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ABSTRACT

A two-day Workshop was held by R&D Associates to consider the importance of catalytic processes in supplying the DOD with fuels and other forms of energy, and with petrochemicals of military importance.

The general conclusions of the Workshop with respect to the DOD are that national direction and guidance of catalytic research is needed, that the defense interests of the United States call for improvements in catalysis, and that ARPA should take part in providing leadership in research and catalysis to ensure that the needs of the DOD are met.

PREFACE

This draft is a summary of material presented both formally and informally at the ARPA Workshop on the needs of the Department of Defense for Catalysis. Emphasis has been given to topics having relevance to the interests of the DOD. The Proceedings of the Workshop are reported in detail in RDA-TR-3501-002, "ARPA Workshop on Needs of the Department of Defense for Catalysis, Volume II - Proceedings." Recommendations prepared by a subgroup of the participants in the workshop, as reported in Volume II, are also presented in this volume.

The Workshop was held in Santa Monica on November 5 and 6, 1973, conducted by R & D Associates, under contract with the Defense Advanced Research Projects Agency. The proceedings of the Workshop, together with transcripts of discussions among the participants, are embodied in Volume II, RDA-TR-3501-002. Since most of the participants, although nationally known in their fields, were unacquainted with catalytic needs and energy problems of the DOD, they spoke instead of what they know how to do with present day catalysts. On this account much of the substance of the Proceedings has to do with catalysis in industry and in university research.

The present volume, Volume I, contains concepts and problems of interest to the DOD as developed in the Workshop and as evolved in conversation with Workshop participants. The author hopes to have abstracted the sense of statements made by the Workshop attendees without altering the intent of their words.

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SECTION 1. SUMMARY OF WORKSHOP FINDINGS WITH RESPECT TO DOD INTERESTS

1.1 DOD INVOLVEMENT WITH CATALYTIC RESEARCH

The DOD is already supporting catalyst research on a small scale to ensure the availability of fuel, because the material science of catalysis is not sufficiently developed today to permit production of alternate fuels, nor supplementary fuels, nor to permit easy interconversion of fuels.

It is reasonable to suppose that industry could invent the catalytic technology to produce new fuels for military use from crudes and coal in domestic large-scale refineries if given sufficient incentive. DOD support for development of mobile processing facilities and appropriate catalysts to produce military fuels from available feedstock at remote locations may be warranted.

Hydrogen as a fuel has transport and storage problems which limit its usefulness in military operations. On the other hand, hydrogen will play a key role in future production of military fuels from coal, oil shale, resid, and other feedstocks. Catalytic production of hydrogen is basic to ensure availability of clean fuels to the military in the future. The technology for making liquid fuels and hydrogen via the Fischer-Tropsch and water gas reactions was improved in Germany during World War II; the German Luftwaffe flew on fuel processed from coal by means of catalysis. However, the Fischer-Tropsch and water-gas technologies have been neglected in the last thirty years.

The Workshop made little reference to missile propellants (solid and liquid) nor explosives, although these are obviously materials essential to operations of the DOD. It is possible that innovative and advanced catalyst research might be important in producing new propellants and explosives in which the rate of combustion is controlled by catalysts.

1.2 ARPA'S ROLE IN CATALYTIC RESEARCH

The research effort called for in development of better, more efficient, more selective forms of present day catalysts, and in development of new genera of catalysts, independent of foreign supplies of platinum and other noble metals, is important for military self-sufficiency and national security. The national research effort envisioned is one of necessarily high risk and requires bold innovation with accompanying expansive test programs to prove the usefulness of the new catalysts. This is a program of advanced research appropriate to ARPA. Although the subject was not addressed in a formal talk at the Workshop, the sense of many Workshop attendees was that the new catalysts developed by this national research program will be essential to self-sufficiency of the U.S. in meeting the energy requirements of all of the services, and also on this account is appropriate to leadership by ARPA.

1.3 REDUCTION IN FUEL REQUIREMENTS FOR REFINING AND CONSERVATION OF FEEDSTOCKS

Because catalysts speed rates of reaction at a given temperature, a given yield can be accomplished using lower temperatures than would otherwise be needed, leading for example to a reduction in the amount of petroleum which must be burned in the refining operation. The selectivity of catalytic reactions allows the yield of specific products to be optimized for a given amount of feedstock put into a reactor. For example, today's catalysts allow the amount of high-octane gasoline per barrel of crude to be more than doubled above that which can be obtained by straight distillation. With the catalysts of the future, it may even be possible to change a barrel of crude into a barrel of gasoline, jet fuel, or any desired combination of end products. However, the examples of these applications to date are few.

1.4 EMPHASIS ON HETEROGENEOUS CATALYSIS

The major catalytic technology in use at the present time is the heterogeneous catalysis of gases and liquids on surfaces of solid catalysts. Therefore, the Workshop concentrated on heterogeneous catalysis. However, all life processes depend on homogeneous catalysis in enzymes and other molecules. There is some activity in industry aimed at attaching homogeneous catalysts to solid supports so they can be used more conveniently as catalysts in commercial reactors. Three-phase heterogeneous catalysis (liquid and gas on solid) is in limited use in desulfurizing residual fuel oil in industry.

1.5 CONCLUSIONS ON TECHNOLOGY

National direction and guidance of experimental catalytic research aimed toward elucidation of a fundamental understanding of catalysis is badly needed. Industry is principally motivated to commercialize new catalytic processes rather than to explore theory, with the result that basic understandings are seldom if ever reached. A research program directed toward reaching basic understanding of catalysis of importance to the DOD is appropriate to ARPA sponsorship.

The technology of catalytic reforming of petroleum has been developed to be very highly selective and controlled, using platinum and mixtures of platinum with certain other metals such as rhenium, germanium, tin, etc., and noble metals generally supported on alumina or on alumina containing a small amount of silica. This technology, mainly directed at production of high octane gasoline, is among the most highly developed catalyst technologies in commercial use; however, while mechanism of most of the reactions is rather fully understood, a great deal needs to be learned concerning theory and concerning mechanism of minor reactions.

Technologies presently used for studying surface properties of catalysts and surface chemistry on catalysts are inadequately developed, so that only fragmentary information has been obtained under conditions of commercial use. The various kinds of measurements already performed have helped in understanding the dynamics and chemical steps for any specific catalyzed reaction but are inadequate to permit prediction of the optimum catalyst system for the given reaction. A concerted collaborative effort to understand the selectiveness, surface chemistry, and surface kinetics for each of the most widely used catalysts is needed. A national service furnishing high quality isotope and other measurements important to catalyst research is needed.

The chemical compositions of the first few Ångstroms of catalytic surfaces can be very different from the bulk composition of the material below the surface. However this difference has been recognized comparatively recently so that much of the published material on previous studies of heterogeneous catalysis may have little or nothing to do with the reactions taking place on the surface.

Removal of heavy metals, which exist in all crude oils and coal, is desired to prolong the life of catalysts and boiler tubes. The U.S. Navy has converted its boilers to burning distillates partly to avoid this problem but, with the increasing shortage of distillates, many have to return to use of resids. Improved methods of heavy metal removal, which might involve new catalysts, could be of great military importance.

Desulfurization is developed only to some degree for sulfur atoms bound in petroleum and coal. Yet sulfur removal seems mandatory to prolong the life of turbine blades and boilers, and to conserve air quality. Removal of sulfur from coal and resid to an acceptably low concentration is a difficult problem that is yet to be solved.

Shale oil technology is in the pilot plant stage. In commercial production it appears that it will become economically competitive with crude at $7 to $8 per barrel. The future rewards to be had by improvement of the catalytic technology of its processing are similar to those to be had in processing of petroleum crude oils.

Fuel cell technology, aimed toward optimization of clean, quiet, portable sources of high power density is clearly of great military importance. To achieve more rapid progress, an expanded research effort is indicated to invent new and better catalysts appropriate to fuel cells.

1.6 ON THEORY

It was generally agreed by the Workshop that the theory of catalysis is largely incomplete. A few of the concepts that appear to have some validity are as follows:

1) Catalytic activity is more related to the electronic properties of surfaces and electrical fields in crystal pores than to the electronic properties of the bulk material.

2) Substances having unfilled, or partly filled, d bands and perhaps f bands, or energy closely equal to the top energy of locally available electrons, are likely to be catalytically active.

3) Catalysis seems to be a function of the closeness of match in molecular geometry and atomic distances of catalytically active surfaces to those of the reacting molecules.

4) Catalysts lower potential barriers; a catalyst which effects a small change in barrier height can produce a rate change of orders of magnitude.

5) Transport effects are understood theoretically and are frequently important.

These concepts are qualitative only; as yet nothing can be calculated with precision. One of the more promising approaches to theoretical understanding may appear to be incorporation of surface states in theories of catalysis.

1.7 PRODUCTION OF MORE RESEARCH SCIENTISTS

The number of scientists in the catalytic research in the U.S. is very small relative to, e.g., the numbers of chemists and engineers, and does not seem to be increasing rapidly. At least in part this is caused by the fact that the number of senior catalyst scientists in universities is small so that they can train only relatively few students. Some participants of the Workshop recommend establishment of a national catalyst institute with teaching capabilities and with part of its research task oriented toward DOD needs, and provision of fellowships for graduate training of catalyst scientists in the universities.

1.8 SHORTAGE OF JET FUEL

The use of jet fuel for peaking power by the electric utilities, both for nuclear and fossile fuel reactors, has more than doubled every two years since 1968, and by 1980 could require one million barrels per day, equal to about one-third to one-half of the total distillate production of U.S. refineries. The competition among the utilities, commercial air traffic, and the military, for jet fuel has come into head-on collision, which will put the DOD into the unpleasant and unpopular position of having to requisition jet fuel from civilian supplies in peacetime.

1.9 SHORTAGE OF NOBLE METAL CATALYSTS

Some very important commercial catalytic processes (such as reforming) depend on platinum or platinum combined with other metals. Because platinum is supplied mainly from South Africa and the USSR, the United States has no assured self-sufficiency in that metal. An advanced research effort to develop non-platinum catalysts is therefore of considerable importance.

1.10 IMPROVEMENT OF COMMUNICATIONS

Many attendees of the Workshop indicated their lack of knowledge of the catalytic requirements of the DOD. They expressed great interest in the onset of communications with the DOD initiated by the Workshop and their willingness to serve as advisors to the DOD on the challenge of insuring self-sufficiency of military energy needs through use of catalysis.

SECTION 2. RECOMMENDATIONS PREPARED BY WORKSHOP

The recommendations arrived at during the ARPA Workshop were collated and clarified directly after its termination by Professors Joe Hightower, W. Keith Hall, Michel Boudart, R. L. Burwell, Jr., and James T. Richardson.

There is room for improvement in almost all commercially important heterogeneous catalytic processes, and research in each should ultimately lead to enhanced activity, greater selectivity, longer life, and more efficient use of raw materials. While some improvements may be effected through more sophisticated engineering design, others can only be expected through development of a basic understanding of the individual steps in a catalytic sequence. The most productive approach to developing or improving catalysts involves simultaneous studies of specific processes and the fundamental aspects of catalysis. Since it is, of course, impossible for the DOD to become involved in all commercial processes, the panel of experts has divided the recommendations into three areas: those aimed at improving the fundamental understanding of catalysis, some specific processes that appear to have a direct bearing on the mission of the DOD, and the formation of a panel to search for new areas where applications of catalysis might have a positive influence on the DOD. These should not be considered as limiting but should serve only as examples of projects that merit DOD support.

2.1 RESEARCH TO EXTEND GENERAL UNDERSTANDING OF CATALYSTS

2.1.1 Surface Physics and Instrumental Techniques

The growing list of spectroscopic and diffraction techniques developed for the study of composition, structure, and electronic states of well-defined surfaces presents new challenges and promises in catalytic research.

In the past, adaptation of a new physical technique to the examination of catalytic materials has taken ten to fifteen years. This is far too long. Attempts to use a new technique directly, without proper adaptations, have frequently lead to early disenchantment. Perhaps this will be avoided by the support of co-operative efforts between chemical physicists and catalytic chemists. Finally, while methods of surface analysis well-suited to the examination of catalytic materials in vacuo are of great interest, priority should be given to those methods which permit the observation of catalytic surfaces at pressures and temperatures used in catalytic processes. The ultimate goal is the determination of composition, structure, and bonding of the surface intermediates propagating the catalytic sequence of elementary processes. Close collaboration between physicists, surface chemists, and materials scientists on the one hand and physical chemists and chemical engineers on the other hand is a necessary condition for swift and successful transfer as advocated here.

2.1.2 Kinetics, Mechanisms

One of the largest present weaknesses in the theory and practice of catalysis is the lack of knowledge concerning the elementary processes that occur inside the catalytic reactor. Such mechanistic knowledge is frequently essential for process control, trouble-shooting, improving catalysts, or discovering alternatives to existing catalytic routes. Regrettably, a knowledge of mechanisms cannot generally be derived from kinetic studies alone, that is, by studies investigating only how the reaction rate (or selectivity) changes with concentration of the reactants, temperature, and time reactants spend in the reactor. These must be supported (and sometimes guided) by much auxiliary data, including work with isotopically labeled tracers, model compounds, and sometimes studies of the chemisorption of various gases. In the latter connection, the use of some of these as selective poisons may result in improvement in selectivity, which is the key feature of practical catalysis. Knowledge of this kind is currently badly needed in the areas of coal gasification and hydrodesulfurization. A central feature of mechanism is a knowledge of the intermediates formed on the catalyst surface. Special techniques have been developed to examine these intermediates which play a key role in the reaction mechanism. A reasonably complete picture of the chemistry of the catalytic process results when such information about intermediates is combined with data from kinetic studies. Such multifaceted approaches should be encouraged.

2.1.3 Physical Properties, Transport Effects

Most catalysts are porous, spongelike solid materials. Their effectiveness frequently is limited not by their intrinsic catalytic activity but by the rate of entry and exit of reactants and products from the pores. When this is the case, physical properties of the solids have overriding effects on their performance as catalysts. Such factors as particle size, pore size and distribution, and thermal conductivity influence the transport properties of reactants that affect reaction rates, selectivities, kinetics, temperature dependencies, catalyst strengths, and poisoning susceptibilities. It is possible to modify these physical characteristics and thereby to synthesize materials with properties controlled in such a way as to maximize performance for the desired reactions. Detailed investigations of the relationship between physical properties and performance are necessary in order to optimize the system. It is recommended that in any system of catalytic interest, the role of physical properties be investigated in order to optimize its performance. This will necessarily involve synthesis of catalysts in which the parameters have been systematically varied for testing.

2.1.4 Activation, De-activation, Poisoning

In use, catalysts suffer decline in activity. Such loss in activity appears to result from the presence in the reactants of poisons that absorb permanently and prevent reaction at the active sites, from change in the area, in the structure of the surface or in the chemical identity of the bulk of the catalyst, and from deposition of by-products on the surface of the catalyst. Such factors substantially influence the efficiency of technical catalytic processes, and they are poorly understood in general. In particular, many catalysts consist of active ingredients such as Pt or Cr_2O_3 deposited on a porous, high area support like Al_2O_3 or SiO_2. The crystallites of Pt, for example, are initially very small (a few nanometers in diameter) with 50% or more of the atoms of Pt often being in the surface of the tiny Pt crystallites. With use, the Pt crystallites grow, the catalytic activity falls, and the selectivity may change. Furthermore, reactivation of a "poisoned" catalyst may result in further enlargement of the crystallites, thus leaving even a smaller fraction of the active atoms on the crystallite surface where they are useful.

Almost no understanding of just what happens during these processes exists, and it is important that additional work be done in this area which is a pervasive problem in heterogeneous catalysis. The other aspect of deactivation are apt to be specific to a particular catalyst and reaction. Work which is imaginative and likely to be of practical use in these other areas is worthy of support. For example, success of a process frequently depends on the ability to re-activate catalysts without causing them to sinter.

2.2 RESEARCH TO SUPPORT SPECIFIC APPLICATIONS OF CATALYSIS

1. Development of catalysts for the optimal conversion of non-petroleum feeds (coal, shale, tar sands, etc.) into usable hydrocarbon fuels.
2. Improve catalytic methods for hydrogen production, a fuel to be used in fuel cells for quiet power generation, for deep-sea recovery vessels, as a heat source to drive turbines, and to produce liquid fuels from coal and shale oil.
3. Develop improved catalysts and an understanding of their function for hydrogenation, methanation, and Fischer-Tropsch synthesis of fuels.

4. Study non-noble metal catalysts for inexpensive, reliable fuel cells that operate on fuels other than hydrogen and oxygen, and with an aim to achieve U.S. independence of foreign supplies of platinum.
5. Investigate the mechanism of catalytic removal of sulfur, oxygen, and nitrogen from fuels.
6. Explore the novel catalytic requirements that would be involved in building small, mobile, shipboard, refineries, to produce hydrocarbon fuels on nuclear powered ships, from coal and oil.
7. Explore the interfacial and catalytic factors involved in decomposition of solid phase propellants and explosives.
8. Investigate any possible catalytic effects involved in the abalation of heat shield materials from missiles or re-entry vehicles.

2.3 COMMISSION PANEL TO INVESTIGATE DOD's NEEDS FOR CATALYSIS

In general, the panel found it difficult to make specific recommendations that would be unique to the DOD's needs. This was largely due to uncertainties on the part of the members as to exactly what the needs are. Most of the areas discussed (e.g., fuels, chemicals, pollution control, etc.) are common both to DOD and civilian uses, and considerable research has already been expended in these areas by the civilian sector. It is therefore recommended that a somewhat smaller panel (perhaps ten people) be commissioned to visit various DOD centers and itemize areas where research in catalysis might be expected to have a unique and positive effect on the DOD's mission, and on DOD self-sufficiency for its energy needs.

Pentagon Is Expected To Seek More Fuel Oil For Second Quarter

By a WALL STREET JOURNAL Staff Reporter

WASHINGTON—Defense Secretary James Schlesinger indicated that the Pentagon probably will request more fuel oil for the second quarter of 1974 than it did this quarter.

However, Mr. Schlesinger didn't say how big an increase the Defense Department might seek for military operations. He testified before a House Armed Services subcommittee studying military fuel needs during the energy crisis.

The Pentagon requested and received an allocation of 637,000 barrels daily for operations this quarter, up 2% from the previous quarter. It also has pending a request for an additional 100,000 barrels daily to rebuild depleted war reserves of fuel oil. The Pentagon's requests go to the Federal Energy Office, with President Nixon authorized to make the final decision.

Mr. Schlesinger said there has been "some degradation" in combat readiness because of training cutbacks ordered to save fuel, but he stressed that the situation isn't alarming. In reply to questions, Mr. Schlesinger also conceded that the Pentagon might, at some point, consider building a government refinery to make petroleum products from crude in the Naval petroleum reserve in northern Alaska. Though he expressed little enthusiasm for such a project, he said the new defense budget will request $17 million for oil exploration on government land in Alaska.