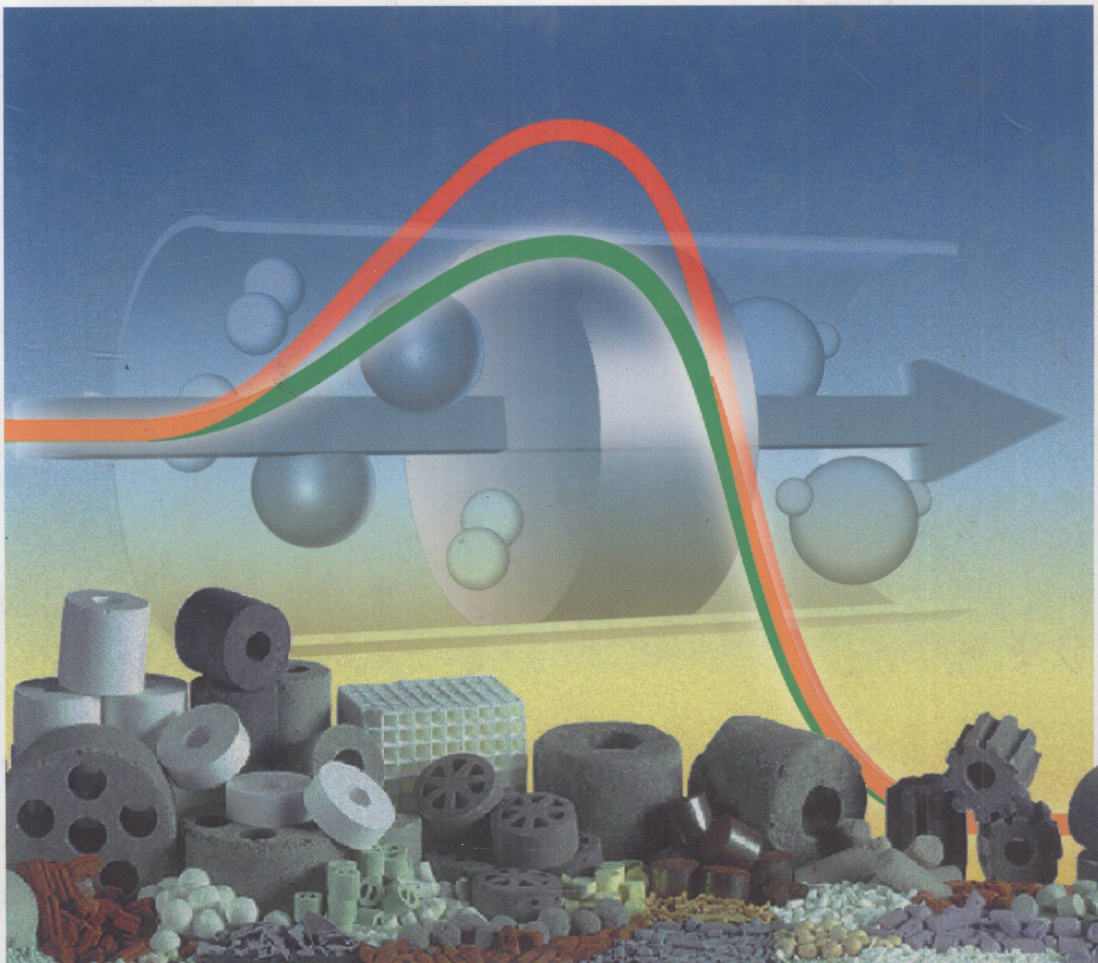
Jens Hagen

WILEY-VCH

Industrial Catalysis

A Practical Approach

Second, Completely Revised
and Extended Edition



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Preface to the Second Edition

During the last years catalysis has made a rapid progress, there can be observed many new applications of catalysts. For obvious reasons catalysis is the key to the success in developing new processes for various fields in industry. The use of suitable catalysts for new processes requires a basic knowledge of catalytic principles.

In this book, my main objective is to present an overview on catalysis, so that both the student and the experienced practitioner can see the broad picture. It was the intention to compile a text of about 500 pages surveying the whole area of catalysis, that means homogeneous catalysis, heterogeneous catalysis, biocatalysis and special topics of applied catalysis. It is felt that sufficient information is given here for a rational approach to be applied in a basic understanding of the phenomenon catalysis.

In the present edition some space is dedicated to special topics such as electrocatalysis, photocatalysis, asymmetric catalysis, phase-transfer catalysis, environmental catalysis, and fine chemicals manufacture. On the basis of fundamental reaction engineering equations, examples for calculation and modeling of catalysis reactors are given with the easy-to-learn PC program POLYMATH. Well over 170 exercises help the reader to test and consolidate the gained knowledge.

The book is based on my own lecture course for chemical engineers at the University of Applied Sciences Mannheim and several vocational training seminars for chemists and engineers in industry. I hope this book will be useful both to students who have studied chemistry or chemical engineering and to graduates and chemists who work in or are interested in the chemical industry.

Grateful appreciation is given to the following companies which provided photographic material: Degussa AG, Hanau and Marl, HTE AG, Heidelberg, and Süd-Chemie AG, Heufeld. I am particular grateful to Prof. V. M. Schmidt, Mannheim, for his valuable advice in electrocatalysis and additional material. I also want to thank the numerous students who followed my courses in Mannheim.

I thank the publishers, for their kind and competent support. I gratefully acknowledge the help of Dr. Romy Kirsten, who directed the project, Claudia Grössl for production, and Dr. Melanie Rohn for copy-editing. Special thanks and appreciation to my wife Julia for her patience, understanding and the encouragement to stay with this project to its completion.

Mannheim, October 2005 *Jens Hagen*

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Preface to the First Edition

Catalysts have been used in the chemical industry for hundreds of years, and many large-scale industrial processes can only be carried out with the aid of catalysis. However, it is only since the 1970s that catalysis has become familiar to the general public, mainly because of developments in environmental protection, an example being the well known and widely used catalytic converter for automobiles.

Catalysis is a multidisciplinary area of chemistry, in particular, industrial chemistry. Anyone who is involved with chemical reactions will eventually have something to do with catalysts.

In spite of years of experience with catalysts and the vast number of publications concerning catalytic processes, there is still no fundamental theory of catalysis. As is often the case in chemistry, empirical concepts are used to explain experimental results or to make predictions about new reactions, with greater or lesser degrees of success.

To date there has been no standard book that deals equally with both heterogeneous and homogeneous catalysis, as well as industrial aspects thereof. The books published up to now generally describe a particular area or special aspects of catalysis and are therefore less suitable for teaching or studying on one's own. For this reason, it is not easy for those commencing their careers to become familiar with the complex field of catalysis.

This book is based on my own lecture course for chemical engineers at the Fachhochschule Mannheim (Mannheim University of Applied Sciences M.U.A.S) and is intended for students of chemistry, industrial chemistry, and process engineering, as well as chemists, engineers, and technicians in industry who are involved with catalysts. Largely dispensing with complex theoretical and mathematical treatments, the book describes the fundamental principles of catalysis in an easy to understand fashion. Numerous examples and exercises with solutions serve to consolidate the understanding of the material. The book is particularly well suited to studying on one's own.

It is assumed that the reader has a basic knowledge of chemistry, in particular, of reaction kinetics and organometallic chemistry. Homogeneous transition metal catalysis and heterogeneous catalysis are treated on the basis of the most important catalyst concepts, and the applications of catalysts are discussed with many examples. The book aids practically oriented readers in becoming familiar with the processes

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of catalyst development and testing and therefore deals with aspects of test planning, optimization, and reactor simulation. Restricting the coverage to fundamental aspects made it necessary to treat certain areas that would be of interest to specialists in concise form or to omit them completely.

I wish to thank all those who supported me in producing this book. Special thanks are due to Dr. R. Eis for all the hard work and care he invested in preparing the figures and for his helpful contributions and suggestions. I am grateful to the following companies for providing photographic material: BASF, Ludwigshafen, Germany; Degussa, Hanau, Germany; Hoffmann-LaRoche, Kaiseraugst, Switzerland; Doduco, Sinsheim, Germany; and VINCI Technologies, Rueil-Malmaison, France. Interesting examples of catalyst development were taken from the Diploma theses of Fachhochschule graduates, of whom K. Kromm and T. Zwick are especially worthy of mention.

I was pleased to accept the publisher's offer to produce an English version of the book. The introduction of international study courses leading to a Bachelor's or Master's degree in Germany and other countries makes it necessary to provide students with books in English. I am particularly grateful to Dr. S. Hawkins for his competent translation of the German text with valuable advice and additional material.

I thank the publishers, Wiley-VCH Weinheim, for their kind support. Thanks are due to Dr. B. Böck, who directed the project, C. Grössl for production, and S. Pauker for the cover graphics.

Mannheim, January 1999 *Jens Hagen*

Abbreviations

A	area [m^2]
A^*	adsorbed (activated) molecules of component A
a	catalyst activity
a_s	area per mass [m^2/kg]
A	electron acceptor
ADH	alcohol dehydrogenase enzyme
ads	adsorbed (subscript)
AES	Auger electron spectroscopy
aq	aqueous solution (subscript)
bcc	body-centered cubic
bipy	2,2′-bipyridine
Bu	butyl C_4H_9-
c_i	concentration of component i [mol/L]
CB	conduction band
C.I.	constraint index
Cp	cyclopentadienyl C_5H_5-
CSTR	continuous stirred tank reactor
D	diffusion coefficient [m^2/s]
d	deactivation (subscript)
D	electron donor
DMFC	direct methanol fuel cell
E	E factor, rate of waste [kg] per product unit [kg]
E_a	activation energy [J/mol]
E_{bg}	bandgap energy [eV]
E_F	Fermi level
E	enzyme
e.e.	enantiomeric excess [%]
eff	effective (subscript)
E_i	ionisation energy
E_r	redox potential [V]
Et	ethyl C_2H_5-
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance spectroscopy

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e	electrons
F	Faraday constant [96 485 C/mol]
fcc	face-centered cubic
ΔG	Gibb's free energy [J/mol]
G	gas (subscript, too)
GHSV	gas hourly space velocity [h^{-1}]
H	Henry's law constant
H_{ex}	external holdup
ΔH_{ads}	adsorption enthalpy [J/mol]
ΔH_f	enthalpy change of formation [J/mol]
H_m	modified Henry's law constant
ΔH_R	reaction enthalpy [J/mol]
H_0	Hammett acidity function
HC	hydrocarbon
HSAB	hard and soft acids and bases
h	hard
hcp	hexagonal close packing
I	inhibitor
IL	ionic liquid
ISS	ion scattering spectroscopy
j	current density [A/m^2]
K	equilibrium constant
K_i	adsorption equilibrium constant of component i
K_i	inhibition constant
K_M	Michaelis constant
k	reaction rate constant
k_0	pre-exponential factor
$k_L a_L$	gas-liquid mass transfer coefficient
$k_S a_S$	liquid-solid mass transfer coefficient
k_{tot}	global mass transfer coefficient
L	liquid (subscript)
L	ligand
LEED	low-energy electron diffraction
LF	liquid flow [L/min]
M	metal
m	mass [kg]
$m_{cat.}$	mass of catalyst [kg]
MAO	methylaluminoxane
Med	mediator, redox catalyst
n	number of moles [mol]
n	order of reaction
$\dot{n}$	flow rate [mol/s]
$\dot{n}_{A,0}$	feed flow rate of starting material A [mol/s]
NAD	nicotinamide adenine dinucleotide cofactor
NHE	normal hydrogen electrode

NSR	NO_x storage-reduction
ODE	ordinary differential equation
Oxad	oxidative addition
P	total pressure [bar]
PEG	polyethylene glycol
PEMFC	proton exchange membrane fuel cell
Ph	phenyl C_6H_5-
PPh_3	triphenylphosphine
PTC	phase-transfer catalysis
p	pressure [bar]
p_i	partial pressure of component i [bar]
py	pyridine
R	ideal gas law constant [J mol^{-1} K^{-1}]
R	recycle ratio
R	alkyl
r	reaction rate [mol L^{-1} h^{-1}]
r_{eff}	effective reaction rate per unit mass of catalyst [mol kg^{-1} h^{-1}]
rel	relative (subscript)
r_d	deactivation rate
S	Tafel slope (electrocatalysis)
S	surface area [m^2/kg]
ΔS	entropy change [J mol^{-1} K^{-1}]
S_p	selectivity [mol/mol] or [%]
S	solid (subscript, too)
SCR	selective catalytic reduction
SIMS	secondary-ion mass spectroscopy
SLPC	supported liquid phase catalysts
SMSI	strong metal-support interaction
SSPC	supported solid phase catalysts
s	soft
s	sample standard deviation
s^2	experimental error variance
S^{-1}	mass index, ratio of all the materials [kg] to the product [kg]
S	substrate
sc	supercritical
STY	space time yield [mol L^{-1} h^{-1}, kg L^{-1} h^{-1}]
T	temperature [K]
TEM	transmission electron microscopy
TF	time-factor [$m_{cat}/\dot{n}_{A,0}$]
TOF	turnover frequency [s^{-1}]
TON	turnover number [mol mol^{-1} s^{-1}]
t	time [s, h]
TPD	temperature-programmed desorption
TPR	temperature-programmed reduction
TS 1	titanium(IV) silicalite zeolite catalyst

U	cell voltage [V]
V	volume [m^3]
$\dot{V}$	volumetric flow-rate
V_R	reaction volume [m^3]
VB	valence band
VOC	volatile organic compound
X	conversion [mol/mol] or [%]
$\bar{x}$	mean value of measurements
$\vec{x}$	positional vector (simplex method)
z	tube length [m]
δ	percentage d-band occupancy
$\in$	excitation energy of semiconductors [eV]
$\in_P$	void fraction of particle
η	catalyst effectiveness factor
η	overpotential [V]
θ_i	degree of coverage of the surface of component i
ν	stretching frequencies (IR) [cm^{-1}]
ν_i	stoichiometric coefficient
ρ	density [g/mL]
$\rho_{cat.}$	pellet density of the catalyst [g/mL]
τ	tortuosity
σ	interfacial tension
ϕ_0	work function [eV]
*	active centers on the catalyst surface

Contents

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