced in multimillion pound quantities for testing in the marketplace. A variety of poly-PMS polymers and copolymers have been produced and compared with the corresponding polystyrene analogues. A number of advantages have been demonstrated. Several other hydrocarbons have been produced by means of various zeolite catalysts for subsequent conversion to the corresponding vinyl analogues.

FUNDAMENTAL STUDIES ON HIGH-ACTIVITY CATALYSTS FOR
OLEFIN POLYMERIZATION

James C. W. Chien

University of Massachusetts

Important new advances have been made on the designing of new catalysts. A prerequisite is that the structure of the catalyst and its relationships to function are completely understood. Olefin polymerization catalysts are more complicated than other catalysts for several reasons. The catalysts require high utilization of Ti sites possessing strict stereospecificity. Control of molecular weight and bulk density are the other necessary features. Because polymerization and crystallization occur simultaneously, diffusion limitation can be a factor.

In recent years a new generation of Ziegler-Natta catalysts has been developed using rather involved procedures. We have characterized each intermediate state during the catalyst preparation with BET surface area, mercury porosimetry, redox titrations, EPR, FTIR, GC-MS, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, electron microscopy, elemental analysis, and other techniques. The kinetics of polymerization were studied by radiotagging of active sites and radio-quenching of growing and dormant chains. The question of monomer diffusion limitation has been resolved by comparing the polymerization of propylene to insoluble isotactic polypropylene and of decene-1 to soluble isotactic poly-(decene-1).

OLEFIN POLYMERIZATION CATALYST TECHNOLOGY

H. L. Hsieh

Phillips Petroleum Company

In the mid-1950's a series of patents on a new ethylene polymer was issued. These patents were all similar in that solid catalysts were used to produce polyethylene at relatively low ethylene pressures. This early technology for high-density polyethylene may be broadly grouped in terms of three different processes, Phillips, Standard Oil of Indiana, and Ziegler. Today, only Phillips and Ziegler are of commercial significance.

The Phillips catalysts were discovered by Hogan and Banks in 1951. The chemistry and technology of these catalysts were extensively studied--since the discovery. Large-pore amorphous silicas, finely divided and promoted with Cr(VI) oxidic species, constitute the catalysts. Formation of active sites occurs from the initial reaction of ethylene with the Cr(VI) surface compound. Polymerization of ethylene is done by suspending the catalyst in a low-boiling paraffin in which ethylene is dissolved. Commercially, production is done at high rates in loop reactors which operate continuous flow at 97-98% conversion per pass. Polyethylene can be produced at the desired molecular weight by varying reactor temperature and catalyst type and by use of hydrogen. Densities ranging from above 0.96 down to 0.925 have been produced commercially by varying catalyst and 1-olefin addition. With the recent modifications and improvements, they make it the most versatile catalyst on the market today. One can achieve broad molecular weight distribution, high-melt indices in the particle form process, and a very wide range of physical properties by simple modification of the catalyst or activation conditions.

The term Ziegler-Natta catalyst is conventionally used to mean a titanium tetrachloride solid used in conjunction with an aluminum alkyl to polymerizing olefins. The use of these catalysts to produce polyethylene initially grew at a much slower pace than the chromium oxide on silica catalysts. The main difficulty with the original Ziegler-Natta catalysts was that yield of polymer per unit of catalyst was so low that the catalyst had to be extracted from the polymer. This greatly increased the cost of using Ziegler-Natta catalysts as compared to chromium oxide on silica catalysts where yield based on chromium was sufficient so that washing was not necessary. This led to a great deal of research on Ziegler-Natta catalysts to find means of improving productivities.

This research effort has paid off and resulted in so-called "second generation" catalysts. These high-productivity catalysts are supported on a variety of carriers. These supported catalysts violate the basic tenet that heterogeneous catalysis, being a surface reactor, is relatively inferior to soluble catalyst systems. Catalysts with very high productivities started appearing in the 1960's and have continued into the 1970's. In more recent

years the primary interest has not been in catalyst productivity, but more in the area of polymer properties. As the polyolefin business becomes more competitive and the cost of production escalates, it becomes more and more important to control precisely such factors as molecular weight, polydispersity, and chain branching.

The other major commercially important polyolefin resin is stereospecifically polymerized polypropylene. The Ziegler-Natta system polymerizes not only ethylene but also propylene. Phillips catalyst does both as well, but the polymerization of propylene with it is of little commercial value. The different stages of development of commercially important catalysts are reviewed. The new generation of supported catalysts which have very high productivities and stereospecificities have been developed. The economic significances of these new catalysts are examined.

PHOTOELECTROLYSIS WITH CATALYST-ACTIVATED
SEMICONDUCTOR ELECTRODES

Adam Heller

Bell Laboratories

Classical catalysts of electrolytic processes that reduce the overpotential of electrode reactions also activate semiconducting photoelectrode surfaces. The photogenerated minority carriers, i.e., electrons in photocathodes and holes in photoanodes, are dissipated by the kinetically competing, potential-dependent reactions of carrier recombination and transfer to the electrolyte. The quantum efficiency of transfer depends on the relative rates of the recombination and transfer reactions. Thus, for example, in the p-InP photocathode, surface recombination can be reduced by a 6-10 Å thick layer of an anodically formed hydrated indium oxide. When a catalyst such as Rh, Re, Ru, or Pt is incorporated in the surface, the quantum efficiency of the hydrogen-generating p-InP photocathode, operating at a potential 0.5 V positive of a reversible hydrogen electrode and at pH0, reaches 0.8. Incorporation of Pt increases the quantum yield by a factor of 10^4 .

Uniform films of platinum group metals of 50-80 Å thickness absorb one-half of the minority carrier generating photons. Further losses are incurred because of reflection. To avoid these losses, the average catalyst film thickness must be on the order of 10-20 Å. Such thin films are usually inhomogeneous: the catalysts are porous or form islands. To assure efficient collection of the photogenerated carriers, neither the diameter of the pores nor the distance between the islands must exceed the diffusion length of the carriers, typically of 10^3 - 10^4 Å when the carriers are not drained by transfer to the electrolyte, and substantially less when they are.

The theoretical limit to the reduction in the voltage bias that can be achieved by substituting a classical hydrogen evolving electrode (such as metallic Pt) by a semiconducting photocathode (such as Pt-activated p-InP) is the height of the barrier to majority carrier transport from the semiconductor to the electrolyte. When the diameter of the pores in the catalyst film or the distance between the catalyst islands is smaller than the minority carrier diffusion length, the effective barrier height is the lesser of the two barriers of the two junctions, one between the semiconductor and the catalyst and the other between the semiconductor and the solution. Since the theory of Schottky junctions predicts that the height of barriers at junctions of p-type semiconductors and metallic catalysts should increase with the work function of the metals (up to its limit in hydrogen-evolving electrodes, i.e., the barrier of the semiconductor H_2/H^+ redox couple junction), one would expect that the gain in bias voltage in photoelectrolytic cells will depend on the catalyst's vacuum work function. One finds, however, no such dependence. The gain in bias at vanishingly small photocurrent densities is the same for all catalysts, even when these are deposited to form nonporous

thick films, and it does not differ substantially from that of the uncatalyzed electrode. This indicates that the work function of the hydrogen-saturated catalyst at the semiconductor surface equals the work function of H_2/H^+ redox couple. G. A. Somorjai suggested that the constancy of the barrier height may be due to the doping of the surface of the p-type semiconductor with hydrogen atoms. These, if ionized to protons and electrons, make the surface strongly n-type. Thus, the result of exposing a p-type semiconductor to hydrogen atoms, either alloyed by the catalyst or formed at the bare semiconductor surface upon photoelectrolysis, would be the formation of a p-n⁺ junction. The p-n⁺ junction has, by definition, the largest barrier and reduces the voltage bias required in a photoelectrolytic cell more than any other possible junction.

To date, the most efficient photoelectrochemical cells are based on hydrogen-generating Rh-activated p-InP photocathodes. The solar-to-hydrogen efficiency of these photocathodes is 13.3% when the efficiency is measured by dividing the electrical power that can be generated from the photoelectrochemically produced hydrogen by the solar irradiance (integrated over all wavelengths), and 16.4% when measured as the ratio of the electrical power conserved in the electrolytic process and the solar irradiance.

THE CATALYZED PHOTODISSOCIATION OF WATER

G. A. Somorjai

Lawrence Berkeley Laboratory and Department of Chemistry
University of California, Berkeley

The dissociation of water to hydrogen and oxygen requires energy of $\Delta G_{298} = 258$ kJ/mole. By irradiating insulators with light of energy greater than this amount, one may produce electrons in the excited state and electron vacancies at the surface that can perform the photochemical reduction ($2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H} \longrightarrow \text{H}_2$) and oxidation ($2\text{OH}^- + 2\oplus \longrightarrow \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + (1/2)\text{O}_2$).

There are several semiconductors, SrTiO_3 , TiO_2 , CdS , and Fe_2O_3 among them, that can photodissociate water. Some possess sites for both reduction and oxidation, while others carry out the two processes at different surfaces. A reversible solid state reaction that involves changes in the transition metal ion oxidation state must accompany the splitting of water. Platinum, rhodium, and ruthenium oxide, when deposited on the semiconductor, serve as catalysts that accelerate the water photodissociation. These additives accelerate the recombination of hydrogen and oxygen atoms, shift the semiconductor Fermi level to a more favorable position that improves the thermodynamic feasibility for the process, accelerate electron transport, and inhibit side reactions like the photoreduction of oxygen. Many of the elementary reaction steps leading to photoproduction of hydrogen and oxygen have been identified and will be discussed.

THE PRESENT STATUS OF INDUSTRIAL PRODUCTION AND USE OF
PHOTOVOLTAIC AND PHOTOCATALYTIC SOLAR ENERGY CONVERSION DEVICES

F. V. Wald

Mobil Solar Energy Corporation

At the present time, no photocatalytic solar energy conversion devices are in industrial production or use. Only single-crystal silicon-based photovoltaic diodes are now being produced in quantities approaching an industrial scale, and a number of "new" generations of polycrystalline and amorphous silicon materials support fabrication on a limited pilot scale. These products are all sold for a variety of remote site applications and even field tests on a large scale, such as multimegawatt utility installations.

In fact, there are at present three different generations of new silicon materials which are fabricated in pilot production runs as a basis for preparing large area solar cells ($\sim 50\text{-}100\text{cm}^2$) on scale of $\sim 10,000$ devices/week to $\sim 100,000$ devices/week or a few hundred kW to several megawatts per year. The scale of operations is sufficient to support the development of simplified and automated cell manufacturing and panel production methods, and the industrial success of photovoltaics very much depends on that, as about one-half to two-thirds of the total photovoltaic module cost is due to these operations.

However, it is thought by most that the true challenge of photovoltaics lies in providing a new materials base of much lower cost, such that it could support very large-scale photovoltaic panel technology at levels of less than \$1/watt.

The four generations of silicon materials which are now being investigated for production thus range from the well-known Czochralski-grown single-crystal material over casting and sheet growth techniques to amorphous silicon films. All of these possess various advantages and disadvantages which the paper will aim to discuss and assess in relation to the levels of upscaling which are necessary if the industry is to have an impact on the power supply picture of the U.S.

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