Industrial Catalysis:

Chemistry and Mechanism

James D. Burrington

Imperial College Press

Industrial Catalysis: Chemistry and Mechanism

James D. Burrington

Published by

Imperial College Press 57 Shelton Street Covent Garden London WC2H 9HE

Distributed by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

Library of Congress Cataloging-in-Publication Data

Names: Burrington, James D., 1951-

Title: Industrial catalysis: chemistry and mechanism / James D. Burrington

(The Lubrizol Corporation, USA).

Description: New Jersey: Imperial College Press, 2016.

Identifiers: LCCN 2015043857 ISBN 9781783268979 (hc : alk. paper)

ISBN 9781783268986 (sc : alk. paper)

Subjects: LCSH: Catalysis--Textbooks. | Organometallic chemistry--Textbooks. |

Chemistry, Technical--Textbooks.

Classification: LCC QD505 .B88 2016 | DDC 660/.2995--dc23

LC record available at http://lccn.loc.gov/2015043857

British Library Cataloguing-in-Publication Data

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

Copyright © 2016 by Imperial College Press

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

Desk Editors: Kalpana Bharanikumar/Catharina Weijman

Typeset by Stallion Press

Email: enquiries@stallionpress.com

Printed in Singapore by Mainland Press Pte Ltd.

Industrial Catalysis: Chemistry and Mechanism

To Rebecca

此为试读,需要完整PDF请访问: www.ertongbook.com

Foreword

Why should we study catalysis?

- The vast majority of high-volume chemicals are produced using catalysis
- Catalysis is the most cost-effective form of chemistry: the highest cost materials are recycled
- Catalysis is the key to solving many of the world's environmental problems

Topics

- Introduction to Industrial Catalysis
- · Acid Catalysis
- · Oxidation Catalysis
- · Polymerization Catalysis
- Reduction Catalysis/ Hydrogenation
- · Environmental Catalysis
- · Catalyst Characterization

Within the context of chemistry as a business, catalysis provides the means by which the vast majority of chemicals (on a volume basis) are produced. This can be understood based on the key features of a catalytic process — the efficient conversion of the lowestcost raw materials to value-added products by processes in which the highest-cost components that effect the reaction are regenerated. In the chemical synthesis laboratory, where the formation of the desired products in the highest purity possible is more important than the cost of its production, these materials are called "reagents," which are consumed in the process and discarded. Every chemist has used such reagents at some point, for example, potassium permanganate for oxidation or lithium aluminum hydride for reduction. Of course, for very high-value products, this strategy also makes commercial sense.

But even in those cases, there are growing environmental and economic driving forces for the use of catalysis as a means to reduce or prevent pollution as opposed to end-of-pipe waste treatment. Pollution that is not produced in the first place makes more cost-effective use of raw materials and reduces environmental impact of chemical operations.

Catalysis has also been a key technology for solving the world's growing emissions limitations, especially for passenger cars and heavy-duty diesel engines for which catalysts are the heart of commercialized emissions reduction devices. Future catalytic scientists and engineers will play a key role in meeting future emission and fuel economy requirements.

Catalysis is truly an interdisciplinary technology, the practice of which requires knowledge of many disciplines, among them, chemistry, chemical engineering and material science. Each of these studies, in their own right, defines a distinct and coherent body of knowledge and each contributes an important perspective on catalysis. And yet, catalysis remains, first and foremost, a chemical phenomenon, and its successful application starts with an understanding of the underlying chemistry. This text attempts to provide a chemical basis for that understanding as a primer for future industrial chemists.

The text is composed of seven chapters: the introduction; four chapters dealing with the major catalytic reaction types of commercial importance: acid catalysis, oxidation, polymerization, reduction/hydrogenation; a chapter devoted to catalytic processes for environmental applications, mainly exhaust gas treatment; and one of methods for analytical characterization.

Chapter 1 (Introduction) is an overview of the history and basic concepts of catalysis and commercial catalytic processes. Chapters 2–6 are presented in three sections: basic Concepts, which covers the fundamental chemical transformations and mechanistic principles, elements of Catalyst Design, which discusses the catalyst parameters important for design of industrial catalysts, and major industrial processes: reaction chemistry and mechanism and catalyst characterizations. Chapter 7 presents the principles and applications of several key analytical methods for catalyst characterization.

In addition to the core areas of study, there are also embedded in the chapters "Toolkit" Topics, which will help the student to master skills associated with the practice of industrial catalysis.

These include:

- (1) The representation of catalytic mechanisms using the Tolman formalism,
- Methods for the preparation of industrial catalysts, especially heterogeneous catalysts,
- (3) Elements of catalyst process engineering, including measurement of process and catalyst efficiency and catalyst design,
- (4) Application of methods of analysis for a given catalyst and reaction situation,
- (5) Analysis of studies in catalysis from the scientific literature.

Toolkit Topic discussions will include practical examples for students to use in the study and mastery of these skills.

Catalysis "Toolkit" Topics

- Representing catalytic mechanisms
- Methods of catalyst preparation
- · Catalysis process
- · Engineering concepts
- Catalyst characterization/ analysis
- · Catalysis literature

Contents

For	Foreword			
1.	An	Introd	luction to Industrial Catalysis	1
	1.1	Histor	rical Background	1
		1.1.1	Early Catalysis Examples	2
		1.1.2	Highlights of Catalysis Technology	2
	1.2	Cataly	sis Definitions	6
	1.3	Kineti	cs and Catalysis	7
	1.4 Thermodynamics .			8
		1.4.3	Thermodynamic Limitation	10
	1.5	Key C	Concepts	11
		1.5.1	Activity: Batch Measures	11
		1.5.2	Activity: Space Velocity	12
		1.5.3	Space Velocity Examples	13
		1.5.4	Activity: Turnover Rate	14
		1.5.5	Turnover Example	15
		1.5.6	Selectivity	17
		1.5.7	Selectivity Example	18

		1.5.8	Selectivity Example 2: Formation of Two Products	19
		1.5.9	Catalyst Life	21
	1.6	Cataly	rtic Mechanism	21
		1.6.1	Representing Mechanisms: "Electron Pushing"	22
		1.6.2	Representing Mechanisms: "Name Reaction" Examples	23
		1.6.3	Elementary Catalytic Reaction Steps	23
		1.6.4	Representing Catalytic Mechanisms: The "Tolman Formalism"	25
		1.6.5	Catalytic Mechanism Example: Hydroformylation of Olefins	25
	1.7	Homo	geneous Versus Heterogeneous Catalysis	26
		1.7.1	Homogeneous Catalysis Example	28
		1.7.2	Heterogeneous Catalysis Example	29
		1.7.3	Advantages of Homogeneous Catalysis	30
		1.7.4	Advantages of Heterogeneous Catalysis	31
	1.8	Major	Industrial Catalytic Process Types	32
		1.8.1	Industrial Examples	33
	1.9	Proble	ems	35
		1.10	Answers to Problems	38
2.	Aci	id Cata	ılysis	43
	2.1	Basic	Concepts	44
		2.1.1	An Acid Catalyst Periodic Table	44
		2.1.2	pKa Acidity Scale	45
		2.1.3	Ho Acidity Scale for Superacids	46
		2.1.4	Superacid Example: Phosphotungstic Acid	47
		2.1.5	Bronsted Versus Lewis Acidity	48
		2.1.6	Some Common Solid Acid Catalysts	49
		2.1.7	Silica-Alumina SiO ₂ /Al ₂ O ₃ Solid Acids	50
		2.1.8	Zeolite Synthesis	52

	2.1.9	Zeolite Acid Sites	52	
	2.1.10	Bronsted and Lewis Acidity Measurements		
		in Solids	53	
	2.1.11	Mechanism of Acid Catalyzed Aromatic Reactions	55	
	2.1.12	Thermodynamics	56	
2.2	Elemen	nts of Acid Catalyst Design	57	
	2.2.1	Active Site Distribution	57	
	2.2.2	Zeolites	58	
	2.2.3	Other Si/Al Frameworks	59	
	2.2.4	Shape Selectivity	60	
	2.2.5	Surface Activity Effects	63	
	2.2.6	Surface Activity: Small Crystallite Example	64	
	2.2.7	Heat Treatment — Phase Formation	66	
	2.2.8	Common Catalyst Supports	68	
	2.2.9	Catalyst Supports: Hydrophobic Versus		
		Hydrophillic Surfaces	68	
2.3	Major	Industrial Processes — Refinery	69	
	2.3.1	Catalytic Cracking	69	
	2.3.2	Disproportionation of Aromatics	71	
	2.3.3	Isobutane/isobutylene Alkylation (Octane)	72	
	2.3.4	Methyl-tert-butyl ether Synthesis	73	
	2.3.5	Methanol-to-Gasoline (MTG)	74	
2.4	Major	Industrial Processes — Chemical	76	
	2.4.1	Benzene Ethylation	76	
	2.4.2	Cumene	76	
	2.4.3	Beckman Isomerization	77	
	2.4.4	Esterification	79	
2.5	Trends	in Acid Catalysis	79	
2.6	Proble	ms	81	
2.7	Answers to Problems 83			

Contents ix

x Contents

3.	Oxidation	n Catalysis	83
	3.1 Conce	epts	84
	3.1.1	Oxidation Catalyst Periodic Table	84
	3.1.2	Oxidation Thermodynamics	85
	3.1.3	Recognizing Organic Oxidation States	85
	3.1.4	Oxidation Catalysis Concepts — Homogeneous	90
	3.1.5	Oxidation Catalysis Concepts — Heterogeneous	90
	3.1.6	Elementary Reaction Steps	91
	3.1.7	Homogeneous Oxidation Catalysis	92
	3.1.8	Hetereogeous Oxidation .	95
	3.2 Eleme	ents of Oxidation Catalyst Design	98
	3.2.1	Metals Substitution	98
	3.2.2	Active Site Isolation	99
	3.2.3	Surface Versus Bulk Composition	101
	3.2.4	Promoters	102
	3.2.5	Oxidation Catalyst Synthesis	102
	3.3 Majo	r Industrial Processes	104
	3.3.1	Epoxidation — Styrene Monomer Propylene	
		Oxide Process	104
	3.3.2	Acrylonitrile	105
	3.3.3	Vinyl Acetate/Wacker Oxidation	105
	3.3.4	Cyclohexanol/One — Cyclohexane Oxidation	107
	3.3.5	Adipic Acid/Nylon 6,6	108
	3.3.6	Maleic Anhydride	109
	3.3.7	Aromatic Oxidation — Terephthalic Acid	110
	3.3.8	Phthalic Anhydride	111
	3.3.9	Aromatic Oxidation — Cumene to Phenol/Acetone	111
	3.4 Probl	ems	113
	3.5 Answ	vers to Problems	116

1.	Pol	ymeriz	ation Catalysis	119
	4.1	Conce	pts	120
		4.1.1	Polymerization Catalyst Periodic Table	120
		4.1.2	Thermodynamics	122
		4.1.3	Polymer Molecular Weight	122
		4.1.4	Polymerization Reaction Mechanisms	125
		4.1.5	Polymerization Mechanisms: Elementary Steps	125
		4.1.6	Anionic Polymerization	127
		4.1.7	Cationic Polymerization	129
		4.1.8	Metal Oxide/Coordination Catalysis	130
		4.1.9	Coordination Catalysis: Ziegler-Natta	131
		4.1.10	Coordination Catalysis: Metallocene	132
		4.1.11	Free Radical Polymerization	133
		4.1.12	Living Polymerization	135
		4.1.13	Living Polymerization: TEMPO Initiator	136
	4.2	Polym	erization Catalyst Design	137
		4.2.1	Metals Substitution: PP Isomers	138
		4.2.2	V-Based Polypropylene Catalysts: Syndiotactic	139
		4.2.3	Ti-Based PP Catalysts: Isotactic	140
		4.2.4	Ligand Effect: Constrained Geometry Metallocenes	141
		4.2.5	Isotactic from Cp* Catalyst	142
		4.2.6	Non-Coordinating Anions	143
		4.2.7	Effect of Solvents: Butadiene Example	145
		4.2.8	Ziegler-Natta Catalyst Synthesis:	
			Particle Microreactor	146
		4.2.9	Single Versus Multiple Site Polyolefin Catalysts	147
	4.3	5	Industrial Processes	149
		4.3.1	Polyethylene and Isotactic Polypropylene:	1.40
		122	TiCl ₄ /AlEt ₂ Cl/MgCl ₂ Ethylene/Propylene Copolymers (EPC)	149
		4.3.2	EUIVICIE/PTODVICIE CODOIVMETS (EPC.)	1.00

		4.3.3	Higher Olefins: Shell Higher Olefin Process (SHOP)	153
		4.3.4	Styrene/Butadiene Emulsion Polymerization (SBR)	154
		4.3.5	Polyethoxylates (Anionic Polymerization)	156
		4.3.6	Polyisobutylene	156
	4.4	Future	Catalysts: Late Transition Metals	
		for Br	anched Polyethylene	158
		4.4.1	Branched Polyethylene	159
		4.4.2	Branching Mechanism	160
	4.5	Proble	ems	161
	4.6	Answe	ers to Problems	166
5.	Rec	duction	/Hydrogenation Catalysis	169
	5.1	Conce	epts	170
		5.1.1	Reduction Catalysis Periodic Table	170
		5.1.2	Thermodynamics	171
		5.1.3	H ₂ activation by Metals/Olefin Hydrogenation	172
		5.1.4	Hydroformylation: CO Insertion	172
		5.1.5	Synthesis Gas Reactions	173
		5.1.6	Synthesis Gas: Non-Dissociative CO Adsorption: MeOH	174
		5.1.7	Synthesis Gas: Dissociative CO Adsorption: Fischer–Tropsch Hydrocarbons	175
		5.1.8	Fischer-Tropsch: Schultz-Flory Distribution	176
		5.1.9	Hydrodesulfurization	177
	5.2	Eleme	ents of Catalyst Design	178
		5.2.1	Metal Substitution Effect: Fe Versus Co in FT	178
		5.2.2	Metals/Ligand Effect: Hydroformylation	180
		5.2.3	Hydroformylation Ligand Effects	181
		5.2.4	Asymmetric Hydrogenation	183
		5.2.5	Promoters and Poisons: Noble Metals	184

			Contents	xiii
	5.3	Major	Industrial Processes	184
		5.3.1	Hydrogenolysis: Hydrocracking and Hydrotreating	184
		5.3.2	Dehydrogenation: Styrene	185
		5.3.3	Hydroformylation/Hydrogenation: Oxo Alcohols	186
		5.3.4	Carbonylation: Methanol to Acetic Acid	187
		5.3.5	Catalytic Reforming	189
		5.3.6	Ammonia Synthesis	190
	5.4	Proble	ms	191
	5.5	Answe	ers to Problems	195
6.	Env	vironm	ental Catalysis	199
	6.1	Conce	pts	200
		6.1.2.	Thermodynamic Considerations	200
		6.1.3	Exhaust Gas Components	201
		6.1.4	Catalytic Conversion of Exhaust Gas	202
		6.1.5	Catalytic Reactions for Removal of Exhaust	
			Pollutants	203
		6.1.6	Temperature of the second contraction of the contra	205
		6.1.7	Catalyst Components and Functions — 3-Way Catalyst	205
		6.1.8	Catalyst Components and Functions — Lean NO _x Catalyst	207
		6.1.9	Catalyst Components and Functions — SCR Catalyst	208
		6.1.10	Catalyst Components and Functions — NO_x Absorber	209
		6.1.11	Catalyst Functions and Components — DOC and DPF	210
		6.1.12	Mechanistic Concepts	211
	6.2		nts of Catalyst Design	212
		6.2.1	Metal Substitution	212
		6.2.2	Promoters and Poisons	212

xiv Contents

		6.2.3	Catalyst Synthesis	214
		6.2.4	Engineering Concepts	214
	6.3	Major	Catalytic Technologies	215
		6.3.1	Diesel Particulate Trap	215
		6.3.2	Diesel Oxidation Catalyst	220
		6.3.3	Diesel NO _x Reduction — SCR	222
		6.3.4	NO_x Trap	226
		6.3.5	Gasoline Engines — 3-Way Catalyst	227
		6.3.6	Future Technology: Fuels Cells	228
	6.4	Proble	ems	230
	6.5	Answe	ers to Problems	233
7.	Cat	talyst (Characterization	237
	7.1	Spectr	roscopic Methods	238
		7.1.1	X-ray Diffraction/X-ray Fluorescence	240
		7.1.2	X-ray Photoelectron Spectroscopy	242
		7.1.3	Extended X-ray Adsorption Fine Structure	244
		7.1.4	Fourier Transform Infrared Spectroscopy	245
		7.1.5	Laser Raman Spectroscopy	246
		7.1.6	Nuclear Magnetic Resonance Spectroscopy	247
		7.1.7	Electron Microscopy	250
		7.1.8	Secondary Ion Mass Spectrometry	251
	7.2	Adsor	ption Methods	252
		7.2.1	BET Surface Area	253
		7.2.2	Porosimetry — Pore Volume and Pore Size Distribution	254
		7.2.3	Thermogravimetric Analysis/Differential	
			Scanning Calorimetry	254
	7.3	Proble	ems	256
	7.4	Answe	ers to Problems	257
Ref	ere	nces		259
Ind	ex			263

1

An Introduction to Industrial Catalysis

While catalysis is a multidisciplinary science, it is first and foremost a chemical phenomenon, and it is the intent of this text to emphasize its chemical aspects. At the heart of catalytic chemistry is the mechanism by which reactants interact with catalyst, catalytic intermediates are interconnected and products are formed. The foundations of mechanism covered in this chapter will be repeatedly used in subsequent discussions of the various catalytic reaction types.

Another important distinction in catalytic science and technology is that of homogeneous versus heterogeneous catalysis. It is not just a distinction based on the number of phases present in the reaction, but one which also encompasses fundamentally different chemistries and process engineering, with distinct advantages and disadvantages. Finally, in this chapter there will be a summary of the major industrial processes and reaction types, covered in greater detail in each of the subsequent chapters.

1.1 Historical Background

As with any new endeavor, it is useful to begin our studies with a historical perspective, a set of definitions, a few basic concepts and some examples which will provide the basis on which the rest of the course will be built.