



Zeolites: Science and Technology

Edited by

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Zeolites: **Science and Technology**

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PREFACE

Zeolites have been the focus of intensive activity and growth in applications over the past 25 years in ion exchange, in adsorption and in catalytic process technology. Beginning with the synthetic zeolites A,X and Y, continuing into the emerging ZSM series, and including selected natural zeolites, applications span the range from large-scale purification and separation to such major petroleum and petrochemical processes as catalytic cracking and aromatics alkylation.

The future promises several new areas of significant use as our energy resource base is expanded. As a result, a NATO Advanced Study Institute on Zeolites was held in Alcabideche, Portugal, May 1-12, 1983. Its purpose was to summarize the state-of-the-art in zeolite science and technology, with particular emphasis on recent developments. This summary is intended to complement presentations of the latest research results at the 1983 International Zeolites Association meeting in Reno, Nevada - USA.

Both the fundamental concepts and industrial applications are addressed in the lectures of the Institute. Individual chapters cover historical development, structure, crystallography and synthesis techniques. Basic principles of adsorption, diffusion, ion exchange and acidity are reviewed. A section on catalysis addresses shape selectivity, transition metals, bifunctional catalysis and "methanol-to-gasoline".

Included in the section on industrial applications are chapters on reactor and adsorber design, catalytic cracking, xylene and n-paraffins isomerization, as well as ion exchange and adsorption.

We would like to thank the members of the Advisory Board for the support given by them to the organization of this meeting; and all lecturers are to be thanked for their clear presentations and written contributions. We particularly wish to acknowledge the efforts of the local committee.

This NATO Advanced Study Institute was made possible through the NATO-ASI Programme. We are much indebted to this organization.

May 1983
Alcabideche

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PART I

HISTORY, STRUCTURE AND SYNTHESIS

MOLECULAR SIEVE ZEOLITE TECHNOLOGY: THE FIRST TWENTY-FIVE YEARS*

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ABSTRACT

In twenty-five years molecular sieve zeolites have substantially impacted adsorption and catalytic process technology throughout the chemical process industries; provided timely solutions to energy and environmental problems; and grown to over a hundred million dollar industry worldwide. The evolution in zeolite materials with improved or novel properties has strongly influenced the expansion of their applications, and provided new flexibility in the design of products and processes.

INTRODUCTION

The year 1979 marked the twenty-fifth anniversary of the commercial birth of molecular sieve zeolites as a new class of industrial materials. They were introduced in late 1954 as adsorbents for industrial separations and purifications. Since that time the fascination with and the elegance of, this unique class of materials has generated a masss of scientific literature describing their synthesis, properties, structure and applications, which probably now numbers well over 15,000 scientific contributions and over 10,000 issued patents. The molecular sieve industry has been projected to have grown into an estimated quarter of a billion dollar market {1} serving all of the major segments of the chemical process industries including major applications in the petroleum refining and petrochemical industries, and has generated a myriad of other adsorption, catalytic,

* This article is used as reference material for J. A. Rabo's lecture on "Historical Aspects of Zeolites".

and most recently ion exchange applications.

Milton reviewed the beginnings and development of molecular sieve zeolites in 1967 {2}. He traced the early discoveries and synthesis of the new zeolites A, X, and Y, which led to their commercial applications as selective adsorbents and catalysts. It will be the purpose of this paper to review the evolution of molecular sieve materials, their synthesis, properties and applications, over the span of 1954 to 1979, with emphasis on the major milestones and trends in these areas. There will be no attempt here to repeat the in depth coverage of zeolite molecular sieves given by Breck {3} or Barrer {4}, or recent up-to-date review articles on the applications of molecular sieve zeolites as adsorbents {6}, catalysts {7,8}, and ion exchangers {9}, and on natural zeolites and their applications {10,11,1,5}.

Success of molecular sieve zeolites has been due primarily to the discovery of new materials whose properties have been engineered into improvements in known processes and into the development of new ones. This discussion will therefore emphasize the materials and properties aspects of molecular sieve zeolites as they evolved and developed into various application areas.

THE EVOLUTION IN MATERIALS

The theme in research on molecular sieve zeolite materials over the twenty-five year period has been a quest for new structures and compositions. Because zeolites are unique as crystalline porous materials, with structure as well as composition controlling properties, there arose the strong conviction that novel and useful properties would result from the discovery of new compositions and structures. Let us now trace the web of change in those discoveries over twenty-five years.

"Low-Silica" Zeolites or Aluminum-Rich Zeolites.

The discovery of zeolites A and X by Milton {12} at the Union Carbide Corporation Laboratories represented a fortunate optimum in composition, pore volume, and channel structure, guaranteeing these two zeolites their lasting commercial prominence out of more than 150 synthetic species known and discovered over the last twenty-five years. Both zeolites are nearly "saturated" in aluminum in the framework composition with a molar ratio of Si/Al near one, the maximum aluminum content possible in tetrahedral aluminosilicate frameworks if

one accepts Loewenstein's rule. As a consequence they contain the maximum number of cation exchange sites balancing the framework aluminum, and thus the highest cation contents and exchange capacities. These compositional characteristics combined give them the most highly heterogeneous surface known among porous materials, due to exposed cationic charges nested in an aluminosilicate framework which results in high field gradients. Their surface is highly selective for water, polar and polarizable molecules which serves as the basis for many of their applications particularly in drying and purification. Their pore volumes of nearly $0.5 \text{ cm}^3/\text{cm}^3$ are the highest known for zeolites and give them a distinct economic advantage in bulk separation and purifications where high capacity is essential to and economic design. Their 3-dimensional channel structures allow the maximum in diffusion characteristics. By a judicious selection of cation composition achieved by facile ion exchange reactions, nearly the entire spectrum of known pore sizes in zeolites can be obtained. The pore sizes achievable by cation exchange of types A and X span the entire range from the smallest pore-sized zeolite known, Cs-A at 0.2nm in size {13} through the 0.3nm potassium A, the 0.4nm sodium A, the 0.5nm calcium A, to the largest known which is about 0.8nm in sodium X. This large pore size of zeolite X was a key to its introduction as a catalytic cracking catalyst.

"Intermediate Silica" Zeolites. The next evolution in zeolite materials was the impetus to synthesize more siliceous zeolites, primarily to improve stability characteristics, both thermal and acid. It was recognized in the early 1950's by scientists at Union Carbide Laboratories that the tetrahedral framework aluminum provided a site of instability for attack by acid and water vapor or steam. Also, the siliceous mineral zeolite mordenite was known with a Si/Al molar ratio of 5 and possessing superior stability characteristics. Breck provided the first success in this quest with the discovery of the third commercially important molecular sieve zeolite type Y {14}, with an Si/Al ratio of from 1.5 to 3.0, and a framework topology like that of zeolite X and the rare zeolite mineral faujasite. Not only was the desired improvement in stability over the more aluminous X achieved, but also the differences in composition and structure had a striking, unpredicted effect on properties that has led to the preeminence of zeolite Y based catalysts in nearly all of the important catalytic applications involving hydrocarbon conversion,

(i.e., cracking, hydrocracking and isomerization) since its initial commercial introduction in 1959.

The next commercially important synthetic zeolite introduced in the early 1960's was a large pore mordenite made by the method of Sand {15} and marketed as "Zeolon" by the Norton Co. {16}, which continued the progression toward higher Si/Al ratio, in this case a value near 5. Again, thermal, hydrothermal, and acid stability improvement was evident. This improved stability coupled with its specific structural and compositional characteristics found it a small but a significant commercial market as both an adsorbent and hydrocarbon conversion catalyst. Type L zeolite, discovered in the early 50's by Breck and Acara {17} with an Si/Al ratio of 3.0 and a unique framework topology, has only recently recieved attention as a commercial catalyst in selective hydrocarbon conversion reactions {18}.

Other zeolites with "intermediate" Si/Al compositions of from 2 to 5 and their own unique framework topologies which have achieved commercial status are the zeolite minerals mordenite, erionite, chabazite, and clinoptilolite, and the synthetic zeolite omega {19} with a typical Si/Al of 3 to 4. Their properties exhibit a common characteristic in terms of improved stability over the "low" silica zeolites. However, unique properties as adsorbents, catalysts and ion exchange materials are also exhibited which reflect their unique structural features. The surface of these intermediate silica zeolites is still heterogeneous and exhibits high selectivity for water and other polar molecules.

"High Silica" Zeolites. The most recent stages in the quest for more siliceous molecular sieve compositions was achieved in the late 1960's and the early 1970's with the synthehsis at the Mobil Research and Development Laboratories of the "high silica zeolites", compositions exemplified first by zeolite beta discovered by Wadlinger, Kerr and Rosinski {20}, and later ZSM-5 discovered by Argauer and Landolt {21}. Subsequently, ZSM-11 {22}, ZSM-21 {24}, and ZSM-34 {25} were described. These compositions are molecular sieve zeolites with Si/Al ratios from 10 to 100 or higher, and with unexpected, strikingly different surface characteristics. In contrast to the "low" and "intermediate" silica zeolites, representing heterogeneous hydrophilic surfaces within a porous crystal, the surface of the high silica zeolites approaches a more homogeneous characteristic with an organophilic-hydrophobic selectivity. They more strongly adsorb the less polar

organic molecules and only weakly interact with water and other strongly polar molecules. In addition to this novel surface selectivity, the high silica zeolite compositions still contain a small concentration of aluminum in the framework and the accompanying stoichiometric cation exchange sites. Thus, their cation exchange properties allow the introduction of acidic OH groups via the well known zeolite ion exchange reactions, essential to the development of acid hydrocarbon catalysis properties.

Silica Molecular Sieves. The ultimate in siliceous molecular sieve compositions, and a much discussed aspiration of early workers in zeolite synthesis in the 1950's, was also achieved in the 1970's with the synthesis of the first pure silica molecular sieve, silicalite {26}, containing essentially no aluminum or cation sites. In the complete absence of strong field gradients due to framework aluminum and exchangeable metal cations which serve as hydrophilic sites, silicalite exhibits a high degree of organophilic-hydrophobic character, capable of separating organic molecules out of water-bearing streams {26}. Silicalite does however contain extraneous or defect hydroxyl groups which contribute a small concentration of hydrophilic sites capable of interacting with water and polar molecules. A related new composition, fluoride-silicalite {27}, completely free of hydroxyl groups, exhibits the ultimate in near perfect hydrophobicity, adsorbing less than 1 wt. % water at 20 torr and 25°C, and even exhibits bulk hydrophobicity: the crystals ($d = 1.7 \text{ g/cm}^3$) actually float on water. Silicalite reportedly {26a} has the same framework topology as zeolite ZSM-5 {28}. Other silica molecular sieve compositions have been reported, including silicalite-2 {29}, and TEA-silicate {30}.

Chemically Modified Zeolites. An alternate method for producing highly siliceous zeolite compositions had its beginnings in the mid 1960's when thermochemical modification reactions that lead to framework dealumination were first reported {31,32}. These reactions include those described as "stabilization," or "ultrastabilization" involving high temperature steaming of ammonium exchanged or acid forms of the zeolite {31}, and framework aluminum extraction with mineral acids or chelates. Repetitive treatments in effect produce zeolites with framework Si/Al compositions and stability characteristics comparable to those observed in the synthesized high silica zeolite compositions. Such highly siliceous variants have been described by Scherzer for zeolite Y

{33}, by Chen {34} and others for mordenite, and by Eberly et al. {35} and Patton et al. {36} for erionite. The stabilized Y zeolite of McDaniel and Maher {31} and the highly siliceous mordenite products of Chen {34}, were reported to be hydrophobic. Although the ultra-stabilized and other dealuminated forms of zeolites emerged at the same time as the synthesized high silica zeolite beta, focus in the former case in the late 60's was on their improved stability characteristics and catalytic applications, rather than on their surface selectivity.

Other highly siliceous analogs or "pseudomorphs" of clinoptilolite and mordenite prepared during the same period by acid extraction {37} have Si/Al compositions like the high silica zeolites and silica molecular sieves. However, their crystallinity, stability, and hydrophobicity are substantially less than the thermally derived ultrastabilized and dealuminated compositions, presumably due to the presence of high concentrations of hydroxyl defects {37b}, and the absence of substantial silicon reinsertion into framework tetrahedral sites.

Natural Zeolites. In contrast to the development of the synthetic zeolites which required their discovery and successful synthesis in the laboratory, the evolution of the natural or mineral zeolites depended on their availability in mineable deposits. The discovery in 1957 of mineable deposits of relatively high purity zeolite minerals in volcanic tuffs in the western United States and in a number of other countries represents the beginning of the commercial natural zeolite era {10}. Prior to that time there was no recognized indication that zeolite minerals with properties useful as molecular sieve materials occurred in large deposits. Commercialization of the natural zeolites chabazite, erionite, and mordenite as molecular sieve zeolites commenced in 1962 with their introduction as new adsorbent materials with improved stability characteristics in various acid natural gas drying applications. Their improved stability over the then prevalent synthetic zeolite adsorbents, types A and X, again reflects their higher intermediate Si/Al ratio of 3-5. The applications of clinoptilolite in radioactive waste recovery and in waste water treatment during the same period of the 60's was based not only on superior stability characteristics but also a high cation exchange selectivity for cesium and strontium, or for the ammonium ion.