

EXPERIMENTAL METHODS  
IN CATALYTIC RESEARCH

VOLUME II

*Preparation and Examination  
of Practical Catalysts*

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*Edited by  
Robert B. Anderson*

*and  
Peter T. Dawson*

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### *Preparation and Examination of Practical Catalysts*

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## PREFACE

In this century catalysis has advanced from a laboratory curiosity to a major component of the chemical and petroleum industries. Catalysis will play an equally important role in new processes for producing alternate fluid fuels. The development of catalysts was initially a mysterious art requiring laborious empirical testing. These tests will probably always be a part of catalyst development, but the process can be performed expeditiously by utilizing the vast store of scientific and practical information currently available and by employing modern research tools. Concurrent with practical developments, new research tools were applied to the investigation of catalysts and catalytic reactions. Some new experimental procedures were developed especially for catalysis, and others were adapted from chemistry and physics. The improved research tools and the concepts resulting from their use have dispelled many of the mysterious aspects of catalysis; however, they have disclosed a host of new and challenging problems.

Since 1935 the experimental methods used in catalytic research have increased both in number and complexity, so that mastery of all of the techniques available is difficult. Volumes II and III provide useful accounts of these methods written by specialists. As in Volume I, each chapter includes a description of the method and its fundamental principles, the apparatus used, the data obtained and their interpretation, and finally an account of special problems related to catalytic research. Volume II considers the preparation and examination of practical catalysts, and Volume III the characterization of surfaces and adsorbed species.

Volume II begins with two chapters on the preparation of catalysts; Chapter 1 presents methods of modifying commercially available zeolitic molecular sieves into useful catalysts. Chapter 2 describes the art of preparing impregnated metal catalysts and provides a scientific basis for many of the

complex processes involved. In Chapter 3 the electron probe microanalyzer, despite its limited resolution, is shown to be a useful tool for studying many problems in practical catalysis. Metallurgists have been masters at utilizing all of the capabilities of the electron microscope, and we have chosen two of them to describe this subject in Chapter 4. Mössbauer spectroscopy is described in Chapter 5; for iron and other Mössbauer nuclides this is an elegant way of determining their chemical structure and environment. Chapter 6 describes modern microbalances, which are sensitive and usually robust instruments capable of measuring adsorption accurately. Finally, the single-pellet reactor is presented in Chapter 7. This simple yet seldom-used technique provides pertinent information on rate, transport, and poisoning phenomena that cannot be obtained in usual experiments.

The authors were asked to describe their specialities at a level understandable to a physical chemist with no experience in their field. These accounts were to provide an adequate introduction to both the experimental procedures and the theory. To a large degree these objectives have been accomplished. The editors have generally accepted the system of units chosen by the authors; these units are probably those that the reader will encounter in the current literature of the particular area.

The editors thank Dr. H. C. Chen and Professor W. N. Delgass for reviewing chapters, and Dr. John Freel, Professors F. E. Massoth, and Indresh Mathur for furnishing unpublished data for Chapter 3.



## CONTENTS OF OTHER VOLUMES

### **VOLUME I**

#### **1. KINETICS OF CATALYTIC REACTIONS**

*Robert B. Anderson*

#### **2. DETERMINATION OF SURFACE AREA AND PORE STRUCTURE OF CATALYSTS**

*W. B. Innes*

#### **3. SURFACE POTENTIALS**

*P. M. Gundry and F. C. Tompkins*

#### **4. FIELD ELECTRON AND FIELD ION EMISSION MICROSCOPY**

*Robert S. Hansen and Nelson C. Gardner*

#### **5. CHEMISORPTION IN ULTRAHIGH VACUUM SYSTEMS**

*Robert S. Hansen and Victor J. Mimeault*

#### **6. LOW ENERGY ELECTRON DIFFRACTION**

*H. E. Farnsworth*

#### **7. MEASUREMENTS OF SEMICONDUCTIVITY, PHOTOCONDUCTIVITY, AND ASSOCIATED PROPERTIES OF CATALYSTS**

*T. J. Gray*

#### **8. SPECTRA OF ADSORBED SPECIES**

*G. Blyholder*

## 9. MEASUREMENT OF ACIDITY OF SURFACES

*Marvin S. Goldstein*

## 10. CONVENTIONAL MAGNETIC METHODS IN CATALYSIS

*L. J. E. Hofer*

## 11. ELECTRON SPIN RESONANCE SPECTROSCOPY

*Richard J. Kokes*AUTHOR INDEX<sup>r</sup>

## SUBJECT INDEX

## VOLUME III

## 1. INTRODUCTION TO SURFACE SPECTROSCOPIES

*Robert L. Park*

## 2. ELECTRON SPECTROSCOPY OF SOLID SURFACES

*H. D. Hagstrum, J. E. Rowe, and J. C. Tracy*

## 3. DIFFRACTION METHODS

*R. A. Armstrong*

## 4. MOLECULAR-BEAM SCATTERING IN CATALYTIC RESEARCH

*Joe N. Smith, Jr.*

## 5. ION-SCATTERING SPECTROSCOPY

*J. M. Poate and T. M. Buck*

## 6. DESORPTION METHODS

*Peter T. Dawson and P. C. Walker*

## 7. INFRARED SPECTROSCOPY

*J. Pritchard and T. Catterick*

## INDEX



# CONTENTS

LIST OF CONTRIBUTORS .....	ix
PREFACE .....	xi
CONTENTS OF OTHER VOLUMES .....	xiii

## 1. MOLECULAR SIEVE ZEOLITES

*A. P. Bolton*

I. Introduction .....	1
II. Molecular Sieve Zeolites .....	2
III. Estimation of Zeolite Purity .....	7
IV. Zeolite Modification .....	13
V. Introduction of Catalytically Active Components .....	39
References .....	42

## 2. PREPARATION AND CHARACTERIZATION OF SUPPORTED METAL CATALYSTS

*R. L. Moss*

I. Introduction .....	43
II. Materials .....	45
III. Methods of Preparation .....	55
IV. Characterization .....	70
V. Concluding Remarks .....	90
References .....	91



### 3. THE USE OF THE ELECTRON PROBE MICROANALYZER IN CATALYSIS

*Gary R. Purdy and Robert B. Anderson*

I. Introduction .....	95
II. The Electron Probe Microanalyzer .....	96
III. Application of the Electron Probe Microanalyzer to Catalysis .....	108
IV. Conclusions .....	135
References .....	136

### 4. TRANSMISSION AND SCANNING ELECTRON MICROSCOPY

*C. M. Sargent and J. D. Embury*

Introduction .....	140
I. Electron Optical Instruments .....	140
II. Principles of Transmission Electron Microscopy .....	149
III. Principles of Scanning Electron Microscopy .....	168
IV. Specimen Preparation for Transmission Electron Microscopy .....	180
List of Symbols .....	184
References .....	184

### 5. MÖSSBAUER SPECTROSCOPY

*Melvin C. Hobson, Jr.*

I. Introduction .....	187
II. Theory .....	189
III. Instrumentation .....	200
IV. Applications .....	209
V. Summary .....	220
References .....	221

### 6. MICROBALANCES IN ADSORPTION AND CATALYSIS

*D. A. Cadenhead and N. J. Wagner*

I. Introduction .....	223
II. Microbalances .....	225
III. Applications .....	240
IV. Summary .....	251
References .....	252

## 7. SINGLE-PELLET DIFFUSION REACTORS

*Eugene E. Petersen*

I. Introduction .....	257
II. Theory of Operation .....	258
III. Experimental Apparatus .....	261
IV. Measurement of Porous Catalyst Parameters .....	266
V. Determination of Mechanism of Catalyst Deactivation .....	269
VI. Conclusions and Comments .....	276
References .....	277
INDEX .....	279



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Numbers in parentheses indicate the pages on which the authors' contributions begin.

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# MOLECULAR SIEVE ZEOLITES

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I. Introduction .....	1
II. Molecular Sieve Zeolites .....	2
A. Types X and Y .....	3
B. Type A .....	3
C. Mordenite .....	4
D. Zeolite L .....	5
E. Erionite .....	5
F. Zeolite $\Omega$ .....	5
III. Estimation of Zeolite Purity .....	7
A. X-Ray Crystallinity .....	7
B. Determination of Surface Area .....	11
C. Determination of Zeolite Purity by Oxygen Adsorption .....	11
IV. Zeolite Modification .....	13
A. Ion Exchange .....	13
B. Removal of Residual Alkali Metal Cations .....	23
C. Effect of Thermal Treatment .....	26
D. Cation Hydrolysis .....	31
E. Stabilized Y .....	36
V. Introduction of Catalytically Active Components .....	39
References .....	42

## I. Introduction

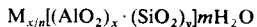
Synthetic molecular sieve zeolites have made a significant impact both technically and commercially on heterogeneous catalysis. Scientific publications on zeolite catalysis have increased from but a few in 1963 to several

hundred a decade later. Zeolite-containing catalysts are currently used commercially by the petroleum and chemical industries in catalytic cracking, hydrocracking, paraffin and olefin isomerization, and aromatic alkylation.

It is possible to controllably modify the physical and chemical properties of a zeolite by effecting changes in pore size, cation species, silica-alumina ratio, and degree of hydration. The controlled variation of these parameters enables a continuous series of catalysts to be prepared of varying activity and selectivity. This characteristic is probably unique in heterogeneous catalysis. The occasional lack of agreement between investigators and the nonreproducibility of catalytic activity and selectivity that is to be found in the literature is probably due to an imperfect understanding of the variabilities encountered during zeolite modification as well as to the use of zeolite samples of less than satisfactory purity. Laboratory synthesis of zeolites can often give rise not only to miscellaneous amorphous impurities but also to other crystalline phases that modify catalytic activity. The large-scale commercial production of types X, Y, erionite, and mordenite in high purity solves the latter problem, and the object of this chapter is to attempt to shed some light on the difficulties encountered during zeolite modification.

## II. Molecular Sieve Zeolites

The term zeolite is a mineralogical name describing a family of crystalline aluminosilicates. Structurally, the zeolites are based on an infinitely extending, three-dimensional network of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra linked by the sharing of oxygen atoms. Chemically, the structural formula of a crystallographic unit cell of a zeolite may be expressed in terms of the oxides,



where M is a cation of valence  $n$ ,  $m$  is the number of water molecules, and the sum of  $x$  and  $y$  is the total number of tetrahedra in the unit cell.

The framework contains channels and interconnected voids, which are occupied by cations and water molecules. Generally the cations are mobile and may be replaced, to varying degrees, by exchange with other cations. The intracrystalline water can be removed, sometimes reversibly. Many zeolites, after dehydration, contain very small channel systems, which are not interpenetrating and which may contain diffusion blocks. For many zeolites complete dehydration irreversibly disturbs the framework structure and location of metal cations so that partial structural collapse occurs. As structurally stable zeolites are required in practical applications, those which have received the most study scientifically and generated the most industrial interest as adsorbents and catalysts are relatively few in number.

Those structures of principal interest in hydrocarbon conversion catalysis are the large-pore zeolites, types X, Y, L,  $\Omega$ , and mordenite. The smaller-pore structures, type A and erionite, are of interest, particularly in "shape selective" catalysis. The salient physical and chemical properties of these materials will be briefly described. Further detailed information on these topics is comprehensively covered by Breck (1).

#### A. TYPES X AND Y

The framework structures of types X and Y are topologically related to the mineral faujasite. The unit cells are cubic with a very large dimension of nearly 25 Å and contain 192 total  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra. The unusually stable and rigid framework structure involves the largest void space of any known zeolite and amounts to over 50 vol % of the crystal. The chemical compositions of types X and Y vary between limits that are related to the synthesis conditions. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of type X is between 2 and 3, and that of type Y between 3 and 6. The framework may be illustrated by a model using skeletal tetrahedra as shown in Fig. 1. The structure consists of truncated octahedra, formed by the  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, joined by six-membered rings. The unit cell contains eight large cavities, each with a free diameter of about 13 Å. The large cavities are interconnected by apertures of twelve-membered oxygen rings having a free diameter of about 7.4 Å. The large-pore system is three dimensional and adsorption measurements show the pore openings to be large enough to admit polysubstituted alkylbenzenes.

#### B. TYPE A

Whereas the unit cells of types X and Y consist of truncated octahedra joined by double six-membered rings, the unit cell of type A is formed by truncated octahedra joined by double four-membered rings (Fig. 1). The three-dimensional channel system consists of large cavities, having a free diameter of about 11 Å, separated by apertures formed by eight-membered oxygen rings. These small apertures, having a free diameter of 4.2 Å, exclude all hydrocarbons except normal paraffins and linear olefins. The characteristic of type A to adsorb normal paraffins from isoparaffins selectively is the basis of the Isosiv normal paraffin separation process. Some of the cations in type A are located close to the apertures and changes in the cation form result in substantial changes in the pore size and consequently in adsorbent characteristics. For example, potassium-exchanged A has a pore size that will admit water and exclude all hydrocarbons.

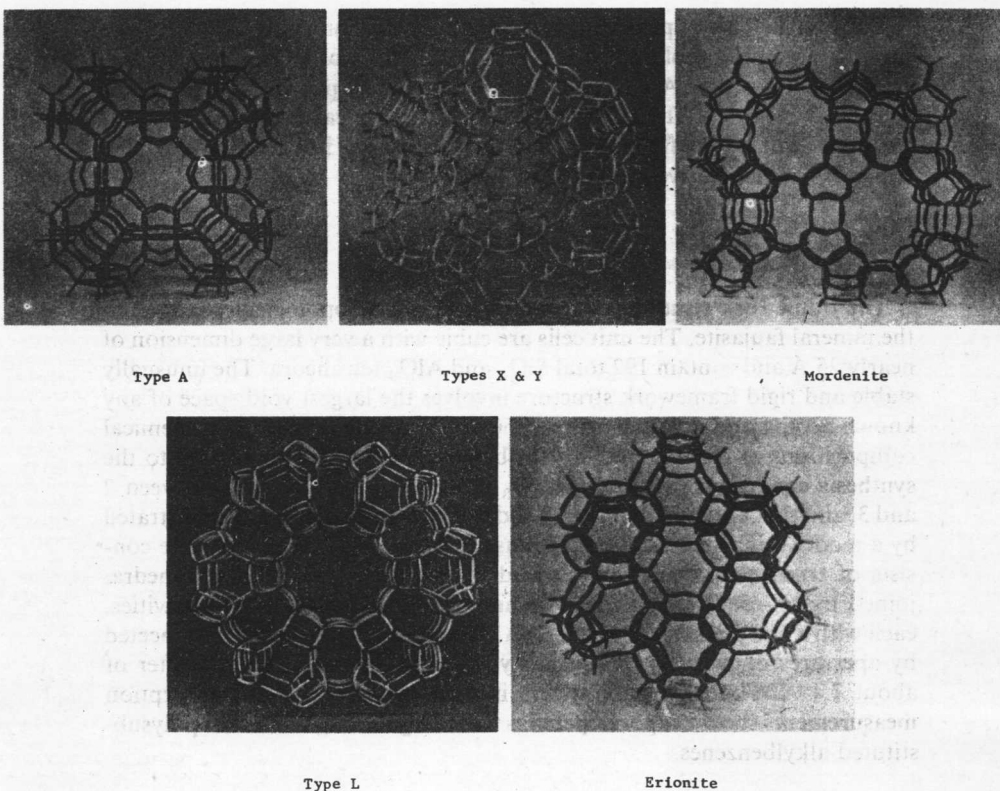


Fig. 1. Projections of some zeolite structures.

### C. MORDENITE

The structure of mordenite, shown in Fig. 1, consists of chains of tetrahedra cross-linked by the sharing of oxygen atoms. Each tetrahedron belongs to one or more five-membered rings in the framework. The high thermal stability of mordenite has been attributed to the presence of the large number of these energetically favored five-membered rings. Unlike types X and Y, mordenite contains no large internal cavities but a collection of one-dimensional pores, 6.7 Å in diameter, similar to a bundle of straws. The dehydrated zeolite has a two-dimensional channel system for small molecules, such as water, but this second pore system is not available to hydrocarbon molecules. The pore system of the mineral form of mordenite is partially blocked by extraneous impurities. However, a synthetic form known as "large-port" mordenite exhibits the adsorption characteristics consistent with the known



structure. The synthetic form has a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of between 9 and 10. The pore system is sufficiently large to admit molecules up to the size of benzene. Mordenite has high acid stability and it is possible to extract most of the structural aluminum with mineral acids without destroying the structure.

#### D. ZEOLITE L

Although type L may be synthesized from systems containing both sodium and potassium ions, the major cation component in this zeolite is potassium. Type L has been synthesized with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios in the range 5–7. The structure of type L is hexagonal and is based upon cross-linking a column of cancrinite units joined by double six-membered rings to three other columns by single oxygen bridges. This arrangement, shown in Fig. 1, gives rise to planar twelve-membered rings that constitute a parallel one-dimensional channel system. These channels have a free diameter of about 1.7 Å. Although the pore size of this zeolite approaches that of types X and Y, the pore volume available for hydrocarbon adsorption is less than half that of types X and Y. Twenty percent of the potassium cations are not available for ion exchange.

#### E. ERIONITE

The framework of this zeolite consists of double six-membered rings and single six-membered rings, which are arranged in parallel planes perpendicular to the hexagonal axis as shown in Fig. 1. This produces cancrinite type cages linked by hexagonal prisms, and these are cross-linked by single six-membered rings perpendicular to the hexagonal axis. This arrangement produces a three-dimensional pore system containing cavities that have internal dimensions of  $15.1 \times 6.3$  Å. The main apertures are formed by eight-membered oxygen rings that have a free dimension of  $3.6 \times 5.2$  Å; each cavity has six apertures. Erionite, which has a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 6, is one of the more siliceous zeolites and one of the most thermally stable, and has an acid stability comparable to mordenite.

#### F. ZEOLITE $\Omega$

The structure of zeolite  $\Omega$  is not definitely proven but is suggested to consist of gmelinite-type cages linked in columns parallel to the hexagonal axis through six-membered rings and linked laterally by oxygen bridges. The pore system is one dimensional and is formed by twelve-membered rings having a free diameter of 7.5 Å. Although the pore size is approximately the same as types X and Y, the void volume  $0.38 \text{ cm}^3/\text{cm}^3$  is considerably