Zeolite Catalysis: Principles and Applications

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To Ratna
Kamal and Pankaj
and
Ankit

PREFACE

The discovery of zeolite catalysts in the late 1950s stimulated the interest of scientists, chemists, physicists, and engineers in the study of zeolite catalysts and reactions catalyzed by zeolites. Catalysis is one of the most intensely pursued subjects in Applied Chemistry and Chemical Engineering. During the last 20 years, zeolite catalysis has had a revolutionary impact on both fundamental and applied catalysis. The use of zeolite as a catalyst is widespread for numerous important processes throughout the chemical and petroleum processing industries. Several new catalytic processes were introduced into petroleum refining with the advent of new synthetic zeolites. Zeolite catalysis and its interpretation have been presented in the form of a book for those who have had little previous exposure to zeolite catalysis and would provide a representative cross section of zeolites used as catalysts. The book demonstrates the complexity of zeolite catalysis along with a comprehensive introduction to the kinds of information that one needs to know in order to work with zeolite catalysts in the laboratory, pilot plant, or commercial installation. From the viewpoint of chemical rection engineering, chemical aspects associated with reactor design are also considered. In this respect the present volume can be useful as a text or reference. I hope this book will meet the needs of a book concerning zeolite catalysis and to convey what the science and practice of the subject are really like.

There are ten chapters in the book, and each chapter has been conceived to give a rounded view on all important aspects of zeolite catalysis including structure, synthesis, characterization, technology, and industrial applications. Each chapter critically reviews its particular area giving ample opportunity for interpretation and discussion. Chapters 1 to 3 cover zeolite structure and synthesis aspects. Chapter 4 explains the role of diffusion in zeolite catalysis. Chapter 5 gives an account on acid catalysis. Chapters 6 and 7 cover the various aspects of metal zeolite catalysis and shape selective catalysis, phenomenona unique with zeolite catalysts. Chapter 8 is devoted to usage of various analytical tools for the characterization of surface and bulk properties of zeloite as a catalyst. Chapter 9 addresses the important subject of deactivation of zeolite catalysts. The last chapter presents the application of zeolite catalysts in various industrial processes. The industrially important processes are chosen to illustrate the role of zeolite catalyst in modification and its economic impact.

The book should be of interest to chemical engineers or chemists working in industry or for those starting research on catalytic systems. It contains material suitable for graduate courses on zeolite catalysis in chemical engineering and for a final year undergraduate course in chemical reaction engineering or petroleum refining. The final manuscript evolved from notes for a graduate course on zeolite catalysis taught in the Department of Chemical Engineering, I.I.T., Kanpur, India

Without the help and criticisms of my students and colleagues, this book could not have been written. The author is indebted to countless individuals in ways that are frequently difficult to recognize and to acknowledge explicitly. Particular thanks are due to J.P. Sharma and P.K. Saini for their careful typing of the manuscript, to D.S. Panesar for drawings of tracings, and J.S. Virdi for helping me at various stages of manuscript preparation. I am very grateful to I.I.T. and the Department of Chemical Engineering for providing financial assistance under the Quality Improvement Program (QIP) in the preparation of this manuscript. I wish to express special gratitude to my wife, Ratna for help in a variety of ways.

It is the Author's hope that this book will contribute to an understanding of zeolite catalysis and be a valuable resource to all those active in catalysis or preparing for a career in industrial catalysis.

Subhash Bhatia
June 1988

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Subhash Bhatia, Ph.D., is a Professor in the Department of Chemical Engineering, Indian Institute of Technology, Danpur, India. Her received his Bachelor of Chemical Technology Degree from Harcourt Butler Technological Institute in 1968, graduation with highest honors. He was a recipient of The University gold medal for securing the highest marks in the Faculty of Technology of Kanpur University. Dr. Bhatia obtained his Master and Ph.D. degrees in Chemical Engineering from the Indian Institute of Technology, Kanpur, India in 1971 and 1976 respectively, graduating with honors. He was a postdoctoral fellow in the Department of Chemical Engineering, University of Saskatchewan, Saskatoon, Canada for two years (1976—1978). Since 1978, he has held successive appointments as Lecturer, Assistant Professor, and currently, Professor of Chemical Engineering at the Indian Institute of Technology. He spent one year (1988—1989) in the Department of Chemical Engineering, The University of Queensland, St. Lucia, Australia as a visiting faculty member.

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Chapter 1

INTRODUCTION

1.1 HISTORICAL DEVELOPMENT

In recent years there have been considerable academic and industrial research efforts carried out in the field of zeolite catalysis.[1-8] There are 34 known natural zeolites and about 100 zeolites which do not have natural counterparts have been synthesized. Of this large number of zeolites, only a few have found commercial application: they are mostly synthetic zeolites and synthetic-analog natural zeolites. Since zeolites were first used in petroleum processing in the 1960s, zeolite catalysis has undergone rapid and dynamic advances. The number of zeolite-related U.S. patents published through 1981 exceeds 5,000 and the zeolite scientific and technical literature contains over 25,000 articles.

A zeolite has been defined by Smith[9] as a ''crystalline aluminosilicate with a tetrahedral framework structure enclosing cavities occupied by cations and water molecules, both of which have enough freedom of movement to permit cation exchange and reversible dehydration''. The term zeolite was originally used to describe just such a material. Later, however, the term was broadened to include all ion exchangers — naturally occurring and synthetic inorganic materials as well as organic ones. Because of the widespread use of crystalline aluminosilicate zeolites in industry today, the name zeolite is now fairly well known.

The major industrial processes that use zeolite catalysts are listed in Table 1, together with their respective zeolite usages.

The major part of zeolite catalysis work has been related to reactions where the zeolite is used as solid acid, e.g., isomerization, cracking, hydrocracking etc. The catalyst of choice for catalytic cracking, the heaviest use of zeolites, is usually a rare earth, magnesium, hydrogen, or ultrastable form of zeolite X and Y, or a combination of these. The next heaviest use, hydrocracking, uses catalysts that are dual function in nature and incorporate CO, MO, W, Ni, Pt, or Pd supported on HY, mordenite, erionite, or ultrastable faujasites. Organic and inorganic chemical technologies currently have little use for zeolite catalysts. However, because of the unique intercrystalline pore-channel systems and the excellent maintenance of catalyst activity of the new organic cation containing zeolites, applications in the organic chemical process industry are increasing.

The increased process applications of zeolites in the chemical industry and the virtual explosion of new zeolite synthesis and characterization studies have generated a number of innovations in zeolite catalysis. Review on zeolite catalysis has therefore in general tended to concentrate more on the work related to acid catalysis.[1,4,10]

In general, zeolites have four properties that make them especially interesting for heterogeneous catalysis:[11,12]

1. They have exchangeable cations allowing the introduction of cations with various catalytic properties.
2. If these cationic sites are exchanged to H^+, they can have a very high number of very strong acid sites.
3. Their pore diameters are less than 10 Å.
4. They have pores with one or more discrete sizes.

In principle, zeolites offer considerable scope for surface modification. The ion exchange properties and the periodicity (crystallinity) of zeolites, for example, enable functional metal ions or complexes to be stablized in a variety of oxidation states and coordination geometries

TABLE 1
Zeolite Usage in the Chemical and Fuel Industries (U.S.) (Based on Approximately 221,500 tons/year)

Process	Wt%	Catalyst examples
Catalytic cracking	90	REY,HY
Hydrocracking	9	CO, MO, W, Ni, HY, mordenite, erionite
Organic chemicals	1	ZSM-5, REY
Inorganic chemicals	1	Mordenite

TABLE 2
Zeolite History[13]

1756	Discovery and naming of first natural zeolite, stilbite
1825	Discovery of natural lecynite
1842	Discovery of natural faujasite
1862	First zeolite synthesis (levynite)
1864	Discovery of natural mordenite
1870—88	First ion exchange studies with zeolites
1890	Discovery of natural erionite
1929	Potential as strong acids described (Pauling)
1930—34	First zeolite structure determinations
1932	Zeolites described as molecular sieves
1942—45	Quantitative separations by molecular sieving
1948	First purely synthetic zeolite made
1948	Synthesis of mordenite
1949	Preparation of acid forms of zeolites
1956—64	Synthesis of zeolites A,X, and Y (Union Carbide)
1962	Introduction of zeolite-based cracking catalysts(Mobil Oil Corp.)
1971—72	Highly-siliceous zeolites (ZSM-5, ZSM-8) synthesized (Mobil Oil Corp.)
1975	ZSM-5 catalysts used in ethyl benzene production
1978	ZSM-5 catalysts used in oil dewaxing
1978	Structure of ZSM-5 and ZSM-11
1980	High resolution electron microscopy and NMR applied to zeolite
1985	Methanol to gasoline plant (ZSM-5 catalyst) due to start up
1986	Synthesis of aluminophosphate and highly siliceous zeolites NU-1 and FU-1

on specific surfaces in a well-defined pore structure. This represents a valuable starting point in the design of catalytic surfaces. A greater emphasis is given to the most recent and more novel application of zeolites to heteregeneous catalysis.

1.2 MAJOR BREAKTHROUGHS

There have been many breakthroughs in zeolite science and technology which have relevance in zeolite catalysis and impact over processes. Tables 2 and 3 give an account of zeolite history and a major breakthrough in zeolite catalysis.

1. Small quantities of zeolites incorporated in silica, silica-alumina, and silica-clay materials significantly improved the properties of petroleum-cracking catalysts. The replacement of the amorphous cracking catalyst by zeolites saved the industry several billion dollars per year.
2. The second milestone was the observation that high conversion rates could be obtained through the intracrystalline pore channel system of zeolites. Weisz and co-workers[15] demonstrated experimentally the shape-selective principles in catalytic process. A

TABLE 3
Major Breakthrough in Zeolite Catalysis[10]

Breakthrough	Date	Ref.
Zeolites introduced in commercial catalytic cracking	1964	14
Shape selectivity demonstrated in chemical reactions	1962	15
Organic cations used as templates for zeolite synthesis	1967 1966	16,17

TABLE 4
Some Large-Scale Processes Based on Zeolite Catalysts[18]

Process	Objective	Catalyst	Main process characteristics
Selectoforming	Octane number and increase in gasoline and LPG production	Ni-erionite	Selective in *n*-paraffin cracking
M-forming	High yield, octane number (ON) increase in gasoline	ZSM-5	Cracking depends on degree of branching
Dewaxing	Liquid fuel from heavy fuel oil; lube oil with low pour points	Ni-ZSM-5	Cracking of high molecular weight *n*-monomethyl paraffins
Xylene isomerization	High yield *p*-xylene production	ZSM-5	High through-put, long cycle life
Ethyl benzene	High yield EB production	ZSM-5	Suppression of side reactions
Toluene disproportionation	Benzene and xylenes from toluene	ZSM-5	—
Methanol to gasoline	Methanol (from coal or natural gas) conversion to high grade gasoline	ZSM-5	Synthesis of hydrocarbon only restricted to gasoline range (C_4 to C_{10}) including aromatics

number of processes where shape selectivity has been demonstrated are

i. Conversion of linear paraffinic hydrocarbons without reaction of the branched substrate.
ii. Selective hydrogenation of piperylene (a linear diolefin) without the conversion of isoprene.
iii. Selective hydrogenation of linear olefins.

Table 4 lists some large-scale processes where zeolite catalysts have been used. A catalytic shape-selective process was commercialized in selecto-forming by Mobil Oil workers.[10] In this process linear paraffins are selectively cracked from petroleum reformate streams. Selective conversion results in a high octane gasoline refinery stream and concomitant production of liquid propane gas (LPG).

A third milestone was the crystallization of synthetic counterparts of certain zeolite minerals from reaction mixtures containing organic cations. Using tetramethylammonium (TMA) cations, Barrer[16] was able to synthesize zeolite A (N-A), zeolite X (N-X), and zeolite Y (N-Y). During this same period, Kerr[17] found that organic cations facilitate the synthesis of new zeolites. He first synthesized zeolites ZK-4 and ZK-5. These breakthroughs were rapidly followed by the synthesis of many zeolites from organic cation-containing mixtures such as omega, ZSM-4, and ZSM-5.

There have been recent reports that elements such as Fe, B, As, Cr, V, and Ge have been used to replace aluminum and silicon in the framework of the pentasil family of zeolites. Pentasil-zeolite has been proposed recently to encompass all members of a family of high silica zeolites. Attempts to synthesize zeolites with this type of framework substitute can probably be attributed to early observations of phosphorus in tetrahedral PO_4 units in the rare zeolites. For obvious reasons, much effort has been directed toward introducing other atoms into the framework of known zeolites such as A, X, Y, and mordenite. Such efforts could result not only in new zeolite structures with unique pore channel and cage systems, but also in the synthesis of new catalytic systems with unusual substrated zeolite "solvent" framework interactions. Such subtrate-zeolite "solvent" framework interactions could lead to highly selective reaction pathways. Perhaps the most interesting of these new pentasil materials are the boralites. X-ray diffraction indicates that the unit cell parameter decreases linearly as the B/(B + Si) ratio increases, suggesting that the boron is incorporated in the framework of the zeolite structure. A large body of experimental evidence in zeolite chemistry and zeolite catalysis suggests that the key distinguishing features of zeolite catalysts used in industrial applications are

1. The catalytic selectivity based on molecular sieve effects or on diffusion limitations.
2. The high concentration of strongly ionic hydrogen (H^+) atoms attached to framework oxygen atoms.
3. The large enhancement of ionization reactions and the stabilization of carbenium ions.
4. The high concentration of hydrocarbon reactants within zeolite crystals, resulting in the enhancement of bimolecular reaction steps over unimolecular reaction steps.

1.3 PRESENT STATUS AND FUTURE DIRECTIONS

A close examination of the most recent developments in the field suggests that the innovations to commercial processes will be accelerated by the use of sophisticated catalyst characterization techniques such as solid state nuclear magnetic resonance (NMR) and high resolution microscopy. These and other analytical techniques will enable the scientist to identify the nature of structural interaction which occurs when homogeneous catalysts, metal clusters, and alloys are isolated in the zeolite intracrystalline environment during chemical reaction. Most importantly, with the aid of these techniques, the key parameters that determine the final zeolite structure during synthesis will be identified. In addition, the location and distribution of Al and other framework substitutes (for example Fe, B, P, Cr) in the zeolite structure will be identified. The interface between homogeneous and heterogeneous catalysis may be closing since the zeolite structure is used as a "solvent" or anchor for homogeneous catalysts, metal clusters, and alloys.[20,21]

There is now a renewed interest in metal zeolite interactions. The roles of the metal cluster and alloys and the effects of zeolite acidity and framework interaction must be delineated before a complete understanding of the unique reactivity is found.[21,22]

The most recent example of the dynamic developments that we may expect in the future resulted from the combined application of at least two of the molecular engineering techniques:

1. Organic cation templating
2. Substitutions of framework Al and Si by other chemical elements

Synthesis of a new class of aluminosphosphate molecular sieves has been reported.[23] The aluminophosphate molecular sieves represent microporous inorganic solids with the potential to be as useful and scientifically challenging as the aluminosilicate zeolites. The new zeolites include both three- and two-dimensional framework structures. The templating effects of TMA species were combined with the substitution of silica by phosphate to generate the new microporous crystalline solids.

The incentives for layered "zeolite like" materials have been generated. Pillared, interlayered clays (approximately 9 Å spacing) have been synthesized with properties similar to zeolites and high activity amphorous catalysts.[24] Thus, the goal of larger pore solid structures for petroleum processes may be near. A modification of the ZSM-5 structure is

TABLE 5
Industrial Use of Zeolite-Containing Catalysts[5]

Utilization	Catalyst usage (tons/year)	Catalyst cost (1984) ($/ton)
Catalytic cracking	150,000	1,200—3,500
Hydrocracking	1,400	12,000—32,000
Chemical	200	1,500—60,000
Pollution control	<100	5,000

thought to be a central catalyst concept in a new *p*-methylstyrene monomer plant planned to be set up by a U.S. company. This shape selectivity is the culmination of molecular structural engineering efforts begun in the 1960s. Technologies of this type offer a glimpse of the future impact of zeolite catalysts on the chemical and fuel industries. The data in Table 5 show the extent that zeolite catalysts are utilized in the refinery and petrochemical industries.

The development of commercial zeolites selected from newly discovered compositions and structures, chemical modifications of present products to generate new useful properties, and a re-evaluation of the host of known zeolites which never achieved commercial success should be attempted. With the world-wide expansion of scientific zeolite centers with the capability of synthesizing zeolites and finding their potential applications, it is likely that this will offer new opportunities in design parameters of reactor design and catalysis. The industrial applications of zeolite used as catalysts will open up entirely new vistas in chemical, petroleum, and petrochemical industries. As coal becomes a developing source of hydrocarbon fuels and chemicals, zeolites should dominate the down-stream secondary catalytic processes used to upgrade products of the Fischer-Tropsche converter. Indeed, the future of zeolite catalysis looks bright.

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Chapter 2

ZEOLITE COMPOSITION AND STRUCTURE

2.1 INTRODUCTION

The properties of a zeolite are dependent on the topology of its framework, the size, shape, and accessibility of its free channels, the location charge and size of the cations within the framework, the presence of faults and occluded material, the ordering of T-atoms, and the local environment of T-atoms. Therefore, structural information is extremely important in understanding the adsorptive and catalytic properties of zeolite catalysts.[1-4]

The behavior of a given zeolite as a diffusion medium, sorbent and molecular sieve is regulated in part by the topology of the anionic framework and the size, charge, and locations of the exchange ions within the framework.

The fundamental building block of all zeolites is a tetrahedron of four oxygen anions surrounding a small silicon or aluminum ion. These tetrahedra are arranged so that each of the four oxygen anions is shared in turn with another silica or alumina tetrahedron. The crystal lattice extends in three-dimension and the −2 oxidation state of each oxygen is accounted for. Each silicon ion has its +4 charge balanced by the four tetrahedral oxygens and the silica tetrahedra are therefore electrically neutral. Each alumina tetrahedran has a residual charge of −1 since the trivalent aluminum is bonded to four oxygen anions. Therefore, each alumina tetrahedron requires a +1 charge from a cation in the structure to maintain electrical neutrality. Figure 2.1 shows the primary building blocks of zeolite. These cations are usually sodium in the zeolites as it is initially prepared, but they can readily be replaced by ion exchange. Ion exchange represents the most direct and useful method for the alteration of zeolite properties.

The silica and alumina tetrahedra are combined into more complicated secondary units, which form the building blocks of the framework zeolite crystal structures. The silica and alumina tetrahedra are geometrically arranged, with Al-O-Al bonds excluded. The unit cell formula is usually written as

$$Mn^{+}_{x/n}\left[(A10_2^-)_x\ (Sio_2)_y\right]_z H_20$$

where M_n^+ is the cation which balances the negative charge associated with the framework aluminum ions. These metal cations, which neturalize the excess anionic charge on the aluminosilicate framework, are usually alkali metal and alkaline earth metal cations and at least some of them must be able to undergo reversible ion exchange if the material is to be classed as zeolite. Water molecules fill the remaining volume in the interstices of the zeolite.

The tetrahedra are arranged so that the zeolites have an open framework structure, which defines a pore structure with a high surface area. This surface area is different from that of amorphous solids such as silica-alumina in that it is a true part of the crystalline solid. Figure 2.2 shows a sodalite cage structure. Therefore, the chemistry of the zeolite surface is determined uniquely by the properties of the crystalline solid, which is a major advantage in elucidating the catalytic chemistry. The three-dimensional framework consists of channels and interconnected voids or cages. The cations and water molecules occupy the void spaces in the structure. The intracrystalline zeolitic water can be removed by thermal treatment, usually reversibly. For many zeolites the structure remains intact and the intracrystalline channels and voids become vacant except for the remaining cations.