

Handbook of Heterogeneous Catalysis

Volume 5

**Edited by
G. Ertl, H. Knözinger, J. Weitkamp**

Handbook of Heterogeneous Catalysis

Volume 5

Edited by
G. Ertl, H. Knözinger, J. Weitkamp



Prof. Dr. G. Ertl
Fritz-Haber-Institute
of the Max Planck Society
Dept. Physical Chemistry
Faradayweg 4-6
D-14195 Berlin
Germany

Prof. Dr. H. Knözinger
Ludwig-Maximilian-University
Institute of Physical Chemistry
Sophienstr. 11
D-80333 München
Germany

Prof. Dr. J. Weitkamp
University of Stuttgart
Institute of Technical Chemistry I
Pfaffenwaldring 55
D-70569 Stuttgart
Germany

This book was carefully produced. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Published by
VCH Verlagsgesellschaft mbH, Weinheim (Federal Republic of Germany)

Editorial Director: Dr. Michael Bär
Production Manager: Hans-Jochen Schmitt

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloguing-in-Publication Data:

Handbook of heterogeneous catalysis / ed. by G. Ertl ... Weinheim : VCH
ISBN 3-527-29212-8

Title page:

Photos courtesy G. Ertl (t.l.); BASF AG, Ludwigshafen, Germany (t.r.); Süd-Chemie AG, Munich, Germany (b.l.); J. Weitkamp (b.r.).

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim (Federal Republic of Germany), 1997

Printed on acid-free and chlorine-free paper

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition: Asco Trade Typesetting Ltd., Hong Kong
Printing and bookbinding: Aubin Imprimeur, Poitiers, France
Printed in France

Foreword

Heterogeneous catalysis has not only become the basis of industrial and environmental chemistry during this century, but also its scientific foundation has been developing with ever increasing speed. The *Handbuch der Katalyse* edited by G. M. Schwab in the period 1941 to 1943 and P. H. Emmett's Catalysis series published between 1954 and 1960 were the first accounts summarizing the then available knowledge of catalysis. Many new and now prosperous specialized journals and review series have been founded in the following decades and the emphasis nowadays given to the field of catalysis within the framework of chemical and chemical engineering education is documented by the increasing number of monographs and text books of the science of catalysis that became available in recent years. The present handbook, published at the verge to the 21. century, is the first comprehensive treatise of heterogeneous catalysis that attempts to describe all facets of the field from the scientific fundamentals to the chemical engineering of industrial processes.

Heterogeneous catalysis is an interdisciplinary area that demands the cooperation of scientists from a multitude of different disciplines. It is based on solid state chemistry and physics, materials chemistry and engineering, surface science, analytical chemistry, theoretical chemistry, reaction kinetics and mechanisms, and reaction engineering. For a comprehensive treatise of the science of heterogeneous catalysis hence, the cooperation of more than 200 experts from all over the world was required. These scientists have contributed highly topical articles ranging from catalyst preparation and characterization through the analysis of catalytic conversions at a molecular level to the reaction engineering aspects of industrial catalysis. We are extremely grateful to all authors for their expert work and enthusiastic cooperation. It is obvious that a work like this handbook cannot be com-

posed of entirely uniform chapters. But we trust that each of the contributions conveys the basic principles of the particular subject to the interested readers. It is also clear that the production of a handbook requires a relatively long period of time. As a consequence the most recent literature could not be covered in all chapters. We believe that this is not too severe a disadvantage because a handbook article is in fact meant to describe generally accepted principles rather than providing an encyclopedic review of a topic. However, we also understand that those authors who submitted their contributions at a very early stage may be disappointed by the time it took to appear in print. We can only apologize for this and call on their understanding for the amount of work that had to be invested by the editors and the publisher to ultimately produce this handbook.

During the planning phase as well as during the preparation of the handbook we have been very fortunate to have extremely stimulating discussions with and expert advice from many colleagues of which we want to mention only a few, namely A. Baiker, P. Courty, E. Gallei, B. C. Gates, K. Kochloefl, J. A. Moulijn, R. Schlögl. We gratefully acknowledge their valuable assistance. Last but not least we are grateful to our partners at VCH, Dr. Mager and Dr. Bär, and to our desk-editor, Dr. Bew, for their highly competent and professional cooperation.

It is our hope that this Handbook of Heterogeneous Catalysis may promote the further development of the field, that it may stimulate the mutually beneficial cooperation between various relevant disciplines, and that it may attract young scientists to devote their interest to a fascinating, interdisciplinary and future-oriented area.

G. Ertl
H. Knözinger
J. Weitkamp

book: to Professor S F A Kettle, Professorial Fellow at the University of East Anglia, for reading the work in manuscript and for making a number of helpful suggestions; to Professor J R Jones, Head of the Department of Chemistry at the University of Surrey, for a careful reading of the book in proof, thereby eliminating some unforced errors; and finally to the publishers for their assistance and cooperation in bringing the work to a state of completion. Any infelicities that might remain are the sole responsibility of the author.

Mark Ladd

Note added at proof

The reader is cautioned to distinguish carefully between the italic ‘vee’ and the Greek *nu*. An example of their occurrence together is in equation (A3.5), p. 458, where the first of these characters is a ‘vee’.

PHYSICAL CONSTANTS AND OTHER NUMERICAL DATA

These data have been selected, or derived, from the compilation of E R Cohen and B N Taylor, *J. Phys. Chem. Ref. Data* (1988) **17**, 1795–1803; the values are reported in SI units. The figures in parentheses after each value represent the standard deviation to be applied to its last two digits; the values of c and ϵ_0 are *defined*. Although the data are presented here with their full precision, we shall rarely need to employ more than about the first four or five significant figures.

Speed of light in a vacuum	c	2.99792458	$\times 10^8$	m s^{-1}
Permittivity of a vacuum	ϵ_0	8.854187817	$\times 10^{-12}$	F m^{-1}
Permeability of a vacuum	μ_0	4π	$\times 10^{-7}$	H m^{-1}
Planck constant	h	6.6260755(40)	$\times 10^{-34}$	J Hz^{-1}
Elementary charge	e	1.60217733(49)	$\times 10^{-19}$	C
Avogadro constant	L	6.0221367(36)	$\times 10^{23}$	mol^{-1}
Atomic mass unit	u	1.6605402(10)	$\times 10^{-27}$	kg
Bohr magneton	μ_B	9.2740154(31)	$\times 10^{-24}$	J T
Rydberg constant	R_∞	1.0973731534(13)	$\times 10^7$	m^{-1}
Rydberg constant for hydrogen	R_H	1.0967758772(13)	$\times 10^7$	m^{-1}
Bohr radius	a_0	5.29177249(24)	$\times 10^{-11}$	m
Boltzmann constant	k_B	1.380658(12)	$\times 10^{-23}$	J K^{-1}
Molar gas constant	R	8.314510(70)	$\text{J K}^{-1} \text{mol}^{-1}$	
		0.0820577(7)	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$	
Molar volume of ideal gas at 273.15 K and 101 325 Pa	V_m	22.41410(19)	$\times 10^{-3}$	$\text{m}^3 \text{mol}^{-1}$
Compton wavelength (electron)	λ_c	2.42631058(22)	$\times 10^{-12}$	m
Rest mass of electron	m_e	9.1093897(54)	$\times 10^{-31}$	kg
Rest mass of proton	m_p	1.6726231(10)	$\times 10^{-27}$	kg
Rest mass of neutron	m_n	1.6749286(10)	$\times 10^{-27}$	kg
Reduced mass of proton and electron pair	μ	9.1044313(54)	$\times 10^{-31}$	kg
Faraday	\mathcal{F}	9.6485309(29)	$\times 10^3$	C mol^{-1}
Ice-point temperature	T_{ice}	273.1500(01)		K

(Farad $\text{F} = \text{C V}^{-1}$; Tesla $\text{T} = 10^4 \text{ G (gauss)} = \text{J C}^{-1} \text{m}^{-2} \text{s}$; Henry $\text{H} = \text{J C}^{-2} \text{s}^2$)

Some of the more important additional units are listed below.

Length

1 Å (ångström unit) = $10^{-10} \text{ m} = 0.1 \text{ nm}$

Energy

$$1 \text{ eV (electronvolt)} \equiv 1.60217733(49) \times 10^{-19} \text{ J}$$

$$1 \text{ cal (calorie)} = 4.184 \text{ J} \equiv 96.485309(29) \text{ kJ mol}^{-1}$$

$$1 \text{ cm}^{-1} \equiv 1.9864673(4) \times 10^{-23} \text{ J} \equiv 1.1962568(5) \times 10^{-2} \text{ kJ mol}^{-1}$$

Pressure

$$1 \text{ atm (atmosphere)} = 101\,325 \text{ Pa (N m}^{-2}\text{)} = 760 \text{ Torr} \equiv 760 \text{ mmHg}$$

Dipole moment

$$1 \text{ D (debye)} = 3.33564 \times 10^{-30} \text{ C m}$$

Contents

4	Organic Reactions 2123	
4.1	Alkylation of Aromatics 2123	
4.1.1	Introduction 2123	
4.1.2	Alkylation of Benzenes, Phenols and Anilines 2124	
4.1.2.1	Acid Catalyzed Synthesis of Alkylbenzenes 2124	
4.1.2.2	Base Catalyzed Synthesis of Alkylbenzenes 2131	
4.1.2.3	Alkylphenols 2131	
4.1.2.4	Alkylanilines 2132	
4.1.3	Alkylation of Binuclear Aromatics 2133	
4.1.3.1	Alkylation of Naphthalene 2133	
4.1.3.2	Alkylation of Biphenyl 2134	
4.2	Isomerization and Transalkylation of Alkylaromatics 2136	
4.2.1	Introduction 2136	
4.2.2	Xylene Isomerization 2136	
4.2.2.1	Fundamental Aspects of Isomerization 2136	
4.2.2.2	Xylene Isomerization Processes 2137	
4.2.3	Toluene Disproportionation 2138	
4.2.4	Selective Toluene Disproportionation 2138	
4.2.5	Selective Ethylbenzene Disproportionation 2139	
4.3	Dehydrogenation Reactions 2140	
4.3.1	Dehydrogenation of Alkanes 2140	
4.3.1.1	Conceptual Approach to the Dehydrogenation Reaction 2140	
4.3.1.2	Catalytic Systems 2142	
4.3.1.3	Kinetics and Mechanism 2146	
4.3.1.4	Reactor Engineering 2146	
4.3.1.5	Commercial Processes for Low Alkanes 2147	
4.3.1.6	Dehydrogenation of Other Alkanes 2149	
4.3.1.7	Future Developments 2150	
4.3.2	Dehydrogenation of Ethylbenzene 2151	
4.3.2.1	Introduction 2151	
4.3.2.2	Thermodynamics 2152	
4.3.2.3	Byproducts 2152	
4.3.2.4	Effects of Diluting Agents, Especially Steam 2152	
4.3.2.5	Catalysts 2153	
4.3.2.6	Kinetics 2156	
4.3.2.7	Application of Membrane Reactors 2156	
4.3.2.8	Dehydrogenation of Ethylbenzene-Related Hydrocarbons 2157	
4.3.2.9	Industrial Processes and Commercial Catalysts 2157	
4.3.3	Dehydrogenation of Alcohols 2159	
4.3.3.1	Scope, Thermodynamics and Common Features 2159	
4.3.3.2	Catalysts 2160	
4.3.3.3	Kinetics 2161	
4.3.3.4	Mechanism 2162	
4.3.3.5	Industrial Applications 2163	
4.4	Hydrogenation Reactions 2165	
4.4.1	Selective Hydrogenation of Hydrocarbons 2165	
4.4.1.1	Introduction 2165	
4.4.1.2	Kinetics and Mechanisms of Selective Hydrogenation of Alkadienes and Cycloalkadienes 2165	
4.4.1.3	Kinetics and Mechanism of the Selective Hydrogenation of Ethyne and other Alkynes 2172	
4.4.1.4	Effect of Carbon Monoxide in Selective Hydrogenation 2174	
4.4.1.5	Comparison of Selective Hydrogenation on Palladium and Platinum 2175	
4.4.1.6	Particle Size Effect 2176	
4.4.1.7	Role of Mass Transfer in Selective Hydrogenation 2178	
4.4.1.8	Partial Hydrogenation of Benzene to Cyclohexene 2181	
4.4.1.9	Selective Hydrogenation Processes in the Downstream Treatment of Naphtha Cracking 2182	
4.4.2	Selective Hydrogenation of Functionalized Hydrocarbons 2186	
4.4.2.1	Introduction 2186	
4.4.2.2	General Considerations 2186	
4.4.2.3	Guidelines for the Selection of a Catalytic Hydrogenation System 2190	
4.4.2.4	Chemoselectivity in Catalytic Hydrogenation 2195	
4.4.2.5	Reviews on Selected Topics 2195	
4.4.3	Regioselective Hydrogenations 2209	
4.4.3.1	Definitions and Scope 2209	
4.4.3.2	General Principles Governing Regioselectivity 2210	
4.4.3.3	Regioselective Catalytic Hydrogenations 2212	
4.4.3.4	Concluding Remarks 2220	
4.4.4	Fat Hydrogenation 2221	
4.4.4.1	Introduction 2221	
4.4.4.2	Hydrogenation of Double Bonds 2221	
4.4.4.3	Catalysts 2223	
4.4.4.4	Fat and Fatty Acid Hardening 2224	
4.4.4.5	Fatty Alcohols 2227	

- 4.5 Hydroformylation 2231
 - 4.5.1 General Remarks 2231
 - 4.5.1.1 Cobalt Catalysts 2232
 - 4.5.1.2 Rhodium Catalysts 2232
 - 4.5.1.3 Catalysts other than Cobalt and Rhodium Compounds 2233
 - 4.5.1.4 Reaction Mechanism 2233
 - 4.5.2 Hydroformylation with Immobilized Metal Complex Catalysts 2234
 - 4.5.2.1 Supported Metal Complex Catalysts 2234
 - 4.5.2.2 Anchored Metal Complex Catalysts 2235
 - 4.5.3 Heterogeneous Metal Catalysts 2241
- 4.6 Selective Oxidations 2244
 - 4.6.1 Epoxidation Catalysis Using Heterogeneous Catalysts 2244
 - 4.6.1.1 Introduction 2244
 - 4.6.1.2 Redox Catalysis 2245
 - 4.6.1.3 Oxygen Adsorption and Reactivity 2246
 - 4.6.1.4 Acid-Base Catalysis 2249
 - 4.6.1.5 Chemistry of Ethylene Epoxidation Catalysis 2249
 - 4.6.1.6 Epoxidation of Propylene 2251
 - 4.6.2 Oxidation of Hydrocarbons 2253
 - 4.6.2.1 Introduction 2253
 - 4.6.2.2 Electrophilic and Nucleophilic Oxidation 2253
 - 4.6.2.3 Selectivity in Hydrocarbon Oxidation 2256
 - 4.6.2.4 Oxidative Dehydrogenation of Alkanes 2258
 - 4.6.2.5 Oxidative Dehydrogenation and Oxidation of Alkenes 2259
 - 4.6.2.6 Oxidative Dehydrogenation of Alkylaromatics 2263
 - 4.6.2.7 Selective Oxidation of Aromatic Hydrocarbons 2265
 - 4.6.2.8 Oxidation of Butane to Maleic Anhydride 2268
 - 4.6.2.9 Structure Sensitivity of Oxidation Reactions 2269
 - 4.6.2.10 Monolayer Oxide Catalysts 2271
 - 4.6.2.11 Dynamics of Oxide Surfaces in Oxidation Reactions 2272
- 4.6.3 Oxidative Dehydrogenation of Alcohols to Aldehydes, Ketones, and Carboxylic Acids 2274
 - 4.6.3.1 Introduction 2274
 - 4.6.3.2 Fundamentals 2274
 - 4.6.3.3 Catalysis on Metals 2275
 - 4.6.3.4 Catalysis on Oxides 2279
- 4.6.4 Wacker Chemistry with Solid Catalysts 2284
 - 4.6.4.1 The Overall Wacker Chemical Cycle 2284
 - 4.6.4.2 Industrial Production of Acetaldehyde via Wacker Chemistry 2285
 - 4.6.4.3 Related Homogeneous Wacker Chemistry 2286
 - 4.6.4.4 Mechanism of Homogeneous Wacker Chemistry 2287
 - 4.6.4.5 Zeolite-Heterogenized Wacker Chemistry 2289
 - 4.6.4.6 Pd and V Combined as Wacker Elements in Heteropolyanion Catalysts 2292
 - 4.6.4.7 Pd/V Couples in Heterogeneous Wacker Catalysis 2294
- 4.6.5 Oxyacetylation: Vinyl Acetate from Ethylene 2295
 - 4.6.5.1 Introduction 2295
 - 4.6.5.2 Properties, Use, and Economics of Vinyl Acetate 2296
 - 4.6.5.3 Liquid-Phase Process 2296
 - 4.6.5.4 Vapor-Phase Process 2296
- 4.6.6 Ammoxidation 2302
 - 4.6.6.1 Introduction 2302
 - 4.6.6.2 Ammoxidation of Alkenes 2302
 - 4.6.6.3 Ammoxidation of Substituted Alkenes 2321
 - 4.6.6.4 Ammoxidation of Aromatics 2322
 - 4.6.6.5 Ammoxidation of Heteroaromatics 2323
 - 4.6.6.6 Ammoxidation of Alkanes 2323
- 4.6.7 Ammoxidation 2326
 - 4.6.7.1 Introduction 2326
 - 4.6.7.2 Cyclohexanone Ammoxidation to Cyclohexanone Oxime 2326
 - 4.6.7.3 ENICHEM Ammoxidation Process 2328
- 4.6.8 Phenol Hydroxylation and Related Oxidations 2329
 - 4.6.8.1 Introduction 2329
 - 4.6.8.2 Early Industrial Processes for Diphenols 2329
 - 4.6.8.3 Phenol Hydroxylation Processes Using Homogeneous Catalysis 2330
 - 4.6.8.4 Phenol Hydroxylation Process Using Heterogeneous Catalysis 2331
- 4.7 Amination Reactions 2334
 - 4.7.1 Amination of Alcohols 2335
 - 4.7.1.1 Aliphatic Alcohols 2335
 - 4.7.1.2 Amino Alcohols, Polyalcohols 2338
 - 4.7.1.3 Amination of Phenols 2339
 - 4.7.2 Amination of Carbonyl Compounds (Reductive Alkylation) 2339
 - 4.7.2.1 Reaction Mechanism 2340
 - 4.7.2.2 Catalysts, Reaction Conditions 2340
 - 4.7.2.3 Selective Synthesis of Primary, Secondary or Tertiary Amines 2340
 - 4.7.2.4 Amination with Bifunctional Amines or Carbonyl Compounds 2341
 - 4.7.2.5 Heterocyclic Ring Formation 2341
 - 4.7.2.6 Stereoselectivity 2342
 - 4.7.3 Amination of Carboxylic Acids and Esters 2342
 - 4.7.4 Amination of Alkenes 2343
 - 4.7.5 Amination of Ethers 2344
 - 4.7.6 Amination of Halogen Compounds 2344
 - 4.7.7 Amination of Hydrocarbons 2345
 - 4.7.8 Amination of Carbon Monoxide and Carbon Dioxide 2346
- 4.8 Halogenation Reactions 2348
 - 4.8.1 Introduction 2348
 - 4.8.2 Halogenation and Halogenating Agents 2348
 - 4.8.3 Halogenation Over Solid Heterogeneous Catalysts 2349
 - 4.8.3.1 Fluorination 2349
 - 4.8.3.2 Chlorination 2349
 - 4.8.3.3 Bromination 2355

- 4.8.3.4 Iodination 2355
- 4.8.4 Conclusion 2355
- 4.9 Acylation of Aromatics 2358
- 4.9.1 Introduction 2358
- 4.9.2 Catalysts 2358
- 4.9.3 Substrates 2359
- 4.9.4 Acylating Agents 2359
- 4.9.5 Reaction Mechanism 2359
- 4.9.6 Acylation Using Aluminosilicate Catalysts 2360
- 4.9.7 Conclusions 2363
- 4.10 Nucleophilic Aromatic Substitution Reactions 2364
- 4.10.1 Introduction 2364
- 4.10.2 Aromatic Substitutions with Oxygen Nucleophiles 2366
- 4.10.3 Aromatic Substitutions with Nitrogen Nucleophiles 2366
- 4.10.4 Nature of Copper-Catalyzed Substitution Pathway 2367
- 4.10.5 Conclusions 2369
- 4.11 Elimination and Addition Reactions 2370
- 4.11.1 Scope and Thermodynamics 2370
- 4.11.2 Common Features 2371
- 4.11.2.1 Mechanism 2371
- 4.11.2.2 Influence of Structure on Rate 2373
- 4.11.2.3 Direction of Elimination and Addition 2374
- 4.11.3 Catalysts 2375
- 4.11.3.1 Surface Structure 2375
- 4.11.3.2 Stop Effect 2375
- 4.11.3.4 Poisoning 2376
- 4.11.4 Kinetics 2376
- 4.11.5 Applications 2377
- 4.11.5.1 Dehydrochlorination 2377
- 4.11.5.2 Dehydration 2378
- 4.11.5.3 Hydrochlorination 2378
- 4.11.5.4 Hydration 2378
- 4.11.5.5 Addition of Alcohols and Organic Acids to Alkenes 2379
- 4.11.5.6 Alkylation and Dealkylation 2379
- 4.12 Oligomerization and Metathesis 2380
- 4.12.1 Oligomerization 2380
- 4.12.1.1 Introduction 2380
- 4.12.1.2 Thermodynamics 2381
- 4.12.1.3 Mechanism of Alkene Oligomerization 2382
- 4.12.1.4 Catalysts for Alkene Oligomerization 2382
- 4.12.1.5 Conclusion 2386
- 4.12.2 Alkene Metathesis 2387
- 4.12.2.1 Introduction 2387
- 4.12.2.2 Applications 2387
- 4.12.2.3 Reaction Mechanism 2390
- 4.12.2.4 Solid Catalysts 2390
- 4.12.2.5 Catalyst Deactivation 2398
- 4.12.2.6 Kinetics 2398
- 4.12.2.7 Concluding Remarks 2399
- 4.13 Polymerization Reactions 2400
- 4.13.1 Phillips Process for Ethylene Polymerization 2400
- 4.13.1.1 Introduction 2400
- 4.13.1.2 Process 2401
- 4.13.1.3 Catalyst 2401
- 4.13.1.4 Polymerization 2402
- 4.13.1.5 Molecular Weight Control 2402
- 4.13.1.6 Catalyst Porosity 2403
- 4.13.1.7 Branching 2403
- 4.13.1.8 Catalyst Modifications 2404
- 4.13.1.9 Future Developments 2404
- 4.13.2 Ziegler-Natta Polymerization 2405
- 4.13.2.1 Introduction 2405
- 4.13.2.2 Conventional (Heterogeneous) Ziegler-Natta Catalysts 2405
- 4.13.2.3 Metallocene Catalysts 2411
- 4.14 Enantioselective Catalysts and Reactions 2422
- 4.14.1 Introduction 2422
- 4.14.1.1 Background and Scope 2422
- 4.14.1.2 Definitions 2422
- 4.14.1.3 Principles of Enantioselective Catalysis 2422
- 4.14.1.4 Historical Developments [10] 2423
- 4.14.1.5 Search for New Enantioselective Reactions and Catalysts 2423
- 4.14.2 Tartaric Acid (Tartrate)-Modified Nickel Hydrogenation Catalysts and Related Systems 2423
- 4.14.2.1 General Aspects 2423
- 4.14.2.2 Important Parameters that Affect Catalytic Performance 2423
- 4.14.2.3 Mechanistic Investigations and Hypotheses for Enantioselection 2425
- 4.14.3 Cinchona-Modified Platinum Hydrogenation Catalysts and Related Systems 2425
- 4.14.3.1 General Aspects 2425
- 4.14.3.2 System Parameters Influencing Catalytic Behavior 2426
- 4.14.3.3 Reaction Pathway, Mass Transfer, and Kinetic Modeling 2428
- 4.14.3.4 Models for Enantiodifferentiation 2429
- 4.14.3.5 Novel Enantiodifferentiating Systems Based on Modified Platinum 2431
- 4.14.4 Miscellaneous Chiral Catalysts 2432
- 4.14.4.1 Modified Metallic Catalysts 2432
- 4.14.4.2 Modified Metal Oxides and Chiral Metal Salts 2432
- 4.14.4.3 Chiral Polymers 2433
- 4.14.5 Synthetic and Commercial-Scale Applications of Solid Catalysts 2433
- 4.14.5.1 Hydrogenations with Ni Tartrate and Pt Cinchona Catalysts 2433
- 4.14.5.2 Addition to C=C Bonds 2434
- 4.15 Biocatalytic Reactions with Immobilized Enzymes 2436
- 4.15.1 Introduction 2436
- 4.15.2 Reactors for Immobilized Enzymes 2437
- 4.15.3 Characterization of Immobilized Enzymes 2439
- 4.15.4 Selected Examples for Reactions Using Immobilized Enzymes 2441
- 4.15.4.1 Production of L-Amino Acids Using Aminoacylase 2441

- 4.15.4.2 Production of 6-Aminopenicillanic Acid and 7-Amino-cephalosporanic Acid Using Amidases 2442
- 4.15.4.3 Production of High-Fructose Corn Syrup Using Glucose Isomerase 2442
- 4.15.4.4 Production of Acrylamide by Means of Nitrile Hydratase 2443
- 4.15.4.5 Production of Glycerol-3-phosphate Using Glycerol Kinase 2443
- 4.15.4.6 Production of (2*R*,3*S*)-Methyl-*p*-methoxy-phenylglycidate Using a Lipase 2444
- 4.15.4.7 Miscellaneous Processes Using Immobilized Enzymes 2445
- 4.15.5 Enzyme Suppliers 2445
- Index 2449

4 Organic Reactions

-
- 4.1 Alkylation of Aromatics
 - 4.2 Isomerization and Transalkylation of Alkylaromatics
 - 4.3 Dehydrogenation Reactions
 - 4.4 Hydrogenation Reactions
 - 4.5 Hydroformylation
 - 4.6 Selective Oxidations
 - 4.7 Amination Reactions
 - 4.8 Halogenation Reactions
 - 4.9 Acylation of Aromatics
 - 4.10 Nucleophilic Aromatic Substitution Reactions
 - 4.11 Elimination and Addition Reactions
 - 4.12 Oligomerization and Metathesis
 - 4.13 Polymerization Reactions
 - 4.14 Enantioselective Catalysts and Reactions
 - 4.15 Biocatalytic Reactions with Immobilized Enzymes
-

4.1 Alkylation of Aromatics

J. S. BECK AND W. O. HAAG

4.1.1 Introduction

The alkylation of aromatic compounds is widely used in the large scale synthesis of petrochemicals, and a great variety of fine chemicals and intermediates. The essential feature of the reaction consists in the replace-

ment of a hydrogen atom of an aromatic compound by an alkyl group derived from an alkylating agent. If the replaced hydrogen is on the aromatic ring, the reaction is an electrophilic substitution and is carried out in the presence of an acid catalyst; if a hydrogen on the side chain of an aromatic is replaced, base catalysts or radical conditions are required. The nature of the alkylation product thus depends on the catalyst used (Fig. 1). The overwhelming majority of commercial alkylations are acid catalyzed. At least three commercial processes are using base-catalyzed alkylations of aromatics.

In view of the great theoretical and practical interest in alkylation, there are several review articles which provide valuable information on both mechanistic and synthetic issues [1-6].

Acid catalysts used for alkylation of aromatic hydrocarbons are Brønsted acids containing acidic protons. These include acidic halides such as aluminum chlorides and boron fluoride, acidic oxides and zeolites, protonic acids, especially sulfuric acid, hydrofluoric acid, and phosphoric acid, and organic cation exchange resins.

It has been established that acidic halides, which are typically Lewis acids, have little or no activity for alkylation when used in a pure state. They are activated by the inadvertent presence or addition of small concentrations of cocatalysts or promoters, such as water, alcohols or hydrogen halides. These cocatalysts interact with the Lewis acids to generate actual or potential Brønsted acids [7]. Metal halides, usually called Friedel-Crafts catalysts, have been used extensively for aromatics alkylation in the past; they are highly active and allow the reactions to be carried out in liquid phase at low temperatures. However, for large scale applications they are being rapidly replaced by solid alkylation catalysts, especially by crystalline aluminosilicates, i.e. zeolites. These are much more desirable for environmental reasons, are noncorrosive, and offer additional advantages for controlling the selectivity via their shape-selective properties. They are less active than the typical Friedel-Crafts catalysts and are, therefore, applied at higher temperature and mostly in the gas phase. This is, however, not necessarily a disadvantage. Alkylations are usually exothermic reactions. For

References see page 2135

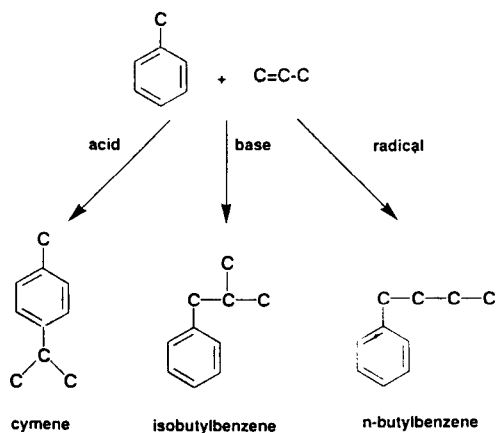


Figure 1. Effect of catalyst type on major products from the reaction of toluene with propylene.

example, the synthesis of ethylbenzene from benzene and ethylene occurs with a reaction enthalpy of -113 kJ mol^{-1} . Operation at high temperature allows much of this heat to be economically recovered, in contrast to low temperature synthesis.

Alkylating agents are alkyl halides, alcohols and ethers, alkenes, alkynes and dienes. Large scale alkylations use alkenes almost exclusively; they do not pose a byproduct problem, and are inexpensively available from thermal or catalytic cracking processes. Alkanes are used in one commercially developed process, M-forming [8]. It combines in situ alkene production via alkane cracking with simultaneous alkylation of aromatics by the alkenes.

Section 4.1.2 discusses general mechanistic and kinetic principles of the alkylation of mononuclear alkylbenzenes, and describes the synthesis of the most important alkylbenzenes, phenols and anilines. Section 4.1.3 covers the synthesis of binuclear aromatics, i.e. alkylated naphthalenes and biphenyls. Related articles are Sections B.4.11 and B.4.12.1.

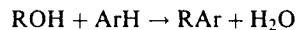
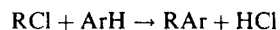
4.1.2 Alkylation of Benzenes, Phenols and Anilines

The introduction of alkyl groups into mononuclear aromatic compounds is a reaction of broad scope and versatility. It can be applied to many aromatic hydrocarbons and heterocyclic compounds and their substituted derivatives. Extensive studies have established many mechanistic principles of general utility that constitute one of the cornerstones of theoretical organic chemistry. The alkylation reactions of benzenes, phenols and anilines display qualitative differences, which justifies treating them separately.

4.1.2.1 Acid Catalyzed Synthesis of Alkylbenzenes

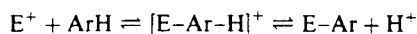
A General Aspects

The net reactions in the alkylation of an aromatic hydrocarbon, ArH , with alkyl halides, alcohols and alkenes are:



a Mechanistic Considerations

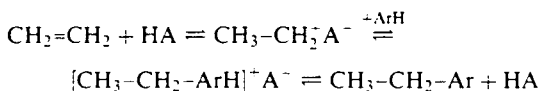
The mechanistic details of alkylation involve first the interaction of the alkylating agent with the acid catalyst to form an activated electrophile, E^+ , which adds to the aromatic ring acting as a nucleophile, followed by proton elimination:



1

where 1 is known as a Wheland intermediate.

In the case of benzene alkylation by ethylene with a Brønsted acid catalyst HA , the reaction sequence can be written as



The activated species, $\text{CH}_3-\text{CH}_2^+\text{A}^-$, is often written for simplicity's sake as a free carbenium ion, $\text{CH}_3-\text{CH}_2^+$. This shorthand notation is very convenient, although in the majority of cases the activated species in its ground state exists as a more or less tight ion pair, and may have a considerable degree of covalent bonding between the carbocation and the anion. As a result, the nature of the anion has a considerable influence on the reactivity and selectivity of the alkylating agent. The completely free carbenium ion is never obtained, although it can be considered to be qualitatively representative of the transition state of the reaction. Therefore, its relative stability is still important for determining the rates and products of alkylation. For example, the GaBr_3 -catalyzed alkylation of benzene with *n*-propylbromide yields mostly *i*-propylbenzene, as a result of a rearrangement of the *n*-propyl cation to the more stable *i*-propyl cation prior to reaction; however, at low temperature *n*-propylbenzene results when *n*-propyl chloride is used. In the alkylation with alkenes over solid catalysts, products derived from the most stable carbenium are usually obtained. Thus, propylene and benzene yield isopropylbenzene with phosphoric acid on kieselguhr ("solid phosphoric acid") and with large pore zeolites. With the medium pore zeolite ZSM-5, isopropylbenzene is also the kinetically preferred primary prod-

Table 1. Relative rates and orientation of entering alkyl groups in the alkylation of toluene [9].

Alkyl group	Relative rate	Isomer distribution (%)			$2 \times \text{para/meta}$
		<i>para</i>	<i>meta</i>	<i>ortho</i>	
Methylation	1.0	26	14	60	3.7
Ethylation	13.7	34	18	48	3.8
Isopropylation	20 000	36.5	21.5	42	3.4
<i>t</i> -Butylation	—	93	7	0	26.6

uct, but at increased temperature and longer contact time, isomerization to an equilibrium mixture of *n*-propyl- and *i*-propylbenzene (ratio 1.8:1) occurs. Such secondary product isomerizations can occur with many catalysts under severe operating conditions.

Large linear alkenes such as 1-octene, usually yield products with aromatics attached to every secondary carbon atom of the alkene chain, indicative of double bond isomerization in the alkene prior to alkylation. This finding, and exceptions to it, will be discussed in subsection 4.1.2.1 I.

b Kinetic Considerations

The effect of alkylating agent nature on the rate of Friedel-Crafts alkylation is illustrated in Table 1, column 2. Isopropylation occurs about 1460 times faster than ethylation. Similar data have been obtained in the REY zeolite-catalyzed alkylation of benzene with alkenes at 100°C where propylene reacted about 300 times faster than ethylene. These data are in directional agreement with the greater ease of protonation of the more substituted alkenes, as indicated by their proton affinities [10]:

ethylene 681 kJ mol⁻¹

propylene 747 kJ mol⁻¹

i-butene 803 kJ mol⁻¹

They reflect the greater rate of formation and reactivity of the corresponding carbenium ions, which follow the sequence primary < secondary < tertiary.

c Substrate Selectivity

The substrate selectivity, i.e. the relative reactivity of various aromatics, is governed by their nucleophilicity and their ability to delocalize the positive charge in the Wheland intermediate **1** by inductive and resonance effects. For instance, methyl substituents in benzene increase the rate, and phenol reacts many orders of magnitude faster than benzene.

It is, therefore, surprising that it is difficult to alkylate phenol over conventional acid catalysts with ethylene to obtain ethylphenol. This reaction requires a temperature above 400°C, whereas propylene reacts at 250°C with phenol, and benzene can be much more

easily ethylated than phenol. This result can be understood by considering the kinetic consequences of the reaction mechanism, which requires interaction of the alkene with the acid site and reaction of the activated alkene with the nonactivated aromatic. In this Eley-Rideal mechanism, the aromatic should not, or only weakly, compete with the alkene for the sites. Although true for benzene, this is not always true for the much more basic phenol. Strong chemisorption of phenol almost completely inhibits the activation of the weakly basic ethylene, but not that of the more basic propylene and isobutylene.

d Positional Selectivity

Positional selectivity, such as the distribution of *ortho*, *meta* and *para* isomers obtained in the alkylation of toluene, depends on the reactivity of the electrophile and on steric factors. The data in Table 1 show that the relative amount of *ortho* isomer drops as the alkylating agent increases in size. The large *t*-butyl group cannot be introduced next to a methyl group, for instance in toluene or *m*-xylene. *p*-Xylene cannot be alkylated by *i*-butene. It has been assumed that this is a result of steric retardation of the rate of alkylation, which is a kinetic effect. However, detailed studies have shown that the Wheland intermediate is not sterically constrained and forms readily, but that the resulting hydrocarbon is unstable relative to the reactants, and *ortho-t*-butylation is not observed for thermodynamic reasons.

The *para:meta* ratios listed in the last column of Table 1 are corrected for the number of available positions in toluene. The numbers reflect the relative reactivity of the *para* and *meta* position in toluene towards an electrophile. They can be correlated with the overall reactivity of toluene versus benzene by the Brown selectivity relationship [11], which results directly from a Hammett free energy relationship [12]. Such correlations are derived from electronic factors and are valid only in the absence of steric constraints. They are observed in homogeneous solution or with amorphous and large pore zeolite catalysts, for example in zeolite Y [13]. When alkylations are performed in the micropores of medium pore zeolite catalysts,

Table 2. Influence of zeolite catalyst on the product distribution during toluene alkylation with ethylene for a toluene:ethylene molar ratio of 2.4 [19].

Parameter	Zeolite type				
	Beta ^a		ZSM-5 ^b		
Reaction temperature (°C)	262	240	403	355	313
Conversion (%)	22.3	16.8	20.4	18.4	7.8
Sum of ethyltoluenes	70.0	70.6	98.2	96.5	94.4
Sum of diethyltoluenes	30.0	29.4	1.8	3.5	5.6

^a Large 12-ring pore, diameter 0.64 × 0.76 nm.^b Medium 10-ring pore, diameter 0.53 × 0.56 nm.

significant and industrially very important deviations from these rules can be obtained. These result from steric control of the reaction transition state [14] or from differences in the diffusion rates of the various product molecules [15]. Recent reviews of the underlying principles and applications of shape selective catalysis are available [16, 17], and specific applications are shown below for individual compounds.

e Depolyalkylation

When higher alkenes are used as alkylating agents that are easily cracked, intact alkylation is sometimes difficult to achieve. For example, the reaction of propylene tetramer with benzene yields the expected C₁₂ alkylbenzene, whereas the isobutene dimer 2,4,4-trimethylpentene yields only *t*-butylbenzene. Thus, the high rate of cracking of this particular C₈ alkene, which contains quaternary carbon atoms, is faster than its rate of alkylation with benzene. If the rate of alkylation is increased by using toluene instead of benzene, some intact alkylation is possible at -50°C. With the highly reactive phenol as a substrate, *t*-octylphenol is readily obtained [3].

f Monoalkylation and Polyalkylation

In many cases, the desired product is that resulting from the introduction of only one alkyl group, i.e. the monoalkylation product. However, the mechanistic considerations discussed above indicate that, for benzene alkylation, consecutive alkylation of the primary product should occur with a greater rate than the first alkylation step. Thus, there is a kinetic bias in favor of polyalkylation. For example, in methanol conversion with ZSM-5 zeolite catalyst, tri- and tetramethyl benzene are the predominant primary products at moderate conversions and temperature, resulting from increasingly rapid methylation, in the sequence benzene < toluene < xylene [18].

Several means exist to maximize the yield of the primary, monoalkylated product. The obvious way is to work with a large molar excess of the aromatic over the alkylating agent. However, this is economically feasible

only for valuable specialty chemicals, in view of the high cost of recovering the excess aromatic. Working under conditions where the aromatic feed and the alkylation products undergo equilibration, such as high temperature, can eliminate the kinetic bias to yield the thermodynamically favored product.

For moderate temperature alkylation, the process of catalytic distillation can provide high yields of the monoalkylation product. This process combines alkylation with continuous withdrawal from the reaction zone of the primary alkylation product, in a so-called cat-still reactor.

The possibility of applying shape-selective zeolites as catalysts provides an economically attractive route for monoalkylate optimization. For example, the data for toluene ethylation in Table 2 indicate that the large-pore zeolite beta produces about 70% ethyltoluene and 30% diethyltoluene, whereas the medium pore ZSM-5 yields over 94% ethyltoluene and less than 6% diethyltoluene [19].

B Ethylbenzene

Ethylbenzene (EB) is predominantly used as a precursor for styrene monomer. With the growth in demand of styrene-containing polymers since the late 1940s, the need for ethylbenzene has increased sharply; the yearly production capacity now exceeds 17 × 10⁶ t. In view of its importance as a major petrochemical, the technical production aspects of ethylbenzene have been examined in detail [20–22]. EB is predominantly produced by the alkylation of benzene with ethylene. The reaction is highly exothermic with a reaction enthalpy of -113 kJ mol⁻¹. Being an indigenous resource, ethanol is used in India as the alkylating agent. An alternative source of ethylbenzene is the C₈ aromatic extract from reformat gasoline, where it is present to about 12–18% in admixtures with xylenes. A distillative EB recovery process from this source was developed in 1957, which provided up to 10% of the total ethylbenzene production. In view of the closeness of boiling points, energy-intensive superfractionation is required for this difficult separation. The large increase in

energy costs since the 1970s have made this process economically unattractive.

The first commercial EB processes were developed in the 1930s by Dow, BASF, Monsanto, Union Carbide-Badger and others. Benzene and ethylene are reacted in a liquid-solid AlCl_3 two-phase system at low pressure and less than 130°C . High-boiling polyethylbenzenes are recycled to the single reactor where thermodynamic equilibrium among the aromatics is established. An improved version was developed by Monsanto in 1974, which operates at $160\text{--}180^\circ\text{C}$ with an AlCl_3 concentration below the solubility limit in a homogeneous liquid phase. This results in improved EB yield and allows recovery of the heat of reaction as low-pressure steam. However, at the low AlCl_3 concentration the catalyst is inhibited by recycled polyethylbenzenes, and a separate transalkylation reactor is required.

A heterogeneous gas phase EB synthesis, the Alkar process, was commercialized by UOP in the 1960s [23]. It operates at 300°C and 60 bar with a solid BF_3 /alumina catalyst, can be used with dilute ethylene streams (5–95%), and allows polyethylbenzenes to be recycled. Because of high maintenance costs caused by severe corrosion, the process has lost its inherent attractiveness [21].

With the advent of zeolite catalysts and the greater importance of environmental issues, new process alternatives to those using metal halide Friedel-Crafts catalysts became attractive. These are noncorrosive and nonpolluting, and require no waste disposal or waste water treatment plants. An example is the Mobil-Badger Ethylbenzene process which was developed in the 1970s [24].

The key to this process is the highly selective and stable zeolite catalyst, ZSM-5. Earlier attempts to use zeolites such as HY, REY, and mordenite failed, because of rapid coke deactivation and poor yields. This is a result of the high hydride transfer activity occurring in the large pores of these catalysts. In the medium pore ZSM-5, bimolecular hydride transfer is greatly retarded for steric reasons. High yields of ethylbenzene (over 99%) can be obtained. Catalyst deactivation is slow, the catalyst can be regenerated by coke burning, and has a long ultimate life.

The process operates in the gas phase at $380\text{--}450^\circ\text{C}$, 20–30 bar pressure, and a high mass of feed per mass of catalyst per hour ($\text{WHSV} > 100$). Because the catalyst is insensitive to many feed impurities, diluted ethylene streams can be used, such as the off-gas from refinery gas-oil crackers. The high reaction temperature allows the recovery of over 90% of the heat of reaction as medium and low pressure steam. Byproduct polyethylbenzenes can be recycled together with recycled benzene to the synthesis reactor for transalkylation (Fig. 2). The reaction section contains two parallel, multitubed reactors which enable continuous

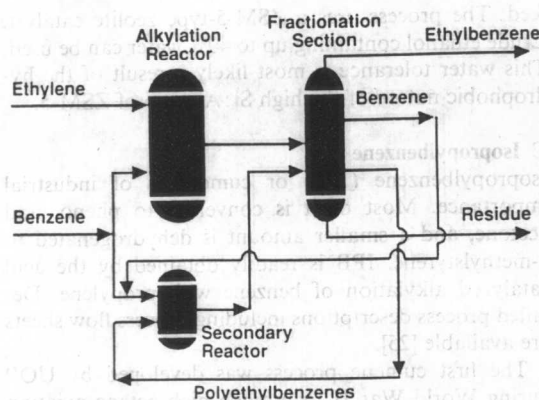


Figure 2. Mobil-Badger ethylbenzene process flow sheet.

operation by being alternately on stream and regenerated. A narrow optimal temperature is maintained with interbed quench by the reactants; this allows optimization of the cycle life and selectivity.

The commercial acceptance of this process has been excellent. More than 25 plants in 10 countries are now licensed to practise this technology. Individual plant sizes vary from 60 000 to 1 000 000 tons per annum; the combined capacity of these plants is nearly 7 000 000 tons per annum.

Alternatives to the vapor phase EB technology involve the liquid phase alkylation of benzene with ethylene. These types of processes also utilize zeolitic catalysts, and several are in commercial development or have been recently licensed. The liquid phase operations have the advantage of decreased byproduct yields.

Another zeolite-based liquid phase EB process has been developed by the Chemical Research and Licensing Company (CR&L), a division of CDTech. It uses the concept of catalytic distillation in which reaction and separation occur in the same reactor. This allows for good heat integration. It has the additional advantage of minimizing the amount of polyalkylation that is normally unavoidable at economically desirable conversions per pass. However, this advanced process does not seem to have been applied commercially as yet.

Ethylene is the preferred alkylating agent for the synthesis of ethylbenzene in countries that have access to the feedstock for ethylene crackers, i.e. light gaseous alkanes or naphtha, either through local production or through imports. In certain countries, ethylene is not readily available. In India, for example, an ethylbenzene synthesis process called ALBENE has been developed and commercialized that utilizes indigenously produced fermentation alcohol as the alkylation

feed. The process uses a ZSM-5-type zeolite catalyst. Crude ethanol containing up to 40% water can be used. This water tolerance is most likely a result of the hydrophobic nature of the high Si:Al ratio of ZSM-5.

C Isopropylbenzene

Isopropylbenzene (IPB) or cumene is of industrial importance. Most of it is converted to phenol and acetone, and a smaller amount is dehydrogenated to α -methylstyrene. IPB is readily obtained by the acid catalyzed alkylation of benzene with propylene. Detailed process descriptions including process flow sheets are available [25].

The first cumene process was developed by UOP during World War II to provide high-octane aviation gasoline. This vapor phase process is still the most widely used commercial process today. It is remarkable that it still uses the same catalyst that was developed 50 years ago by Ipatieff [26]. The catalyst is prepared by depositing phosphoric acid on kieselguhr, a diatomaceous earth consisting essentially of silica, followed by calcination. Condensation to polyphosphoric acid and reaction with the silica occurs, producing silicophosphoric acid, usually referred to as "solid phosphoric acid" (SPA). A low water partial pressure, which depends on the temperature, has to be maintained in the reactor to prevent complete dehydration to catalytically inactive P_2O_5 . The process operates at 200–250 °C and 15–35 bar. Since the catalyst does not have transalkylation activity, the production of diisopropylbenzenes (DIPB) is usually kept low by using a high benzene to propylene ratio in the reactor, which adds to the distillation costs. Alternatively, a separate transalkylation reactor can be used to convert the DIPB to cumene. The overall yield of cumene is typically 96%, and with transalkylation 98%.

Building on their experience with their liquid phase ethylbenzene process, Monsanto commercialized in the mid-1980s an improved cumene process, using $AlCl_3/HCl$ as catalyst. With a cumene yield of 99% based on benzene, a higher selectivity, and lower energy requirements, this process offers a lower process cost than the UOP process.

However, the corrosiveness of the system, requiring expensive construction materials, and the need for disposal of the $AlCl_3$ -containing waste stream, are disadvantages.

Zeolites have been investigated extensively as alternative catalysts for cumene synthesis. The catalyst used in the Mobil-Badger EB process, the medium pore ZSM-5, is not suitable for cumene production. As a result of the relatively narrow pores, the bulkier cumene tends to isomerize to the less bulky *n*-propylbenzene. Consequently, the zeolite must contain pores of sufficient dimensions to effect the formation of cumene, and also allow any polyalkylated species to

pass through so that they may eventually be transalkylated. Associated problems include increased formation of diisopropylbenzenes, and very rapid deactivation, since larger polyalkylated species are not easily desorbed.

Research in this area has focused on the use of the larger 12-ring zeolites including effectively unidimensional 12-ring systems such as mordenite, and intersecting 12-ring systems such as zeolite beta. Indeed, in a recent patent by Chevron, zeolite beta is used for both the alkylation and transalkylation steps as a result of its large accessible 12-ring pore system [27]. The system is capable of converting a mixture of benzene and DIPB to additional IPB product.

Dow Chemical has recently reported [28] the production of IPB, based on modified mordenite zeolites. The advantages of such zeolite-based processes again rely on their ability to effect transalkylation, the non-corrosive nature of the material, and reduction of catalyst costs as the materials may be regenerated.

In the Dow technology, which has been commercialized, two highly dealuminated mordenite catalysts are used for the alkylation and transalkylation steps. The alkylation catalyst is silica bound, and has an $SiO_2:Al_2O_3$ ratio of 156 and the transalkylation catalyst has an $SiO_2:Al_2O_3$ ratio of 108. The dealuminated mordenite is highly active for alkylation: at temperatures as low as 130 °C, all propylene is consumed. The selectivity to cumene increases at higher benzene to propylene ratios. In this low temperature range, the mordenite catalyst is less selective to cumene than the standard supported phosphoric acid catalysts. This lower selectivity manifests itself in additional production of *para*-diisopropylbenzene; however, this material is handled in the subsequent transalkylation step over the more active mordenite catalyst described above. The high *para*-diisopropylbenzene selectivity may be attributed to the shape-selective influence of the mordenite catalyst.

In commercial operation, the low-temperature operation of the mordenite system is quite important because higher temperatures favor the production of *n*-propylbenzene, a troublesome impurity because it is difficult to separate from cumene, even by distillation. Therefore, conditions which lead to the production of this material need to be avoided. Typical product yields for the specified mordenite catalyst are shown in Table 3.

In comparison with the UOP process, there are some advantages and disadvantages. The selectivity to cumene of the nonzeolite system is greater than that of the zeolites; however, overall IPB yields may be increased with a modified mordenite via its excellent transalkylation activity.

Mobil-Badger have recently introduced a new commercial process for cumene production. This liquid