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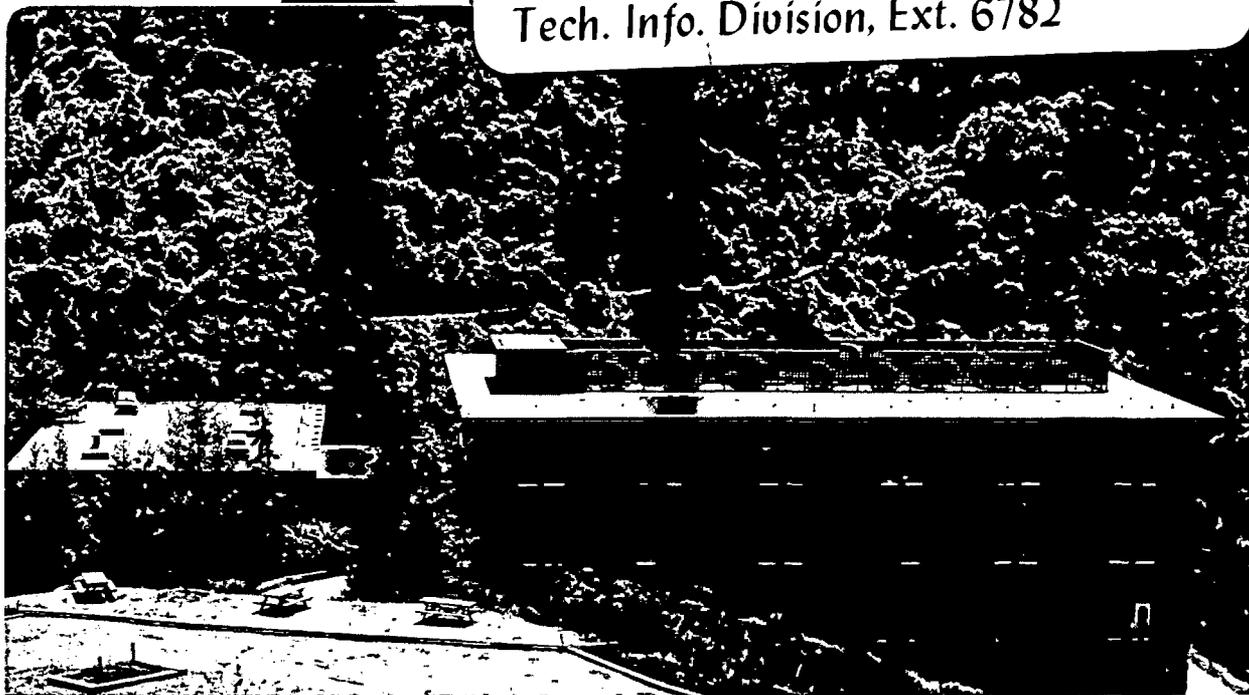
RECENT ADVANCES IN HETEROGENEOUS CATALYSIS

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RECENT ADVANCES IN HETEROGENEOUS CATALYSIS

G. A. Somorjai and P. R. Watson

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory,
and Department of Chemistry,
University of California, Berkeley, CA 94720

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INTRODUCTION

The study of heterogeneously catalyzed reactions is, despite its long and varied history, an area of active and tremendous concern for both academic and industrial researchers. The events of the last decade have shown us that we cannot rely on traditional feedstocks for the future. As a result the chemical industry worldwide has embarked on programs of catalytic research aimed at tailoring catalysts that can more efficiently crack poorer grades of crude oil or are able to catalyze the formation of fuels and commodity chemicals from new carbon sources such as biomass and synthesis gas, CO and H₂. Environmental concerns have resulted in new breeds of catalysts such as are used in automobile exhaust systems.

Paralleling these new technical developments there has been a resurgence of interest in providing microscopic descriptions of catalyst structure and behavior. Much of the impetus for this revitalization in heterogeneous catalysis research has been the rapid and impressive development, both in an instrumental and theoretical manner, of experimental tools that are sensitive

to various atomic scale properties of surfaces.

Many of the electron and photon spectroscopies have been developed by surface scientists are being employed with increasing regularity and success for both model and actual catalysts. As a result it is becoming clear that we can achieve a detailed microscopic description of the surface properties of a catalyst and start to find correlations between these properties and catalytic performance and new insights into the catalytic process. Thus we are standing at an exciting time in the history of heterogenous catalysis. Many bold new technical developments are underway, and it appears that in some cases we are drawing ever closer to the catalytic chemists' dream of having a sufficiently detailed understanding of atomic scale factors that determine the performance of a catalyst and the mechanistic details of the catalytic performance to be able to tailor new catalysts with suitable properties to perform specific functions.

In view of this wealth of information this survey limits us by its size to the discussion of a few selective areas of modern catalysis science. Selection of topics and their treatment reflect the interests of the authors, and it is certainly not complete since we neglect, for example, some important aspects of modern catalysis science such as carbon monoxide chemistry as is already covered in this volume. However, the subjects we have chosen we consider to represent an interest in selection of recent discoveries which show to advantage the cutting edge of both new technological and scientific advances.

NEW TECHNIQUES OF CATALYSIS RESEARCH

Over the past 15 years a very large number of experimental techniques have been developed that can inspect heterogeneous catalyst surfaces on the atomic scale.¹ Many of these techniques are directly applicable to the investigations of the small catalyst particles in a configuration that is very similar to that used in the industrial technology. These systems contain catalyst particles of 20-150 Å in size that are dispersed on high surface area supports. Photoelectron spectroscopy (XPS) can determine the composition of the particles and the oxidation states of surface atoms as many successful experiments testify. Extended X-ray absorption fine structure studies (EXAFS), using X rays from the high intensity synchrotron or rotating anode sources, can determine the coordination number of surface atoms of the small atomic clusters and the surface composition. Most of the other surface sensitive probes must be employed using external surfaces as they cannot find their way inside the small pores of the catalyst supports or they cannot back scatter readily. These probes are usually low energy electrons or ions instead of photons that must also be employed in high vacuum to obtain reproducible results. These surface techniques are utilized on model catalyst systems that are fabricated by the deposition of small particles on the external surfaces of oxide films. Often single crystal surfaces of metals or oxides, catalysts with well defined structure and composition are used in these investigations. Low energy electron diffraction (LEED) determines the atomic surface structure of the clean surface and of monolayers of adsorbates as long as the surface species are well ordered. High resolution electron energy loss spectroscopy (HREELS) determines the vibra-

tional spectra of adsorbed atoms and molecules and can readily detect hydrogen on surfaces. Auger electron spectroscopy (AES) determines the surface composition along with XPS. Ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy (SIMS) are sensitive probes of the surface composition. These are perhaps the most frequently used techniques of modern surface science for studies of catalysts that joined many other techniques in this field (infrared spectroscopy, isotope labeling, electron spin resonance, Mossbauer spectroscopy, to name a few) to provide a picture of the catalyst surface structure and composition on the molecular scale.

Catalysis is a kinetic phenomenon, and studies in this field require the determination of rates and product distribution. Usually these studies have to be carried out at high pressures and high temperatures. In order to bridge the pressure gap that exists between the conditions necessary to analyze the surface structure and composition (high vacuum) and those required for catalytic reaction studies a low pressure-high pressure reaction cell was developed which combines surface science and catalytic studies.² The sensitivity of this small reactor is so high that it can readily determine reaction rates and product distributions for sample catalysts no larger than 1 cm^2 in surface area. Such small area samples can be prepared with uniform structure and composition that is usually difficult with high surface area catalysts. Thus the correlation between the catalyst surface structure and the composition on one hand, and its reaction rate and product distribution on the other can be reproducibly studied and determined. As a result, the atomic scale characteristics of complex catalysts that make them active and selective are being uncovered.

NEW-OBSERVATIONS AND CONCEPTS EMERGING FROM SURFACE SCIENCE STUDIESa. Surface Irregularities, Steps, and KinksAre Active Sites for Breaking Chemical Bonds

Studies of transition metal crystal surfaces revealed the importance of atomic height steps and kinks to break H-H, C-H, C-C, and CO bonds with near zero activation energies.³ On terrace sites of higher symmetry there is often a small activation energy for bond scission that decreases the rates of these elementary surface chemical processes as compared to the chemical reaction rates at the surface defects. By suitable manipulation of the surface structure, the relative concentrations of the various surface irregularities can be altered that, in turn, can change the rates of competing surface reactions and thus the product distribution. By blocking some of these small concentration surface sites with sulfur or other chemically inert metals, the reaction selectivity can often be improved.

b. The Oxidation State of Surface Atoms Can Strongly Influence the Selectivity of Catalytic Reactions.

Recently the catalyzed hydrogenation of CO has been investigated on transition metal and metal oxide surfaces.⁴ Very different rates and product distributions were found as the oxidation state of the surface atoms are altered. Rhodium metal produces largely methane from CO and H₂, while Rh₂O₃ produces olefins and oxygenated products such as acetaldehyde. LaRh₂O₃ yields alcohols in high concentrations. Iron metal is readily poisoned by the building of a multilayer of carbon during the CH₂ reaction. Fe₃O₄, on the other hand, remains active and selective and exhibits a product distribution very different from that of iron.

It appears that the changing binding energies and dissociation probabilities of adsorbed molecules as the oxidation states of surface atoms are changed strongly influence the surface concentrations of adsorbed species and the nature of the reaction intermediates. As a result, the reaction rates and product distribution are also altered.

c. Monolayers of Carbonaceous Deposits on the Catalyst Play Important Roles in Determining Catalytic Activity and Selectivity

There are many hydrocarbon reactions that occur at relatively low temperatures ($<200^{\circ}\text{C}$); these are hydrogenation, dehydrogenation, and isomerization to name a few. These reactions occur with high turnover numbers while others need higher temperatures ($>200^{\circ}\text{C}$). These reactions include dehydrocyclization and hydrogenolysis. C^{14} isotope labeling experiments revealed that carbonaceous overlayers form on the catalyst surface in both temperature regimes.⁵ During the low temperature reactions, the carbonaceous deposits rehydrogenate at a rate that is faster than the turnover number. Thus the catalytic reactions take place on the metal surface in this circumstance. However, at high temperatures, the rate of rehydrogenation of the carbonaceous deposits is much slower than the turnover number of the hydrocarbon reactions. As a result the reaction must take place on top of the carbonaceous layer -- not on the metal surface. This finding necessitates the rethinking of many of the reaction schemes that assumed the surface reactions to occur only on the metal surface. The importance of the chemical bonding of the adsorbates to the carbonaceous fragments and the hydrogen transfer between the fragments and the adsorbed molecules is clearly indicated by these studies and influence reactivity and selectivity of hydrocarbon reactions.

d. The Role of Additives, Electron Donors and Acceptors During Catalytic Reactions

The formulation of many catalysts include the addition of electron donors, mostly alkali metals or electron acceptors, halogens or oxygen. For example, alkali salts are added to iron catalysts used in ammonia synthesis or to the iron catalyst used for the hydrogenation of carbon monoxide. Chlorine is added to platinum reforming catalysts that are dispersed on alumina support.

These additives play several important roles through which they influence reactivity and selectivity. These roles are being verified by recent surface science studies. Potassium helps to remove carbon from iron surfaces as CO_2 by a catalytic side reaction that involves the formation of KOH and perhaps also K_2CO_3 . Potassium increases the heat of adsorption of N_2 on iron, and increases the activation energy for dissociation of N_2 to atomic nitrogen. It also increases the dissociation probabilities of carbon monoxide on iron and the heat of adsorption of carbon monoxide on platinum.

Charge transfer between the additives and the catalyst leads to charge redistribution that can modify the oxidation states of surface atoms. Chlorine is known to facilitate the redispersion of noble metal particles. Thus the surface structure of catalysts can be altered by additives most likely through their effect of the changed relative surface free energies of the various crystal faces. Oxygen adsorbed at a kink site on platinum surfaces was found to exhibit enhanced catalytic activity in hydrogenolysis reactions.

BUILDING OF NEW CATALYSTS

a. Advances in Alloy Catalysis--Bimetallic Clusters

There has been a long-standing interest in exploring the electronic factor in catalysis through the use of bimetallic catalysts.⁶ New developments in the preparation and characterization of highly dispersed bimetallic cluster catalysts have resulted in successful commercialization.⁷ A supported bimetallic catalyst can be made quite simply by impregnating a high surface area support, such as silica or alumina, with an aqueous solution of salts of the two metals of interest. The dried material is then reduced in hydrogen to provide highly dispersed particles. Alternatively, the starting point can be a molecular complex containing two metal atoms already bound together. An example is the use of SiO₂ impregnated with (Co₂Rh₂)(CO)₁₂ as a catalyst precursor.⁸ These procedures result in the formation of very small metal clusters dispersed on the surface of the carrier. An interesting question is whether the clusters will be monometallic or contain atoms of both metals. On statistical grounds we might expect them to be bimetallic, and this has been shown experimentally even for cases in which individual metals show very low bulk miscibility.

Direct experimental verification has emerged in various ways. First, a catalytic reaction is used to probe the interaction between the two metallic components. A favorite reaction has been the hydrogenolysis of ethane to methane. An example of this type of investigation has been performed by Sinfelt for the Cu-Ru and Cu-Os systems supported on silica.⁹ In these cases addition of copper to the Group VIII metal markedly reduced the hydrogenolysis activity. Experiments of this type demonstrate clearly that the two metals are not isolated from each other on the carrier surface and

provides evidence for the existence of bimetallic clusters. From the point of view of practical catalysis, such systems are of interest as inhibition of hydrogenolysis may improve the selectivity to more desirable reactions such as dehydrocyclization and isomerization.

The second approach to characterizing the bimetallic nature of these cluster catalysts has been that of X-ray diffraction which has been applied with some success to naphtha reforming catalysts containing two Group VIII metals (e.g., Pt-Pd, Pt-Rh, Pt-Ir).¹⁰

Platinum and iridium crystallize in the fcc structure and form solid solutions in all proportions in the bulk. The lattice parameter is a function of the composition and hence can be used to demonstrate the presence of bimetallic clusters in silica supported Pt-Ir catalysts. The X-ray diffraction pattern from a mixture of 10% Pt-SiO₂ with 10% Ir-SiO₂ shown a broad line due to the overlapping of lines from individual clusters of Pt and Ir, estimated to be 56 Å and 27° in size, respectively. The pattern from a bimetallic cluster catalyst (10% Pt, 10% Ir-SiO₂) shows a single symmetric line corresponding to clusters of 49⁴ size and a lattice parameter corresponding to a 1:1 mixture of Pt and Ir, in agreement with the overall composition.

The application of X-ray diffraction to more highly dispersed catalysts becomes very difficult. In order to obtain information on more highly dispersed clusters a third technique, that of extended X-ray absorption fine structures (EXAFS), has been developed (see section 2). EXAFS results on a 1% Ru-Cu on silica catalyst,¹¹ indicate that the ruthenium component is very similar to the ruthenium in a silica-supported ruthenium reference catalyst with an average coordination number of $\underline{11}+1$. The

ruthenium atoms are coordinated mainly to other ruthenium atoms and only to a minor extent to copper atoms. However, the copper component of the bimetallic cluster has an average coordination number of 9 ± 2.5 and appears to have a more equal distribution of copper and ruthenium nearest neighbors. These results are consistent with a cluster in which the copper is present on the surface of a small core of ruthenium atoms.

The ruthenium-copper catalyst is complex in the sense that a distribution of cluster sizes is observed by electron microscopy which may exhibit some variation in shape. The EXAFS results, especially the average coordination number of ruthenium close to 12, indicate that the majority of the clusters have a three-dimensional form and that rafts of two atomic layers are only a minor component, which had been suggested previously.

Automotive Exhaust Catalysts

The use of catalytic converters to reduce the emissions of unburned hydrocarbons, CO and nitrogen oxides in exhaust gases, has a history going back over 40 years. As early as 1949, Houdry¹² developed mufflers for trucks used in confined spaces such as mines and warehouses. Remarkably, one of these anticipated developments that were to occur on a large scale in the 1970's was a catalyst of monolith-porcelain rods with an alumina washcoat on which platinum was deposited.

The impetus that opened up this new field of catalytic chemistry was given by the United States Federal Clean Air Act of 1970 which set standards of emission that could not readily be met by the existing technology of internal combustion engines and spurred an intensive research effort. The initial maximum concentration of emissions were specified to

reduce carbon monoxide and hydrocarbon emissions by 90% or more of those previously emitted. Control on nitrogen oxide emissions came somewhat later. Enforcement of the law was delayed and interim standards adopted, but all new cars (with the exception of Honda which uses an improved combustion system) sold in the U.S. since 1976 have been equipped with catalytic converters.

Exhaust Gas Composition

Ideally, the automotive engine receives a stoichiometric mixture of air and gasoline (14.7:1 by weight) which is completely combusted to CO_2 , H_2O , and N_2 . In practice, lean mixtures (16:1) are desirable for economical cruising, and rich mixtures (12:1) for starting and acceleration. The combustion process is never complete so that the exhaust gases contain carbon monoxide, hydrocarbons, hydrogen, and oxygenated organics such as formaldehyde. Some of the nitrogen in the air is oxidized to nitrogen oxides during combustion.

The major problems associated with designing catalytic converters is not just one of finding a catalytic system that will produce the required reductions in emissions, but one that will keep on doing its job for many thousands of miles and under an extremely wide range of operating conditions.

The major difficulty is the requirement of efficient operation under transient conditions. In most major catalytic processes employed in the chemical industry, continuous steady-state operating conditions are utilized. In the urban car we have to deal with start-up conditions and

with the recurring transient conditions of stop-and-start urban driving. The concentrations of the major pollutants can change drastically with air-to-fuel ratio during acceleration. The exhaust gas temperature may vary between 300 and 1000°C¹³ while the gas flow rate may change by an order of magnitude or more, and typically affords a contact time with the catalyst of only a few milliseconds.¹⁴

Further constraints on the choice of catalyst are that the oxidizing atmosphere of the auto exhaust contains not much more than a stoichiometric amount of oxygen and about 15 mole-% water. The catalyst should also have a lifetime that is a substantial fraction of the lifetime of the car. An efficient automotive catalytic converter must operate well within narrow ranges in the four variables: gas flow rate, temperature, gas composition, and poison concentration. The catalytic system can tolerate occasional excursions from these ranges, but prolonged variations are not permitted.

Catalyst Strategies A large research effort has gone into finding suitable catalysts that will lower nitrogen oxide, carbon monoxide, and hydrocarbon emissions, within the constraints detailed above. The catalytic reduction of NO by a reducing agent such as CO or H₂ proceeds at reasonable rates on a number of catalysts, but if oxygen is present it will be preferentially reduced. Therefore, it is necessary to provide a net reducing atmosphere to reduce NO to nitrogen. This is in contrast to the oxidizing conditions needed to convert CO and hydrocarbons to CO₂ and water.

Of the many types of catalysts tested, the most successful for both oxidation and reduction appear to be the platinum group metals. These are

usually dispersed as small crystallites on alumina. Three major support shapes are spheroids, wire mesh, and monolithic honeycombs. A washcoat of high surface area alumina is usually placed on the ceramic surface to act as the substrate for the metal. Unfortunately, the use of such catalysts places a heavy demand on the continued availability of noble metals which are principally mined in the Soviet Union and South Africa. Research to find a suitable non-noble metal catalyst substitutes for the presently used platinum based catalysts is an active and important area of research at present.¹⁵

The most successful automobile emission catalyst is the "3-way redox" system. Simultaneous oxidation and reduction can take place in a single catalytic bed, provided that the air-to-fuel ratio is maintained close to the stoichiometric 14.7:1. In this window NO_x conversion to N_2 is still high, while CO and hydrocarbon is still over 80%. In order to achieve the precise metering necessary to maintain the stoichiometric ratio, a feedback control mechanism, equipped with an oxygen sensor to measure oxygen pressure in the exhaust gas, must be provided. The prime catalysts for the redox system are rhodium, platinum, palladium, or rhodium-platinum catalysts. This catalyst is the workhorse of the auto emission control technology at present.

Poisoning

The use of platinum-type emission catalysts necessitate the elimination of potential poisons from gasoline, most prominently lead compounds. All automobiles equipped with catalytic converters must use unleaded gasoline. This means that the octane number of the gasoline must be boosted by catalytic reforming or cracking and by additives other than tetramethyl lead. In turn, more crude oil must be processed since the yield of gasoline

from the crude decreases with increasing octane requirement.

Strong Metal Support Interaction (SMSI)

In many important applications such as automotive exhaust purification, gasoline octane improvement, and the manufacture of fats and oils, the catalyst consists of small metal particles distributed in the pores of a porous inorganic oxide. These support oxides, such as alumina or silica, have high surface areas, often greater than 200 square meters per gram. A dilute solution of a metal salt can be dispersed over this large area and, subsequently, reduced, resulting in very small metallic particles of the order of 20 Å in size. As a result, most of the catalyst atoms are surface atoms and, as the catalytic reactions occurs on the catalyst surface, this represents a more efficient catalytic utilization of the available metal, a particular economic benefit in the case of expensive catalysts such as the noble metals.

The function of the catalyst support is, therefore, to provide an efficient dispersion of the metallic catalyst and to maintain it under processing conditions by keeping the particles far enough apart to prevent agglomeration. This view of the function of the support being a merely physical role has been borne out in large measure in practice. In general, the support has not been thought to exert profound effects on the activity or selectivity of supported-metal catalysts,¹⁶ and there has been no need to invoke any large degree of metal-support interaction. However, the intimate association of metal and support provides a potential for such an interaction and, in some cases, it has been shown that the nature of the support can influence catalytic activity.

More recently, there has appeared evidence for a type of metal-support interaction of a more pronounced nature. This has been termed,

"strong metal-support interaction," or SMSI in which there is direct physical evidence of strong bonding as well as alterations of catalytic properties.

Characteristics of SMSI

The most obvious characteristics of a system exhibiting SMSI are shown in the strongly altered chemisorption properties. The chemisorption of H_2 and CO are used on routine basis to measure both the dispersion of the metal to allow rate measurement on the basis of surface instead of total metal atoms, and in the case of CO to gain chemical information from studies of the CO stretching frequency. The indicator of SMSI behavior is a severely depressed ability for the supported metal atoms to chemisorb H_2 or CO. The noble metal impregnated TiO_2 is first reduced in H_2 and then evacuated before chemisorption measurements are made. After reduction at $200^\circ C$, the hydrogen chemisorption values (expressed as ratio of hydrogen atoms adsorbed to total metal atoms) are typical of those found on familiar supports such as alumina or silica. Reduction at $500^\circ C$, however, leads to a drastic reduction in the ability of the metals to adsorb hydrogen, reducing the chemisorption to all but undetectable levels. Similar behavior is seen for CO chemisorption. Explanations such as agglomeration of the metal, due to structural collapse in the presence of strongly bound hydrogen molecules from the reduction process, were discounted by careful experimental procedures.

Titanium oxide is not the only support to show such behavior, nor is activation at $500^\circ C$ a necessary prerequisite for SMSI behavior. The oxides of titanium, vanadium, manganese, and niobium are able to suppress the chemisorption of hydrogen onto iridium by an order of magnitude when activated in hydrogen for one hour at $350^\circ C$. The ratio of hydrogen atoms

adsorbed to metal atoms continues to decline as the reduction temperature is raised. The supports which have been tested for SMSI behavior are listed in Table II. For supports such as alumina and silica, hydrogen chemisorption continues at a high level for reduction temperatures up to 500°C. If the temperature is raised to 700°C, hydrogen chemisorption drops slightly due to particle agglomeration. Thus several binary transition oxides show striking metal-support interactions, whereas others do not. A possible explanation for this can be found by examining the reducibility of the oxides to metal or a lower oxide. A clear correlation can be traced between SMSI behavior and reducibility. Those transition metal oxides that are highly resistant to reduction do not show a strong metal support interaction. Those that are easily reducible (TiO_2 , or Nb_2O_5), or are already unsaturated (MnO , V_2O_3) do. The sluggish behavior of Ta_2O_5 , which only shows a substantial SMSI effect if reduced at $>400^\circ\text{C}$, can be correlated with its intermediate reducibility.

Metal-Substrate Bonding

The effect of SMSI supports on the supported metal atoms has been seen directly using an electron microscope in a series of elegant experiments by Baker et al.¹⁹ A clearer difference was seen for Pt/TiO_2 than for other supports such as alumina, silica, and carbon. Much smaller particle diameters were seen for reduction on titania; moreover, the particles were thin and flat, only a few atoms thick as opposed to the usual hemispherical aggregates. High temperature oxidation transformed the thin particles to thicker hemispheres. Reduction would reverse this behavior with melting of the thickened platinum aggregates into thin rafts. Clearly, the support metal interaction must be sufficient to outweigh the cohesive forces within

the metal aggregates. At the same time, the TiO_2 support reduced to Ti_4O_7 which could be reoxidized. The changes in chemisorption and structural properties which characterize the SMSI state are strongly suggestive of a substantial electronic interaction at the metal-oxide interface. Consideration of experimental results with theoretical studies, using molecular orbital methods,⁵ suggests that two important needs have to be satisfied to allow SMSI behavior.

1. Oxygen anions must be removed from the surface to allow a close approach of a metal atom to a surface cation.
2. The surface transition metal cations of the support must be reduced thereby acquiring d-electrons. The concomitant loss of surface anions allows a metal-cation approach with electron transfer to the metal resulting in an ionic attractive interaction.

Thus surface reduction fulfills the twin needs of removing oxygen and reducing the support cation, e.g. Ti^{4+} to Ti^{3+} . Clearly these supports that contain metal cations which are highly resistant to reduction, e.g. Al_2O_3 , would not be able to exhibit this type of behavior. This interpretation is supported by X-ray photoelectron studies which show charge transfer from reduced surface cations to the supported metal in Pt/TiO_2 ²¹ and Pt/SrTiO_3 .²²

The observed suppression of H_2 and CO chemisorption on SMSI catalysts is rather difficult to account for. Present explanations center on the unusual and flat topography of the metal particles which do not provide the correct ensemble of metal atoms for effective adsorption and the altered oxidation states of the metal ions at the surface.

SMSI Catalysts

As chemisorption must be an essential step in any catalytic reaction, we might expect the strongly altered chemisorption characteristics of supported metal catalysts in the SMSI state to be reflected in different catalytic properties. In particular, for CO-H₂ synthesis gas chemistry, the repression of CO and H₂ chemisorption might lead us to expect lowered activity, different selectivities, and decreased deactivation rates as compared to non-SMSI catalysts. Indeed, there are several selective SMSI catalysts under intense experimental scrutiny at present. Unfortunately, published catalytic data for SMSI catalysts is as yet meager. Studies of methane production from CO and H₂ by Vannice and Garten,²³ using supported nickel and ruthenium catalysts, have shown up to 10-fold greater activity when the metals were dispersed on a titania support rather than on alumina, silica, or carbon. In situ infrared studies showed only small amounts of CO on the titania supported metal, but larger amounts if the carrier was silica or alumina. In general, the SMSI catalysts showed a lower selectivity for methanation and a higher yield of olefins. Clearly, a weakened surface-substrate interaction can lead to many beneficial catalytic effects.

The nature of the strong metal-support interaction still poses some important questions, particularly as to how the oxide-support-to-metal charge transfer changes from system to system. If we can understand the details of such variation and the response in terms of catalytic efficiency and product distribution, it may well be possible to design new catalysts with improved properties.

New Zeolite Catalysts

Zeolites are the largest volume catalyts used presently in the petroleum refining and chemical technologies.²⁴ These alumina-silicates are prepared with various concentrations of aluminum ions in the tetrahedral silica framework. The Bronsted acidity of the catalyst can be correlated with the Al^{3+} concentration in the crystal lattice. By using clever synthetic routes, zeolites with variable pore sizes are prepared that permit one to carry out "shape selective" catalysis. Molecules that are small enough to enter the cannels in the crystal lattice which are of molecular dimensions (~12-22 Å range) will react, undergo hydro-cracking, and isomerization, while molecules which are too large to enter the pores remain unreacted. These catalysts are of very large internal surface area and exhibit ordered lattice structures and high thermal stability.

Recently, researchers from the Linde Division of Union Carbide, and from Mobil Oil Corporation have reported the synthesis of a new class of zeolites with very large silicon to aluminum ion ratio chemical composition. The materials are made of silicon and oxygen atoms almost exclusively, but the removal of the aluminum ions does not prevent the formation of the large internal surface area structures. These new zeolites, one of which is named sylicalite by the Union Carbide researches, are often hydrophobic--rejecting water while adsorbing hydrocarbons. The small concentration of aluminum ions left behind in the silica framework can be used to ion exchange metals of various types into the structure, thus producing a new class of catalysts with low Bronsted acidity.

The most successful new zeolite is called ZSM-5 by the Mobil

researchers. The catalyst has been employed in a new technology to produce high octane gasoline with a large concentration of aromatic molecules from methanol. Since methanol can be readily produced from CO and H₂, this new technology represents a breakthrough for indirect liquification of synthesis gas, CO and H₂ to high octane fuel. ZSM-5 has also been used to isomerize toluene and for various selective reactions of olefins. The new catalyst is much more resistant to coking than the more acidic zeolites, and maintains the same thermal stability.

At present, zeolites provide new and exciting opportunities to develop catalytic technologies of great importance, both in the chemical and petroleum industries. As a result of new advances of catalyst synthesis, it is likely that an entirely new family of zeolites with intriguing chemical properties will become available in the near future.

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TABLE I. Hydrogen Chemisorption on TiO₂ Supported Group VIII Metals. H/M is the Ratio of Hydrogen Atoms Adsorbed to Total Metal Atoms. (B)

<u>Metal (2 Wt%)</u>	<u>H/M Reduction @ 200°C</u>	<u>Reduction @ 500°C</u>
Rh	0.71	0.01
Pd	0.93	0.05
Pt	0.88	0.00

TABLE II. Supports Showing SMSI Activity with Ir¹⁴

<u>SMSI Supports</u>	<u>Non-Interacting Supports</u>
TiO ₂	Al ₂ O ₃
V ₂ O ₃	SiO ₂
MnO	Sr ₂ O ₃
Nb ₂ O ₅	H ₂ O
Ta ₂ O ₅ *	MgO
	ZrO ₂
	Y ₂ O ₃
	Cr ₂ O ₃ §

*Sluggish

§Some slight suppression of H₂ Chemisorption.

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720