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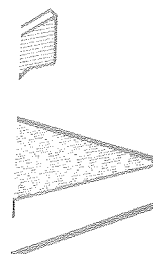
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First Berkeley CATALYSIS AND SURFACE SCIENCE CONFERENCE

July 1980

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**First Berkeley
CATALYSIS AND
SURFACE SCIENCE
CONFERENCE**

July 1980

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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PROGRAM
FIRST BERKELEY CATALYSIS AND SURFACE
SCIENCE CONFERENCE
July 16-18, 1980
Lawrence Berkeley Laboratory
Berkeley, California

Wednesday, July 16

8:15	Pick up at hotel entrance — bus transportation to LBL
8:15-9:00	Check in at desk in Bldg. 50 Auditorium Lobby
9:00	Opening remarks by LBL Director, D. A. Shirley

AMMONIA SYNTHESIS

Chairman: G. A. Somorjai

9:10	M. Boudart and C. Yuan (Stanford University) <i>Kinetics and Mechanism of the Ammonia Synthesis</i>
9:55-10:10	Discussion
10:10-10:25	Coffee break
10:25-11:10	A. Nielsen (Haldor Topsoe Company) <i>Exploratory and Applied Research</i>
11:10-11:25	Discussion
11:25-12:10	L. C. Axelrod (Pullman-Kellogg Company) <i>The Manufacture of Ammonia</i>
12:10-12:25	Discussion
12:30	Lunch break. Lunch is available at the LBL Cafeteria

HOMOGENEOUS CATALYSIS BY TRANSITION METALS

Chairman: R. G. Bergman

1:45-2:30	E. L. Muetterties (LBL/UC Berkeley) <i>Scientific Background</i>
2:30-2:45	Discussion
2:45-3:30	Dennis Forster, A. Hershman, and D. E. Morris <i>Mechanistic Pathways in the Catalysis of Olefin Hydrocarboxylation by Metal Complexes</i>
3:30-3:45	Discussion
3:45-4:00	Coffee break
4:00-4:45	G. W. Parshall (E.I. Du Pont) <i>Commercial Applications of Reactions Catalyzed by Soluble Complexes of Cobalt and Rhodium</i>
4:45-5:00	Discussion
5:00	Bus transportation from LBL to hotels
6:30	Bus transportation from hotels to Lawrence Hall of Science
6:45-7:30	Social hour
7:30	Banquet and After-Dinner Speaker, Dr. Glenn T. Seaborg
9:00	Bus transportation to hotels

Thursday, July 17

8:00 Bus pick-up at hotels

ETHYLENE OXIDATION

Chairman: D. A. Shirley

8:30-9:15 W. M. H. Sachtler, C. Backx, and R. A. van Santen
(Shell Research B.V.)

Mechanism of Ethylene Epoxidation

9:15-9:30 Discussion

9:30-9:45 Coffee break

9:45-10:30 J. V. Porcelli
(Halcon Research & Development Corporation)

Exploratory Research

10:30-10:45 Discussion

10:45-11:30 J. C. Zomerdijk (Shell International)
*Technology for the Oxidation of Ethylene to Ethylene
Oxide*

11:30-11:45 Discussion

11:45-1:00 Lunch break. Lunch is available at the LBL Cafeteria

HYDROGENATION OF CARBON MONOXIDE

Chairman: Heinz Heinemann

1:00-1:30 G. A. Somorjai (LBL/UC Berkeley)
The Formation of C₁ Hydrocarbons

1:30-2:00 A. T. Bell (LBL/UC Berkeley)
*Catalytic Synthesis of Hydrocarbons over Group VIII
Metals*

2:00-2:20 Discussion

2:20-3:05 J. A. Cusumano, D. L. King and R. L. Garten
(Catalytica Associates)
*A Technological Perspective for Catalytic Processes
Based on Synthesis Gas*

3:05-3:20 Discussion

3:20-3:40 Coffee break

3:40-4:25 J. C. Hoogendoorn and M. Dry (SASOL)
The Technology of the Fischer-Tropsch Process

4:25-5:00 Discussion

5:00 Bus transportation to University of California Faculty
Club

5:30 Wine tasting at Faculty Club

6:30 Bus transportation to hotels

Friday, July 18

8:00 Bus pick-up at hotels

ZEOLITE CATALYSIS

Chairman: A. T. Bell

8:30-9:15 G. T. Kerr (Mobil Research & Development Corporation)
*The Synthesis and Properties of Two Catalytically
Important Zeolites*

9:15-9:30 Discussion

9:30-10:05 Coffee break

10:05-10:50 Jule A. Rabo (Union Carbide Corporation)
Unifying Principles in Zeolite Chemistry and Catalysis

10:50-11:05 Discussion

11:05-11:50 Heinz Heinemann (LBL/UC Berkeley)
Technological Applications of Zeolites in Catalysis

11:50-12:05 Discussion

12:05 Closing remarks

12:10 Bus transportation to hotels

AMMONIA SYNTHESIS: KINETICS AND MECHANISM

M. Boudart and C. Yuan

Stanford University

At temperatures around 700 K and at low pressure, the rate determining process in ammonia synthesis appears to be the dissociative chemisorption of dinitrogen. This proceeds without the help of hydrogen on a surface covered mostly by adsorbed nitrogen.

The role of textural promoters, e.g. alumina in commercial catalysts, is to prevent sintering in two possible ways: by avoiding contact between iron surfaces and/or by building up elastic stresses in the iron crystallites. The role of structural promoters, e.g. potassium oxide, may be to neutralize the acidity of the textural promoter or to decrease the work function of iron. Surface analysis by Auger electron spectroscopy or by selective chemisorption reveals that only a few percent of the reduced surface of a commercial catalyst consists of iron.

The evidence for ammonia synthesis being a structure sensitive reaction will be reviewed. The idea that (111) planes or C_7 surface atoms on iron surfaces may be providing more active sites for the reaction will be assessed together with the evidence for the nonuniformity of iron catalytic surfaces.

Finally a comparison will be made between the activity of various metals in ammonia synthesis.

AMMONIA SYNTHESIS

Anders Nielsen

Haldor Topsøe A/S

Improvements of complex catalyst systems such as promoted and stabilized catalysts have until now been obtained primarily by exploratory research, guided by progress in the improved understanding of the properties of catalyst surfaces, and of the individual steps of the reaction network.

The presentation will primarily deal with ammonia synthesis on iron and on ruthenium and with the stabilization and promotion of such catalysts.

The bulk and surface structures of traditionally doubly and triply promoted iron ammonia synthesis catalysts are reviewed. Efforts to increase their activity have followed paths of increasing the active surface area on one hand, and on improving the specific activity per unit of area on the other hand.

One way of stabilizing small iron particles is the use of suitable supports, and catalyst systems on magnesium oxide and carbon supports will be discussed. Another approach is the use of stabilizers different from those of conventional catalysts. Turnover frequencies for differently prepared unsupported and for MgO-supported iron catalysts with different particle size will be referred to. Many promoters have been explored for improving the specific activity. The discussions will deal with alkali metals, alkali metal oxides, beryllium oxide, cobalt, titanium, and rare earth oxides.

Upon introduction of prereduced catalysts, a new avenue was opened for further promotion of iron ammonia synthesis catalysts, namely by impregnation on the pore surface created during the reduction process. Another avenue of research has aimed at obtaining a better pore structure in the catalysts, in order to improve the mass transfer inside the particles during use. Examples of these avenues will be discussed.

Work on various ruthenium catalysts will be reviewed, particularly with a view to the effect of different supports and promoters.

In the applied research we obtain the knowledge that allows the design of ammonia converters based on a given catalyst. This means accumulation of rate data maybe in the form of a rate equation and an optimization of operating conditions. Rate data at a number of process conditions will be compared and the consequences of improvements of catalyst activity discussed.

Future planning of exploratory research will be guided mainly by research work into the science of ammonia synthesis including research into the natural systems which reduce nitrogen to ammonia and calculations of the orbitals in configurations that reasonably represent active sites--metal clusters--and their bonding with simple molecules like hydrogen and nitrogen.

THE MANUFACTURE OF AMMONIA

L. C. Axelrod

Pullman-Kellogg Co.

An examination of the market for ammonia confirms that demand remains a function of population growth and a gradual increase in the standard of living in developing countries. Synthetic materials are using an increasing share of the ammonia manufactured. Rate of growth of production facilities will continue to depend on availability of financing and development of infrastructure for distribution and use.

A review of feedstock availability indicates that natural gas should continue to be the primary feedstock for manufacture of ammonia although a specific case can be made for coal when the synthesis gas production is incremental to another coal conversion project.

The incentives for continued development effort are thus established on the basis of market growth and changing economic evaluation with feedstock availability, escalation in feedstock prices and increased investment cost as major variables.

Against this background, available and emerging technology for manufacture of ammonia will be discussed. The emphasis will be on the necessity for being able to evaluate the economics for any given situation. This will be demonstrated by a brief discussion of number of processes for making synthesis gas from various feedstocks and the effect of combining them with various flow-sheets for ammonia synthesis.

HOMOGENEOUS CATALYSIS

Earl L. Muetterties

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

Catalysis of chemical reactions by discrete molecular species typically comprises a series of elementary steps. The number of steps may be quite large but despite the reaction complexity, labelling, kinetic and spectroscopic studies have enabled a molecular characterization of the catalytic cycle for many basic and important classes of catalytic transformations. Olefin metathesis and asymmetric synthesis of organic molecules are two such class reactions that recently have been delineated in a mechanistic context. Such mechanistic studies are of great general value: (1) they are a rich source of fundamental information about coordination chemistry, (2) they provide a basis for the design of more efficient or selective catalysts, (3) they collectively provide the basis for the design of catalysts for new types of catalytic reactions and (4) they identify reaction intermediates that may be formally related to intermediates in catalytic reactions effected at a gas-solid or liquid-solid interface. Mechanistic studies of reactions catalyzed by coordination complexes will be the major theme of this discussion.

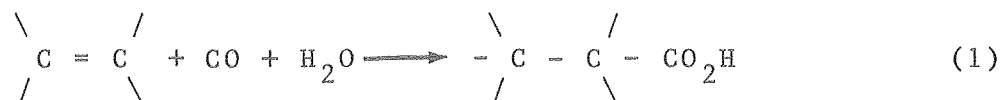
Molecular complexes that contain two or more metal centers present the possibility of effecting catalytic reactions in which more than one metal center is involved in some steps within the reaction cycle. However, most molecular clusters are not especially reactive under mild conditions and many suffer fragmentation processes in their reactions. Synthesis approaches to reactive polynuclear metal complexes with robust polynuclear frameworks will be discussed. Specific polynuclear metal complexes that are very active catalyst precursors will be described and the mechanistic information about the catalytic cycles will be discussed fully.

MECHANISTIC PATHWAYS IN THE CATALYSIS OF
OLEFIN HYDROCARBOXYLATION BY METAL COMPLEXES

D. Forster, A. Hershman, and D. E. Morris

Monsanto Company

The hydrocarboxylation of olefins (eq. 1) is catalyzed



by several metal complex systems; in particular cobalt, rhodium, iridium and palladium complexes are especially effective. Studies have been conducted aimed at elucidation of the mechanism of the reaction with the iodide-promoted rhodium and iridium catalysts and a nucleophile - promoted cobalt catalyst.

A comprehensive understanding of the iridium-catalyzed reaction has been achieved by use of a combination of techniques including in situ spectroscopy and kinetic studies, as well as the synthesis and characterization of reaction intermediates. We have found that the rate-determining step in the catalytic cycle varies with the choice of reaction conditions.

In the rhodium-catalyzed reaction, the key metal-carbon bond promotion step has been investigated by use of radiotracer techniques. This approach allowed a distinction to be made between two interpretations which were indistinguishable by kinetic measurements.

The cobalt-catalyzed reaction has been investigated by several groups, and the speaker will review the evidence gathered to date on the mechanism. The role of the nucleophile is almost certainly that of acyl removal from the metal by external attack.

COMMERCIAL APPLICATIONS OF REACTIONS CATALYZED BY
SOLUBLE COMPLEXES OF COBALT AND RHODIUM

G. W. Parshall

E. I. du Pont de Nemours and Company

Cobalt and rhodium are the metals of choice in half of the two dozen commercial applications of homogeneous catalysis. In 1977, processes catalyzed by soluble compounds of these two metals produced about six million metric tons of organic chemicals.

The largest application is the cobalt-catalyzed air oxidation of hydrocarbons such as butane, cyclohexane, toluene and the xylenes. The chemistry of these processes is very complex. The metal complex is primarily involved as a catalyst to selectively decompose the organic hydroperoxides that arise from radical chain reactions of the hydrocarbons with oxygen.

Soluble cobalt and rhodium complexes are also used extensively to catalyze reactions of carbon monoxide. Hydroformylation, the reaction of an olefin with CO and H₂ to form an aldehyde, is used in manufacture of both linear and branched chain alcohols, which are used in detergents, synthetic lubricants and plasticizers. Carbonylation of methanol to form acetic acid is the fastest growing process for this basic industrial chemical. This process should find increasing favor in the future because it is based entirely on synthesis gas which is available from many different feedstocks. In the past, cobalt carbonyl derivatives were the preferred catalysts for all these reactions of carbon monoxide. Now, however, soluble rhodium catalysts are used increasingly because they operate at lower pressures and are often more selective.

Cobalt catalysts are also used in production of polyesters and polybutadiene. Rhodium compounds are used on a smaller scale to make trans-1,4-hexadiene and *l*-DOPA and pyrethrin precursors. The large scale use of these two metals in catalytic processes (both homogeneous and heterogeneous) has contributed to a dramatic increase in price that may restrict their future growth.

MECHANISM OF ETHYLENE EPOXIDATION

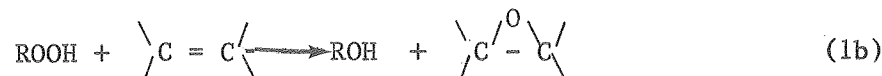
W. M. H. Sachtler, C. Backx and R. A. van Santen

Koninklijke/Shell-Laboratorium, Amsterdam

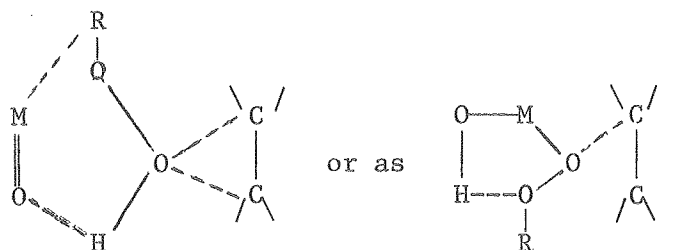
Whereas the liquid-phase epoxidation of alkenes is catalyzed by various homogeneous catalysts, epoxidation in the gas phase with high yields appears to be known for ethylene with silver as the catalyst.

This paper will review facts and ideas of homogeneous and heterogeneous epoxidation catalysis and attempt to identify the chemistry common to both fields.

Numerous epoxidation reactions in solution follow the general scheme:

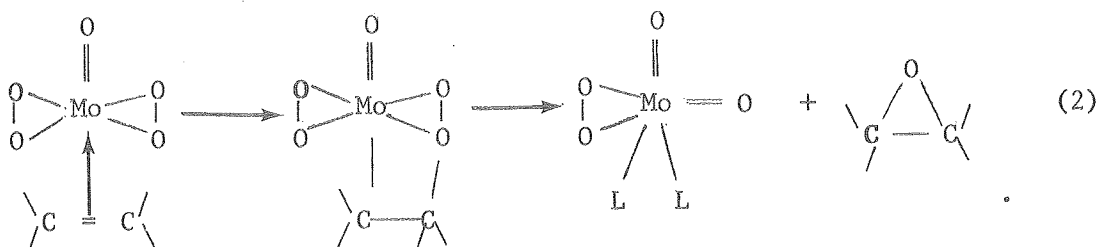


The mechanism of the non-catalyzed reaction has been described by Ugo as a nucleophilic addition of ROO^- to the alkene. For $R = CH_3CO$ a "butterfly" intermediate stabilized by the $C=O$ group has been proposed. Accordingly (1b) can be catalyzed by Lewis acids, in which case the intermediates are written either as



Here the presence of an $M=O$ group seems to be essential to stabilize the intermediate.

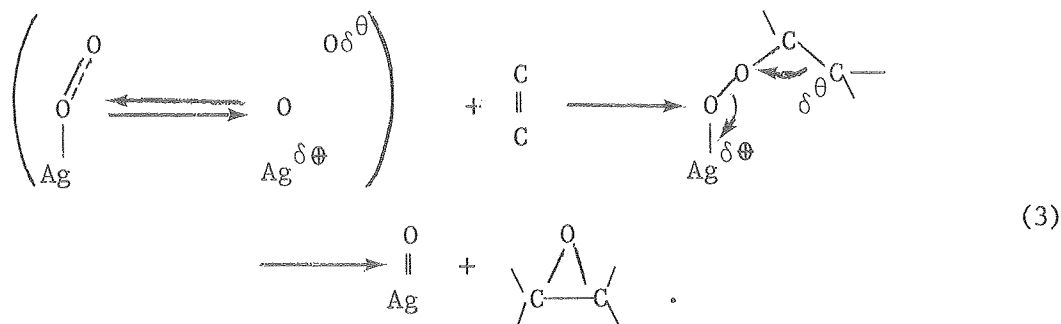
A second type of a highly selective and stoichiometric epoxidation reaction makes use of metal super-oxo complexes, in particular of Mo and W. For $M-O-O$ e.g., Mimoun postulates the formation of a five-membered ring:



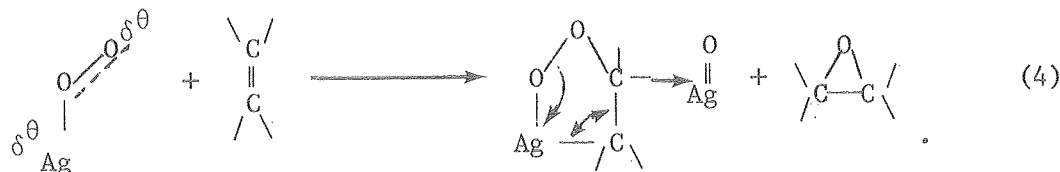
In this scheme the highly positive charge of Mo^{6+} is essential. In the case of a lower valent ion such as Rh^+ an aldehyde is formed instead of an epoxide, and with Pt^0 and Pd^0 Ugo observed cleavage of the $\text{C} = \text{C}$ bond.

A common feature of processes (1) and (2) is the presence of the $-\text{O}-\text{O}-$ group in the oxidizing complex, only one of these two oxygen atoms being transferred to the alkene. The only homogeneous system lacking such a dioxygen group and claimed to epoxidize alkenes at least to some extent is reported to be the $\text{TlCl}_3 + \text{H}_2\text{O} + \text{C}_3\text{H}_6$ system, where a Wacker-type intermediate is visualized.

The direct gas-phase oxidation of ethylene with oxygen catalyzed by silver is rate limited by adsorption of oxygen. One group of authors assumes that the mechanism is basically similar to (1) and (2), i.e. only the non-dissociative mode of oxygen is utilized for epoxidation, which might explain the unique role of silver. The mechanism can then be formulated as involving either a stepwise nucleophilic attack of the olefin



Or, in analogy to (2), the formation of a cyclic peroxo species:



The second oxygen atom will either be consumed by subsequent reaction with ethylene molecules forming H_2O and CO_2 or recombine with another oxygen atom to give adsorbed dioxygen and thus be available for a second epoxidation. Evidence in support of this is the IR observation of adsorbed dioxygen-ethylene complexes at temperatures below 100°C (Kilty et al.) and the detection of O_2^- by ESR (Clarkson).

Another group of authors postulates an entirely different mechanism, by which epoxidation is due to interaction of ethylene with monoatomic oxygen. In this case the main evidence consists in the absence of infrared absorption bands of adsorbed dioxygen-ethylene complexes under the reaction condition (Force & Bell).

The well-known effect of chlorine enhancing the selectivity has been rationalized with either model. Besides the IR and ESR data mentioned, there is some other evidence of potential mechanistic relevance:

(1) Herzog and Koboyashi found that replacement of O_2 by N_2O led to a drastic decrease of epoxidation selectivity.

(2) Imre observed that the concentration of oxygen atoms below the silver surface increases above the equilibrium value upon addition of ethylene to gaseous dioxygen under conditions where the epoxidation selectivity is high. This result agrees with the mechanism:



(3) Our recent results on the adsorption of oxygen on the (110) plane of a silver single crystal obtained by TPD, HRELS and LEED show that at 200°C at least two adsorption states coexist. One state consists of atomic oxygen adsorbed on the surface in a fourfold coordinated site up to a maximum coverage of $\theta = 0.5$, which is desorbed at 310°C. The second state consists of atomic oxygen present as subsurface oxygen, also with a maximum coverage of $\theta = 0.5$, which is not desorbed and does not diffuse into the bulk below 400°C. Ethylene oxide is formed only if both surface and subsurface oxygen are present.

(4) Cant and Hall observed an increase of the selectivity when C_2H_4 was replaced by C_2D_4 . The absolute rate of epoxide formation was enhanced but that of total combustion decreased.

We found that the isotope effect decreases when the silver surface is pre-covered with chlorine. These results suggest that the same kind of adsorbed oxygen can result either in epoxide or in $CO_2 + H_2O$. Moderation of the surface with chlorine favors the epoxidation route.

(%) Upon alloying Ag with Au, Geenen et al. found that the selectivity of epoxidation decreases. This finding, which is at variance with previous results obtained by Frank and Beachall, might be explained by assuming that subsurface oxygen is needed for the epoxidation reaction and that this is absent in the gold alloys.

The implication of each of these observations will be discussed.

ETHYLENE OXIDATION

J. V. Porcelli

Halcon Research and Development Corporation

The steps involved in developing commercially successful catalysts are described, as seen by the speaker during his twenty years at Halcon/Scientific Design. The Halcon/SD ethylene oxide process is one of the three major processes being practiced world-wide for the production of ethylene oxide by ethylene oxidation over a silver catalyst. It is one of the two major processes offered for license and is the only major process for which the licensor does not commercially practice the technology itself. This fact, combined with the continuous licensing activities by Halcon/SD for over 25 years, has greatly influenced the way a new ethylene oxide catalyst is developed, in that a suitable catalyst must remain available for even the oldest plants.

In the case of Halcon/SD, the process and catalyst were originally developed together, leading to the startup of the first commercial plant utilizing this technology in 1952. The process, as then practiced, is briefly described and the evolution of the process is followed, primarily from the standpoint of those factors influencing catalyst characteristics and performance. The uses of air versus oxygen as oxidant, reaction staging, flammability considerations and reactor design and stability are discussed.

Since process and catalyst are intimately related, the criterion for success of a catalyst is overall process economics, rather than merely selectivity or productivity. Therefore, at Halcon/SD the development of ethylene oxide catalysts has been based primarily on performance in reaction environments at each stage in the development process. A number of different reaction systems have been devised over the years, differing vastly in scale and complexity. The advantages and shortcomings of some of these are described. In recent years, the techniques available to study the catalytic surface under non-reacting conditions have made substantial progress and some of these are also described. The prospects for development of superior ethylene oxide catalysts in the future based on a combination of modern techniques are discussed.

TECHNOLOGY FOR THE OXIDATION OF ETHYLENE TO ETHYLENE OXIDE

J. C. Zomerdijk

Shell International

It is now some 20 to 25 years since direct oxidation technology of ethylene to ethylene oxide using a silver-containing catalyst started gradually to replace the then standard chlorohydrin technology, both for reasons of improved process economics, and for avoiding the use of chlorine with the associated aqueous effluent problems. Both air and high purity oxygen can be used as the oxidizing agent for the reaction, and although a limited number of incidents have occurred in the reaction section since the introduction of this technology, it is now fully accepted that the direct oxidation concept, coupled with a reliable automatic shut down system, gives safe operation and allows the achievement of high plant on-stream factors.

As experience with direct oxidation has accumulated, various process improvements have been implemented. The tightening of product specification, the introduction of better safety systems, the need to minimize effluent streams, and the application of more advanced equipment have all led to a more sophisticated and mature plant design. Recently the introduction of catalysts which give a considerably improved selectivity, and the improved design optimization for better heat economy have further improved the overall process.

This article will describe in more detail the present status of the technology with an emphasis on the process using pure oxygen. The major design criteria resulting from the system of design equations will be described with particular reference to current design concepts, especially those relating to the safety system, the heat recovery system, and the use of advanced catalysts. The consequences of increasing plant capacities, the sizing of larger reactors, the impact of the energy saving drive, and the influence of tighter environmental control will also receive detailed attention. Others will describe the mechanisms of the reaction; therefore, only a brief description of the chemistry of the reaction and side-reactions involved will be given.

Ethylene oxide is probably the most versatile petrochemical at the disposal of the industry today. In Western Europe between 50 to 55% of the ethylene oxide is converted into glycols, in USA up to about 65%, and in Japan between 70 to 75%. The remaining part of the ethylene oxide is converted into glycol ethers, surface active agents, ethanolamines, polyglycols, polyols, ethylene di-amines, and a number of further derivatives. Bearing in mind a reasonable growth rate of ethylene oxide and its derivatives in the next decade, it appears justified to continue spending further efforts on catalyst and process research with the aim of higher efficiency on ethylene and energy to keep pace with the increasing costs.

As this subject is part of a symposium on surface catalysis, direct routes to ethylene glycol bypassing ethylene oxide will not be discussed. In any case, as almost 50% of the oxide is needed for derivatives other than ethylene glycols, a need for ethylene oxide as such will continue to exist.

THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE.

THE FORMATION OF C_1 HYDROCARBONS

G. A. Somorjai

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

Few reactions have a more distinguished history than the catalytic hydrogenation of carbon monoxide. It was first reported in 1902 by Sabatier and Senderens who produced methane from CO and H_2 over nickel. The production of methanol was announced by BASF as early as 1913. Then in 1926 Fischer and Tropsch published their classical work reporting on the synthesis, near atmospheric pressures, of various higher molecular weight hydrocarbons. Commercialization of this discovery proceeded rapidly, and in 1943 the production of synthetic fuel from CO and H_2 was over 20,000 barrels per day. After World War II basic research in the mechanism of the hydrogenation of CO was continued in Professor Emmett's laboratory at Johns Hopkins University and in the U.S. Bureau of Mines in the U.S. as well as in England and in Japan.

Basic research and development of the catalytic hydrogenation of carbon monoxide has proceeded rapidly in recent years. Using modern surface diagnostic techniques, the atomic level mechanisms of this reaction are being unraveled. As a result it will become possible to produce single component hydrocarbons from methane to ethylene glycol or benzene instead of obtaining an undersirable mixture of hydrocarbons as was obtained 40 years ago. This reaction has attracted researchers in the fields of catalysis science because it uses small, easily available molecules and, because using various ratios of CO and H_2 , the production of hydrocarbons of different types is thermodynamically feasible.

It is appropriate to subdivide the processes which occur during the catalytic hydrogenation of carbon monoxide as follows: (1) methanation, (2) methanol formation, (3) polymerization reactions which yield a mixture of high molecular weight hydrocarbons, (4) formation of oxygenated organic molecules, and (5) the insertion of CO molecules (carbonylation) to form C_2 or C_3 products. We would like to know the mechanisms for forming these different products under a variety of experimental conditions. These include a molecular level understanding of the catalyst surface structure, the oxidation state of the active sites, the structure of the reaction intermediates, and the role of the various additives which have been found useful in extending the catalyst's life and improving its performance. While such a complete understanding of the reaction mechanism does not exist, many of the elementary reaction steps and the surface structures and composition of the active catalysts have been verified by careful studies of given catalyst systems.

This lecture will focus on the kinetics and mechanisms of formation of C₁ hydrocarbons, methane and methanol. The kinetics and the thermodynamics of these reactions over various transition metal compound catalysts will be reviewed. The surface composition of the active catalysts as obtained by electron spectroscopy studies will be discussed. The importance of the water-gas shift reaction in controlling the surface concentration of reaction intermediates will be reviewed along with studies of bonding of CO, H₂ and of the reaction intermediates using the various techniques of surface science. Finally, the roles of additives that alter the rate and the product distribution will be discussed.

CATALYTIC SYNTHESIS OF HYDROCARBONS OVER
GROUP VIII METALS

Alexis T. Bell

Lawrence Berkeley Laboratory and Department of Chemical Engineering
University of California, Berkeley

It is well established that a broad spectrum of organic products can be produced by the catalytic hydrogenation of carbon monoxide, and that the composition of the products obtained can be altered radically through the control of catalyst composition, reaction conditions, and reactor configuration. Moreover, in certain instances a single product or a very narrow range of products can be obtained. Examples of such cases include the synthesis of methane, methanol, and ethylene glycol. By contrast, the selective synthesis of gasoline blending stocks, C₅ - C₁₂ hydrocarbons, has proven much more difficult to achieve. This problem has stimulated active research aimed at better defining the surface chemistry involved in the synthesis of hydrocarbons containing two or more carbon atoms and the means by which catalyst modifications influence product distribution.

This talk will review our present understanding of the catalytic synthesis of higher molecular weight hydrocarbons, with primary focus on what has been established regarding group VIII metals. The first part of the talk will deal with the chemistry involved in the initiation, propagation, and termination of hydrocarbon chain growth and with the structure of the reaction intermediates. The connection between reaction pathways and the product distribution will be discussed, and the influence of secondary reactions of olefins will be examined. The second part of the talk will be concerned with the effects of catalyst composition on catalyst activity and selectivity. The means by which metal dispersion, metal-support interactions, alloying, compound formation, and the addition of modifiers affect catalyst performance will be reviewed, and explanations for the influence of these factors will be proposed.

A TECHNOLOGICAL PERSPECTIVE FOR CATALYTIC PROCESSES BASED ON SYNTHESIS GAS

J. A. Cusumano, D. L. King, and R. L. Garten

Catalytica Associates, Inc.

Continuously increasing oil prices, a dwindling supply of indigenous petroleum crude, and the existence of extensive coal reserves has made the conversion of coal to chemicals and clean-burning fuels an increasingly important part of the national energy programs for a number of industrial nations. In particular, there is a growing interest in the production and use of synthesis gas as a feedstock for the manufacture of fuels and chemicals. Most of the proposed routes are catalytic in nature, and are directed at overcoming the limitations of the chemistry which is the basis for the classical Fischer-Tropsch synthesis. Indeed, a common aspect of much of the recent work has been to bypass the selectivity limitations of Fischer-Tropsch synthesis which are conveniently described by the Schulz-Flory distribution function. The latter has been used for many years to describe various homogeneous polymerization processes. Over the past several years, research efforts have led to new selective routes to various fuel fractions; to petrochemical feedstocks including light olefins and various aromatics; to commodity chemicals such as ethylene glycol, ethanol, acetic acid, and to a number of other fuels and chemicals.

Although the chemistry and catalysis for many of these new routes look promising, there are still a number of technical challenges to be met before they are commercially viable. Innovations in both homogeneous and heterogeneous catalysis will play a key role in meeting these challenges. In this presentation, some of the key technical problems of synthesis gas chemistry are reviewed, and those areas of catalysis which could have an impact on the solution of these problems are identified.

THE TECHNOLOGY OF THE FISCHER-TROPSCH PROCESS

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For the purpose of this paper, the Fischer-Tropsch process is understood to be the reaction between hydrogen and carbon monoxide to produce predominantly hydrocarbons. The reaction is highly exothermic and the development of the technology for its industrial application has two major objectives: the construction of reactor systems which can remove the heat of reaction fast enough to avoid local overheating of the catalyst, and the development of catalysts which maintain their activity and selectivity over as wide a range of temperatures as possible.

From the catalyst point of view, the objective has not yet been achieved to the extent that one would like and the accent has therefore been on the development of reactors which can remove the heat of reaction, at the same time keeping the reaction temperature within limits. The Fischer-Tropsch reaction has its main importance as a large scale producer of synthetic motor fuels, and the ideal reactor should be of a type which is not too complicated and can be scaled-up to very large capacities. At present there are three reactor types which fulfill the requirements: the fixed-bed tubular reactor, developed from the small reactors used in the German plants of the 1940s; the fluid-bed reactor, developed from reactor systems used in the oil refinery industry; and the slurry-bed reactor. The fixed-bed and fluid-bed reactors have been in commercial use for many years in the Sasol plant in Sasolburg in South Africa. The slurry-bed reactor has not yet been built on a large enough scale to evaluate its potential commercial behavior with full confidence.

The paper will give some comparisons of the three systems as obtained in the Sasol research laboratories.

The Fischer-Tropsch reaction is by nature not very selective and a range of hydrocarbons and associated oxygenated products will be obtained. The range of the spectrum of selectivity can be controlled by factors such as gas composition, catalyst composition, and operating parameters. The reactor system does not influence the selectivity. However, the range of hydrocarbons desired may dictate the choice of reactor system. If the product range required consists mainly of high molecular weight hydrocarbons which will be liquid even under the actual reaction conditions, then obviously a fluid-bed reactor is not the right answer and either the fixed-bed or the slurry-bed reactor should be considered. On the other hand, if predominantly smaller molecules are required, such as in the production of synthetic motorfuels, then all three reactor systems could be used. Under these conditions, however, the fluid-bed system, which lends itself more easily for scale-up to very large size, will have an industrial advantage.

In the Sasolburg plant, both the circulating fluid-bed and the fixed-bed systems have been in use and have given satisfactory performance in their own areas of application. For the Sasol Two and Sasol Three plants which are specifically built as large scale motorfuel producers, the choice went to the Synthol system which uses Sasol's technology for catalyst and large scale circulating fluid-bed reactors.

The paper will give a review of the potential and flexibility of the Sasol Synthol system as a producer of motorfuels, building blocks for petrochemicals and substitute natural gas.

THE SYNTHESIS AND PROPERTIES OF TWO CATALYTICALLY IMPORTANT ZEOLITES

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Zeolites (crystalline aluminosilicates) comprise a unique group of crystalline solids. All members of the group have a porosity such that essentially all the atoms (or ions) contained within the crystal constitute a surface available to foreign or guest molecules. Such tremendous surface areas per unit mass play an obvious role in heterogeneous catalysis. The uniformly-sized channels or ports that produce the porosity vary in size on a molecular-size scale resulting in selectivities for guest molecules of specific sizes and shapes. Hence, shape- and size-selective catalysis can be achieved. Aluminosilicates chemically consist of tetrahedrally coordinated silicon and aluminum atoms joined to one another by oxygen atoms. This gives rise to an anionic charge associated with each aluminum atom. When the cation compensating for this anionic charge is a proton, the acidity produced is comparable to that of the very strongly acidic perchloric acid. These three properties (1) large surface area, (2) shape- and size-selectivity, and (3) very strong acidity play the key roles for the important catalytic applications of zeolites.

Of the presently known thirty five naturally-occurring zeolites, the crystal structures of twenty seven have been elucidated and all but about ten have been prepared synthetically. A dozen or so crystalline aluminosilicates have been prepared which are purely synthetic, i.e., they have no naturally-occurring counterparts. Of all the known zeolites, natural and purely synthetic, two are outstanding in the realm of catalysis: a synthetic faujasite known as zeolite Y and a purely synthetic zeolite designated zeolite ZSM-5. Zeolite Y is the active component in cracking catalysts used in the manufacture of gasoline, and ZSM-5 has a number of important applications in the petrochemical and petroleum refining areas. These two zeolites are discussed in terms of their synthesis, crystal structure, crystal chemical properties, and their sorptive properties which are governed by their intracrystalline channel diameters.

UNIFYING PRINCIPLES IN ZEOLITE CHEMISTRY AND CATALYSIS

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The unusual chemical environment of the zeolite surface and especially the crystal field of the surrounding crystal lattice render it a strong solid electrolyte. Zeolites interact strongly with polar and polarizable atoms and molecules resulting in unusually strong adsorption, or even ionization of adsorbed species.

The adsorption properties of zeolites well demonstrate the strong electrostatic interaction between zeolites and occluded molecules. The redox chemistry of zeolites testifies that the interaction often goes beyond physical interaction even to the extent of ionization of the adsorbed molecules. Reactions resulting in the ionization of adsorbed molecules which would otherwise be endothermic by as much as ~ 126 kcal/mole in the gas phase readily proceed at moderate temperatures because of the "solvation" effect of the zeolite on the ionic products.

Mechanistic studies show that ionization of hexanes or their reaction intermediates does not occur on alkali zeolites, and that the cracking of hydrocarbons proceeds by a radical mechanism. It is worth noting that the ionization energy of hexanes and their radical fragments is ≈ 170 kcal/mole, significantly higher than the free energy change of redox reactions readily occurring in zeolites. The radical mechanism over alkali zeolites shows distinct differences in product distribution from the non-catalyzed thermal process. These differences are explained on the basis that zeolites concentrate the reactants in the zeolite, resulting in a strong enhancement of bimolecular reaction steps over unimolecular reaction steps. Thus, zeolites generate a substantially higher reactant concentration relative to the gas phase outside the zeolite crystal.

In the cracking of hydrocarbons over H-Y zeolite, an unusually strong Bronsted acid activity is observed. The product distribution indicates great enhancement of H redistribution, presumably through hydride ion shifts. Here again, as with K-Y, bimolecular reaction steps (H redistribution) are favored over unimolecular reaction steps (fragmentation). The cause of this phenomenon is that zeolites concentrate the reactants in the zeolite pore-and-cavity system. Enhanced concentration of reactants on catalyst surfaces is, of course, characteristic of any heterogeneous catalyst. However, from the mechanistic evidence reviewed here, it appears that this concentration effect is greater with zeolites than with other amorphous acidic catalysts.

THE TECHNOLOGY OF ZEOLITE CATALYSIS

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While zeolites have been used for some time as adsorbents (drying agents) and ion exchangers, the first large-scale application of zeolites as catalysts was their introduction as major components of cracking catalysts in the early 1960s. Considering that catalytic zeolite technology is thus less than twenty years old, it is remarkable that ten large-scale commercial processes using zeolite catalysts have been developed in this time span.

The introduction of zeolite cracking catalysts revolutionized the petroleum industry. It permitted higher conversions and greater selectivities to gasoline and thus materially reduced the volume of crude oil that had to be refined to meet gasoline demand. Better than 90% of the free world's cracking capacity now uses zeolite catalysts. The paper will discuss some of the chemistry and technology involved and will further mention catalyst and unit improvements made in recent years.

Shape selective catalysis is another subject that deserves detailed attention. Processes considered are: selectoforming of naphthas; isomerization of xylenes, both in the presence and absence of hydrogen; catalytic hydrodewaxing of both distillates and lube oils; alkylation of benzene with ethylene; toluene disproportionation; and processes which have not quite reached the commercial scale, such as methanol conversion to gasoline. The role of zeolites in potentially modifying Fischer-Tropsch reactions is mentioned.

Relationships between catalyst characteristics, operating conditions, and regeneration properties as well as unit designs will be considered and discussed.

