

APPLIED INDUSTRIAL CATALYSIS

VOLUME 1

Edited by
Bruce E. Leach

Applied Industrial Catalysis

Volume 1

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BRUCE E. LEACH

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Preface

Industrial catalysis contributes significantly to our modern economy and life-style. The objective of these volumes is a practical description of catalysis by industrial scientists. Excellent reference works on catalyst theory, kinetics, and reaction mechanisms already exist, but reviews of practical operation of commercial units are rarely published by industrial scientists.

Industrial catalysis is influenced not only by science but also by business, economics, markets, and politics. These factors are discussed in various chapters. The reader should recognize that in most cases competitive technology exists for the synthesis of chemical intermediates. The examples given represent current industrial practice but obviously do not disclose proprietary information.

This first of three volumes begins with a review of the importance of industrial catalysis and its effect on our life-style and environment (Chapter 1, by B. E. Leach). In Chapter 2, E. F. Sanders and E. J. Schlossmacher describe how to take a laboratory catalyst to successful commercialization with a minimum of problems. In Chapter 3, J. M. Berty presents techniques for evaluating a catalyst in laboratory reactors. In Chapters 4 and 5, D. C. McCulloch and M. D. Edgar, respectively, describe in detail two major refinery processes—hydrotreating and reforming. In Chapters 6 and 7, specific processes for polyethylene (J. P. Hogan) and polypropylene (K. B. Triplett) manufacture are reviewed. Ethylene oxide synthesis is described in Chapter 8 by J. M. Berty. Oxychlorination of ethylene to ethylene dichloride is the subject of Chapter 9 by J. S. Naworski and E. S. Velez. Methanol carbonylation to acetic acid is reviewed by R. T. Eby and T. C. Singleton in Chapter 10. Additional general catalysis and specific processes will be presented in chapters to be published in subsequent volumes.

The editor acknowledges Drs. D. P. Higley, R. J. Convers, and M. L. Shannon, who assisted in reviewing chapters. Their critical comments and helpful suggestions are appreciated. Dr. C. M. Starks, who encouraged me to edit this work, and Sherry Martin, who assisted with communications with the authors, deserve special recognition. I also wish to thank my wife, Sharon, who supported me in the many extra hours of work necessary for this project.

It is the editor's hope that this book will be of value to all those active in catalysis and also that it will promote an understanding of industrial catalyst research and processes that could be valuable to seniors and graduate students preparing for industrial careers.

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CHAPTER 1

Industrial Catalysis: Chemistry Applied to Your Life-Style and Environment

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I. Industrial Catalysis: Definition, Scope, and Importance

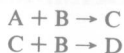
Catalysis is a major factor in industrial research, process selection, plant design, and plant operation. The success of the chemical industry is based largely on catalyst technology. The discovery of new catalysts and their application have historically led to major innovations in chemical processing. Market, business, and political factors combine to encourage or require further improvements in catalyst technology with time.

It is the interaction of business, markets, economics, and politics with chemistry that distinguishes industry from academia. Chemical principles and the laws of thermodynamics still apply. The definition of a catalyst is the same—a material that changes the rate of a reaction without itself being consumed. Catalysts have no effect on the position of equilibrium, and one cannot make a reaction proceed that is forbidden by the laws of thermodynamics. A catalyst acts to lower the activation energy barrier for reactions that have a net decrease in free energy. The alternate reaction paths provided by catalysts within the laws of thermodynamics and chemistry add value to feedstock materials in the refining and chemical processing industry.

The fundamental aspects of adsorption on active sites are adequately covered in most catalysis reference works. The catalysis scientist should be knowledgeable about adsorption and kinetic experiments and their results. For example, in the reaction $A \rightarrow B$ (Fig. 1), a series of steps in the catalytic reaction can be considered: (1) external diffusion, $k_{\text{ext. diff.}} = k_g S_{\text{ext}}$; (2) internal diffusion, $k_{\text{int. diff.}} = k_g S_{\text{int}} \eta$; (3) adsorption, k_{ads} ; (4) surface reaction, k_s ; (5) desorption of B; (6) internal diffusion of B; and (7) external diffusion of B.

In external diffusion the size and shape of the catalyst particle, the volume/diameter ratio of the reactor, and the space velocity are factors that influence the amount of channeling, the type of flow, the extent of back-mixing, and the residence time. Guidelines for catalyst evaluations in laboratory reactors are given in Chapter 3.

Internal diffusion is dependent on the pore structure of the catalyst. Pores are arbitrarily placed in three size categories according to pore diameter: micropores, $<15 \text{ \AA}$; mesopores, $15-150 \text{ \AA}$; macropores, $>150 \text{ \AA}$. The pore diameter affects internal diffusion. The surface area of many catalysts is primarily internal surface, so most interactions and collisions occur with the internal surface. Pores have a variety of structures, and there is an effectiveness factor in the equation expressing internal diffusion rates that depends on how difficult it is for reactants to diffuse in or out. Often it is not so critical to know the value of k for internal diffusion as to know whether the reaction occurs primarily on the external surface or within the pores of the catalyst and to recognize the consequences. For example, in a consecutive reaction



where C is the desired product and D is to be minimized, there are two recognized methods for achieving the desired result. The pore size can be kept small enough so that the reaction occurs primarily on the surface of the catalyst particles. Examples include most hydrocarbon oxidation catalysts where a decreased rate of reaction due to reduced surface area (internal) is

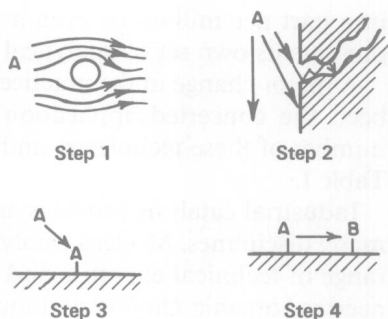


Fig. 1. Steps in the catalytic reaction.

acceptable to gain selectivity of product. Specific examples are given in Chapter 8.

Alternatively, a large pore size can be selected so that there is facile diffusion out of the pore system before C can react further with B. This approach reduces the internal surface area, whereas in the case of very small pores the internal surface is inaccessible.

Another example of pore size importance is found in the hydrodesulfurization of heavy crude oils. Rapid catalyst deactivation is associated with particular pore sizes, and approaches based on supports of either small [1] or large [2] pore diameter have been developed.

Theory has often come after discovery. Ideally, the objective is to design a catalyst based on first principles. This objective is not yet within the capability of catalysis science. In addition, the complicating factor of economics must be addressed in the industrial setting.

Optimization of the added value to feedstocks requires a knowledge and interaction of chemistry and economics. This is a special challenge to the scientist or engineer in industrial catalysis. Both catalytic science and economics change with time. This ensures that new and improved catalysts will continue to be developed. These catalysts will be used to process historic and new feedstocks. The variables encompassed by new catalysts, new and modified processes, and the changing economics of alternate feedstocks taken together with political and environmental restraints make for many exciting and challenging technical endeavors within the industry.

The scope of catalysis in industry ranges from theoretical predictions of catalytic activity to the art of catalyst forming. It includes both work on the frontiers of catalysis science and the careful recommendation of a particular commercial catalyst that meets a specific customer's feedstock and reactor design criteria. It includes catalyst regeneration, testing, and quality control, as well as catalyst selection. Finding and removing a catalyst poison present

in a part per million or even a part per billion quantity in the feedstock presents its own set of analytical and chemical challenges.

A major change in the practice of catalysis in the past several decades has been the concerted application of analytical techniques to catalysts. A number of these techniques and their application in catalysis are given in Table I.

Industrial catalysis provides an opportunity for technical exchange with many disciplines. Modern catalysts must rely on the integration of a broad range of technical expertise and experimental capabilities. Chemical engineering, organic chemistry, inorganic chemistry, coordination chemistry, analytical chemistry, and surface science are all essential in understanding and developing catalysts (Fig. 2).

At a time at which the conversion to SI units is in progress and with older

TABLE I
Analytical Techniques Frequently Used in Catalysis

Characterization	Technique
Bulk	Surface area analysis
	Pore volume analysis
	X rays
	Scanning electron microscope
	Electron microprobe
	Infrared spectroscopy
	Elemental analysis
	Surface acidity
	Loss on ignition
	Thermal gravimetric analysis
	Density
	Bulk crushing strength
	Particle size analysis
	NMR
	ESR
Surface	X-ray scattering
	Laser Raman spectroscopy
	Extended x-ray adsorption fine-structure microscopy (EXAFS)
	X-ray photoelectron spectroscopy (ESCA)
	Scanning electron microscope (SEM)
	Auger electron spectroscopy (AES)
	Ion-scattering spectroscopy (ISS)
	Secondary ion mass spectroscopy (SIMS)
	Magnetic susceptibility
	Selective surface area
	Selective adsorption
	Programmed temperature desorption

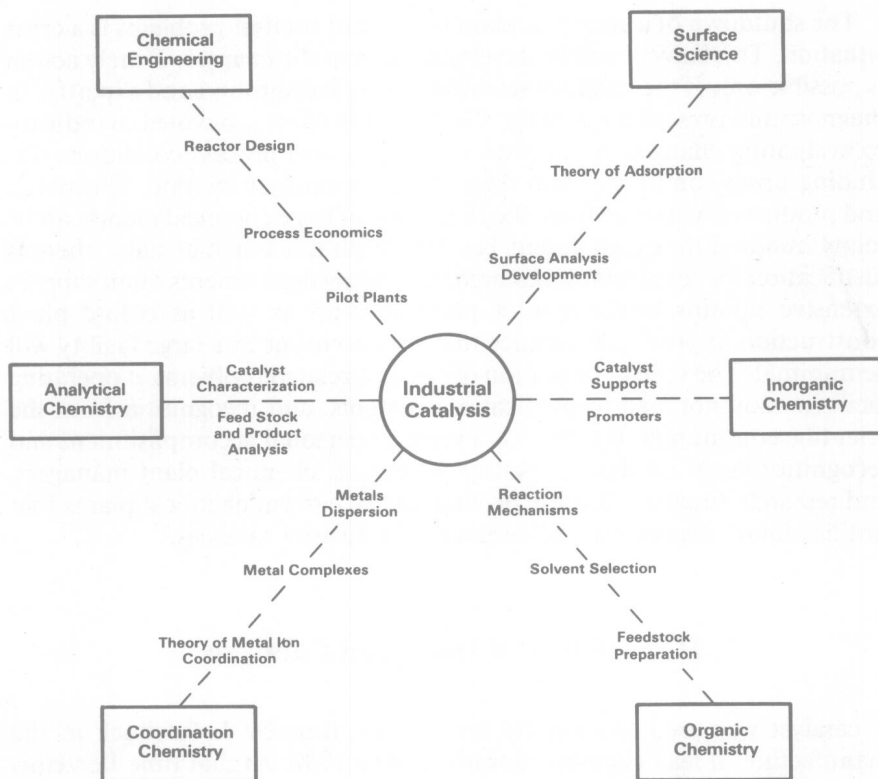


Fig. 2. Technical dependence of industrial catalysis.

units still widely used, there is a communication problem. This book reflects problems that will continue for many years. For this reason a common nomenclature and units table is provided in the Appendix to this volume. Although the reader may find it confusing to see temperature in degrees centigrade, degrees Fahrenheit, and kelvins all in the same chapter, this is the reality of the situation one is faced with in industry.

The scope of catalysts in the chemicals industry is so extensive that it is rare to find a research problem that cannot be redefined in terms of catalysis. Thus although the research problem title and the objective may be stated in business and economic language, the scientific methodology required for achieving the project goals often involves the practice of catalytic science. The major innovations in the petrochemical industry in the past 25 yr have involved breakthroughs in catalyst research. In most industrial research problems, catalyst selection or improvement is the key to the success of the project. This heavy dependence on catalysis can be seen in both exploratory and applied research.

The shutdown of a chemical plant because of catalyst problems is a crisis situation. This subject will be developed later in the chapter. Timely action is possible only if the catalysis scientist has the background and expertise to diagnose and prescribe a remedy. Considerable effort is devoted in industry to evaluating changes in catalysts, feedstocks, and process conditions (including upset conditions) and their effect on catalyst lifetime, selectivity, and productivity. Losses from the shutdown of large chemical plants can be many hundred thousand dollars per day. With this much at stake, there is justification for considerable research. Operating departments often support extensive piloting facilities after plant start-up as well as before plant construction to provide insurance that the downtime at a large facility will be minimal. The speedy resolution of catalyst-related problems at operating facilities may not lead to publications, patents, and recognition from the scientific community, but there is a sense of personal accomplishment and recognition from catalyst marketing managers, chemical plant managers, and research directors. It is the profitability of current chemical plants that justifies future expansion and research in industrial catalysis.

II. History of Industrial Catalysis

A catalyst was used industrially for the first time by J. Roebuck in the manufacture of lead chamber sulfuric acid in 1746. At that time Berzelius had not yet used the word "catalysis"—that came in 1836. Early development occurred in inorganic industrial chemistry with processes for carbon dioxide, sulfur trioxide, and chlorine production in the 1800s. P. Sabatier and R. Senderen in 1897 found that nickel was a good hydrogenation catalyst. P. Sabatier [3], in his book *Catalysis in Organic Chemistry*, gives an excellent perspective of catalysis in the early 1900s. It was a time when answers to questions about transition states, adsorption, and mechanisms were difficult to obtain, and yet Sabatier was asking the right questions. His idea of temporary unstable intermediate compounds being formed in catalysis was correct. He lamented the unsatisfactory state of knowledge, yet the period 1900–1920 saw advances in many areas. It was the time of Ostwald, Gibbs, Bosch, Ipatief, Einstein, Planck, Bohr, and Rutherford, among others. Scientists such as E. Fischer, Kekulé, Claisen, Fittig, Sandmeyer, Faworsky, Deacon, Dewar, Friedel, and Crafts had made their contributions to organic chemistry just prior to 1900.

Initially most catalysts were relatively pure compounds. Multicomponent catalysts were studied after 1900 at Badische Anilin- & Soda-Fabrik (BASF). Haber discovered ammonia synthesis at high pressure using osmium or uranium catalysts. Bosch and associates at BASF developed the use of

magnetite promoted with alumina and alkali. This research project is described by A. Mittasch [4] in detail.

The ammonia synthesis industry is based on promoted iron catalysts. A catalyst was developed to supply hydrogen via the water gas shift reaction by the BASF group.

Bosch at BASF next attempted to reduce carbon monoxide with hydrogen at high pressures to produce alcohols and higher hydrocarbons. This work led to methanol synthesis using alkali-promoted zinc oxide plus chromium oxide in 1923. Synthetic hydrocarbons were made from synthesis gas in 1927 by Fischer and Tropsch.

The adsorption of reactants on catalyst surfaces was first thought to be important in the 1900–1920 period. Langmuir–Hinshelwood and Rideal–Eley mechanisms were proposed. The adsorption of gases by solids and particularly the adsorption of hydrogen presented many unknowns. For example, it was not known why the quantity of hydrogen adsorbed varied or indeed how a substance like palladium could adsorb so much hydrogen.

A major development in the 1920s occurred when H. S. Taylor distinguished among activated adsorption, chemisorption, and physical adsorption. He also developed the concept of active centers.

In the 1930s a number of advances occurred that aided in the study of adsorption:

- (1) Isotopes became available in 1933.
- (2) Brunauer and Emmett discovered how to measure the surface area and pore geometry of catalysts using physical adsorption.
- (3) Beeck used evaporated metal films for basic catalytic studies.
- (4) Roberts made tungsten filaments—for the first time “clean” surfaces could be studied because tungsten could be heated hot enough to clean metal surfaces.
- (5) Rideal made other metal filaments and films.

Adsorption studies dominated catalysis science for a time while the new techniques were being applied. In the 1950s attention shifted to the nature of the interactions between the active center and the adsorbate, and today spectroscopic methods continue to reveal information about bonding in catalysts.

A survey of catalytic development is given in Fig. 3. The past 60 yr have been very active ones in the development of new catalytic processes. A list [5] of the more recent of these has been compiled by Halcon International (Table II). Other significant catalyst developments include the family of ZSM zeolites discovered by Mobil Oil Corporation, the carbonylation of methanol to acetic acid practiced by Monsanto Company, and a new generation of catalysts for refining, polyolefins, oxychlorination, etc.

Few heterogeneous catalyst compositions remain constant for as long as a

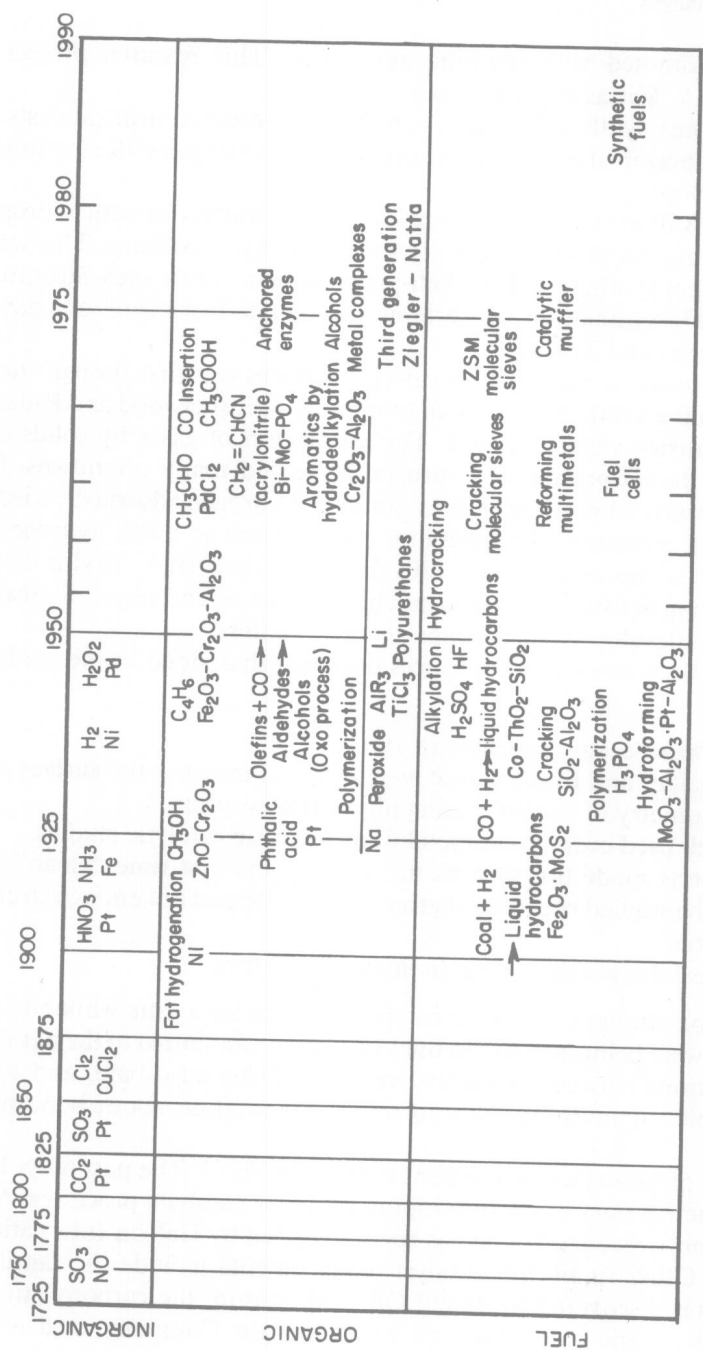


Fig. 3. Survey of catalytic development. Adapted with permission from Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, John Wiley & Sons, Inc.

TABLE II

Chemical Processing Developments of the Last 25 Yr as Compiled by Halcon International^a

Approximate date	Product	Development	Company ^b		
			Chemical	Oil	Process engineering
Before 1957	Isocyanates-urethanes	Urethanes and foams (polyether polyols, one-shot foam, etc.)	Bayer	Wyandotte	Houdry
1953+	Ammonia	High-pressure synthetic gas	—	—	Pullman, Kellogg
1955	Maleic anhydride	High-yield benzene oxidation	—	—	Halcon
1958	High-density polyethylene, polypropylene	New catalysts	Montecatini	Phillips, Avisun	—
1958	α -Olefins	New catalysts	Ethyl	Gulf, Conoco	—
1958+	Terephthalic acid	Air oxidation of <i>p</i> -xylene pure product	Halcon	—	Amoco
1959	Acetaldehyde	Vapor phase ethylene oxidation	Wacker	—	Hoechst
1960-1970	Oxidation alcohols	Improved catalysts	UCC, ICI	Exxon, Shell	—
1964	cyclohexanol, cyclohexanone (for nylon)	Cyclohexane oxidation, boric system	—	—	Halcon
1965+	Vinyl chloride	Oxychlorination of ethylene	Goodrich, Monsanto, Stauffer, PPG	—	—
1965	Acrylonitrile	Propylene ammoxidation	—	SOHIO	—
1965	HMDA (for nylon)	Acrylonitrile electrohydrodimerization	Monsanto	—	—
1967+	Vinyl acetate	Ethylene + acetic acid + O ₂ , vapor phase	Bayer, Celanese, Hoechst, USI	—	—
1968	Acetic acid	High-pressure methanol + CO	BASF, DuPont	—	—

Table II (continues)