

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME 20

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME 20

HONORARY ADVISORY BOARD

H. ROBERTSON
Berkeley, California

P. H. RABALAIS
Madison, Wisconsin

G. N. RAY
London, England

M. CALVIN
Berkeley, California

J. KOSSUTH
Chicago, Illinois

E. H. SNELL
London, England

H. G. TAYLOR

M. CALVIN
Berkeley, California

J. KOSSUTH
Chicago, Illinois

E. H. SNELL
London, England

H. G. TAYLOR

M. CALVIN
Berkeley, California

J. KOSSUTH
Chicago, Illinois

E. H. SNELL
London, England

J. H. DE BOER
Delft, The Netherlands

W. A. GIBBS
Ottawa, Canada

P. W. SALTER
Canberra, Australia

J. H. DE BOER
Delft, The Netherlands

W. A. GIBBS
Ottawa, Canada

P. W. SALTER
Canberra, Australia

J. H. DE BOER
Delft, The Netherlands

W. A. GIBBS
Ottawa, Canada

P. W. SALTER
Canberra, Australia

ACADEMIC PRESS

DON

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME 20

EDITED BY

D. D. ELEY

*The University
Nottingham, England*

HERMAN PINES

*Northwestern University
Evanston, Illinois*

PAUL B. WEISZ

*Mobil Research and
Development Corporation
Princeton, New Jersey*

CURRENT ADVISORY BOARD

M. BOUDART

Stanford, California

M. CALVIN

Berkeley, California

J. H. DE BOER

Delft, The Netherlands

P. H. EMMETT

Baltimore, Maryland

J. HORIUTI

Sapporo, Japan

W. JOST

Göttingen, Germany

G. NATTA

Milano, Italy

E. K. RIDEAL

London, England

P. W. SELWOOD

Santa Barbara, California

H. S. TAYLOR

Princeton, New Jersey



1969

ACADEMIC PRESS, NEW YORK AND LONDON

ADVANCES IN CATALYSIS
AND RELATED SUBJECTS
VOLUME 20
COPYRIGHT © 1969, BY ACADEMIC PRESS, INC.

ALL RIGHTS RESERVED

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, RETRIEVAL SYSTEM, OR ANY
OTHER MEANS, WITHOUT WRITTEN PERMISSION FROM
THE PUBLISHERS.

ACADEMIC PRESS, INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
Berkeley Square House, London W1X 6BA

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 49-7755

ACADEMIC PRESS
PRINTED IN THE UNITED STATES OF AMERICA

Contributors

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

MICHEL BLANCHARD,* *Faculty of Sciences, University of Lille, Lille, France* (267)

M. BOUDART, *Department of Chemical Engineering, Stanford University, Stanford, California* (153)

ROBERT L. BURWELL, JR., *The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois* (1)

SIDNEY W. FOX, *Institute of Molecular Evolution and Biochemistry Department, University of Miami, Coral Gables, Florida* (373)

JEAN EUGENE GERMAIN,† *Faculty of Sciences, University of Lille, Lille, France* (267)

P. C. GRAVELLE, *Institut de Recherches sur la Catalyse and Faculté des Sciences de l'Université de Lyon, Villeurbanne, France* (167)

GARY L. HALLER, *The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois* (1)

FRANK D. MANGO, *Shell Development Company, Emeryville, California* (291)

H. MORAWETZ, *Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York* (341)

KIYOSHI MORIKAWA,‡ *The Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguroku, Tokyo, Japan* (97)

MASAHIDE OKADA,§ *The Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguroku, Tokyo, Japan* (97)

Y. ONO, *Chemistry Department, Princeton University, Princeton, New Jersey* (135)

JOHN F. READ, *The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois* (1)

* Present address: Faculté des Sciences, Université de Poitiers, France.

† Present address: Ecole Supérieure de Chimie Industrielle de Lyon, France.

‡ Present address: Japan Gasoline Co. Ltd., New-Ohtemachi Bldg., Ohtemachi, Chiyodaku, Tokyo, Japan.

§ Chiba Institute of Technology, Narashino, Chiba Prefecture, Japan; Present address: Faculty of Engineering, Kumamoto University, Kumamoto, Japan.

DUANE L. ROHLFING, *¶ Biology Department, Massachusetts Institute of Technology, Cambridge, Massachusetts (373)*

TAKAYASU SHIRASAKI, *The Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan (97)*

KENZI TAMARU, *Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo (327)*

KATHLEEN C. TAYLOR, *The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois (1)*

S. J. TEICHNER, *Institut de Recherches sur la Catalyse and Faculté des Sciences de l'Université de Lyon, Villeurbanne, France (167)*

J. TURKEVICH, *Chemistry Department, Princeton University, Princeton, New Jersey (135)*

¶ Present address: Department of Biology, University of South Carolina, Columbia, South Carolina.

Preface

The present volume presents a departure from our usual procedure, since in addition to the comprehensive reviews by Frank D. Mango, H. Morawetz, and Duane L. Rohlfs and Sidney W. Fox, it contains seven chapters based on papers given at a recent symposium and therefore partakes more of the character of accounts of personal research.

The Symposium, entitled The Ipatieff Centenary Symposium, was organised by Professor H. Pines at Evanston in September, 1967. Vladimir Nikolaevich Ipatieff lived from 1867 to 1952 and a short obituary notice by one of his pupils and a previous editor of these *Advances*, V. I. Komarevsky, will be found in Volume 5. Articles by Ipatieff with his colleague Louis Schmerling will be found in Volumes 1 and 2. Ipatieff's influence on catalysis, both academic and industrial, has been profound. In his day he helped to emphasize in a healthy fashion the chemical aspects of the subject at a time when physical investigations, inspired by the contribution of Irvin Langmuir, would otherwise have been dominant. His interest in the aluminum halides surely followed on the classical Russian tradition established by Menschutkin and others shortly after the original discoveries of Friedel and Crafts. In the present group of Symposium papers that by Germain and Blanchard lies closest to Ipatieff's field of interests. Although the contributions vary in length, and while some lay emphasis on generalization while others are concerned with specific contributions, together they contribute a valuable cross section of modern activity in catalysis, drawn from the USA, France, and Japan.

The review article by Frank D. Mango emphasizes a new aspect of reactivity that has been developed recently from theoretical organic chemistry. The articles by Morawetz and Rohlfs and Fox are concerned with models for enzyme catalysis, a rapidly growing field of academic and industrial interest.

It is our hope that every catalytic chemist will find one chapter of specific interest in this volume. Also, if his eye should stray over the

other articles, he may find stimulating analogies for his own field. After all, the results of x-ray diffraction reveal that active sites on enzymes are often in pits rather than on promontaries and analogies may therefore be drawn between enzymes and zeolites. If one cuts down a supported metal crystallite sufficiently one ends up with a single metal atom, presumably chelated as in metalloenzymes. The interaction of gases with chromia on nickel oxide, and also with electron donor-acceptor complexes, may be discussed in terms of semiconductor band theory, which in turn may be related to some aspects of enzyme behavior. These are just some of the analogies which may be drawn between the apparently widely spaced articles in the present volume.

September, 1969

D. D. ELEY

The Symposium entitled "The Latest Developments in Catalysis" organized by Professor H. Pines at Evanston in September, 1967, Vladimir Nikolaevich Ipatiev lived from 1907 to 1982 and a short obituary notice by one of his pupils and a previous editor of these Advances, V. I. Komarevsky, will be found in Volume 8. Articles by Ipatiev with his colleagues Louis Scheraga will be found in Volume 1 and 2. Ipatiev's influence on catalysis, both academic and industrial, has been profound. In his day he helped to emphasize in a healthy fashion the chemical aspects of the subject at a time when physical investigations inspired by the contribution of Irvin Langmuir, would otherwise have been dominant. His interest in the aluminum halides surely followed on the classical Russian tradition established by Friedel Clausen and others shortly after the original discoveries of Friedel and Crafts. In the present group of Symposium papers that by German and Blanchard lies closest to Ipatiev's field of interest. Although the contributions vary in length, and while some lay emphasis on generalization while others are concerned with specific contributions, together they contribute a valuable cross section of modern activity in catalysis drawn from the USA, France, and Japan.

The review article by Frank D. Mango emphasizes a new aspect of reactivity that has been developed recently from theoretical organic chemistry. The articles by Morawate and Hocking and Fox are concerned with catalysts for enzyme catalysis, a rapidly growing field of academic and industrial interest.

It is our hope that every catalytic chemist will find one chapter of specific interest in this volume. Also, if his eye should stray over the

Contents of Previous Volumes

Volume 1

The Heterogeneity of Catalyst Surfaces
for Chemisorption

HUGH S. TAYLOR.

Alkylation of Isoparaffins

V. N. IPATIEFF AND LOUIS SCHMERLING.

Surface Area Measurements. A New Tool
for Studying Contact Catalysts

P. H. EMMETT.

The Geometrical Factor in Catalysis

R. H. GRIFFITH.

The Fischer-Tropsch and Related Pro-
cesses for Synthesis of Hydrocarbons by
Hydrogenation of Carbon Monoxide

H. H. STORCH.

The Catalytic Activation of Hydrogen

D. D. ELEY.

Isomerization of Alkanes

HERMAN PINES.

The Application of X-Ray Diffraction to
the Study of Solid Catalysts

M. H. JELLINEK AND I. FANKUCHEN.

Volume 2

The Fundamental Principles of Catalytic
Activity

FREDERICK SEITZ.

The Mechanism of the Polymerization of
Alkenes

LOUIS SCHMERLING AND V. N. IPATIEFF.

Early Studies of Multicomponent Cata-
lysts

ALWIN MITTASCH.

Catalytic Phenomena Related to Photo-
graphic Development

T. H. JAMES.

Catalysis and the Adsorption of Hydrogen
on Metal Catalysts

OTTO BEECK.

Hydrogen Fluoride Catalysis

J. H. SIMONS.

Entropy of Adsorption

CHARLES KEMBALL.

About the Mechanism of Contact Catalysis

GEORGE-MARIA SCHWAB.

Volume 3

Balandin's Contribution to Heterogeneous
Catalysis

B. M. W. TRAPNELL.

Magnetism and the Structure of Catalyt-
ically Active Solids

P. W. SELWOOD.

Catalytic Oxidation of Acetylene in Air for
Oxygen Manufacture

J. HENRY RUSHTON AND K. A. KRIEGER.

The Poisoning of Metallic Catalysts

E. B. MAXTED.

Catalytic Cracking of Pure Hydrocarbons

VLADIMIR HAENSEL.

Chemical Characteristics and Structure
of Cracking Catalysts

A. G. OBLAD, T. H. MILLIKEN, Jr., AND
G. A. MILLS.

Reaction Rates and Selectivity in Catalyst
Pores

AHLBORN WHEELER.

Nickel Sulfide Catalysts

WILLIAM J. KIRKPATRICK.

Volume 4

Chemical Concepts of Catalytic Cracking

R. C. HANSFORD.

Decomposition of Hydrogen Peroxide by
Catalysts in Homogeneous Aqueous
Solution

J. H. BAKENDALE.

Structure and Sintering Properties of
Cracking Catalysts and Related Mate-
rials

HERMAN E. RIES, Jr.

Acid-base Catalysis and Molecular Structure

R. P. BELL.

Theory of Physical Adsorption

TERRELL L. HILL.

The Role of Surface Heterogeneity in Adsorption

GEORGE D. HALSEY.

Twenty-Five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen

HELMUT PICHLER.

The Free Radical Mechanism in the Reactions of Hydrogen Peroxide

JOSEPH WEISS.

The Specific Reactions of Iron in Some Hemoproteins

PHILIP GEORGE.

Volume 5

Latest Developments in Ammonia Synthesis

ANDERS NIELSEN.

Surface Studies with the Vacuum Microbalance: Instrumentation and Low-Temperature Applications

T. N. RHODIN, Jr.

Surface Studies with the Vacuum Microbalance: High-Temperature Reactions

EARL A. GULBRANSEN.

The Heterogeneous Oxidation of Carbon Monoxide

MORRIS KATZ.

Contributions of Russian Scientists to Catalysis

J. G. TOLPIN, G. S. JOHN, AND E. FIELD.

The Elucidation of Reaction Mechanisms by the Method of Intermediates in Quasi-Stationary Concentrations

J. A. CHRISTIANSEN.

Iron Nitrides as Fischer-Tropsch Catalysts

ROBERT B. ANDERSON.

Hydrogenation of Organic Compounds with Synthesis Gas

MILTON ORCHIN.

The Uses of Raney Nickel

EUGENE LIEBER AND FRED L. MORRITZ.

Volume 6

Catalysis and Reaction Kinetics at Liquid Interfaces

J. T. DAVIES.

Some General Aspects of Chemisorption and Catalysis

TAKAO KWAN.

Noble Metal—Synthetic Polymer Catalysts and Studies on the Mechanism of Their Action

WILLIAM P. DUNWORTH AND F. F. NORD.

Interpretation of Measurements in Experimental Catalysis

F. B. WEISZ AND C. D. PRATER.

Commercial Isomerization

B. L. EVERING.

Acidic and Basic Catalysis

MARTIN KILPATRICK.

Industrial Catalytic Cracking

RODNEY V. SHANKLAND.

Volume 7

The Electronic Factor in Heterogeneous Catalysis

M. McD. BAKER AND G. I. JENKINS.

Chemisorption and Catalysis on Oxide Semiconductors

G. PARRAVANO AND M. BOUDART.

The Compensation Effect in Heterogeneous Catalysis

E. CREMER.

Field Emission Microscopy and Some Applications to Catalysis and Chemisorption

ROBERT GOMER.

Adsorption on Metal Surfaces and Its Bearing on Catalysis

JOSEPH A. BECKER.

The Application of the Theory of Semiconductors to Problems of Heterogeneous Catalysis

K. HAUFFE.

Surface Barrier Effects in Adsorption, Illustrated by Zinc Oxide

S. ROY MORRISON.

Electronic Interaction between Metallic Catalysts and Chemisorbed Molecules

R. SUHRMANN.

Volume 8

- Current Problems of Heterogeneous Catalysis
J. ARVID HEDVALL.
- Adsorption Phenomena
J. H. DE BOER.
- Activation of Molecular Hydrogen by Homogeneous Catalysts
S. W. WELLER AND G. A. MILLS.
- Catalytic Syntheses of Ketones
V. I. KOMAREWSKY AND J. R. COLEY.
- Polymerization of Olefins from Cracked Gases
EDWIN K. JONES.
- Coal-Hydrogenation Vapor-Phase Catalysts
E. E. DONATH.
- The Kinetics of the Cracking of Cumene by Silica-Alumina Catalysts
CHARLES D. PRATER AND RUDOLPH M. LAGO.

Volume 9

- Proceedings of the International Congress on Catalysis, Philadelphia, Pennsylvania, 1956.

Volume 10

- The Infrared Spectra of Adsorbed Molecules
R. P. EISCHENS AND W. A. PLISKIN.
- The Influence of Crystal Face in Catalysis
ALLAN T. GWATHMEY AND ROBERT E. CUNNINGHAM.
- The Nature of Active Centers and the Kinetics of Catalytic Dehydrogenation
A. A. BALANDIN.
- The Structure of the Active Surface of Cholinesterases and the Mechanism of Their Catalytic Action in Ester Hydrolysis
F. BERGMANN.
- Commercial Alkylation of Paraffins and Aromatics
EDWIN K. JONES.
- The Reactivity of Oxide Surfaces
E. R. S. WINTER.
- The Structure and Activity of Metal-on-Silica Catalysts
G. C. A. SCHUIT AND L. L. VAN REIJEN.

Volume 11

- The Kinetics of the Stereospecific Polymerization of α -Olefins
G. NATTA AND I. PASQUON.
- Surface Potentials and Adsorption Process on Metals
R. V. CULVER AND F. C. TOMPKINS.
- Gas Reactions of Carbon
P. L. WALKER, JR., FRANK RUSINKO, JR., AND L. G. AUSTIN.
- The Catalytic Exchange of Hydrocarbons with Deuterium
C. KEMBALL.
- Immersional Heats and the Nature of Solid Surfaces
J. J. CHESSICK AND A. C. ZETTMELMOYER.
- The Catalytic Activation of Hydrogen in Homogeneous, Heterogeneous, and Biological Systems
J. HALPERN.

Volume 12

- The Wave Mechanics of the Surface Bond in Chemisorption
T. B. GRIMLEY.
- Magnetic Resonance Techniques in Catalytic Research
D. E. O'REILLY.
- Base-Catalyzed Reactions of Hydrocarbons
HERMAN PINES AND LUKE A. SCHAAP.
- The Use of X-Ray K-Absorption Edges in the Study of Catalytically Active Solids
ROBERTS A. VAN NORDSTRAND.
- The Electron Theory of Catalysis on Semiconductors
TH. WOLKENSTEIN.
- Molecular Specificity in Physical Adsorption
D. J. C. YATES.

Volume 13

- Chemisorption and Catalysis on Metallic Oxides
F. S. STONE.
- Radiation Catalysis
R. COEKELBERGS, A. CRUCQ, AND A. FRENNETT.

Polyfunctional Heterogeneous Catalysis

PAUL B. WEISZ.

A New Electron Diffraction Technique,
Potentially Applicable to Research in
Catalysis

L. H. GERMER.

The Structure and Analysis of Complex
Reaction Systems

JAMES WEI AND CHARLES D. PRATER.

Catalytic Effect in Isocyanate Reactions

A. FARKAS AND G. A. MILLS.

Volume 14

Quantum Conversion in Chloroplasts

MELVIN CALVIN.

The Catalytic Decomposition of Formic
AcidP. MARS, J. J. F. SCHOLLEN, AND
P. ZWIETERING.Application of Spectrophotometry to the
Study of Catalytic Systems

H. P. LEFTIN AND M. C. HOBSON, Jr.

Hydrogenation of Pyridines and Quino-
lines

MORRIS FREIFELDER.

Modern Methods in Surface Kinetics: Flash
Desorption, Field Emission Microscopy,
and Ultrahigh Vacuum Techniques

GERT EHRLICH.

Catalytic Oxidation of Hydrocarbons

L. YA. MARGOLIS.

Volume 15

The Atomization of Diatomic Molecules by
Metals

D. BRENNAN.

The Clean Single-Crystal-Surface Ap-
proach to Surface Reactions

N. E. FARNSWORTH.

Adsorption Measurements during Surface
Catalysis

KENZI TAMARU.

The Mechanism of the Hydrogenation of
Unsaturated Hydrocarbons on Transi-
tion Metal Catalysts

G. C. BOND AND P. B. WELLS.

Electronic Spectroscopy of Adsorbed Gas
Molecules

A. TERENIN.

The Catalysis of Isotopic Exchange in
Molecular Oxygen

G. K. BORESKOV.

Volume 16

The Homogeneous Catalytic Isomerization
of Olefins by Transition Metal Complexes

MILTON ORCHIN.

The Mechanism of Dehydration of Alco-
hols over Alumina Catalysts

HERMAN PINES AND JOOST MANASSEN.

 π Complex Adsorption in Hydrogen Ex-
change on Group VIII Transition Metal
CatalystsJ. L. GARNETT AND W. A. SOLLICH-
BAUMGARTNER.Stereochemistry and the Mechanism of
Hydrogenation of Unsaturated Hydro-
carbons

SAMUEL SIEGEL.

Chemical Identification of Surface Groups

H. P. BOEHM.

Volume 17

On the Theory of Heterogeneous Catalysis

JURO HORUIT AND TAKASHI NAKAMURA.

Linear Correlations of Substrate Reac-
tivity in Heterogeneous Catalytic Reac-
tions

M. KRAUS.

Application of a Temperature-Program-
med Desorption Technique to Catalyst
Studies

R. J. CVETANOVIC AND Y. AMENOMIYA.

Catalytic Oxidation of Olefins

HERVEY H. VOGEL AND CHARLES R.
ADAMS.The Physical-Chemical Properties of
Chromia-Alumina CatalystsCHARLES P. POOLE, Jr. AND D. S.
MACIVER.Catalytic Activity and Acidic Property of
Solid Metal SulfatesKOZO TANABE AND TSUNEICHI TAKE-
SHITA.

Electrocatalysis

S. SRINIVASEN, H. WROBLA, AND
J. O'M. BOCKRIS.

Volume 18

Volume 19

Stereochemistry and Mechanism of Hydrogenation of Naphthalenes on Transition Metal Catalysts and Conformational Analysis of the Products

A. W. WEITKAMP.

The Effects of Ionizing Radiation on Solid Catalysts

ELLISON H. TAYLOR.

Organic Catalysis over Crystalline Aluminosilicates

P. B. VENUTO AND P. S. LANDIS.

On Transition Metal-Catalyzed Reactions of Norbornadiene and the Concept of π Complex Multicenter Processes

G. N. SCHRAUZER.

Modern State of the Multiplet Theory of Heterogeneous Catalysis

A. A. BALANDIN.

The Polymerization of Olefins by Ziegler Catalysts

M. N. BERGER, G. BOOCOCK, AND R. N. HAWARD.

Dynamic Methods for Characterization of Adsorptive Properties of Solid Catalysts

L. POLINSKI AND L. NAPHTALI.

Enhanced Reactivity at Dislocations in Solids

J. M. THOMAS.

II. Expansion of Chromia	1
III. Surface Coordinative Unsaturation	2
IV. Oxidation and Reduction of Surface Cr^{3+}	12
V. Possible Forms of Chemisorption on Chromia	17
A. Coordinative Adsorption	13
B. Simple Adsorption at Basic Sites	13
C. Heterolytic Dissociative Adsorption	14
D. Reductive Adsorption	16
E. Ligand Displacement Adsorption	17
VI. Chemisorption on Chromia as a Function of Activation	19
A. Experimental Methods	19
B. Experimental Results with the Chromatographic Technique	29
C. Experimental Results with the Vacuum Microbalance	22
VII. Results of Catalytic Experiments	23
A. Techniques	25
B. Effect of Conditions of Activation upon the Rate of Hydrogenation of 1-Hexene	29
C. Effect of Poisoning by Oxygen and Carbon Monoxide	33
D. Isomerization of 1-Hexene	34
E. Experiments with <i>trans</i> -2-Hexene and 4-Methyl-1-pentene	36
F. Reaction between Deuterium and Hexenes	37
G. Isotopic Exchange between Deuterium and Cyclopentane and Hexane	41
H. Isotopic Exchange between Deuterium and Toluene or Benzene	42
I. Hydrogen-Deuterium Equilibration	47
VIII. Processes in the Hydrogenation of Hexenes and in Isotopic Exchange	47
A. Hydrogenation	48
B. Deuterogenation	49
C. Isomerization	51
D. Isotopic Exchange between Deuterium and Hexenes	52
E. Isotopic Exchange of Alkanes	55
F. Isotopic Exchange of Toluene and Benzene	56

Contents

CONTRIBUTORS	v
PREFACE	vii
CONTENTS OF PREVIOUS VOLUMES.....	xiii

Chemisorptive and Catalytic Behavior of Chromia

ROBERT L. BURWELL, JR., GARY L. HALLER, KATHLEEN C. TAYLOR,
AND JOHN F. READ

I. Introduction	2
II. Preparation of Chromia	4
III. Surface Coordinative Unsaturation	7
IV. Oxidation and Reduction of Surface Cr^{3+}	12
V. Possible Forms of Chemisorption on Chromia	13
VI. Chemisorption on Chromia as a Function of Activation	17
VII. Results of Catalytic Experiments	28
VIII. Processes in the Hydrogenation of Hexenes and in Isotopic Exchange	47
IX. The Nature of Active Sites.....	60
X. Chemical Mechanism	73
Appendix A. Spectra of Chromias	91
Appendix B. Impurities in Chromia	92
References	93

Correlation among Methods of Preparation of Solid Catalysts, Their Structures, and Catalytic Activities

KIYOSHI MORIKAWA, TAKAYASU SHIRASAKI, AND MASAHIDE OKADA

I. Introduction	98
II. Traditional Methods of Preparation of Supported Nickel Catalyst ..	98
III. Superhomogeneous Coprecipitation (SHCP) Method	105
IV. Cation-Exchange Method	112
V. Palladium on Aluminosilicate by Complex-Ion Exchange.....	122
VI. Palladium on Active Charcoal	128
VII. Nickel-Phosphorus Alloy	131
VIII. Conclusion	132
References	132

Catalytic Research on Zeolites

J. TURKEVICH AND Y. ONO

I. Introduction	135
II. Determination of the Catalyst Stability on Dehydration	140

III. Kinetic Studies on the Nature of Cracking Sites.....	142
IV. Experimentation	143
V. Experimental Results	144
References	152

Catalysis by Supported Metals

M. BOUDART

I. Introduction	153
II. Interaction between Metal and Support	154
III. Surface Area of the Metal	156
IV. Structure-Insensitive or Facile Reactions.....	158
V. Structure-Sensitive or Demanding Reactions	161
VI. Conclusion	163
References	165

Carbon Monoxide Oxidation and Related Reactions on a Highly Divided Nickel Oxide

P. C. GRAVELLE AND S. J. TEICHNER

I. Introduction	168
II. Preparation and Properties of a Highly Divided Nickel Oxide.....	170
III. Chemisorptions on Pure Nickel Oxide	176
IV. Surface Interactions between Gases and Adsorbed Species.....	196
V. Room-Temperature Oxidation of Carbon Monoxide	209
VI. Room-Temperature Oxidation of Carbon Monoxide on Doped Nickel Oxides	226
VII. High-Temperature (200°) Oxidation of Carbon Monoxide on Nickel Oxide	245
VIII. Decomposition of Nitrous Oxide on a Highly Divided Nickel Oxide at 250°	256
IX. Conclusions	262
References	264

Acid-Catalyzed Isomerization of Bicyclic Olefins

JEAN EUGENE GERMAIN AND MICHEL BLANCHARD

I. Introduction	267
II. Experimentation	268
III. Isomerizations in the C_8H_{12} Series	270
IV. Isomerizations in the C_9H_{14} Series	274
V. Isomerizations in the $C_{10}H_{16}$ Series	279
VI. Discussion	282
References	289

Molecular Orbital Symmetry Conservation in Transition Metal Catalysis

FRANK D. MANGO

I. Introduction	291
II. Cycloaddition Reactions	297
III. Electrocyclic Reactions	311
IV. Sigmatropic Transformations	316
V. Summary and Conclusions	323
References	324

Catalysis by Electron Donor-Acceptor Complexes

KENZI TAMARU

I. Introduction	327
II. EDA Complexes of Phthalocyanines	328
III. Anthracene-Sodium Complexes	330
IV. Catalytic Hydrogenation over EDA Complexes	334
V. EDA Complexes with Organic Electron Donors	335
VI. Photocatalysis over EDA Complexes	338
References	339

Catalysis and Inhibition in Solutions of Synthetic Polymers and in Micellar Solutions

H. MORAWETZ

I. Introduction	341
II. Some Characteristics of Enzymic Catalysis	342
III. Reaction Rates in Solutions of Long-Chain Macromolecules	345
IV. Catalysis and Inhibition in Micellar Solutions	359
V. Critique of the Use of Synthetic Polymers and Micelles as Enzyme Models	366
References	369

Catalytic Activities of Thermal Polyanhydro- α - Amino Acids

DUANE L. ROHLFING AND SIDNEY W. FOX

I. Introduction	373
II. Properties of Thermal Polyamino Acids	377
III. Catalysis by Thermal Polyamino Acids	378
IV. Reactions Catalyzed by Thermal Polyanhydroamino Acids	379
V. Summary of Catalytic Actions of Thermal Polyamino Acids	409
VI. Significances of the Catalytic Activity of Thermal Polyamino Acids	410
VII. Conclusions	415
References	416

AUTHOR INDEX	419
SUBJECT INDEX	431

Chemisorptive and Catalytic Behavior of Chromia

ROBERT L. BURWELL, JR., GARY L. HALLER,
KATHLEEN C. TAYLOR, and JOHN F. READ

*The Ipatieff Catalytic Laboratory, Department of Chemistry
Northwestern University, Evanston, Illinois*

I. Introduction	2
II. Preparation of Chromia	4
III. Surface Coordinative Unsaturation	7
IV. Oxidation and Reduction of Surface Cr^{3+}	12
V. Possible Forms of Chemisorption on Chromia	13
A. Coordinative Adsorption	13
B. Simple Adsorption at Basic Sites	13
C. Heterolytic Dissociative Adsorption	14
D. Reductive Adsorption	16
E. Ligand Displacement Adsorption	17
VI. Chemisorption on Chromia as a Function of Activation	17
A. Experimental Methods	18
B. Experimental Results with the Chromatographic Technique ..	20
C. Experimental Results with the Vacuum Microbalance	22
VII. Results of Catalytic Experiments	28
A. Technique	28
B. Effect of Conditions of Activation upon the Rate of Hydrogenation of 1-Hexene	29
C. Effect of Poisoning by Oxygen and Carbon Monoxide	33
D. Isomerization of 1-Hexene	34
E. Experiments with <i>trans</i> -2-Hexene and 4-Methyl-1-pentene ..	36
F. Reaction between Deuterium and Hexenes	37
G. Isotopic Exchange between Deuterium and Cyclopentane and Hexane	41
H. Isotopic Exchange between Deuterium and Toluene or Benzene	42
J. Hydrogen-Deuterium Equilibration	47
VIII. Processes in the Hydrogenation of Hexenes and in Isotopic Exchange	47
A. Hydrogenation	48
B. Deuteration	49
C. Isomerization	51
D. Isotopic Exchange between Deuterium and Hexenes	52
E. Isotopic Exchange of Alkanes	55
F. Isotopic Exchange of Toluene and Benzene	58