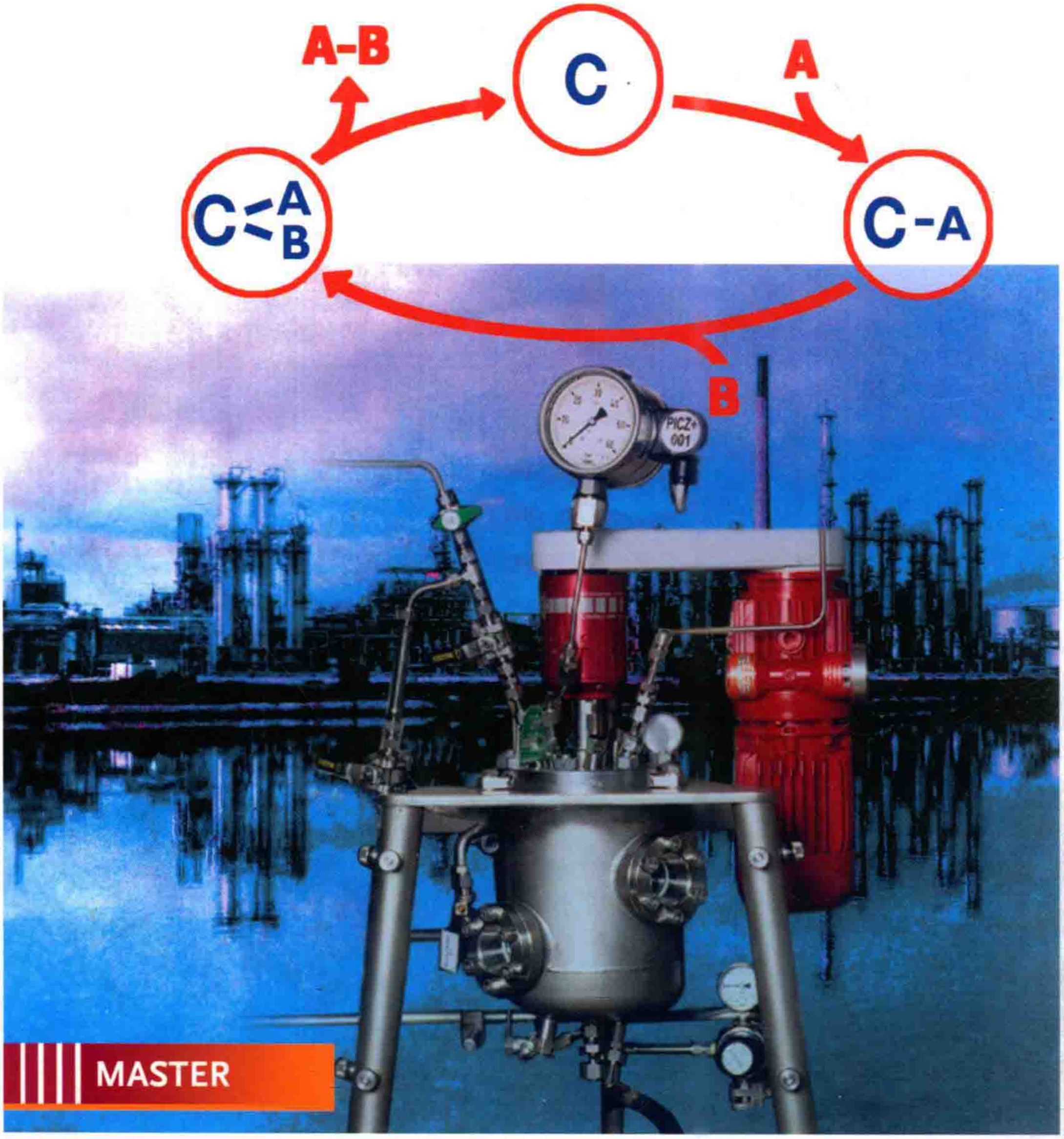
Arno Behr and Peter Neubert

WILEY-VCH

Applied Homogeneous Catalysis



MASTER

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Furthermore, the authors gratefully acknowledge the companies Parr Instrument and Biotage for permission to display their laboratory equipment.

The cover picture shows a facility for the production of 1-alkenes developed by the company Shell (see chapter 22) as well as a pressure reactor by the company Büchi Glas (Uster, Switzerland) (see chapter 13), both of which are also gratefully acknowledged.

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Applied Homogeneous Catalysis

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Foreword

Catalysis represents a key technology that is of fundamental importance for the future development of humankind. The economic importance of catalysis lies in the outstanding creation of valuable products that are found in all areas of our daily life, including nutrition, health, and other day-to-day products. Whilst it may not be too surprising that there are many books available on the subject of catalysis in general, a comprehensive English textbook on *applied* homogeneous catalysis has not yet been produced – until now.

Today, we can distinguish between homogeneous, heterogeneous, and biocatalysis. Homogeneous catalysis in the broadest sense consists of acid–base catalysis and catalysis involving metal compounds. Although, in a homogeneous liquid phase the latter can follow either a radical or coordinative pathway, respectively, homogeneous catalysis is considered to involve reactions that follow a coordination mechanism that is catalyzed by transition metal-containing complexes or metal organic compounds. Thus, homogeneous catalysis represents a truly interdisciplinary field of science in which chemists from all disciplines work together.

During the last few decades, homogeneous catalysis has been applied widely in industry, and it can be assumed that its market share will further increase significantly. Moreover, its industrial implementation requires close cooperation with engineers, as parameters such as the chemical reaction, reactor type, product separation, and process design must each be considered in comprehensive fashion. One of the most important aspects of this book is the interdisciplinary and holistic approach taken towards industrial catalytic processes. Notably, in addition to details of mechanisms and the elementary steps of transition metal catalysis, descriptions are provided of both reactors and separation methods. Unfortunately, however, due to the broad field of the topics incorporated this book can provide only an overview. Yet, chemists and engineers engaged in catalysis will find a wealth of useful information in this book, which may serves simultaneously as both a textbook and a reference book. On that basis, it is recommended for use by chemistry students, chemistry-related engineering students, and also to professionals from industry.

In order to structure the broad field of homogeneous catalysis, and to provide "learning reasons," Part I of the book sheds light on the basic properties of catalysts and process engineering (solvents, analytical methods, reactor choice, catalyst recycling, separation processes, etc.). Subsequently, Part II contains the details of industrially conducted processes (C–C coupling, C–O reactions, oxidations, etc.). Finally, in Parts III and IV, an overview is provided of modern developments, including tandem reactions, combinatorial chemistry, new classes of ligand, nanocatalysis, shifting feedstocks, miniplants, and the future developments of homogeneous catalysis.

The most striking feature of the book is the wealth of practical information that it contains. For example, details can be found of chemical suppliers and equipment manufacturers, including their internet addresses. Furthermore, the comprehensive and well-structured literature section can be employed to expand the readers' knowledge. As is typical for such a textbook, each chapter closes with a section that contains questions (and answers!), where the questions are chosen specifically to test the readers' knowledge and understanding that they should have acquired from the book.

Today, the scientific world is comprised of "real people," whose contributions allow the development of a scientific domain. Consequently, as a special feature the photographs of some of the research workers who have been merited with having made significant contributions to homogeneous catalysis are included, to add a "personal" touch.

Undoubtedly, this book will greatly enrich the field of applied homogeneous catalysis, and Arno Behr has clearly written a volume for which the market has long been waiting. In addition, Peter Neubert has provided an excellent translation.

Prof. Dr Dr h.c. Willi Keim
Institute of Technical and Macromolecular Chemistry at RWTH Aachen University, Germany

Preface

How should this textbook be used?
By reading the following sections, you will find details of:
- The contents and structure of the book.
- The structure of each chapter.
- Which tools will best help you when reading the book and learning the different topics.
- Who has written and arranged the book.

By whom has this textbook been written?
- This book provides information on *homogeneous transition metal catalysis and its applications* in the chemical industry. It does not cover acid–base, heterogeneous, and biocatalysis or organocatalysis.
- This book is not a reference book for specialists in catalysis, but rather an *introductory textbook* for students at the bachelor and master degree levels. A basic knowledge in chemistry is assumed of the reader, but not in catalysis. However, those professionals in the industry may find useful information here about certain products and processes.

What is the structure of the book?
The Applied Homogeneous Catalysis (AHC) section of the book is structured as four main parts, each of which contains about ten chapters. Consequently, there are 40 chapters in total, while a final chapter proposes future developments in homogeneous catalysis.
- **Part I** contains the *Chemical Basics* of organotransition metal chemistry. Here can be found chapters on catalysts, ligands, thermodynamics, and kinetics.
- **Part II** contains the *Process Engineering Fundamentals.* Here will be found information regarding the technical realization of catalytic reactions, together with details of reactor technologies and catalyst separation processes.
- **Part III** describes the most important *Homogeneous Catalyzed Reaction Types,* which are illustrated by typical industrial examples. Some reactions will also be described that will very likely be used in future for the synthesis of fine chemicals or pharmaceuticals.

- **Part IV** lists some *New Trends,* such as nanocatalysis, high-throughput experimentation, or green solvents, all of which may soon become commonplace in the field of homogeneous catalysis.

How is each chapter designed?

- The chapters are made as *compact as possible,* and are of comparable lengths. It is possible to work through a chapter in about an hour. For example, a lecturer can present the contents of one chapter in a single lesson, and then ask students to practice the topics in a later lesson.
- The important *fundamental terms and definitions* are explained at the start of each chapter.
- The chapter *text* is subdivided into several sections, and contains clear figures, equations, tables, and photographs.
- At the end of the chapter any new reactions are illustrated by a "*Typical Experiment,*" providing a concrete description of the chemical reaction in the laboratory.
- Each chapter ends with "*Take-Home Messages,*" where the most important topics are summarized. This enables a quick repetition of the major points of the chapter.
- In the *Literature Appendix* of each chapter can be found a host of references, beginning with the newest citations and going back for the past ten years. Here too can be found the details of books and reviews, as well as some important references that provide the chance to extend your current knowledge. The citations are always given in the sequence: author(s)/(shortened) title/journal/volume/year/pages.
- For each of the 40 chapters can be found ten test questions: the so-called "*Exercise Questions.*" These questions were named in this way because, when you have studied the text thoroughly, it should be possible to answer them very quickly! In total, there are 400 "*Exercise Questions,*" for which the different topics can be memorized and numerous questions solved via typical examples. All answers to the tests, as well as relevant explanations, are given at the end of the book.

Which additional tools will help you?

- Scientific results are always collected by *scientists.* So, in order to provide a closer relation to these people, I asked some of my colleagues to send me their photographs, and these are included in the book. Unfortunately, because the space in the book was very restricted, it was impossible to include everybody's photograph, so some people who were left out may not be happy with me! My apologies!
- In the *Literature Appendix,* some *practical lists* can be found that contain information concerning the manufacturers and/or distributors of chemicals, catalysts, solvents, apparatuses, and so on. Of course, these lists are not necessarily complete – they are only suggestions.
- Some important apparatuses and plants are illustrated in photographs, or as simplified *schemes.* Although these can provide a first impression of the equipment, the details may not be available at this stage.
- When useful, some *internet addresses* have been given which – of course – can change, or may even disappear after a time. Please note that none of the information provided in this book is given with any guarantee.

- Throughout the book, certain *graphical symbols* draw attention to important current topics:

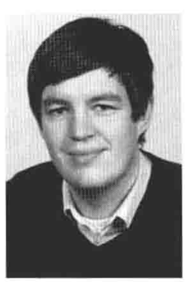
	Technical information
	Typical experiment
	Mechanism
	Exercises
	Internet addresses
	Renewable resources
	Asymmetric catalysis

Who has written and arranged this book?

The first German edition of this textbook was written in 2006/2007 by Arno Behr, who is Professor of Technical Chemistry and Catalysis at the Technical University Dortmund, Germany. Subsequently, based on the high demand for the book in German-speaking countries, in 2010/2011 it was actualized, tightened and translated into English by A. Behr and P. Neubert, to provide help in the curricula of English-speaking countries. We wish you much pleasure and success as you browse through its chapters!

Dortmund, June 2011

Arno Behr



Peter Neubert

Abbreviations

AAA	Acetamidoacrylic acid 28
ACA	Acetamido cinnamic acid 28
Acac	Acetylacetonate
ADMET	Acyclic diene metathesis 23
Amphos	Ligand 17
AMS	Accessible molecular surface 7
Ar	Aryl group
BASPHOS	Ligand 28
BINAP	Ligand 7 and 9
Binaphos	Ligand 20
BINAS	Ligand 17
Binol	Ligand 36
Biphephos	Ligand 7
BISBIS	Ligand 17
BMIM	Butyl-methyl-imidazolium 34
bn	Billion
BR	Butadiene rubber 24
Bu^n	*n*-butyl group
Bu^i	*iso*-butyl group
Bu^t	*tert*-butyl group
Bz	Benzyl group
CAL	Croton aldehyde 28
CAMP	Ligand 9
CAN	Chemical Abstract Number
Cat.	Catalyst
CatASium	Ligand 28
CDT	Cyclododecatriene 28
CIP	Cahn–Ingold–Prelog rules 9
CM	Cross-metathesis 23
CMC	Critical micelle concentration 17
CN	Coordination number
CNRS	Centre National de la Recherche Scientifique

COC	Cycloolefin copolymers 24
cod	1,5-Cyclooctadiene
COT	Cyclooctatetraene 22
Cp	Cyclopentadienyl ligand
cp	Centipoise (viscosity unit)
CSTR	Continuous stirred-tank reactor 13
Cy	Cyclohexyl group
dba	Dibenzylidene acetone ligand 6
DBF	*N,N*-Dibutylformamide
DBN	Nitrogen ligand 36
DBU	Nitrogen ligand 36
DCp	Dicyclopentadiene
DeguPHOS	Ligand 28
DET	Diethyltartrate 29
DFT	Density functional theory 7
diop	Ligand 7 and 9
DIPAMP	Ligand 9
DMF	Dimethylformamide
DMIT	Itaconic dimethyl ester 28
DMSO	Dimethylsulfoxide
DMT	Dimethylterephthalate 29
DOPA	3,4-Dihydroxyphenylalanine 9 and 28
DPEphos	Ligand 7
DPFphos	Ligand 7
dppb	Bis(diphenylphosphino)butane 7
dppe	Bis(diphenylphosphino)ethane 7
dppf	Bis(diphenylphosphino)ferrocene 7
dppm	Bis(diphenylphosphino)methane 7
dppp	Bis(diphenylphosphino)propane 7
DuPhos	Ligand 7 and 28
E	Electric field strength 8
e	Electron
E_A	Activation energy 11
e.e.	Enantiomeric excess 4 and 9
EF	Electrostatic factor
E-factor	Environmental factor 3
EMIM	Ethylmethylimidazolium 34
EPC	Enantiopure compound 9
EPDM	Ethylene propylene diene monomer rubber
ER	Eudysmic ratio 9
ESI	Electrospray ionization 12
Et	Ethyl group
et al.	And others
ETH	Swiss Federal Institute of Technology
eV	Electronvolt 12

EXAFS	Extended X-ray absorption fine structure 12
FBS	Fluorous biphasic system 18
FEAST	Further exploitation of advanced Shell technology 23
FTIR	Fourier transform-infrared spectroscopy 12
HAM	Hydroaminomethylation 32
ht	head-tail (linkage)
HDPE	High-density polyethylene 24
hh	head-head (linkage)
HMPT	Hexamethylphosphoric acid triamide
HPLC	High-performance liquid chromatography
Hz	Hertz 12
ICP	Inductively coupled plasma 12
IFP	Institut Français du Pétrole
IL	Ionic liquid 34
IM	Imdiazolium cation 34
IR	Infrared (spectroscopy) 12
ITA	Itaconic acid 28
JosiPHOS	Ligand 28
K	Equilibrium constant 10
k	Reaction rate constant 11
L	Ligand
L-DOPA	see: DOPA
LDPE	Low-density polyethylene 24
LLBT	Liquid–liquid biphasic technique 17
LLDPE	linear low-density polyethylene 24
LPO	Low-pressure oxo process 20
M	Metal, usually transition metal
MAA	Methyl acetamido acrylate 28
MAC	Methyl acetamido cinnamate 28
MAO	Methylalumoxane 24
Me	Methyl group
Mes	Mesityl group (2,4,6-trimethylphenyl-)
mil	Million
Monophos	Ligand 28
MPI	Max Planck Institut
MS	Mass spectroscopy 12
MTBE	Methyl-*tert*-butylether
MTO	Methyltrioxorhenium 29
MW	Microwaves 39
n:iso	ratio of linear to branched isomers
nbd	Norbornadiene ligand
NHCs	Carbene ligands 36
NMO	*N*-methylmorpholine-*N*-oxide 29
NMR	Nuclear magnetic resonance spectroscopy 12
NorPHOS	Ligand 7

OAc	Acetate group
OCT	Olefins conversion technology 23
OES	Optical emission spectrometry 12
ON	Oxidation number
OTf	Triflate group (trifluoromethanesulfonate)
P	Productivity 4
PAMP	Ligand 9
PC	Propylene carbonate
PCHC	Poly(cyclohexenecarbonate) 26
PE	Polyethylene 24
PEG	Polyethylene glycol 34
PennPHOS	Ligand 28
PETPP	Polyethoxylated triphenylphosphine 17/18
Ph	Phenyl group
PHIP	*Para*-hydrogen-induced polarization 12
PHOPHOS	Ligand 17
Pip	Piperidyl group
PO	Propylene oxide 29
PP	Polypropylene 24
ppb	Parts per billion
PPC	Poly(propylene carbonate) 26
PPG	Polypropylene glycol
ppm	Parts per million
Pr^n	*n*-propyl group
Pr^i	*iso*-propyl group
PTA	Phosphotriazaadamantane 17
PTC	Phase-transfer catalysis 17
PTHF	Poly(tetrahydrofuran) 34
PVP	Poly(vinylpyrrolidone)
QALE	Quantitative analysis of ligand effects 7
Q-Factor	Safety factor 3
R	Organic chain
(*R*).	Rectus; enantiomer descriptor 9
RCH/RP	Ruhr Chemie/Rhône-Poulenc process 20
RCM	Ring-closing metathesis 23
RIM	Reaction injection molding 23
RMIM	Alkylmethylimidazolium 34
ROM	Ring-opening metathesis 23
ROMP	Ring-opening metathesis polymerization 23
RON	Research octane number
RoPHOS	Ligand 28
rpm	Revolutions per minute 13
RT	Room temperature
(*S*)	Sinister; enantiomer descriptor 9
S	Selectivity

SA	Sorbic acid 28
Salen	Ligand 29
SAPC	Supported aqueous-phase catalysis 16
SCF	Supercritical fluids 34
SHOP	Shell higher olefin process 22
SILP	Supported ionic liquid-phase catalysis 34
Siphos	Ligand 28
SLPC	Supported liquid-phase catalysis 16
SM	Self-metathesis 23
SSC	Solvent-stabilized colloids 37
STM	Scanning tunneling microscopy 37
STY	Space–time yield 4
t	tonne (metric)
$t \cdot a^{-1}$	tonnes per annum = annual tonnes
TangPHOS	Ligand 20
TBAI	Tetrabutylammonium iodide
TBHP	*tert*-butyl hydroperoxide 29
TEM	Transmission electron microscopy 37
TEMPO	Tetramethylpiperidin-1-yl)oxyl 29
TetraPHOS	Ligand 7
th	tail-head (linkage)
THF	Tetrahydrofuran
TML	Thermomorphic liquid system 18
TOF	Turnover frequency 4
Tol	Tolyl group
TON	Turnover number 4
TPA	Terephthalic acid 29
TPAP	Tetrapropylammonium perruthenate 29
TPP	Triphenylphosphine
TPPDS	Triphenylphosphine disulfonate 17
TPPMS	Triphenylphosphine monosulfonate 17
TPPTS	Triphenylphosphine trisulfonate 17
Triphos	Ligand 7
Tripod	Ligand 7
TRPTC	Thermoregulated phase-transfer catalysis 18
tt	tail-tail (linkage)
TTN	Total turnover number 4
UCC	Union Carbide Chemicals
UCST	Upper critical solution temperature 18
UHMWPE	Ultra-high-molecular-weight polyethylene 24
v	Reaction rate 11
VE	Valence electrons 5
X	Conversion 4
Xantphos	Ligand 7
XRD	X-ray diffraction 37

Xyl	Xylyl group
XyliPHOS	Ligand
Y	Yield 4
Y	Nucleophilic group 25

Contents