



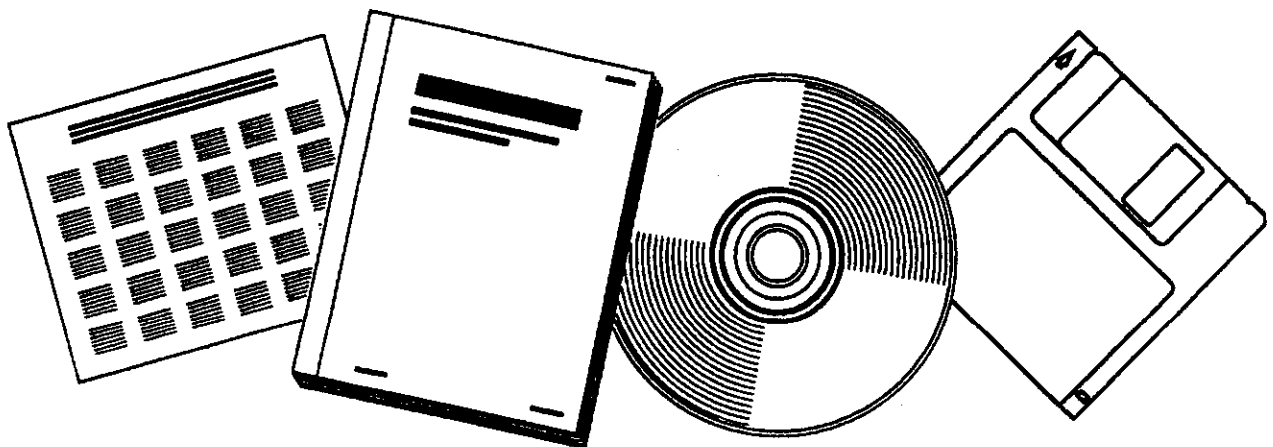
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**PROCEEDINGS OF THE WORKSHOP ON NEEDS FOR
FUNDAMENTAL RESEARCH IN CATALYSIS AS
RELATED TO THE ENERGY PROBLEM HELD AT RICE
UNIVERSITY, HOUSTON, TEXAS ON JUNE 24/25,
1974**

RICE UNIV., HOUSTON, TEX

25 JUN 1974



**U.S. DEPARTMENT OF COMMERCE
National Technical Information Service**

WORKSHOP ON NEEDS FOR
FUNDAMENTAL RESEARCH

IN

CATALYSIS
AS RELATED TO THE
ENERGY PROBLEM

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held at
Rice University
Houston, Texas
June 24-25

sponsored by
Energy-Related General
Research Office
Research Directorate
National Science Foundation

PROCEEDINGS OF THE
WORKSHOP ON NEEDS FOR FUNDAMENTAL RESEARCH IN
CATALYSIS AS RELATED TO THE ENERGY PROBLEM

Rice University
June 24-25, 1974

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I. SUMMARY AND RECOMMENDATIONS

A. Summary

Catalysis plays a vital role in processes involving energy production. To identify areas where fundamental research in catalysis is needed to improve these energy-related processes, a Workshop was held at Rice University on June 24-25, 1974. The twenty-eight delegates and ten observers from universities, industries, and governmental agencies selected specific areas within five broad energy-related categories where fundamental information is needed.

In most of these cases current application has far surpassed the basic understanding of the chemical and physical factors that govern the processes; however, future practical advances will be enhanced by development of such fundamental information. Also, the Workshop suggested new areas where catalysis may reasonably be applied to novel energy conversion systems. Finally, the Workshop addressed the broad issue of fundamental research in catalysis, a multidisciplinary subject embracing chemistry, physics, engineering, and materials science, just to name a few. Although most of the attention was focused on heterogeneous catalysis, homogeneous catalysis and enzyme systems were also considered.

B. Recommendations

The Workshop identified three areas where fundamental research in catalysis should have a positive impact on the energy problem.

1. Fundamental experimental research
 - a. Reaction mechanisms and intermediates
 - b. Surface characterization
 - c. Catalyst deactivation and modeling
2. Catalytic theory aimed at developing a microscopic understanding of catalysis
3. Exploratory research on energy systems

Much effective research in catalysis requires sophisticated expensive equipment. When sound, well-defined proposals involving use of such equipment are deemed worthy of support, it is recommended that special attention be paid to insuring that requisite equipment is available to qualified scientists.

In view of the decrease of fundamental research by U.S. industries, it is recommended that serious consideration be given to increasing support for fundamental research in catalysis and for the training of students in this field, which is so important in both energy supplies and energy utilization.

These programs should focus on development of basic understanding; they should avoid duplication of (or competition with) those being undertaken by industry.

II. INTRODUCTION

The recent "energy crisis" has focused national attention on the need to develop new economical domestic sources of fuel supplies. The Dixy Lee Ray report to President Nixon, entitled "The Nation's Energy Future," (AEC Report WASH-1281, December 1973) identified a number of areas where technological advances are needed in order for the United States to regain energy self-sufficiency. Advances in some of these areas are limited by design and engineering scale-up difficulties. In other areas, however, development of desirable processes is hampered by the absence of sufficient fundamental data on which to build. The field of catalysis is an outstanding example of this case.

Catalytic processes are already significant factors in this nation's economy, and each year they are involved in the production of manufactured goods valued at well over \$100 billion (Haensel and Burwell, "Catalysis," Sci. Am. 225, 46 (1971)). In addition to this industrial productivity, catalysis plays a role in defense technology, in the space program, in environmental quality, and in food supplies. New knowledge in catalytic science will be needed in order to solve the energy problem.

The projected results that can be expected from advances in catalysis as a result of intensive research are numerous. These include the formation of new industries and improved efficiencies in established industries, more economical generation of electrical power, new sources of synthetic fuel, low pollution transportation, and lower temperature processes making use of waste-heat. Frequently the whole key to success or failure of a proposed energy process depends upon the development of catalysts that are selective for the desired reactions and durable enough to withstand the severe processing conditions that are anticipated. There is room for improvement in almost all commercially important heterogeneous catalytic processes, and fundamental research in each should ultimately lead to enhanced activity, greater selectivity, longer life, and more efficient use of raw materials. The most productive approach to developing or improving catalysts involves simultaneous studies of specific processes and the fundamentals of catalysis.

These concepts are consistent with the stated goals, of the 93rd Congress, namely: improving environmental quality, maintaining United States leadership in science and technology, strengthening the national economy, and solving the energy crisis (Rothberg, "Catalysis: Legislative and Policy Aspects of a Technology to Improve Environmental Quality, Energy Supply, and Industrial Productivity," Congr. Res. Service, Q125-US-D1, 73-89-SP, April 2, 1973).

The objectives of the Workshop were to identify areas where research in catalysis reasonably can be expected to have an impact on the development of new and improved energy conversion cycles. Delegates to the Workshop were asked to provide in advance a "position paper" listing specific areas in which both fundamental and applied research in catalysis would be productive. From these it was possible to divide the delegates into six subgroups, corresponding to their interests and expertise. Each subgroup prepared written reports that were then discussed and amended by the entire delegation. The resulting reports form the chapters that follow.

Copies of this report may be obtained from the

National Technical Information Service (NTIS)
Department of Commerce
Springfield, Virginia 22151
(703) 321-8543.

III. PRODUCTION AND USE OF CARBON MONOXIDE AND HYDROGEN MIXTURES

A. Summary and Recommendations

The committee on the production and utilization of CO and H₂ recognizes that extensive technology exists for the production of synthesis gas from gaseous liquid and solid hydrocarbons, including natural gas, liquid petroleum and coal. Extensive technology also exists for the utilization of synthesis gas in such processes as methanation, methanol synthesis, Fischer-Tropsch, and water gas shift. However, with few exceptions, very little is known about the basic chemistry involved in these extensive fields. Therefore, the committee strongly recommends that NSF support a broad program of fundamental research to develop a high level of understanding of these reactions. Some important research areas are:

1. Studies of the reaction mechanisms and kinetics, with emphasis on selectivity and catalyst stability. These studies should utilize catalysts that are well-characterized by modern techniques as well as single crystal metal surfaces.
2. Exploratory research for new reaction pathways for some of the processes. This recommendation is explained in greater detail below.

B. Specific Processes

1. Gasification - Gasification catalysis can be applied to solid, liquid, and gaseous fossil fuels. Solid materials include coal, char, shale, and tar sands. Liquids include petroleum and its fractions from naphtha to vacuum residuum and heavy crudes. Methane reforming is the chief area of interest in the gasification of gases. All of these gasification areas have in common the production of carbon monoxide and hydrogen, and the mechanism of catalysis in each can be related. Fundamental studies of simpler systems, such as the steam reforming of methane, should be helpful in postulating catalytic mechanisms for more difficult systems such as coal.

Research using well defined catalysts (e.g. single crystals) to study mechanism, kinetics, effects of various reaction constituents on the catalyst as well as temperature and time should be emphasized for methane reforming and carbon gasification. One specific area for investigation is the study of alkali oxides with graphitized chars to investigate their catalytic effects. In addition to the basic steam-carbon reaction, attention should be given the carbon-carbon dioxide reaction that occurs in all of the reaction systems.

Such efforts may lead to development of improved gasification techniques and possibly a combination catalyst. Such a combination catalyst for steam-carbon gasification, water-gas shift, and methanation would enable all reactions to be carried out in the same reactor simultaneously with the overall effect of producing methane and carbon dioxide directly from carbonaceous material and steam.

2. Methanation - Synthesis gas reacts over a number of transition metal catalysts to form methane, $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$. This is the reverse of the steam reforming of methane and will accordingly benefit from fundamental research on steam reforming. The reaction is catalyzed by Ni, Co, Fe, Ru, Mo (as sulfide) and CoMo (as sulfide), but Ni is the usual catalytic element because of its high activity and selectivity. In spite of the simple reaction system, the mechanism of this reaction is not known, and the reason for nickel's outstanding specificity to methane is not understood. There are problems associated with the use of nickel catalysts which could be solved by careful fundamental research, such as the causes of catalyst deactivation. Is this due to poisoning by sulfur, fouling by carbon, or poor stability of the metallic structure? Possibly bimetallics or more complex alloys could be made which would retain their activity longer. Nickel compositions vary one from the other in the degree of water-gas-shift which they catalyze. More fundamental knowledge is needed to understand the minor differences which affect selectivity during methanation. Finally, because molybdenum and cobalt-molybdenum compositions can be used in sulfided form in methanation, there is the possibility that a practical sulfur resistant methanation catalyst system can be discovered.

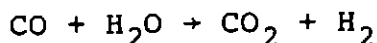
3. Synthesis of methanol and higher alcohols - Higher alcohols are considered here because they normally arise as byproducts of methanol synthesis and can confer beneficial properties on a methanol fuel. The known important catalysts are ZnO , CuO , Cr_2O_3 , and ThO_2 . It is recommended that fundamental studies of kinetics, mechanisms, activity, selectivity and stability of these catalysts be carried out using modern physical and physicochemical techniques. It is known that the addition of alkali to such catalysts can shift selectivity toward higher alcohol yields; accordingly, research on methanol catalysts should include promotions by alkalis and related substances. Thorium catalysts at high temperatures and pressures produce branched hydrocarbons, largely iso- C_4 's. Improved catalysts that may carry out these reactions under less severe conditions seem desirable. In commercial practice, synthesis is carried out in a recycle loop with low conversion per pass; this suggests that more active catalysts might

be sought which could operate at lower temperatures and/or are more resistant to deactivation by sintering and poisoning. Since the Cu-based catalyst is very susceptible to sulfur, poisoning studies and research for S-resistant catalysts appear in order. Finally, it would be desirable to develop a new, single catalytic pathway for converting CH_4 to methanol by direct oxidation under mild conditions.

4. Fischer-Tropsch Synthesis - Studies should be made to supplement the substantial work done before 1960, using recently developed research tools for catalyst characterization and product analysis. Typical iron and cobalt catalysts should be studied with the objectives of determining factors leading to high activity and stability, and developing methods for controlling selectivity, particularly to limiting products to a given molecular type and a small range of carbon numbers. For iron the effect on selectivity of K_2O and interstitial phases (carbides, nitrides, carbonitrides, and corresponding borides if they can be prepared) needs to be studied. Binary alloys of Fe, Co, or Ni plus other reducible metals should be examined as new catalyst types.

The reaction mechanism should be re-examined using all available research tools to identify intermediates, the nature of the chain growth process, and factors influencing formation of branched carbon chains, olefins, and oxygenates.

5. Water-Gas Shift Reaction -



Typical Catalysts	High Temp	800°F.	Fe_3O_4
	Low Temp	400°F.	CuO , Cr_2O_3

Co and Mo catalysts also are often used because of sulfur resistance.

Quite a lot is already known about the mechanism of the water-gas-shift reaction. It is recommended that future exploratory research be directed to the development of a homogeneous catalyst in a scrubber system. The process could be simplified and costs reduced in this way. Mechanistic studies should be carried out with a view to improving the system. It is felt that any improvements in understanding could also contribute to gaining a better understanding of currently used heterogeneous catalysts.

In view of the ability to use inexpensive catalysts, economics favor continuing use of currently developed water gas shift catalysts, and there is consequently less incentive to develop new and improved heterogeneous catalysts than in other areas that deal with the production and synthesis of CO and H_2 .

IV. LIQUEFACTION AND DOWN-STREAM PROCESSES: COAL, TAR, SHALE OIL, AND RESIDUUM

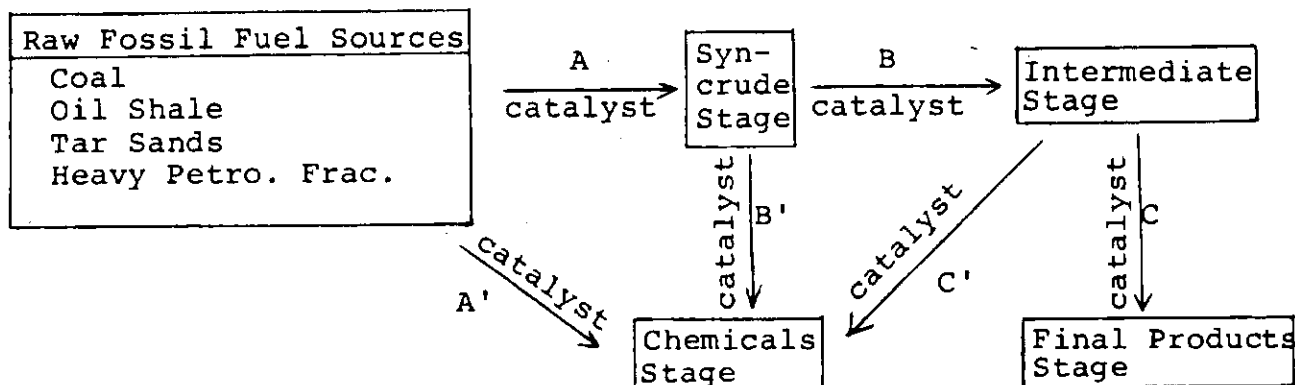


Figure 1: Frame of Reference

A. Physiochemical Characterization of Raw Materials and Primary Products

1. For the efficient catalytic processing of fossil fuels, it is highly desirable to have a much better understanding of the chemical nature of the initial material (as far as possible) and of the products obtained on primary processing (e.g., liquefaction). To the extent possible, key classes of components present in the fossil fuels should be identified, especially as these relate to the catalytic reactivity in processing. Important structural features should be analyzed, and model compounds may be studied in order to better understand the chemical changes occurring during catalytic processing.
2. Specifically with respect to coal, much more information is needed on the surface chemistry, the effect of adsorbed oxygen (even a monolayer), and the effect of variation in the methods of contacting the coal surface with potential catalysts during primary processing.
3. A more detailed chemical understanding should be obtained of the primary products such as "asphaltene" and "oil," resulting from processing steps such as solvation or hydrogenation. This is needed in order to discriminate the action of different catalysts in changing the product distribution, and chemical composition, obtained during primary processing.

B. Processes for Conversion of Fossil Fuels to a Synthetic Crude (Stage A, Figure 1).

1. Coal liquefaction/conversion
 - a. It is necessary to achieve some understanding, in mechanistic detail, of the mode of action of present

catalysts (e.g., SnCl_2 , ZnCl_2 , FeSO_4 , Co/Mo, Ni/Mo) in the liquefaction and hydrodesulfurization of coal--especially since liquefaction and hydrodesulfurization do not generally occur to the same extent. Such research may even involve the use of crystalline catalysts, of relatively simple systems such as CoS, MoS_2 , etc., in order to understand variations of selectivity and reactivity over a range of reaction conditions. There is also a need to determine how such catalysts are deactivated and, possibly, reactivated.

b. A search for entirely new systems of catalysts that can operate on coal may be worthwhile. In the case of effective catalysts, emphasis should be placed on a possible relation (correlation) between catalyst nature and the resultant product distribution. The ability to influence product distribution--i.e., selectivity--may prove extremely important.

c. Directly related to the question of selectivity is the desirable search for catalysts, or catalytic processing methods, that will permit direct conversion of coal to useful chemicals--e.g., the selective cleavage of polynuclear aromatics to mononuclear aromatics (Stage A', Figure 1).

d. It is desirable to seek new catalytic methods to (a) remove the impurities S, N, and O (unless these are desired for specialty chemicals production), and (b) remove the metals Fe, Ti, Ni, and V.

e. Research is needed on the fundamentals of catalyzed solvent conversion of coal. This includes basic research on the catalyzed use of hydrogen donors and of hydrogen carriers as solvents, involving either internal (in situ) or external re-hydrogenation with a catalyst.

f. The catalytic hydrocracking of coal may be fruitfully studied by the use of appropriate model compounds (see Item A, above).

g. Understanding is needed, and lacking, on the nature of the thermal and the catalytic (hydrogenolytic) breaking of bonds in coal.

h. The possible use of coal-derived minerals (residue or ash), either directly or with some chemical processing, as catalysts for coal conversion deserves investigation.

i. There is potential use for the catalytic conversion of coal with steam-carbon monoxide, rather than hydrogen. Differences in rates, product composition, and selectivity may be observed.

j. Differences in the catalytic conversion of solvent-refined coal, in distinction to coal itself, should be studied.

2. Production of shale oil - The use of enzyme catalysis for the in situ conversion of kerogen to more readily extractable material deserves examination.

3. Fundamental studies of stages "A" and "B" Figure 1 - Further studies of the catalytic use of massive amounts of Lewis acids (e.g., ZnCl_2 and $\text{ZnCl}_2\text{-AlCl}_3$) and proton acid - Lewis acid combinations for hydrogenation, hydrocracking, and isomerization are desirable. A need exists for:

- a. Information about the dependence of these processes on the acidity of the medium.
- b. Evidence that the temperatures and pressures of the processes can be substantially reduced. (Recent work has shown that benzene can be saturated and ring-opened to produce a mixture of isohexanes at 50°C and 150 psig H_2 in HF-TaF_5 .)
- c. Methods to regenerate the acid systems, particularly when nitrogen poisoning, the conversion of ZnCl_2 to ZnS , and other inhibiting processes occur.
- d. Mechanistic information that might be obtained by isotopic labeling studies of the massive amounts of acids.

C. Conversion of Synthetic Crudes and Intermediates (Stages B and C, Figure 1)

Desirable studies would include:

1. Exploration of the possibility of non-hydrogenative catalytic methods for denitrogenation of shale oil or other high-nitrogen stocks.
2. Development of low pressure hydrogenative methods for desulfurization, denitrogenation, and deoxygenation.
3. Catalytic cracking of synthetic oils, or representative model compounds, from the standpoint of:
 - a. Mechanistic studies
 - b. Characterization (including valence state, chemical environment, and catalytic properties) of the metallic impurities (Fe, Ti, Ni, V) that may be deposited on or in the catalysts during the cracking of heavy feedstocks.
4. New catalytic routes to chemical products that place emphasis on energy conservation.

D. Homogeneous Catalysts

Homogeneous catalyst systems, whether free or anchored, may be applied to any of the fossil fuel processing procedures discussed above. In this case, research is appropriate on the stability of the homogeneous catalysts to high temperatures and to high levels of sulfur, oxygen, and nitrogen compounds.

Addendum: It is recommended that, when programs are considered worthy of funding but instrumentation necessary for accomplishing the objective is not available to knowledgeable investigators, special attention is given to insuring that appropriate instrumentation be provided.

V. CATALYSIS IN ENERGY CONVERSION WITH EMPHASIS ON ELECTROCATALYSIS

A. The Oxygen Electrode

1. Fundamental

- a. The oxygen activation mechanism limits the efficiency of both fuel-cell and electrolysis operations. In view of the need for a low over-potential at high current densities in both operations, a critical review of the literature on oxygen mechanisms could provide new insights, correlations, and ideas for progress.
- b. Renewed experimental programs should be undertaken on the mechanism of the oxygen electrode, in directions indicated by the literature search.
- c. In connection with multi-component catalysts, we need reproducible methods of preparation and methods for proper characterization--especially of the surface compositions of multi-component catalysts, with the use of recently developed surface analytical techniques. Concurrently, the effects of such composition on electrocatalysis and on stability need to be determined.
- d. The true surface conditions on electrodes during reactions should be determined.

2. Exploratory - The catalytic regeneration of possible cathode redox species, e.g., Tl^+ , V, Cr, and NO_2^- should be investigated.

B. The Fuel Anode

1. Fundamental

- a. Studies are needed of the surface of anodes consuming carbonaceous fuel, with the use or adaptation of available methods, including optical ones. Surface species, including carbon "templates" and surface polymers, should be identified if possible.
- b. A critical review of the hydrocarbon electrode is also needed.

2. Exploratory

- a. Though Pt is a satisfactory anode catalyst for hydrogen and hydrazine, a substitute (alloy?) is needed for cost reasons.
- b. To obviate the problems with carbonaceous fuels, it may be useful to find a redox anode in order to decouple the fuel catalysis from the electrode.
- c. Can the carbonaceous fuel- H_2O reaction be catalyzed on the anode at low temperatures?

C. Electrodes Generally

1. Fundamental

- a. More meaningful studies are desirable of metal sintering and of poisoning of metal catalysts by sulfur and

other materials. These lower the efficiency and shorten the life of energy conversion and interconversion devices.

2. Exploratory
 - a. Better conductive supports for catalysts at the electrode are needed.
 - b. The direct conversion of chemical to mechanical energy has been demonstrated (cf. Kuhn and Katchalsky). Is it possible to find electrodes that would change dimensions cyclically during reaction? Such mechanical action might be used to improve power density.

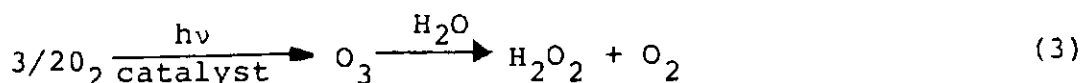
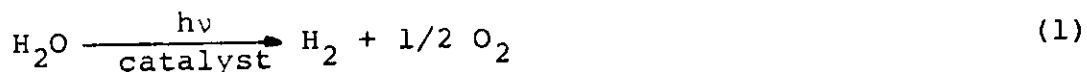
D. Miscellaneous

1. Exploratory
 - a. The "proton cell" (Shedlovsky) should be reconsidered for its potential usefulness.
 - b. The stability of organometallic and inorganic oxygen carriers should be improved for use in homogeneous catalysis (e.g., homogeneous oxidation coupled with surface reduction).
 - c. To suppress dendrite formation on zinc electrodes, negative catalysts would be useful. An example might be adsorption of a poison at the gas-liquid interface.
 - d. Can liquid-phase combustion be catalyzed to obtain high power density? Are there homogeneous catalysts for use in molten salts?
 - e. Can we find recycleable catalysts for more uniform burning temperatures in electric power plants using fossil fuels?
 - f. Can catalytically active compounds be found for use in turbines, to obtain more uniform burning temperatures?

VI. NON-CONVENTIONAL CATALYTIC PROCESSES

A. Introduction

Reliable sources of energy available for the very long term include: a) nuclear fusion, b) harnessing the tides, c) geothermal energy, and d) solar energy. Although materials developments may be needed for the first three, no obvious catalytic problems are apparent. With solar energy conversion and utilization, on the other hand, some possibilities are obvious. The basic problem is the conversion of the relatively large amount of energy contained in sunlight into any other form of energy except heat. This report deals with more efficient energy conversion processes and with transformations leading to conversion of light into stored chemical energy. Some examples of the latter include:



Many others could be added to this list. The lowest frequency needed for such reactions corresponds to the Gibbs free energy deficit if one quantum is required for the conversion of one molecule. However, coupled systems analogous to chlorophyll, in which several quanta are stored and used, are conceivable.

Much has been written concerning the desirable features of a hydrogen economy. Besides the obvious ecological benefits, economic benefits are very considerable, not only in dollars, but in conservation of fossil fuels. For example, coal is hydrogen deficient; to provide the hydrogen needed to upgrade it requires the overall conversion of one atom of C to CO_2 for each 2H_2 produced (not counting the heat required for the coal gasification step). The possibility of finding a direct photochemical means of decomposing H_2O into its elements is thus a challenging problem of considerable potential benefit to society, could a solution be found.

Other possible energy storage chemistry may in the long run prove more tractable and nearly as advantageous. For example, CO produced in reaction (2) may be reacted with H_2O to produce H_2 ; the direct photocatalytic oxidation of CH_4 to CH_3OH is another.

In the subsequent sections these possibilities and others are discussed in more detail. In many instances, heterogeneous

catalysis is discussed or implied, but this is for convenience. Real solutions may equally well be found in homogeneous systems. It is our belief that much research is needed on the chemical effects of the interaction of light with matter.

B. Photocatalysis

In many reactions of interest, the energy per quantum of solar energy which reaches the earth is inadequate to excite the reactant molecules. Thus, a catalyst is sought which will combine with the reactant molecules in such a way that visible quanta may be absorbed to promote the reaction. However, the basic understanding of photocatalytic processes, both in heterogeneous and homogeneous systems, is in its infancy. Systematic fundamental research is needed (including study of model systems) before design and prediction of catalytic materials for specific reactions will be possible.

1. While a complete description of the types of studies required is not possible or desirable, some of the more obvious and important possibilities may be considered. For homogeneous systems, detailed studies of the nature of the excited states of the transition metal catalyst (or of the reactant) are needed and development of ideas about the relationships between the nature of the excited state and chemical reactivity is essential. Included within this should be studies of the mechanism, kinetics, and, where possible, identification of intermediates.

To bridge the gap between homogeneous and heterogeneous systems, the study of photocatalytic behavior of cluster compounds involving several metal ions may be important. These could involve systems with the same metal ions in different environments and/or oxidation states or a couple of different metal ions. In heterogeneous catalysis, initial studies of photoactivated adsorption or desorption mechanisms need to be carried out. These studies can be correlated with present theory and thus lead to a more complete understanding of photocatalyzed reactions. There are a variety of heterogeneous reactions which could possibly turn out to be photocatalytic. Among these are the interesting class of photochemically assisted electrochemical reactions.

2. Application to Dissociation of Water to Produce H_2 - Chemical reactions are known which produce either oxygen or hydrogen (but not both simultaneously) from water, while the other reactant is either reduced or oxidized in the process. In these cases, the system could be made photocatalytic if the adsorbed component from the water molecule could be preadsorbed.

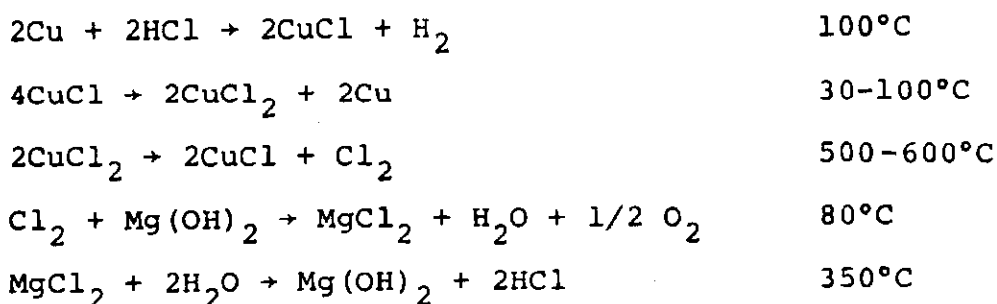
It is convenient to consider the problem by dividing it into several steps:

- a. It is known that water is chemisorbed on transition metal oxides in the form of OH groups. These oxides are inexpensive and provide a wide range of physical properties. Theoretical and experimental research is required to understand the intrinsic surface states on these materials and how these surface states interact with water to cause dissociation and chemisorption.
- b. It is possible that quanta of visible radiation may promote dissociation of the O-H groups into oxygen and hydrogen ions. This may be accomplished by absorption of radiation by the O-H bond, weakened by chemisorption, or by the catalyst itself. The nature of the chemisorbed species and connected substrate must be investigated as well as its interaction with visible radiation.
- c. The oxygen and hydrogen ions produced must be separated, neutralized and converted to gaseous molecules. This can be done by electrolysis. Thus, research is needed on systems where the catalyst is operating as anode or cathode, with and without radiation. Other processes to accomplish final conversion of the ions into separated molecules may be possible which are more economic than electrolysis. Such processes should be considered and investigated.

C. Applications to Other Systems

The application of photocatalysis is not limited to the production of hydrogen. Other chemical processes exist in which energy may be stored and all of these are potential candidates for the utilization of photochemical energy. Indeed, a commercial process for the production of lactams (cyclic amides) is already on stream in Japan. Other potential reactions for the conversion of photo energy to chemical energy were mentioned in the introduction.

Another related application is in various chemical energy conversion cycles where one or more steps are endothermic and therefore normally require very high temperatures to accomplish. With these, it may be possible to replace the thermal energy required by photochemical energy. Consider the cycle to produce H_2 and O_2 from H_2O .



Substantial savings of thermal energy could be obtained if the third step could be photochemically assisted.

D. Energy Conversion Cycles to Increase Efficiency

Many energy conversion processes are wasteful in energy since thermodynamic efficiencies are not realized. Catalysis could play a vital role in energy conservation through the development of more efficient steps in these processes.

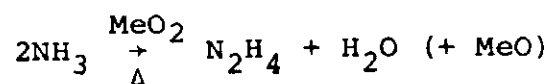
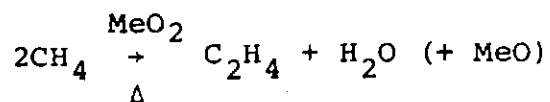
The magnitude of the potential energy savings by increasing efficiency of energy conversion processes is enormous. In the U.S. in 1970, 75% of the energy used for transportation was lost; this corresponds to 40% of all the domestic and imported petroleum utilized in that year. In fact, almost 50% of the total energy (including oil, coal, gas, nuclear, etc.) utilized for all applications was lost. This corresponds to a waste of 15 million barrels of oil/day! Specific examples are as follows:

1. Power Cycles - The efficiency of power cycles using turbines could be increased if chemical energy accumulated in the gas is released at the turbine blade. Research is needed in order to assess the types of reactions necessary to develop proper materials, and to provide adequate design data.

2. Use of Catalytic Processes in Energy Transmission - Suggestions have been made for the transmission of energy in the form of chemicals. For example, with solar or nuclear energy as the primary source, heat is provided for endothermic reactions (such as steam reforming) to yield a product which may be transported or piped to a distant point. An exothermic process (such as methanation) may then be used to produce heat and a product which is recycled back to the primary source. Potential reactions should be catalogued and catalysts developed to meet the requirements of temperature, etc. Although many existing catalytic processes are suitable, it is possible that greater efficiencies may be realized through the development of novel systems specifically for this purpose.

3. Waste Heat Utilization - With the projected proliferation of nuclear reactors in the future, utilization of waste heat from such reactors could be used in catalytic processes, thus making the process more economically attractive. Areas should be identified where this is applicable.

4. High Temperature Reactions - There are a number of scattered references where hydrocarbons have been oxidized by metal oxides resulting in cyclic conversion processes. Theoretically, the following reactions are possible:



Studies of the nature of solids which can function at high temperatures for selectively conducting these reactions could be of importance. This is especially true if waste heat were utilized in heating the metal oxide and in its regeneration.

5. Enzyme Conversions - More efficient conversion of cellulose waste is of importance. For example, can more efficient enzymes be obtained for providing high yields of ethanol? A more efficient conversion of cellulose waste to gaseous hydrocarbons would also be desirable.

6. Internal H_2 Production - Catalysts for the catalytic production of "in situ" hydrogen from H_2O , are needed, e.g., the use of $H_2O + CO$ in conversion processes such as residuum HDS and coal liquefaction would be beneficial. This could reduce or eliminate the tremendous capital required for hydrogen plants.

7. Methanol Synthesis - An improved catalyst for CH_3OH synthesis which functions at lower pressures and temperatures and is more tolerant of sulfur than the current best catalyst would be highly desirable. It is suggested that research on supported metal complexes be initiated with this end in mind. Another desirable possibility is an efficient direct oxidation of CH_4 to methanol.

VII. PROBLEMS RELATED TO POLLUTION CONTROL

A. Introduction

In considering the way a deeper understanding of chemical catalysis will benefit the ultimate solution of pollution control problems, attention will be focussed exclusively on the cleanup of waste or effluent streams. It should be kept in mind that it may well be economically advantageous to consider source cleanup (e.g., generally an upgrading of a fuel for either a moving or a stationary source); this source processing might well involve chemical catalysis.

It cannot be over-emphasized that the objectives of NSF-sponsored basic research should be to add to the total knowledge of the scientific community, i.e., to provide a deeper fundamental understanding of various catalytic reaction mechanisms as outlined below and not necessarily to provide a short-range solution to quite specific problems. For example, it is anticipated that a detailed understanding of the nature of the catalyst surface both in the presence and absence of a reacting system will greatly clarify many of the mysteries generally associated with research in chemical catalysis.

A reasonable point of view would be to conduct research on well-defined model systems (e.g., specific crystallographic orientations of various monocrystalline catalyst surfaces) and then to progress to more realistic systems and conditions insofar as this is compatible with a characterized system. Unfortunately, this kind of a research effort often involves rather sophisticated and expensive instrumentation. Nevertheless, since the information which will be forthcoming from such an experimental program is of such vital importance, it is strongly recommended that NSF not preclude the support of permanent equipment grants, e.g., of \$25K-40K, to competent individual principal investigators.

B. Auto Exhaust Catalysts

The use of catalysts to control three pollutants, CO, hydrocarbons (HC), and NO_x in auto exhaust, allows adjustment of engines of today's vehicles for maximum fuel economy. Hence, for a properly optimized car with exhaust catalysts, cleaner air is achieved with better utilization of energy, although catalysts do require the removal of lead additive for octane enhancement and thus may result in lower compression, less efficient engines. It is very important to increase our fundamental understanding of processes effecting durability of auto exhaust catalysts under actual use conditions. These processes are mainly identified as thermal deactivation and poisoning. Problems for basic research indicated below are related to these areas, and a basic understanding hopefully would eventually lead to the formulation of improved catalysts.

1. Removal of CO and HC

a. Sintering mechanism(s) of supported noble metal catalysts - Is sintering of Pt or Pd on alumina caused by diffusion or by evaporation/redeposition (e.g., of platinum-oxides)? These studies should also consider possible noble metal-support interactions and effect(s) of reaction atmosphere at temperatures relevant to auto exhaust applications (up to approximately 1,000°C).

b. Relative catalytic activities of crystallographic planes - Explanations of differences found (if any) between the various crystallographic planes (hkl) of noble metals and base metal oxides, e.g., Pt, Pd, Cr_2O_3 , etc., are desired with the hope that such information (together with the stability information of most active planes under reaction conditions) may eventually lead to ways of stabilizing a preferred crystal habit in a polycrystalline media.

c. Sintering mechanisms of practical substrate materials - These studies must consider the effects of atmosphere (oxidizing as well as reducing), starting phases, additions, and temperature levels relevant to auto exhaust applications. It is hoped that such basic studies could lead to better stabilization of supports, e.g. alumina, as far as their surface area and phase composition are concerned.

d. Chemical engineering - Since many catalytic auto emission control applications are transport limited, it is important to investigate mass and heat transfer characteristics of various catalyst geometries (e.g., monolithic supports) and modeling. Such studies should allow prediction of more effective systems.

e. Fundamental poisoning studies - Studies of noble metal (e.g., Pt, Pd, etc.) and base metal oxide poisoning by Pb and S under well defined conditions and on well defined surfaces using tools such as LEED, AUGER, Ion Scattering, Photoelectron Spectroscopy, Field Ion Microscopy, etc. are needed. Such studies must include probes for catalytic activity, e.g., by mass spectroscopy.

f. Substitutes for noble metal catalysts - Since the U.S. has essentially no noble metal natural resources that can be economically mined, substitutes for these metals should be sought. Two possible candidates are base metal oxides or mixed oxides, and novel systems such as alloys, solid solutions, and non-stoichiometric compounds. Any such materials must certainly exhibit acceptable durability towards thermal deactivation and poisoning under auto exhaust environment.

2. NO_x Removal

a. A good catalyst for decomposition of NO under oxidizing conditions is desired. It would be directly applicable to Diesel exhaust which cannot be controlled for NO_x by reduction because it is too lean. Studies on a) mechanism of $2\text{NO} + \text{N}_2$ reaction b) determining rate limiting step (removal of oxygen from the surface?) would be desirable. Such basic studies may indicate the probability of technical success of NO decomposition.

b. One of the ways of controlling NO_x emissions is by TWC (Three Way Conversion), that is simultaneous reduction of NO_x and oxidation of CO and HC in a single catalyst bed by close control of air/fuel ratio (of feed to catalyst) near the stoichiometric point. This is accomplished by a closed-loop system employing an oxygen sensor (so-called λ -sensor) and a feed back system. By this mode of operation of the engine, better fuel economy is obtained than by using the "dual-bed" approach which requires rich air/fuel ratio setting of the engine.

Studies are needed regarding a) the reaction mechanisms of TWC catalysis b) development of an understanding that will result in a way to increase the useful air/fuel ratio region of operation (so-called "delta" or "window"). The latter will allow longer successful operation of catalysts.

c. Factors that result in deterioration of NO_x reduction catalysts under "redox" cycling conditions should be studied. Negative aspects of "dual-bed" approach as far as fuel economy is concerned must be considered in setting the priorities of research work on NO_x reduction catalysis.

C. Stack Gas Cleanup

1. Power House Stack Gas - The use of high sulfur content fuels can create a SO₂ emission problem, and the use of high nitrogen fuels can produce a NO problem. In addition, the combustion itself produces NO.

A proposed method of SO₂ removal involves its catalytic oxidation to SO₃ followed by chemical removal of the SO₃. The commercial processes now in use demand an efficient and durable catalyst resistant to deactivation by fly ash. Research aimed at development of new catalytic approaches to SO₂ removal should be encouraged.

The removal of NO can be accomplished by NO decomposition or by selective catalytic reduction in a narrow temperature range in an oxidizing atmosphere by either NH₃ or H₂. The decomposition problem has already been mentioned.

The reduction of the NO, in preference to reduction of oxygen, is probably a result of the strong chemisorption of the NO. Basic research directed towards understanding the surface characteristics of the catalysts that are responsible for this selective reduction would aid in the selection of catalysts for this type of operation. NO removal can also proceed via oxidation to NO₂, which can be catalytic, followed by NO₂ adsorption.

2. Sulfur Recovery From H₂S Streams - In a number of processes for the removal of S from fuels or from stack gases where the fuel is burned under reducing conditions, H₂S can be produced. This H₂S can be recovered and S produced from it by partial oxidation of the H₂S (Claus Reaction). Basic research that might lead to alternative catalytic approaches for H₂S removal would merit support.

D. Miscellaneous Catalytic Conversions

There is a need for research to develop more efficient catalytic processes for the oxidation of pollutants in effluent streams, both in the liquid and vapor phases, from chemical, paint, electroplating and other already established industries, particularly where this clean-up is now done by more energy consuming processes.

As coal conversion comes into increasing use, there will develop clean-up problems for the effluent streams that almost certainly will involve catalysis. Continued research on the fundamental aspects of these problems should speed development of the necessary pollution control processes.

VIII. FUNDAMENTAL STUDIES IN CATALYSIS

A. Important Research Needs

A better understanding of catalysis would significantly accelerate the development of successful catalytic processes in the energy area. However, certain aspects of such a fundamental understanding are likely to be more immediately useful than others. Among the important needs are:

1. A wider exploratory investigation of catalyst compositions other than those generally used in the past with particular attention to surface composition and structure. Possible objectives are catalysts to replace noble metals and sulfur resistant catalysts.
2. Exploratory studies aimed at new catalytic processes with reference to production of fuels or to energy conversion processes, e.g., $2\text{H}_2\text{O} + 2\text{C} \rightarrow \text{CO}_2 + \text{CH}_4$, conversion of polynuclear aromatics to mononuclear species (aimed at coal or petroleum resid conversion). Exploratory studies should also be aimed at new catalytic processes which have the potential of reducing energy consumption in the chemical industry.
3. Development of a quantum mechanical understanding of the nature of the adsorbate-surface bond and of reactions among adsorbates. The absence of such theory has seriously impeded development of mechanistic understanding of heterogeneous catalysis.
4. Thermodynamics of adsorption. There is a great paucity of experimental work dealing with enthalpies and entropies of adsorption as a function of composition and surface coverage.
5. Geometrical location of adsorbed species. The most useful techniques appear to be low energy electron diffraction (LEED) with emphasis on intensity profiles, angular dependence of photoemission, and extended x-ray adsorption fine structure (EXAFS).
6. Electronic levels of adsorbed species. Promising techniques are photoemission and field emission spectroscopy. The experimental investigations under items (4), (5) and (6) should be closely correlated with the theoretical developments of item (3).
7. Chemical mechanisms of heterogeneous catalytic reactions with emphasis upon reactions likely to be useful in the energy area. Possible examples are hydrodesulfurization, the various hydrogenations of carbon monoxide and carbon dioxide, steam reforming of hydrocarbons and catalytic oxidation of hydrocarbons. A reliable determination of any reaction mechanism will generally require the use of two or more appropriate techniques, for example, isotopic-tracer studies, kinetics, stereochemistry, infrared and nuclear spectroscopies and selectivity studies. Such coupled studies are encouraged.

8. Catalyst deactivation. The loss of catalytic activity due to poisoning, sintering, coking and the reaction of components of the catalyst is a very important commercial problem. Any new ideas likely to be useful in this area should be given high priority.

B. Potential Manpower Shortage

The implementation of many of the above recommendations, particularly those related to (1), (2), and (7), will be difficult in the present situation in American universities, i.e. the near absence of faculty working in heterogeneous catalysis in the chemistry departments of the "top-thirty" universities. This will have an increasingly severe effect upon manpower availability and upon research capabilities. In turn, this will limit the ability of the nation to respond to crucial energy needs. We recommend that the NSF commission a study to evaluate the consequences of this situation and make appropriate recommendations.

APPENDIX A

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Rice University
June 24-25, 1974

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APPENDIX B

Sub-Groups Responsible for Various Chapters in Report
 NSF Workshop on Energy/Catalysis
 Rice University
 June 24, 25, 1974

I. SUMMARY AND RECOMMENDATIONS

<u>Hightower</u>	Keulks
Hall	Weller

II. INTRODUCTION

<u>Hightower</u>	Keulks
Hall	Weller

III. PRODUCTION AND USE OF CARBON MONOXIDE AND HYDROGEN MIXTURES

<u>Oblad</u>	Steffgen	Knudsen	Reucroft
Anderson	Coughlin	Plummer	

IV. LIQUEFACTION AND DOWN-STREAM PROCESSES: COAL, TAR, SHALE OIL, AND RESIDUUM

<u>Bailey</u>	Pennington	Venuto
Emmett	Pittman	Weller

V. CATALYSIS IN ENERGY CONVERSION WITH EMPHASIS ON ELECTROCATALYSIS

<u>Cohn</u>	Harkins	Shalit
Bett	Palmer	

VI. NON-CONVENTIONAL CATALYTIC PROCESSES

<u>Richardson</u>	Hall	Swift
Berry	Morin	Willett

VII. PROBLEMS RELATED TO POLLUTION CONTROL

<u>Kummer</u>	Benson	Weinberg
Aykan	Hightower	

VIII. FUNDAMENTAL STUDIES IN CATALYSIS

<u>Burwell</u>	Keulks	Pollitzer	Schrieffer
Eischens	Libby	Roth	

denotes section chairman

BIBLIOGRAPHIC DATA SHEET		1. Report No. _____	2. _____	PB 236 683	
4. Title and Subtitle Workshop on Needs for Fundamental Research in Catalysis as Related to the Energy Problem				5. Report Date June 24/25/1974	
7. Author(s) Joe W. Hightower, W. Keith Hall, George W. Keulks, Sol W. Weller				8. Performing Organization Rept. No. _____	
9. Performing Organization Name and Address Rice University P.O. Box 1892 Houston, Texas 77001				10. Project/Task/Work Unit No. _____	
				11. Contract/Grant No. GP44178	
12. Sponsoring Organization Name and Address National Science Foundation 1800 G Street, N.W. (Research Directorate) Washington, D.C. 20550				13. Type of Report & Period Covered Catalysis June 24/25/1974	
15. Supplementary Notes				14. _____	
16. Abstracts This is a report of the proceedings and recommendations of a workshop on fundamental research in catalysis related to energy problems held at Rice University June 24-25, 1974. Research areas given special attention were: the production and use of carbon monoxide and hydrogen mixtures, liquefaction, electrocatalysis, and pollution control. Consideration was also given to non-conventional catalytic processes with particular attention to those, such as photo-catalysis, which may bear on solar energy utilization. It was emphasized that fundamental research in catalysis is very important to the long-range aspects of energy conversion. Singled out for emphasis were: reaction mechanisms, surface characterization, catalyst deactivation, catalytic theory, exploratory research on energy systems, and equipment.					
17. Key Words and Document Analysis. 17a. Descriptors <div style="display: flex; justify-content: space-between;"> <div> Surface Chemistry Catalysis Catalysts Enzymes Surface Properties Photochemical Reactions </div> <div> Any opinions, findings, conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. </div> </div> <p style="text-align: right;">PRICES SUBJECT TO CHANGE</p>					
17b. Identifiers/Open-Ended Terms NSF Energy Related General Research Workshop in Catalysis					
Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Commerce Springfield VA 22151					
17c. COSATI Field/Group 0704, 0704, 0704, 0601, 0616, 1407, 0705					
18. Availability Statement Release Unlimited				19. Security Class (This Report) UNCLASSIFIED	
				20. Security Class (This Page) UNCLASSIFIED	
				21. No. of Pages	