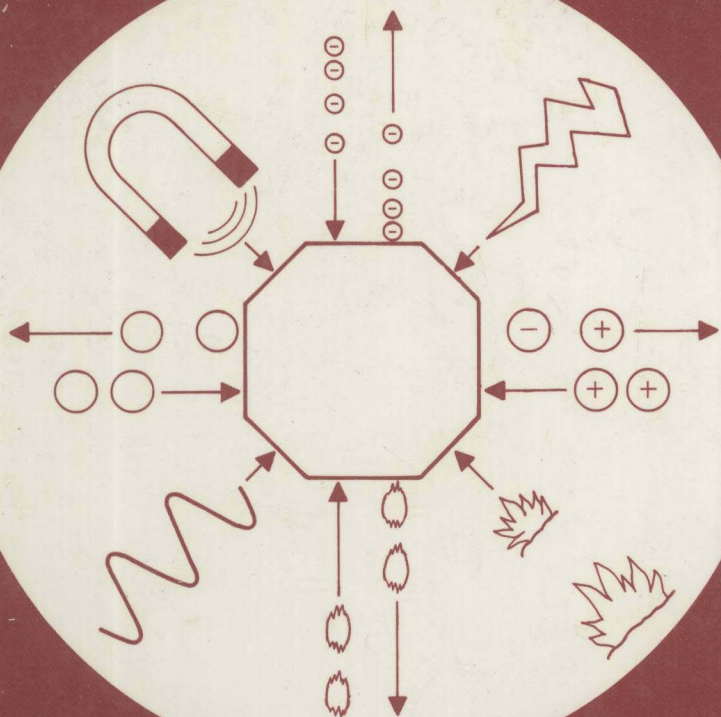


studies in surface science and catalysis



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FUTURE OPPORTUNITIES IN CATALYTIC AND SEPARATION TECHNOLOGY

M. Misono, Y. Moro-oka and S. Kimura
(editors)

Studies in Surface Science and Catalysis

Advisory Editors: B. Delmon and J.T. Yates

Vol. 54

FUTURE OPPORTUNITIES IN CATALYTIC AND SEPARATION TECHNOLOGY

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ELSEVIER

Amsterdam — Oxford — New York — Tokyo 1990

ELSEVIER SCIENCE PUBLISHERS B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
655, Avenue of the Americas
New York, NY 10010, U.S.A.

ISBN 0-444-88592-7

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Printed in The Netherlands

PREFACE

The production of useful materials and the removal of polluting substances are fundamental to chemical technology, and in this respect catalytic and separation processes play essential roles. In order to cope with increasing societal demands, such as finding solutions for the shortage of natural resources and global environmental pollution, rapid and significant progress in the technology is required.

This book is due to the success of the seminar on Selective Reactions and Separation, held at Oiso, Japan, February 1-5, 1988. The seminar was organised by ASPRONC (The Association for the Progress of New Chemistry) as the fourth in the series of seminars on Frontier Technology. ASPRONC was inaugurated in 1986 and its membership is comprised of major companies in the chemical industry and various sectors interested in chemistry. The present editors together with Professor Tamaru served as coordinators of the seminar. The aim of this seminar was to explore the frontiers of catalytic and separation technology and to discuss the requirements for its future development.

The interesting lectures and active discussions stimulated us to prepare this book. Each lecturer was invited to write a chapter based on his lecture. We note with pleasure that the contents of the lectures have been significantly revised and expanded. We also added two chapters which were thought to be appropriate. We would like to express our sincere thanks to all of the authors. We are also indebted to Dr. J. F. Roth and Professor B. Delmon, who kindly assisted in the realization of this book. Further, we are grateful to ASPRONC for their permission to publish this book based on the above seminar.

It is our hope that this book will have a positive contribution to make in the future development of chemical technology.

Makoto Misono
Yoshihiko Moro-oka
Shoji Kimura

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Chapter I

PRESENT AND FUTURE OF CATALYTIC AND SEPARATION TECHNOLOGY

Chapter I.1

FUTURE OPPORTUNITIES IN INDUSTRIAL CATALYSIS*

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In the past few decades many new industrial chemical processes of major commercial importance have been developed and in most cases novel catalytic technology has formed the foundation of the process innovation. However, in the past two years we have seen increasing evidence of a disparity in the United States between the industrial and academic perspectives on the future importance of catalysis. In June 1986, Chemical Week published a very extensive report on the current state of catalysis in which it was pointed out that industrial research in catalysis in the United States was being dismantled, phased down and dramatically curtailed. In contrast to this there is the widely-known and widely-heralded Pimentel report, published at the end of 1985 under the sponsorship of the National Research Council and providing a forward-looking vision of future opportunities in chemistry. In this report catalysis is identified as one of the key intellectual frontiers in chemistry and is recommended as one of the top five areas for priority funding. Thus we have a very wide discrepancy between the analysis and conclusions of the Pimentel report and the perspectives and actions of the United States chemical industry.

It is valuable as we begin to address the question of future opportunities to bring into focus the size and importance of existing catalytic technology. The total worldwide annual market for catalysts for petroleum, petrochemical, and chemical applications was estimated at \$2.2 billion in a study conducted some years ago by Chemical Hitech of Switzerland. The average value of catalysts as a percentage of the product produced therefrom is conservatively estimated as 0.2%. From these two numbers, one concludes that the worldwide value of products made via catalytic technology is in excess of one trillion dollars per year. Clearly catalysis is a technology of major financial importance. There is every reason to expect that the societal needs that are served by the molecules and materials currently made via catalytic technology will continue. These needs

* Adapted from Catalysis 1987, Studies in Surface Science and Catalysis, Vol. 38, pp. 925-934, 1988, Elsevier Science Publishers B.V., Amsterdam.

will be served either by the existing materials or replacement materials made, in either case, most likely by catalytic technology. What then is the situation? The abandonment of industrial catalysis research could be rationalized by assuming that the current slate of products of catalysis is of large volume but low growth and apparent technology maturity. It could be argued that new advances are unlikely that would justify the costs and risks of replacing current technology. However, some do not believe that this is the case but rather that there will be many new opportunities for catalysis. Even in the case of existing large volume commodity chemicals, there will be some significant opportunities, but they will not arise from incremental improvements but rather from major changes. Advances consisting of discontinuities will be required, and the creation of these discontinuities will involve a much higher level of creativity and technical challenge.

In trying to address a specific need or opportunity for radically new catalytic chemistry how does one proceed? There are a couple of myths around. One of these is that it is now possible to scientifically design new catalysts as a result of the information and insights being provided by advanced instrumental techniques in surface science or in computer science. This is simply not true. These surface and computer science techniques have very much increased our ability to characterize catalytic materials or processes, but we are still far away from being able to a priori design a catalyst, that is, prescribe its chemical composition in order to catalyze a reaction in some significantly new way. The most progress that is apparent in a priori design is in the field of homogeneous catalysis, and that is the area that will most likely make the greatest further progress, at least in the near term.

One can consider future opportunities in catalysis in terms of what new industrial developments might occur in the future. These new developments will be the result of either being able to do something new not now practiced commercially or of being able to significantly improve an existing process. Stated another way, we can try to identify some of the unsolved problems or limitations of current industrial catalysis and, in a few cases, to suggest directionally what new approaches might be worth considering.

The three key elements of any catalytic process are the raw materials or feedstock, the catalyst and the products. The catalyst itself can be viewed as providing a challenging materials problem. The functional property we are interested in for a catalyst is its ability to control or orchestrate, if you please, the interaction of feedstock molecules in such a way as to produce favorable reaction rates and selectivities at attractive economics. In attempting to think about future developments in chemical catalysis, one

convenient approach is to consider the basic elements and to project possible emerging developments that could be stimulated or driven by them.

Let us first consider the area of feedstocks.

Methane has always been an attractive, low cost feedstock in those areas of the world where it is abundant and accessible. It is used to produce methanol, ammonia, hydrogen and synthesis gas. One of the major unsolved challenges for catalysis would certainly be a catalyst that promotes the one step direct oxidation of methane to methanol. If such a catalyst were developed, it could have far-reaching implications. It might lead to the production of synthesis gas via methanol dissociation rather than the reverse process which we practice today, namely, the formation of methanol from synthesis gas in a thermodynamically limited low conversion process which employs a large amount of recycle. The synthesis gas in turn is made via endothermic steam reforming of methane. Other uses can be seen for methanol produced via direct methane oxidation and synthesis gas derived from same. This synthesis gas could be shifted in the usual way to produce hydrogen.

Recently we have seen some new results in the literature that signal both increased activity and progress in selective methane oxidation. While they are a long way from practicality, they do represent significant progress over previous results. We should take heart in the knowledge that there are enzymes which oxidize methane to methanol with very high selectivity. Personally, I believe that when practical systems are developed for the oxidation of methane to methanol, they will employ organometallic complexes at relatively mild conditions rather than metal oxides at high temperature. Recently we are also seeing new research results in which the products of direct methane oxidation are not methanol but higher hydrocarbons such as ethane and ethylene. These results also are somewhat removed from current practicality, but they may be harbingers of important future developments.

Methanol itself is an attractive feedstock, even when produced by existing technology from synthesis gas. One particularly valuable new use for methanol would be its oxidative coupling to ethylene glycol, if it could be achieved in high selectivity. Perhaps leads to such a coupling reaction may emanate from the exploratory research now underway on direct alkane activation or from the increasing number of laboratories throughout the world taking a new look at hydrocarbon oxidation catalysis.

Certainly one of the major advances in catalysis of the past decade has been the discovery by Mobil of the ZSM-5 and related zeolites and their applications to such reactions as methanol conversion to gasoline or to ethylene. At the present time, and for the foreseeable future, these technologies do not appear to be competitive in most parts of the world with existing technology based on current hydrocarbon feedstocks. If, however,

vast new sources of methane were discovered with an accompanying large reduction in methane price [and there are a few prophets who see this coming] and if this was coupled with the development of new low cost technology for direct oxidation of methane to methanol, the situation might change in a dramatic and revolutionary way. In this scenario, of course, the dominant fossil fuel feedstock for methanol is methane and not coal as the alternate to crude oil. Also, of course, the production of gasoline from methanol which is now practiced commercially in New Zealand could become generally competitive.

Normal butane is a feedstock that is both abundant and low in relative cost as a source of carbon for producing organic molecules. Recently this low cost, combined with new catalytic technology, has led to normal butane replacing benzene as the feedstock of choice for oxidation to produce maleic anhydride. While butane is clearly emerging as the preferred feedstock, it is interesting to note that the present best catalysts available for butane oxidation function at high temperatures and only afford about a 50% molar selectivity. This obviously leaves considerable opportunity for improvement. Besides its existing uses, maleic anhydride itself is a potential feedstock for a number of reduction products such as γ -butyrolactone, tetrahydrofuran and 1,4 butanediol. 1,4 butanediol is now a large volume intermediate for the engineering thermoplastic PBT and for other specialty polymers. The traditional route to 1,4 butanediol has been via Reppe chemistry from acetylene and formaldehyde. Recently several companies have announced their intention to pursue maleic anhydride reduction to produce 1,4 butanediol. Lower cost maleic anhydride would decidedly solidify its attractiveness as the feedstock for making these C_4 oxygenates, and improved butane oxidation catalysis should provide the key to such lower cost. Monsanto and Dupont have just formed a partnership to develop a higher selectivity moving bed butane oxidation process.

Finally the feedstock we have been hearing so much about since the oil embargo of 1973 is synthesis gas-carbon monoxide plus hydrogen. This is the feedstock that is potentially derivable from coal. While at first there was almost a stampede to learn how to make anything and everything from synthesis gas, there later emerged some rationalization in terms of economics. It is now rather widely recognized and agreed upon that for the foreseeable future the only organic molecules that can be made from synthesis gas at competitive economics are small molecules with a relatively high oxygen to carbon ratio. In general it appears to be uneconomical to synthesize a methylene group from synthesis gas. In essence it's an inefficient and costly process because it involves taking a hydrogen-rich molecule like methane, converting it into a

hydrogen-deficient molecule, namely carbon monoxide, then reducing it back to a hydrogen-rich moiety such as a methylene group. With the economic facts of life in hand, there are very few new syntheses based on syn gas that offer much potential. For almost a decade it appeared as though one major driving force in industrial catalytic research was the effort to make chemicals and fuels from synthesis gas. The disappearance of that thrust left a vacuum.

Let us now move away from feedstocks and look at the catalyst per se as a driving force for the emergence of new catalytic technologies.

There are three types of catalysts that appear to have very high potential for major impact in new catalytic technology of the future, namely, homogeneous catalysts, molecular sieves and membrane reactor catalysts.

In recent years, however, it has become clear that many of the so-called "homogeneous catalysts" can, in fact, be prepared and used in a variety of solid state forms that have basic catalyst properties -- activity and selectivity -- almost identical to their soluble liquid phase counterparts. What we have called homogeneous catalysts for so many years should, in fact, be called "metal complex catalysts." Our second group of major-impact catalysts, molecular sieves, are best exemplified by zeolites which are crystalline alumino-silicate compositions which have very small well-defined pores and cage structures. In recent years there have emerged newer types of molecular sieves such as the ALPOs and SAPOs developed by Union Carbide and also a variety of pillared compositions. Important catalytic applications for these newer types of molecular sieves are now beginning to surface. The next catalyst type on the list, the membrane reactor catalyst, has not yet received much attention. It consists of compositions that have both membrane and catalyst components.

Homogeneous catalysis has long been heralded as an approach that can provide us with some of the exquisite features of enzymes -- high activity at mild conditions and high selectivity. These features were certainly fully realized in the Monsanto acetic acid process and contributed to the exceptionally low unit capital costs of that process. But looking broadly at chemical process technology, has homogeneous catalysis really fulfilled its promises? Has it really come of age? There is some indication that it has and that perhaps the best is yet to come.

Several years ago, my former colleague, Dr. Denis Forster, conducted a review of major new chemical processes that had been commercialized in the 1970's. It was found that in the manufacture of the top 50 large volume organic chemicals, 17 new processes had emerged in the 1970's and that 11 of these involve a homogeneous catalyst as a key element characterizing the new technology.

TABLE 1. Process innovation in the 70's*

<u>Product</u>	<u>Key Process Change</u>
Higher olefins	2 homogeneous + 1 heterogeneous
Butanol	Homogeneous
Plasticizer alcohols(2)	2 homogeneous
Adiponitrile	Homogeneous
Hexamethylene diamine	Heterogeneous
Propylene oxide	Homogeneous
N-propyl alcohol	Homogeneous
Vinyl acetate	Heterogeneous
Isocyanates	Homogeneous
Acrylic acid	Heterogeneous catalyst
Acetic acid	Homogeneous
Maleic anhydride	Heterogeneous
Styrene(3)	Homogeneous (Monsanto)
	Homogeneous (Halcon)
	Heterogeneous (Mobil)
Ethylene glycol	Homogeneous

* Survey by D. Forster

Clearly homogeneous catalysis has been an approach that led to a significant number of new process innovations prior to 1980. Since 1980 the chemical industry has not seen the introduction of many major new catalytic processes of any kind -- homogeneous or heterogeneous.

Although they have not been commercialized, several noteworthy new homogeneous catalysts have been discovered. Anionic ruthenium hydrides, new compositions of matter, have been found by Pez and co-workers that reduce nitriles to amines with very high selectivity to primary amines. Also, this type of catalyst provides the first example of homogeneous catalysis applied to the selective hydrogenolysis of saturated esters to alcohols. This homogeneous reaction proceeds at reaction conditions milder than those required by the conventional heterogeneous catalysts such as the copper chromites. Industrially aliphatic amines such as C_2 and C_3 amines are made by the reaction of the corresponding alcohol and ammonia. Since the alcohols are usually made from the olefin of the same carbon number, it would be desirable to avoid the alcohol and synthesize the amine by a direct interaction of the olefin and ammonia. Just such a reaction by homogeneous catalysis has also been reported by Pez and co-workers for the first time. Soluble inorganic amides promote the direct amination of ethylene or propylene by ammonia to give the corresponding primary amine in high conversion and high selectivity. The ammonia addition in the case of propylene occurs in a Markovnikov manner so that the product is isopropyl amine. It would be potentially useful to have a catalyst that would promote ammonia addition to olefins in an anti-Markovnikov manner. Such a possibility seems to lend itself particularly to homogeneous catalysis where it is possible to achieve

unusual selectivity control via the choice of ligands. Witness, for example, the extraordinary degree of optical stereospecificity that has been achieved in asymmetric hydrogenation catalysis by choice of ligands. The DuPont company discovered and developed some time ago, and has been practicing commercially on a very large scale via homogeneous catalysis, the anti-Markovnikov addition of HCN to butadiene to produce adiponitrile. One can visualize other olefin addition reactions that might be controlled to give preferentially anti-Markovnikov addition in situations where such control has not been achieved previously. Recently Trogler has reported anti-Markovnikov olefin hydration using soluble platinum complexes. The conversion of synthesis gas to methanol via homogeneous catalysis was reported for the first time a few years ago. Although the selectivity so far achieved is relatively modest, this is a worthy target for novel catalysis. The present commercial process for methanol is a low conversion one, limited by thermodynamics. A catalyst more active at lower temperature could provide significant advantages.

The general area of selective oxidation of hydrocarbons is one that also seems destined to find its breakthroughs via homogeneous catalysis. Dr. James Lyons of Suntech has reported achieving via homogeneous catalysis a one step oxidation of propylene to acrylic acid in very high selectivity. This reaction is also applicable to the one step oxidation of isobutylene to methacrylic acid. These one step oxidations contrast with the two step high temperature oxidations that are currently practiced commercially using metal oxide catalysts.

Zeolites made their first big splash in catalysis as cracking catalysts for petroleum refining. In the past decade Mobil has developed varieties of ZSM-5, a synthetic zeolite catalyst that not only converts methanol to high grade gasoline but also is being applied commercially for the isomerization of xylenes to p-xylene, the production of ethylbenzene from benzene and ethylene and the dewaxing of petroleum distillates. Rarely has any single new catalyst or catalyst type had such a breadth of industrial applicability. Furthermore, it has been reported that a modification of ZSM-5 can also selectively alkylate toluene with ethylene to produce para-ethyl-toluene. This, in turn, can be dehydrogenated to p-methyl styrene -- a monomer that should be capable of being produced in large volume at economics comparable to that of styrene. Polymer made from p-methyl styrene is reported to have distinct property advantages over polystyrene. Thus a new development in zeolite catalysis may pave the way to the development of a new large volume monomer and polymer. A world scale styrene plant today is of the order of one billion pounds per year. Unfortunately, this alone provides a major hurdle for any new competitive product to overcome since scale alone provides a major benefit in economics of manufacture.

Many other new zeolite or non-zeolitic molecular sieve compositions are possible as well as new catalytic applications for such materials. For example, during the past few years Union Carbide has reported the synthesis of several families of new crystalline sieves such as the ALPOs which are aluminophosphates and the SAPOs which are silica aluminophosphates. The latter are ion exchangeable. These new sieves are already yielding new catalytic results. A small pore aluminophosphate catalyst converts methanol to light olefins in high conversion and selectivity. Selectivity of more than 90% to C_2-C_4 olefins has been reported. Catalysts made from medium and large pore silicoaluminophosphates have given octane improvement in petroleum refining.

Most of the applications of zeolites to date have been in hydrocarbon conversion reactions, particularly as applied to petroleum refining. Zeolites should also have utility in the synthesis of chemicals wherever sites of strong acidity or size selectivity control are desired. To illustrate, Air Products has received a patent teaching the use of zeolites as catalysts for the selective amination of olefins such as ethylene or propylene. It may be possible to achieve the control of aromatic substitution reactions through the use of molecular sieve-based catalysts.

The other area of promise cited before was that of membrane reactor catalysis. During the past several decades most chemical process innovations have been in the reactor section of the process, as expressed for example via new catalytic synthesis technology, while in the separation section distillation has served as the common workhorse technique. However, it appears that we are at the threshold of some major changes in separation technology, that these changes will have substantial impact broadly on chemical process technology, and that the changes will include significant shifts from separation by distillation to separation by synthetic membranes and molecular complexes. Although synthetic polymeric membranes have been around for several decades, their main industrial applications had been in liquid phase separations such as water desalination. Then in 1979 Monsanto successfully introduced commercially gas separation membranes for the recovery of hydrogen. Since then Monsanto and several other companies have introduced membrane technology for the production or separation of several other gases including nitrogen, carbon dioxide and oxygen. There has been a literal explosion of activity in membrane research throughout the world, some of which is aimed strongly at gas separation opportunities.

Besides their obvious impact in the separation area, it appears that membranes will also be of importance in a new barely emerging area that can be described as membrane reactor catalysis. The basic premise is that of combining or integrating membrane separations with catalysis. Membranes are

capable of achieving separations of incredible subtlety based in some cases on very small differences in molecular sizes or in others based on marked differences in physical or chemical reactivity. Just as zeolites permit one to combine shape selectivity with catalysis, membranes should allow us to combine any of several separation pathways with catalysis to achieve new control of reaction selectivity.

Based on public disclosures, the most active center of membrane catalysis research has been the Soviet Union. A recent 1986 paper published by Gryaznov reported on the extensive activities that have been underway at many institutions in the Soviet Union both at the research pilot plant and commercial scale. One of the most heavily targeted areas is that of selective hydrogenation as applied to the hydrogenation of acetylenic molecules and dienes, the production of vitamin K₄, the synthesis of the fragrance linalool. It has also been applied to the dehydrogenation of cyclohexane diol to pyrocatechol.

Let me quote some euphoric statements from the end of Gryaznov's paper. "Thus, membrane catalysts that are permeable only to hydrogen are extremely promising and are unprecedented in actual practice throughout the world. What is fundamentally new here is that they are completed design elements of a commercial reactor. Priority in our country should be given to the use of membrane catalysts in all plants that utilize the selective hydrogenation of acetylenic alcohols to ethylenic alcohols, nitro compounds to amines, and to the hydrogenation of cyclopentadiene to monomer for synthetic rubber." Russian inventors have to date received 58 Soviet invention certificates and 86 patents issued in several western countries including the U.S. In short it appears that the Russians are at the early commercialization stage in membrane catalysis whereas in the U.S. we are barely at the exploratory research stage.

One can point out a couple of possible opportunities for membrane catalysis that were not mentioned in the Russian review paper. These are in the general area of equilibrium-limited reactions where equilibrium is so unfavorable under ordinary conditions that catalysis is not feasible at reasonable conversion levels. One example is the production of ethylene, the largest volume organic chemical produced in the world. One common method of producing ethylene is via the thermal pyrolysis of ethane at very high temperature of 700°C or higher. This is a rather brutal process that proceeds in a hot tube and gives rise to a number of undesirable by-products. The capital intensity of this process is very high and equals or exceeds 50¢ per annual pound of product. In principle it should be possible to catalytically dehydrogenate ethane at much lower temperatures if the equilibrium constraint could be removed. Can it be developed to give such important products of dehydrogenation as ethylene, butadiene or styrene? There are other