### CATALYSIS

**Principles & Basic Concepts** 

The book Catalysis: Principles and Basic Concepts covers a wide range of topics and issues such as heterogeneous, homogeneous, photo-catalysis, bio-catalysis, phase transfer catalysis, energy and environment. Enough importance is given to the quality and stress to each chapter. The materials in this book are presented in a simple and lucid manner so that any science stream person can understand the concepts, role and issues without any difficulty. This book is useful to UG and PG students of chemistry and chemical engineering, researcher and scientists in catalysis, teachers of catalytic stream of chemical sciences including chemists and chemical engineers from industry. One of the most important aspects of energy is to develop method for exploiting, converting, and optimizing energy sources. Catalysis serves as a crosscutting science in this aspect, with the potential to lead and to bring out of the energy crisis. All round efforts are made to include as many as required chapters for the introductory courses and some advance stage level courses on catalysis for chemical sciences. Catalysis is an interdisciplinary subject and required to be flourished to undergraduate and graduate curriculum in chemistry and chemical technology. This book shall help as a suitable text or reference book for such curriculum.

Arun V. Salker, is presently a Professor at Department of Chemistry, Goa University, Goa. He obtained Ph.D. degree from IIT-Bombay and did his Post-Doctoral Research at University of Karlsruhe, Germany. He was a visiting Professor at Kungpook National University, South Korea, in 2003-04. He served Goa University for last 30 years in Research and teaching in Catalysis, Material Chemistry and Environmental Chemistry. He was the Head of Chemistry Department, during the period 2009 to 2012 and 'Dean' Faculty of Natural Science, for the period May 2014 to May 2017. He has nearly ninety research publications in reputed international and national journals, hundred paper presentations in Symp./conferences, granted two Indian patents to his credit and guided several Ph.D. students and published two books including this one. In recognition to his contribution of teaching and research, the Department of Higher Education, Govt. of Goa, conferred on him "Goa State Award for Meritorious Teacher" in Higher Education for the year 2015.





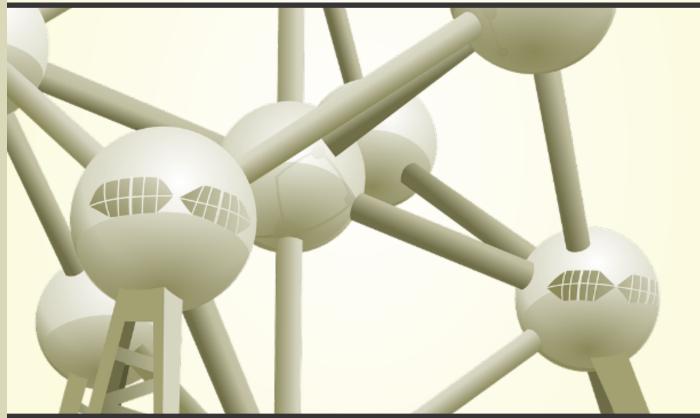
# ISBN 978-93-88716-51-2

# Principles

## CATALYSIS

#### PRINCIPLES AND BASIC **CONCEPTS**

A.V. Salker





Salker





# CATALYSIS Principles & Basic Concepts

**A.V. Salker** Ph.D. Department of Chemistry Goa University, Goa India





#### MEDTECH

A Division of

Scientific International Pvt. Ltd.

Copyright © Publisher

First Edition: 2019

All rights reserved. No Part of this publication may be reproduced or transmitted in any form or by any means—electronic or mechanical, including photocopy, recording, or any information storage and retrieval system—without permission in writing from the publisher.

**Disclaimer:** Every effort has been made to avoid any error or omission in this publication. It may be noted that neither the author nor the publisher will be responsible for any damage or loss of action to any one of any kind, in any manner, therefrom.

ISBN: 978-93-88716-51-2 (PB) ISBN: 978-93-88716-52-9 (HB)

The authors, editors, contributors and the publisher have, as far as it is possible, taken care to ensure that the information given in this text is accurate and up-to-date. However, readers are strongly advised to confirm that the information complies with current standards of practice.

Every effort has been made where necessary to contact holders of copyright to obtain permission to reproduce copyright material. If any have been inadvertently overlooked, the publisher will be pleased to make the necessary arrangements at the first opportunity.

Published by: Vinod Kumar Jain, Scientific International (Pvt.) Ltd.

Registered Office: • New Delhi: 4850/24, Ansari Road, Daryagani,

New Delhi-110002

Branch Offices: • Bengaluru: House No. 1665, Ground Floor, 18th Main, BSK 2nd Stage, Bengaluru-

560070

• Guwahati: House No. 31, 1st Floor, KKB Road, Chenikuthi, Opp. Sirdi Sai Bidya

Mandir High School, PO-Silpukhuri, District-Kamrup, Guwahati-781003

• Kerala: Ponary House, Paudua Raod,

Konthuruthy - 682013

Thevara PO-Ernakulam district, Kerala, India

• Kolkata: 127/G, Manicktala Main Road, Kankurgachi, Near Yogodyan, Kolkata-

700054

Printed in India\*\*

#### Contents

Preface.		(vi)
CHAPTER	1: Origin and Development of Catalysts	1–9
1.1	Introduction	1
1.2	Brief Historical Background	2
1.3	Importance of Catalysts	3
1.4	Green Chemical Processes	5
1.5	Atom Economy	6
1.6	Turnover Number and Frequency	7
•	Suggested Reading	7
•	Exercise	7
•	Objective Type Questions	8
CHAPTER	2: Introduction to Heterogeneous Catalysis	10–21
2.1	Catalysis and Catalyst	10
2.2	General Mechanisms in Heterogeneous Catalysis	11
	2.2.1 Langmuir-Hinshelwood	11
	2.2.2 Rideal-Eiley	11
	2.2.3 Precursor	12
	2.2.4 Mars-van Krevelen	12
2.3	Active Sites	12
2.4	Solid Catalyzed Fluid Reaction	13
2.5	The Physico-chemical Properties of Solid Catalysts	14
2.6	Surface Catalysis	14
2.7	Acidity and Basicity on Surfaces	. 15
	2.7.1 Acidic Surface	16
	2.7.2 Basic Surface	. 17
2.8	Diffusion in Catalysis	17
	2.8.1 Knudsen Diffusion	18
2.9	Heat and Mass Transfer	18
	Suggested Reading	20
•	Exercise	20
	Objective Type Questions	21
Снартел	3 : Adsorption Phenomenon	22–47
3.1	Introduction	22
3.2	Adsorption	22
3.3	Physical and Chemical Adsorption	23

3.4	Heat of Adsorption	26
3.5	Applications of Adsorptions	27
3.6	Scattering, Trapping and Sticking	27
3.7	What is Adsorption?	28
3.8	The Adsorption Isotherm	29
3.9	Freundlich Adsorption Isotherms	31
3.10	The Langmuir Adsorption Isotherm	32
	3.10.1 Testing the Langmuir Equation	34
3.11	The BET Isotherm	35
	3.11.1 Criticism of the BET theory	39
	3.11.2 Surface Area from BET Isotherm	40
3.12	Types of Adsorption Isotherms	41
3.13	BJH Method	43
× •	Suggested Reading	44
•	Exercise	44
•	Objective Type Questions	45
Снартен	4: Types of Catalysts	48–71
4.1	Introduction	48
4.2	Different Types of Catalysts Generally Used	49
4.3	Preparation of Metal Catalysts	49
4.4	2018년 15일 전문의 1일 전 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	49
4.5	Supported Metal Catalysts	50
	4.5.1 Bimetallic Catalysts	52
	4.5.2 Bi-functional Catalysts	52
	4.5.3 Magnetic Ferrite Support	52
4.6	Zeolites	53
	4.6.1 Metal Ion Exchanged Zeolites	55
	4.6.2 Shape Selectivity	55
	4.6.3 Acidity of Zeolites	56
	4.6.4 Application of Zeolites	57
4.7	Carbon	57
	4.7.1 Classification of Carbon	57
	4.7.2 General Properties	58
	4.7.3 Chemical Properties	58
	4.7.4 Structure	59
	4.7.5 Activation Process	60
	4.7.6 Raw Materials	61
	4.7.7 Carbonization Method	61
	4.7.8 Carbon Containing Functional Groups	62
	4.7.9 Graphene	63
	4.7.10 Applications	63

CONTENTO						
CONTENTS						ix
						10

0.000				
	4.8	Nanopa	articles	64
		4.8.1	Natural	. 64
		4.8.2	Metal-based Nanoparticles	64
		4.8.3	Applications and Precautions	65
	4.9	Method	ds of Preparations	66
		4.9.1	Co-precipitation Method	66
		4.9.2	Sol Gel Method	67
		4.9.3	Combustion Method	67
		4.9.4	Hydrothermal Synthesis	67
		4.9.5	Sonochemical Method	68
		4.9.6	Mechanical Attrition	68
		Sugges	sted Reading	69
		Exercis	se	69
	•	Object	ive Type Questions	69
C	APTER	5 : C	haracterization, Spectroscopic and Structural Aspects	72–105
	5.1	Charac	eterization of the Catalysts	72
		5.1.1	X-ray Diffraction (XRD)	/72
		5.1.2	Thermal Analysis Methods (DTA/TG and DSC)	74
		5.1.3	Infrared (IR) Spectroscopy	76
		5.1.4	Scanning Electron Microscopy (SEM)	78
		5.1.5	Transmission Electron Microscopy (TEM)	79
		5.1.6	X-ray Absorption Spectroscopy	80
		5.1.7	X-ray Photoelectron Spectroscopy (XPS)	82
		5.1.8	Auger Electron Spectroscopy (AES)	86
		5.1.9	Diffuse Reflectance Spectroscopy	87
		5.1.10	Nuclear Magnetic Resonance (NMR)	88
		5.1.11	Raman Spectroscopy	89
	5.2	Surface	e Area and Porosity	89
		5.2.1	Temperature Program Desorption (TPD)	91
		5.2.2	Mercury Porosimetry	92
	5.3	Low E	nergy Electron Diffraction	93
	5.4		e Size and Dispersion	94
		5.4.1	Static Method	94
		5.4.2	Physical Methods	95
		5.4.3	Particle Size Distribution Analysis	95
	5.5	Structu	ural Aspect of Solid Catalysts	95
		5.5.1	Crystal Structure Determination	96
		5.5.2	Bravais Lattice	97
		5.5.3	Crystal Planes	100
			그는 사람들이 나는 그는	100

X			CO	NTENTS
		All the second s		

	5.6	Types of Solids	100
		5.6.1 Ionic Solids	100
		5.6.2 Molecular Solids	101
		5.6.3 Atomic Solids	101
		5.6.4 Metallic Solids	101
	5.7	Surface and Bulk Composition	101
		5.7.1 Dynamics of Surface Reconstruction	102
	•	Suggested Reading	103
	•	Exercise	103
	•	Objective Type Questions	103
Сн	APTE	R 6 : Surface Reactions and Kinetics	106–124
	6.1	Thermodynamic for Surface Reactions	106
	6.2	Mechanism of Surface Reactions	108
		6.2.1 Hydrogen Oxidation	. 109
		6.2.2 Oxidation of Ethylene	109
		6.2.3 Hydrogenation of Ethylene	110
		6.2.4 Oxidation of Carbon Monoxide (CO)	110
		6.2.5 Ammonia Preparation	111
		6.2.6 Nitrous Oxide (N <sub>2</sub> O) Decomposition	112
		6.2.7 Decomposition of Isopropanol	112
		6.2.8 Adsorption on Metals	113
	6.3	Semiconductors	113
	6.4	operating resource	114
	6.5	Qualitative Prediction from Active Site Theory	115
	6.6	The Rate Determination	116
	6.7	Rate Expression	117
		6.7.1 Rate Constant for Bimolecular Reaction	118
		6.7.2 Experimental Methods for Rate	119
		6.7.3 Differential and Integral Reactors	120
		6.7.4 Methodology of Kinetic Analysis	120
		6.7.5 Static Method for Rate Determination	121
		6.7.6 Circulation Method	122
	•	Suggested Reading	122
	•	Exercise	122
	•	Objective Type Questions	123
CH/	PTER	7: Catalyst Deactivations and Regenerations	125–134
	7.1	Introduction	125
	7.2	Activity and Life of the Catalyst	125
	7.3	Deactivation	126
		7.3.1 Deactivation by Sintering	126

		7.3.2 Deactivation by Coking	127
		7.3.3 Other Methods of Deactivation	128
	7.4	Promoters	128
	7.5	Poisons	129
		7.5.1 Favourable Poisoning	131
	7.6	Regeneration of the Catalysts	132
		Suggested Reading	133
	•	Exercise	133
	•	Objective Type Questions	133
Сн	APTER	8 : Theories in Heterogeneous Catalysis	135–152
	8.1	Introduction	135
	8.2	Catalysis by Semiconductors	135
		8.2.1 Band Structure	135
		8.2.2 Fermi Energy	136
		8.2.3 Electronic Conductivity	136
	8.3	Boundary Layer Theory for Chemisorptions	138
	8.4	Theory of Wolkenstein	139
		8.4.1 Electronic Transition in Chemisorptions	139
		8.4.2 Equilibrium between Various Forms of Chemisorptions	140
		8.4.3 Fermi Level and the Surface	141
	8.5	Adsorption Change Electronic Property	142
		8.5.1 Carbon Monoxide Sensors	143
		8.5.2 Hydrocarbon Gas Sensors	144
	8.6	Theories of Catalysis by Metals	146
		8.6.1 Structural Factors by Metals	146
	8.7	Electronic Factors in Catalysis by Metals	148
		8.7.1 Molecular Orbital Approach	148
		8.7.2 Electronic Structure of Metals	149
	•	Suggested Reading	150
		Exercise	151
	•	Objective Type Questions	151
Сн	APTE	9: Introduction to Homogeneous Catalysis	153–160
	9.1	Introduction	153
	9.2	Homogeneous Catalytic Reactions	154
		9.2.1 Merits and Demerits of Homogeneous Catalysis	155
	9.3	Intermediate Stages During Catalytic Reactions	155
	9.4	Activation Energy	156
	9.5	Scheme for Calculating the Kinetics	157
		Suggested Reading	159
		Exercise	159
		Objective Type Questions	159

Снартей	2 10 : Acid Base Catalysis	161–167
10.1	Introduction	161
10.2	Acid Base Catalyzed Reactions	162
	10.2.1 Specific Acid Catalysis	162
	10.2.2 Specific Base Reactions	163
	10.2.3 Specific Acid-base Catalysis	163
	10.2.4 General Acid Catalysis	164
	10.2.5 General Base Catalysis	164
	10.2.6 General Acid-Base Catalysis	165
10.3	Conclusion	165
•	Suggested Reading	166
•	Exercise	166
•	Objective Type Question	166
Снартей	11: Decomposition of H <sub>2</sub> O <sub>2</sub>	168–174
11.1	Introduction	.168
11.2	General Rate Expression	. 168
11.3		169
11.4	Decomposition of $H_2O_2$ by $MoO_4^{2-}$	171
•	Suggested Reading	173
	Exercise	174
•	Objective Type Questions	174
Снартен	2 12 : Selected Examples of Homogeneous Catalytic Rea	ctions 175–194
12.1	Introduction	175
12.2	Metal Centered Catalysis in Complex Compounds	175
12.3	Mosanto Acetic Acid Process	177
12.4	Carboxylation Reactions	178
12.5	Hydrogenation	180
12.6	Hydroformulation	182
12.7	The Wacker Process	183
12.8	The Heck Reaction	185
12.9	Suzuki Coupling Reaction	187
12.10	Dimerization of Ethane to 1-Butene	189
12.11	Isomerization of Alkenes	190
12.12	Asymmetric Catalysis	191
	12.12.1 Monsanto L-DOPA Process	191
	12.12.2 S-Naproxen	191
	12.12.3 L-Menthol	192
	12.12.4 Jacobsen Epoxidation	192
	12.12.5 Sharlpess Epoxidation	192
•	Suggested Reading	192
•	Exercise	193
•	Objective Type Questions	193

Снартег	13: Catalytic Polymerization Reactions	195–201
13.1	Introduction	195
13.2	Preparation of the Zeigler-Natta Catalysts	195
13.3	Examples of Homogeneous and Heterogeneous Catalytic Polymerizations	196
•	Suggested Reading	200
•	Exercise	200
•	Objective Type Questions	200
Снартен	14: Photo-catalysis	202–210
14.1	Introduction to Homogeneous Photo-catalysis	202
14.2	Sensitized Photolysis Reactions (Homogeneous)	202
	14.2.1 Photo-sensitized oxidations (Homogeneous)	203
	14.2.2 Photo-sensitized Decomposition and Reactions (Homogeneous)	204
14.3	Heterogeneous Photo-catalysis	204
	14.3.1 Photo-oxidation Reaction	205
	14.3.2 Generation of Hydrogen from Alcohol	205
	14.3.3 Photocatalytic Decomposition	206
	14.3.4 Heterogeneous Photosynthesis of Amino Acids on Pt-TiO <sub>2</sub>	206
14.4	Light Assisted Photo-degradation of Dyes	207
•	Suggested Reading	209
•	Exercise	209
•	Objective Type Questions	210
Chaptéi	t 15 : Bio-catalysis	211–222
15.1	Introduction	211
15.2	Nomenclature and Classification of Enzymes	211
15.3	Role of Metal Ions and Metalloenzyme	212
	15.3.1 Zinc Metalloenzymes	213
	15.3.2 Copper Metalloenzymes	213
15.4	General Properties of Enzymes	214
15.5	Demerits of Enzymes	214
15.6	Action of Enzymes	214
	15.6.1 Lock and Key Model	215
	15.6.2 Induced Fit Model	215
15.7	Coenzymes	216
15.8	Enzyme Catalysed Kinetics	216
15.9	Mechanistic Pathways of Few Enzymatic Reactions	218
	15.9.1 Applied Enzymatic Processes	219
15.10	Factors Affecting Enzymes Activity	220
15.11	Applications	221
	Suggested Reading	221
	Exercise	221
	Objective Type Questions	221

Снартей	16: Phase Transfer Catalysis	223-229
16.1	Introduction	223
16.2	Mechanism of PTC	224
16.3	Selected Examples	224
16.4	Advantages	227
16.5	Disadvantage	227
16.6	Applications	227
•	Suggested Reading	227
•	Exercise	228
•	Objective Type Questions	228
Снартей	17 : Catalysts for Energy and Environment	230–249
17.1	Introduction .	230
17.2	Catalytic Gasification	231
17.3	Electricity from Gas Turbine	231
17.4	Steam Reforming	232
17.5	Electrocatalysis	232
17.6	Fuel Cells	235
	17.6.1 Hydrogen-Oxygen Fuel Cell	235
	17.6.2 Alkaline Fuel Cell	236
	17.6.3 Phosphoric Acid Fuel Cell	237
	17.6.4 Methanol Fuel Cell	237
	17.6.5 Molten Carbonate Fuel Cell	238
	17.6.6 Solid Oxide Fuel Cell	239
17.7	Environmental Pollution	240
17.8	Catalysts for Environmental Pollution Control	243
17.9	Emission Control for Automobiles	244
17.10	Diesel Emission Control	245
17.11	Selective Catalytic Reduction	246
•	Suggested Reading	246
•	Exercise	247
•	Objective Type Questions	247
Append	ix	250–253
1.	Useful Constants	250
2.	Answers to Objective Questions	251
Index		254–258