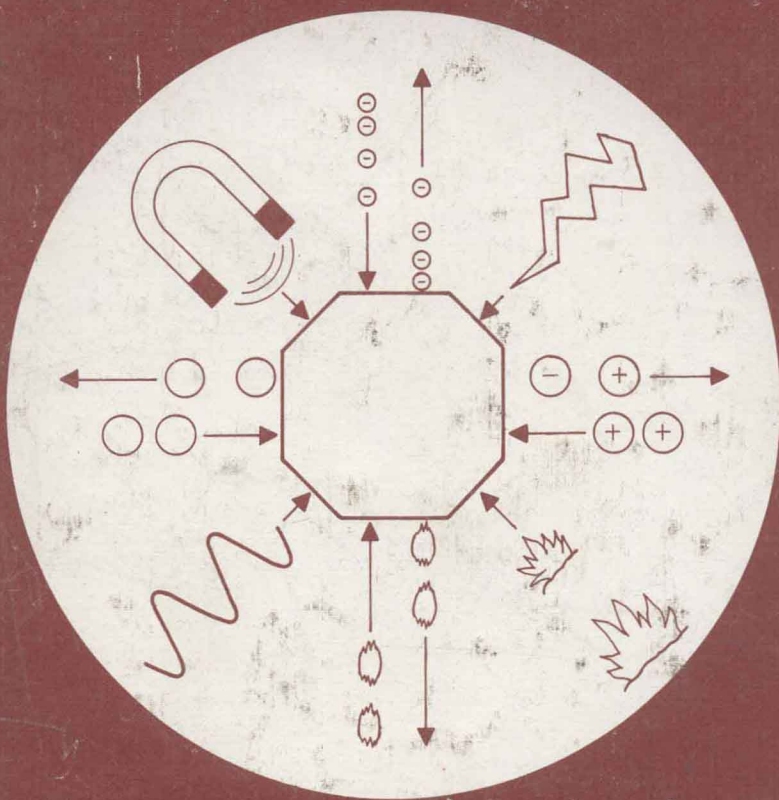


studies in surface science and catalysis



46

ZEOLITES AS CATALYSTS, SORBENTS AND DETERGENT BUILDERS

Applications and Innovations

H.G. Karge
J. Weitkamp
(editors)

elsevier

(Studies in Surface Science and Catalysis

Advisory Editors: B. Delmon and J.T. Yates

Vol. 46)

ZEOLITES AS CATALYSTS, SORBENTS AND DETERGENT BUILDERS

Applications and Innovations

Proceedings of an International Symposium, Würzburg, F.R.G.
September 4–8, 1988

Editors

H.G. Karge

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-1000
Berlin 33 (West)*

J. Weitkamp

*University of Stuttgart, Institute of Chemical Technology I, Pfaffenwaldring,
D- 7000 Stuttgart 80, F.R.G.*



ELSEVIER

Amsterdam — Oxford — New York — Tokyo 1989

ELSEVIER SCIENCE PUBLISHERS B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
655, Avenue of the Americas
New York, NY 10010, U.S.A.

Library of Congress Cataloging-in-Publication Data

Zeolites as catalysts, sorbents, and detergent builders : applications and innovations : proceedings of an international symposium, Wurzburg, F.R.G., September 4-8, 1988 / editors, H.G. Karge, J. Weitkamp.

p. cm. -- (Studies in surface science and catalysis ; 46)
Proceedings of the International Symposium on "Zeolites as Catalysts, Sorbents, and Detergent Builders."

Includes indexes.

Bibliography: p.

ISBN 0-444-87383-X

✓ 1. Zeolites--Congresses. ✓ 2. Sorbents--Congresses. ✓ 3. Detergents, Synthetic--Congresses. I. Karge, H. G. (Hellmut G.) II. Weitkamp, J. (Jens) III. International Symposium on "Zeolites as Catalysts, Sorbents, and Detergent Builders" (1988 : Wurzburg, Germany)

IV. Series.

TP245.S5Z385 1989

660'.2995--dc20

89-1464

CIP

ISBN 0-444-87383-X (Vol. 46)

ISBN 0-444-41801-6 (Series)

© Elsevier Science Publishers B.V., 1989

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V./Physical Sciences & Engineering Division, P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Special regulations for readers in the USA — This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the publisher.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

Although all advertising material is expected to conform to ethical (medical) standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality or value of such product or of the claims made of it by its manufacturer.

Printed in The Netherlands

Studies in Surface Science and Catalysis 46

ZEOLITES AS CATALYSTS, SORBENTS AND DETERGENT BUILDERS

Applications and Innovations

PREFACE

This symposium was one of the smaller zeolite meetings held in between the big International Zeolite Conferences. It is the latest in the series of meetings which started in 1978 in Szeged, Hungary, and continued in 1980 in Villeurbanne (Lyon), France; 1982 in Bremen, FRG; 1984 in Prague, Czechoslovakia; 1985 in Siófok, Hungary; and 1987 in Nieuwpoort, Belgium. These conferences are intended to cover selected fields from the broad area of zeolite research and application. For the Würzburg Symposium emphasis was placed on zeolite catalysis, sorption and detergent builders. With respect to catalysis, particular attention was paid to the synthesis of fine chemicals with the help of zeolite catalysts. An overview of this important field was given in two invited lectures which were complemented by a number of related oral and poster contributions. Special efforts were made to bring together experts from industry and academia. This endeavour was successful, as was reflected both in the invited lectures, oral and poster presentations and in the composition of the audience. An expected trend was the ever increasing interest in the so-called new generation molecular sieves both for research and application. A remarkable number of the presented studies were devoted to these materials. Innovations, however, were mostly visible in developing and refining methods and techniques of investigation either in experiment or theory. Obviously, successful application of highly sophisticated tools of solid state and surface science to problems of zeolite research now becomes possible. This seems to promise a growth in our knowledge of and deeper insight into the subtle details of zeolite properties and behaviour.

Hellmut G. Karge
Fritz Haber Institute
Max Planck Society, Berlin

Jens Weitkamp
Institute of Chemical Technology I
University of Stuttgart

January, 1989

ACKNOWLEDGMENTS

The organizers of the international Symposium on "ZEOLITES AS CATALYSTS, SORBENTS AND DETERGENT BUILDERS", held at Würzburg, Federal Republic of Germany, September 4-8, 1988 express their appreciation to the members of the International Scientific Committee who carried out the difficult and important task of paper selection.

They also wish to thank the members of the Executive Staff for their great efforts made during preparation and running of the symposium. Particular thanks are due to Mrs. R. Stottko for the coordination and execution of the finances, to Dr. St. Ernst for his active participation in the organizational work and to Mrs. M. Rahimi, Mrs. E. Stankewitz and Mrs. J. Reiffel for their most valuable assistance in preparing the proceedings.

Furthermore, the organizers thank the authors for submitting their manuscripts for publication in these proceedings and the referees for spending time and effort in order to ensure the high scientific standard of the contributions.

Last but not least, the help and generous financial support of collaborating organizations and sponsors from the industry is gratefully acknowledged.

Hellmut G. Karge

Jens Weitkamp.

INTERNATIONAL SCIENTIFIC COMMITTEE

H. BEYER, Hungarian Academy of Sciences, Budapest, Hungary.

S. CARTLIDGE, Grace GmbH, Worms, FRG.

P. CHRISTOPHLIEMK, Henkel KGaA, Düsseldorf, FRG.

J. DWYER, The University of Manchester, England.

F. FAJULA, Ecole Nationale Supérieure de Chimie, Montpellier, France.

F. FETTING, Technische Hochschule Darmstadt, FRG.

W. HÖLDERICH, BASF AG, Ludwigshafen, FRG.

W. KEIM, RWTH Aachen, FRG, and DMGK, Hamburg, FRG.

A. KISS, Degussa AG, Hanau, FRG.

H. KRAL, Dechema, Frankfurt/M., FRG.

E.-I. LEUPOLD, Hoechst AG, Frankfurt/M., FRG.

R. MAUREL, Institut de Recherches sur la Catalyse, Villeurbanne, France.

I.E. MAXWELL, Koninklijke/Shell, Amsterdam, The Netherlands.

L. MOSCOU, Akzo Chemie BV, Amsterdam, The Netherlands.

G. ÖHLMANN, Academy of Sciences of the GDR, Berlin-Adlershof, GDR.

L. PUPPE, Bayer AG, Leverkusen, FRG.

M.S. SPENCER, ICI, Billingham, England.

J.B. UYTTERHOEVEN, Katholieke Universiteit Leuven, Belgium.

EXECUTIVE COMMITTEE

R. AMBERG, Berlin (West).

C. H. BERKE, Stuttgart, FRG.

A. BREHM, Oldenburg, FRG.

C.-Y. CHEN, Oldenburg, FRG.

H. DARMSTADT, Berlin (West).

St. ERNST, Oldenburg, FRG.

TH. KROMMINGA, Stuttgart, FRG.

D. LINDNER, Oldenburg, FRG.

G.W. MÜLLER, Stuttgart, FRG.

M. NEUBER, Karlsruhe, FRG.

W. NIESSEN, Berlin (West).

E. PERNKLAU, Stuttgart, FRG.

E. STANKEWITZ, Berlin (West).

R. STOTTKO, Berlin (West).

W. WACHSMANN, Berlin (West).

FINANCIAL SUPPORT

Akzo Chemie, Ketjen Catalysts, Amsterdam, The Netherlands.

BASF AG, Ludwigshafen, FRG.

BP International Limited, Sunbury-on-Thames, England.

Bayer AG, Leverkusen, FRG.

Degussa AG, Frankfurt, FRG.

Deutsche Forschungsgemeinschaft (DFG), Bonn, FRG.

Deutscher Akademischer Austauschdienst (DAAD), Bonn, FRG.

DGMK German Society for Petroleum Sciences and Coal Chemistry,
Processing and Application Division, Hamburg, FRG.

Exxon Chemical Holland B.V., Rotterdam, The Netherlands.

Grace GmbH, Worms, FRG.

Henkel KGaA, Düsseldorf, FRG.

Hoechst AG, Frankfurt, FRG.

Institut Français du Pétrole, Rueil Malmaison, France.

International Zeolite Association (IZA).

Kali-Chemie AG, Hannover, FRG.

Max-Planck-Gesellschaft, München, FRG.

Perkin Elmer GmbH, Überlingen, FRG.

Rütgerswerke AG, Frankfurt, FRG.

SKW Trostberg AG, Trostberg, FRG.

Süd-Chemie AG, München, FRG.

I. CATALYSIS AND CATALYSIS-RELATED PROPERTIES

CONTENTS

Preface	XIII
Acknowledgments	XIV
International Scientific Committee	XIV
Executive Committee	XV
Financial Support	XV

I. CATALYSIS AND CATALYSIS-RELATED PROPERTIES

Skeletal Rearrangement Reactions of Olefins, Paraffins and Aromatics over Aluminophosphate based Molecular Sieve Catalysts J.A. Rabo, R.J. Pellet, P.K. Coughlin, E.S. Shamsoum	1
Catalytic and Physical Properties of Silicon-Substituted $AlPO_4$ -5 Molecular Sieves K.J. Chao, L.J. Leu	19
On the Nature of the Catalytic Activity of SAPO-5 Ch. Minchev, V. Kanazirev, V. Mavrodinova, V. Penchev, H. Lechert	29
Molecular Orbital Calculations on the Structural and Acidic Characteristics of Aluminophosphates ($AlPO_4$), Silicoaluminophosphates (SAPO) and Metaluminophosphate (MeAPO) Based Molecular Sieves R. Carson, E.M. Cooke, J. Dwyer, A. Hinchliffe, P.J. O'Malley	39
Relation between Paraffin Isomerisation Capability and Pore Architecture of Large-Pore Bifunctional Zeolites J.A. Martens, M. Tielen, P.A. Jacobs	49
Respective Influences of the Geometric and Chemical Factors in the Conversion of Aromatics over Acidic Zeolites F. Fajula, M. Lambret, F. Figueras	61
Para-Selectivity of Pentasil Zeolites J.-H. Kim, S. Namba, T. Yashima	71

Hydrogen Spillover in the Conversion of n-Alkanes on Zeolites	
K.-H. Steinberg, U. Mroczek, F. Roebner	81
Intermediates in the Formation of Aromatics from Propene and 2-Propanol on H-ZSM-5 Zeolites	
H. Lechert, C. Bezouhanova, C. Dimitrov, V. Nenova	91
Zeolite and Matrix Structures and their Role in Catalytic Cracking	
C.J. Groenenboom	99
Evaluation of Non-Commercial Modified Large Pore Zeolites in FCC	
E. Jacquinot, F. Raatz, A. Macedo, Ch. Marcilly	115
Surface-Metals Interactions in Fluid Cracking Catalysts During the Upgrading of Vanadium Contaminated Gas Oils	
M.L. Occeilli, J.M. Stencel	127
Highly Dispersed Pt and Pt-Cr Clusters in Pentasils and their Activity in Transformations of Lower Alkanes	
E.S. Shpiro, G.J. Tuleuova, V.I. Zaikovskii, O.P. Tkachenko, T.V. Vasina, O.V. Bragin, Kh.M. Minachev	143
Conversion of Light Alkanes into Aromatic Hydrocarbons.	
3. Aromatization of Propane and Propene on Mixtures of HZSM5 and of Ga ₂ O ₃	
N.S. Gnep, J.Y. Doyemet, M. Guisnet	153
Shape-Selective Catalysis in Zeolites with Organic Substrates Containing Oxygen	
R.F. Parton, J.M. Jacobs, D.R. Huybrechts and P.A. Jacobs	163
The Use of Zeolite Catalysts for the Synthesis of Nitrogen-Containing Organic Intermediates	
W.F. Hoelderich	193
Comparison of the Alkylation of Anisole and Phenol with Methanol on Pentasil and Ultrastable Zeolites	
R.F. Parton, J.M. Jacobs, H.v. Ooteghem, P.A. Jacobs	211
Acidity Effect of ZSM-5 Zeolites on Phenol Methylation Reaction	
N.S. Chang, C.C. Chen, S.J. Chu, P.Y. Chen, T.K. Chuang	223

A new Catalyst for MIBK Synthesis - Palladium on ZSM-5 Zeolites P.Y. Chen, S.J. Chu, N.S. Chang, T.K. Chuang, L.Y. Chen	231
Acetylene Hydration on Zeolite Catalysts: An I.R. Spectroscopic Study of the Surface Species Gy. Onyestyák, J. Papp Jr., D. Kallo	241
Preparation and Characterization of Mo-HY Zeolites A. Mészáros-Kis, J. Valyon	251
Propylene Metathesis Reaction over Mo/Y-Zeolites M. Łaniecki	259
Molybdenum-Oxide-Modified Pentasil Zeolites I.M. Harris, J. Dwyer, A.A. Garforth, C.H. McAteer, W.J. Ball	271
Surface and Catalytic Properties of the New Zeolite Type LZ 132 Z. Tvarůžkova, M. Tupá, P. Jiru, A. Nastro, G. Giordano, F. Trifirò . . .	281
PtRh-Doped Zeolites as Three-Way-Catalysts: SIMS Analysis as a Tool for the Selection of Suitable Zeolite Types C. Plog, J. Haas, J. Steinwandel	295
Transformation of Ethanethiol over Zeolites M. Ziółek, P. Decyk, M. Derewiński, J. Haber	305
Study of the Structure and the Redox Reactivity of NaX Encapsulated Co(II)-Phthalocyanine G. Schulz-Ekloff, D. Wöhrle, V. Iliev, E. Ignatzek, A. Andreev	315
Selective Reduction of Nitric Oxide over Zeolite-Supported Iridium Catalyst R. Myrdal, St. Kolboe	327
Metal-Doped Zeolites for Selective Catalytic Reduction of Nitrogen Oxides in Combustion Gases J. Haas, J. Steinwandel, C. Plog	337

Preparation of NiHZSM-5 Catalyst for Isomerization of C₈ Aromatics.

Solid-State Incorporation of Nickel

B. Wichterlová, S. Beran, L. Kubelková, J. Nováková, A. Smiešková,

R. Šebík 347

Formation of Carbocations from C₆ Compounds in Zeolites

I. Kiricsi, H. Förster, G. Tasi 355

An Infrared and Catalytic Study of Isomorphous Substitution in
Pentasil Zeolites

M.F.M. Post, T. Huizinga, C.A. Emeis, J.M. Nanne, W.H.J. Stork 365

Calorimetric Investigation of the Acidity of Dealuminated Y-Type
Zeolites Using Various Basic Probes

A. Auroux, Z.C. Shi, N. Echoufi, Y. Ben Taarit 377

The Acidity of a Modified Faujasite Structure, Zeolite CSZ-1

S. Cartlidge, R.L. Cotterman, M.L. Howes 389

Control of Catalytic Properties of ZSM-5 made by Fast and
Template-free Synthesis

A. Tišler, P. Polanek, U. Gírrbach, U. Müller, K.K. Unger 399

Theoretical Studies of Brønsted Acidity in Zeolites

R. Vetrivel, C.R.A. Catlow, E.A. Colbourn, M. Leslie 409

NMR and IR Studies of Zeolites of the Erionite Type

F. Roebner, K.-H. Steinberg, D. Freude, M. Hunger, H. Pfeifer 421

Specific Platinum Particles Properties in Basic Zeolites

A. de Mallmann, D. Barthomeuf 429

II. SORPTION

Fundamental Research and Modeling for a Technical Process of Selective
Adsorption of Normal Paraffins ("Parex"-Process of DDR) by Zeolite A

W. Schirmer, K. Fiedler, H. Stach, M. Suckow 439

Sorbex Technology for Industrial Scale Separation

J.A. Johnson, A.R. Oroskar 451

Gas Oil Dearomatization by Adsorption

A. Laktić, J. Mühl, I. Beck, M. Beer 469

Modeling Diffusion Pathways in MFI Materials by Time-Resolved
Powder Diffraction Techniques

B.F. Mentzen 477

Measurement of Intracrystalline Diffusivities of HZSM-5 Zeolite at
Higher Temperatures and Predictions of Shape Selectivity

K. Hashimoto, T. Masuda, M. Kawase 485

Measurement of Hydrocarbon Diffusion Coefficient in a Non-Isobaric
Chromatographic Column of Zeolite Crystal Powder

E. Aust, W. Hilgert, G. Emig 495

Molecular Mobility of Benzene and p-Xylene in MFI Type Zeolites

M. Bülow, J. Caro, B. Röhl-Kuhn, B. Zibrowius 505

Diffusion of n-Hexane and 3-Methylpentane in H-ZSM-5 Crystals of
Various Sizes

P. Voogd, H. van Bekkum 519

A Comparative Study by Deuteron Solid State NMR Spectroscopy of the
Dynamics of Benzene and Olefins in Faujasite- and Mordenite-Type Zeolites

B. Boddenberg, R. Burmeister, G. Spaeth 533

Probing the Hydrogen Sorption States in Zeolites A by Infrared
Spectroscopy and Low-Temperature Gas Chromatography Supplemented by
Theoretical Calculations

H. Förster, W. Frede, G. Peters 545

Fourier-Transform Infra-Red Photoacoustic Spectroscopy, A Useful Technique
for the Study of Strongly Physisorbed Molecules

J. Philippaerts, E.F. Vansant, Y.A. Yan 555

Adsorption Properties of Large Crystals of ZSM-5 Zeolite as a Function
of the Degree of Dealumination

J. Kornatowski, M. Rozwadowski, A. Gutsze, K.E. Wisniewski 567

Self-Consistent-Charge X α Calculations of Sorption Complexes of Nitrous Oxide Attached to Transition Metal Occupied Zeolite Clusters	
O. Zakhariyeva-Pencheva, M. Grodzicki, H. Förster	575
IR Study of the Adsorption of Benzene on HZSM5	
A. Jentys, J.A. Lercher	585
Adsorption Separation of Methylanthalene Isomers on X and Y Zeolites	
V. Solinas, R. Monaci, E. Rombi, M. Morbidelli	595
Oxygen Enrichment of Air with Molecular Sieve Zeolites Using the PSA/VSA Technique	
G. Reiß	607
Adsorption and Diffusion of Different Hydrocarbons in MFI Zeolite of Varying Crystallite Size	
D.H. Lin, V. Ducarme, G. Coudurier, J.C. Vedrine	615
High Resolution Sorption Studies of Argon and Nitrogen on Large Crystals of Aluminophosphate AlPO ₄ -5 and Zeolite ZSM-5	
U. Müller, K.K. Unger, D. Pan, A. Mersmann, Y. Grillet, F. Rouquerol, J. Rouquerol	625
A new Potential Large-Scale Application of Zeolites as Fire-Retardant Material	
H.K. Beyer, G. Borbély, P. Miasnikov, P. Rózsa	635

III. ION EXCHANGE AND DETERGENT BUILDING

Industrial Production of Zeolites	
E. Roland	645
Calcium and Magnesium Exchange in Na-A, Na-X and their Precursor Gels	
L.V.C. Rees	661
Fundamentals of Phosphate Substitution in Detergents by Zeolites - Cobuilders and Optical Brighteners	
M.J. Schwuger, M. Liphard	673

Zeolite A - A Builder for Liquid Detergents?

H. Leonhardt, B.-M. Sax 691

Development and Performance of Zeolite-A-Built Non-Phosphate Detergents

H. Upadek, P. Krings 701

Simultaneous Separation of Suspended Solids, Ammonium and Phosphate Ions from Waste Water by Modified Clinoptilolite

J. Olah, J. Papp, A. Mészáros-Kis, Gy. Mucsi, D. Kallo 711

IV. MODIFICATION AND CHARACTERIZATION

Framework and Non-Framework Al Species in Dealuminated Zeolite Y

P.J. Grobet, H. Geerts, M. Tielen, J.A. Martens and P.A. Jacobs . . . 721

Characterization of Calcined FAPO-5

S. Schubert, H.M. Ziethen, A.X. Trautwein, F. Schmidt, H.-X. Li,

J.A. Martens, P.A. Jacobs 735

Control of Pore-Opening Size of Zeolites

Y.F. Chu, C.F. Keweshan, E.F. Vansant 749

A new Structural-Modification Technique for Zeolites:

Chemisorption of Si_2H_6

Y. Yan, J. Verbiest, J. Philippaerts, E.F. Vansant, P. De Hulsters . . . 759

Dealumination of the Zeolites Offretite and Erionite Studied by Solid-State ^{29}Si - and ^{27}Al -MAS NMR Spectroscopy

K.P. Lillerud, M. Stöcker 769

Galliation and ^{18}O -exchange Reactivities of ZSM-5 and ZSM-11

A. Endoh, K. Nishimiya, K. Tsutsumi, T. Takaishi 779

Thermal Decomposition of Ironpentacarbonyl in Zeolites of Faujasite Type.

A Study of the Influence of Argon, H_2 , H_2/CO Gas Mixture and Various Si/Al Ratios Using Mössbauer, ESR and Mass Spectroscopy

H.M. Ziethen, A.X. Trautwein 789

Investigation of Ultra Stable Y by Differential Thermal Analysis after Injection of Water Vapour	
A. Yoshida, K. Inoue	801
Properties of Hydrothermal Low-Damaged 5A and 10X Zeolites	
R. Schöllner, H. Siegel	811
Phase Transformations and Changes in Lattice Parameters of ZSM-5 as a Function of Al Content and Temperature	
G.T. Kokotailo, L. Riekert, A. Tißler	821
The Effect of Sorbates and Elevated Temperatures on the Structures of Some Zeolite Catalysts	
C.A. Fyfe, G.T. Kokotailo, H. Strobl, H. Gies, G.J. Kennedy, C.T. Pasztor, G.E. Barlow	827
The Effect of Temperature and Sorption of p-Xylene and Benzene on the Structure of ZSM-5	
G.T. Kokotailo, L. Riekert, A. Tißler	843
The Characterization of Modified ZSM-5 Catalysts prepared via a Solid-state Reaction for Propane Aromatization	
Y. Yang, X. Guo, M. Deng, L. Wang, Z. Fu	849
Author Index	859
Subject Index	863
Studies in Surface Science and Catalysis (other volumes in the series). . .	869