

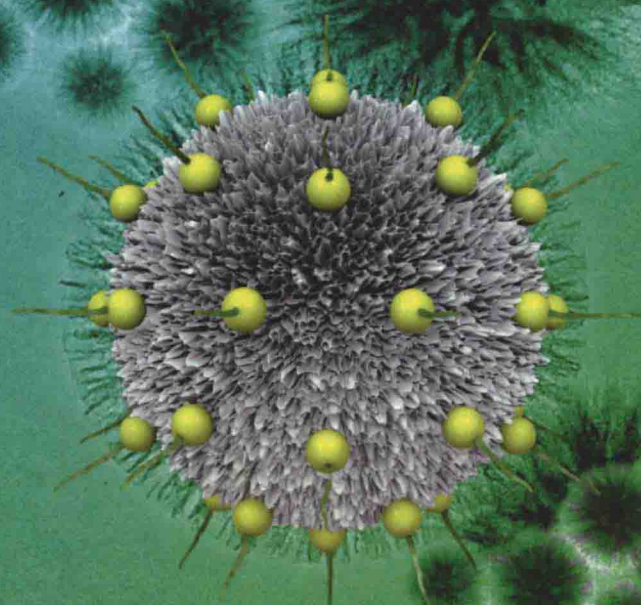
Nanocatalysis

Synthesis and Applications

Edited by

Vivek Polshettiwar and Tewodros Asefa

With a Foreword by Graham Hutchings



WILEY

NANOCATALYSIS

Synthesis and Applications

Edited by

Vivek Polshettiwar

Nanocatalysis Laboratory
Department of Chemical Sciences
Tata Institute of Fundamental Research
Colaba, Mumbai, India

Tewodros Asefa

Department of Chemistry and Chemical Biology
Department of Chemical and Biochemical Engineering
The Rutgers Catalysis Research Center (RCRC)
Rutgers, The State University of New Jersey
Piscataway, NJ, USA

WILEY

Cover Design: John Wiley & Sons, Inc.
Cover Illustration: © Vivek Polshettiwar

Copyright © 2013 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Nanocatalysis : synthesis and applications / edited by Vivek Polshettiwar, Tewodros Asefa.
pages cm

“Published simultaneously in Canada”—Title page verso.

Includes bibliographical references and index.

ISBN 978-1-118-14886-0 (cloth)

1. Nanostructured materials.
 2. Catalysts.
 3. Nanostructured materials—Industrial applications.
 4. Catalysts—Industrial applications.
- I. Polshettiwar, Vivek II. Asefa, Tewodros.

TA418.9.N35N2466 2013

660'.2995—dc23

2012049879

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

NANOCATALYSIS



FOREWORD

This book, entitled *Nanocatalysis: Synthesis and Applications*, edited by Vivek Polshettiwar and Tewodros Asefa, who are both active researchers in this exciting field, comprises a broad range of authoritative sections that are authored by world-class researchers. The book is an important addition to the rapidly growing area of nanocatalysis. The book gives comprehensive perspectives on a wide array of research topics related to nanocatalysis, by highlighting the importance of nanocatalysis in areas ranging from the efficient production of commodity and value-added chemical products to renewable energy and environmental remediation—topics that are of contemporary interest worldwide from government and industry to academia as well as to society as a whole. The book comprises several different topics related to nanocatalysis with topical areas distributed throughout the text, including fundamental aspects of nanocatalysis, surface science, and mechanistic and theoretical studies on how nanocatalysts function. In addition, the range of applications of nanocatalysis in several areas is also covered, including energy and environment. Therefore, researchers in both industry and academia alike, as well as new students and seasoned researchers, will appreciate reading the book.

The timing of this book could not be any better—as can be witnessed by the large number of research publications being reported in the journals concerned with nanoscience and nanotechnology in general, which relate to nanocatalysis in particular. The field of nanocatalysis has attracted intense interest over the last two decades, although, of course, the use of nano-sized materials as catalysts has been a research topic for many decades. The strength of this book is that it brings together the key areas in this broad subject in an easily accessible way. Readers will readily be able to obtain quick information on a variety of topics from synthesis and characterization of nanocatalysts as well as their applications. So, we should thank the two editors for embarking on this project and bringing together this key collection of studies on nanocatalysis. As an active researcher in the field of nanocatalysis, I strongly feel that this book will also stimulate new cutting-edge research activities in the area. However, at the same time, this book gives a wealth of fundamental information that is highly relevant for newcomers to the field as well as providing basic information to graduate and undergraduate students alike. I also consider that the text will be a valuable resource to lecturers with interests in teaching the principles of nanocatalysis. Moreover, I expect the book to inspire more researchers to work on a variety of new research aspects related to nanocatalysis and the development of novel and improved nanocatalysts, especially directed to many of

the contemporary grand challenges of our generation that the world faces today in areas such as renewable energy, production of value-added chemical products, and synthesis of materials in a “greener” or sustainable way, as well as environmental remediation. The book is, therefore, a very valuable resource.

Professor Graham J. Hutchings FRS
Director of the Cardiff Catalysis Institute
The Cardiff School of Chemistry
Cardiff University, UK

PREFACE

Catalysis lies at the heart of chemical processes that lead to a variety of chemical products and synthetic materials. This can be highlighted by the fact that about more than 80–85% of synthetic materials and commercial chemical products see at least one, if not more, catalyst at some point of their synthesis. This means, the synthesis of many useful household products, such as medicines, detergents, polymeric fibers, perfumes, fuels, paints, lubricants, and a myriad of other value-added chemical products essential to humans, would have been neither possible nor feasible in the absence of catalysts.

Catalysts are chemical substances that enable the (“smooth”) transformation of fine chemicals into value-added chemical products or synthetic materials. Catalysts play major roles in such conversions of many different chemical species into important final products by enabling the chemical transformations to take place effectively, that is, in an economical manner, with less by-products, with less energy consumption, or by giving the desired products in larger amount in relatively shorter reaction times.

Besides many conventional chemical processes where catalysts have already been used, the emergence of the grand challenges in areas such as renewable energy and environmental problems that our world faces has made the development of catalysts capable of contributing to the production of renewable energy and environmental remediation among the “holly-grail” research areas worldwide currently. Furthermore, in the face of dwindling fossil fuel sources, the development of catalysts that allow the transformation of CO₂ into fuels and the conversion of water into H₂ in a viable manner has become very vital and contemporary research area today.

Catalysts are traditionally divided into two major groups based on the type of phase of the catalyst is in relative to the catalytic reaction mixtures, that is, homogeneous or heterogeneous catalysts. Homogeneous catalysts are those that exist in the same phase as the reactants. They are generally soluble organic or organometallic complexes and often give chemo-, regio-, and stereoselective products. However, they are relatively difficult to separate from reaction mixtures for reuse at the end of reactions. On the other hand, there are solid or insoluble catalysts, also called heterogeneous catalysts. In many instances, the solid catalysts contain homogeneous catalysts supported on neutral or catalytic-active solid support materials such as porous silica or alumina. These types of catalysts are easily separable and reusable at the end of reactions; however, they often give relatively poor reaction yields, compared with many of their homogeneous counterparts.

The fields of nanoscience and nanotechnology have been unquestionably thriving over the last two or so decades. The positive societal impacts of nanoscience and nanotechnology have also now become clear to scientists and engineers alike, and even to the public, although much work still remains in understanding the potential biological and health effects of many nanomaterials. One of the first examples where the applications of nanoscience and nanotechnology were successfully demonstrated has been in

the area of catalysis; that is, nanoscience and nanotechnology has made it possible for a class of nanomaterials with potential applications in catalysis (or nanocatalysts) to come alight. Many nanomaterials with different interesting catalytic properties have actually been documented, and some of them have also been commercially used. In fact, even before systematic research on nanocatalyst development began or unbeknownst to many, several materials with nanoscale sizes have been successfully used as catalysts in many reactions. Nanocatalysts are interesting from a point of view of being in between homogeneous and heterogeneous catalysts, although this classification is not quite strict. In other words, nanocatalysts exhibit quasihomogeneous or quasiheterogeneous catalytic properties, and thus allow for rapid and selective chemical transformations, with excellent product yield and ease of catalyst separation and recovery. Nanocatalysis can thus be simply defined as the use of nanoscale materials in catalysis, often with effective catalytic properties, that is, efficient catalytic activities as well as ease of catalyst separation, recovery, and reuse.

The objective of the book is to review the development and progress of nanocatalysts and nanocatalysis over the past two decades and to provide readers with well-compiled information about the status of the field on the synthesis and applications of various nanocatalysts for the production of industrially and pharmaceutically important compounds and synthetic materials. The book is also prepared to give quick and highly compiled information on various topics related to nanocatalysts and nanocatalysis to students, faculty, and industrial personnel, who are working in catalysis research. This, in turn, is expected to promote further advances in the field.

The information in the book has been compiled in 19 chapters. The first chapter provides some introduction on nanocatalysts and nanocatalysis. The next six chapters are devoted to nanocatalysts or nanocatalysis for carbon–carbon and carbon–heteroatom coupling reactions. The next two chapters are devoted to nanocatalysts and nanocatalysis for fine chemical synthesis. The subsequent four chapters are devoted to the use of nanocatalysts for oxidation–hydrogenation-type reactions. The four next chapters are also devoted to the topic of nanomaterial-based photocatalysis and the use of nanocatalysis to produce nonconventional sources of energy. The last two chapters focus on the use of nanocatalysts in the chemical industry.

Many of the chapters are written in such a way that they dwell on the synthesis and characterization of nanocatalysts and their properties and applications in synthesis. Each chapter has been contributed by different groups of researchers worldwide, who have expertise in various aspects of nanocatalysts and/or nanocatalysis. Each team has used recent literature in its respective areas of expertise. Thus, we hope that the book will give a broad perspective on the design and synthetic methods to various types of nanocatalysts and their applications. In addition, the various types of advanced characterization methods described in most of the chapters will highlight the current state-of-the-art of various spectroscopic and microscopy tools used for elucidation of nanocatalysts and nanocatalysis. Moreover, methods used for probing the activities of catalysts and the strategies utilized to improve the catalytic activities and selectivities of nanocatalysts should give further information for the researchers working in the area.

We edited this book because we realize that there are several missing areas of interest in the field of nanocatalysis today, especially in light of the rapid progress being made

in the field and the enormous number of papers being published in the area. In addition, although there are few other books written on topics related to nanocatalysis, this book focuses on nanocatalysts and contains a comprehensive review and a fair distribution of synthesis and characterization of nanocatalysts and application of nanocatalysts and nanocatalysis in areas ranging from pharmaceutical products to renewable energy materials and biotransformations.

The book is possible only because of the involvement of many outstanding researchers worldwide, who devoted a significant amount of their time to make contributions to the different sections of the chapters in the book. They are the real craftsmen of this very comprehensive book. We are, therefore, indebted to all of them, who have contributed enormously to make this book possible. We also acknowledge the support we have received from our coworkers, friends, and family members throughout the process of putting the book together.

Vivek Polshettiwar and Tewodros Asefa

LIST OF CONTRIBUTORS

Editors

Vivek Polshettiwar, Nanocatalysis Laboratory, Department of Chemical Sciences, Tata Institute of Fundamental Research, Mumbai, India

Tewodros Asefa, Department of Chemistry and Chemical Biology and Department of Chemical and Biochemical Engineering, The Rutgers Catalysis Research Center (RCRC), Rutgers, The State University of New Jersey, Piscataway, NJ, USA

Authors

Abhinandan Banerjee, Department of Chemistry, University of Saskatchewan, Saskatoon, SK, Canada

A. V. Biradar, Department of Chemistry and Chemical Biology and Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ, USA

Vitaliy Budarin, Department of Chemistry, Green Chemistry Centre of Excellence, University of York, Heslington, York, UK

Victorio Cadierno, Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain

Jeong Ho Chang, Korea Institute of Ceramic Engineering and Technology, Seoul, South Korea

Rafael Chinchilla, Department of Organic Chemistry and Institute of Organic Synthesis, University of Alicante, Alicante, Spain

James H. Clark, Department of Chemistry, Green Chemistry Centre of Excellence, University of York, Heslington, York, UK

Natalia J. S. Costa, Laboratory of Nanomaterials and Catalysis, Institute of Chemistry, USP, São Paulo, Brazil

S. Das, Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, NJ, USA

Aziz Fihri, Nano-Catalysis Laboratory, KAUST Catalysis Centre, King Abdullah University of Science and Technology, Thuwal, KSA

Joaquín García-Álvarez, Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain

- Sergio E. García-Garrido**, Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain
- Anirban Ghosh**, Tata Chemicals Ltd, Innovation Center, Pune, India
- Zhong He**, Department of Chemical, Biological and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, NJ, USA
- Balaji R. Jagirdar**, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India
- Suresh Babu Kalidindi**, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India; Anorganische Chemie II, Ruhr Universität Bochum, Bochum, Germany
- Kiyotomi Kaneda**, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan
- Deepa Khushalani**, Materials Chemistry Group, Tata Institute of Fundamental Research, Mumbai, India
- Rajiv Kumar**, Tata Chemicals Ltd, Innovation Center, Pune, India
- Debashish Kundu**, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India
- Brigid Lanigan**, Department of Chemistry, Green Chemistry Centre of Excellence, University of York, Heslington, York, UK
- Jin Hyung Lee**, Korea Institute of Ceramic Engineering and Technology, Seoul, South Korea
- Soo Youn Lee**, Korea Institute of Ceramic Engineering and Technology, Seoul, South Korea
- Yong Li**, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
- Jones Limberger**, Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, Porto Alegre, Brazil
- Gaoqing Lu**, ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering and AIBN, The University of Queensland, Qld, Australia
- Biswajit Mishra**, Materials Chemistry Group, Tata Institute of Fundamental Research, Mumbai, India
- Takato Mitsudome**, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan
- Adriano L. Monteiro**, Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, Porto Alegre, Brazil
- Nirmalya Mukherjee**, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India
- K. S. Nagabhushana**, Tata Chemicals Ltd, Innovation Center, Pune, India
- Carmen Nájera**, Department of Organic Chemistry and Institute of Organic Synthesis, University of Alicante, Alicante, Spain

- Radha Narayanan**, Department of Chemistry, University of Rhode Island, Kingston, RI, USA
- Brindaban C. Ranu**, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India
- Debabrata Rautaray**, Tata Chemicals Ltd, Innovation Center, Pune, India
- Liane M. Rossi**, Laboratory of Nanomaterials and Catalysis, Institute of Chemistry, USP, São Paulo, Brazil
- Debasree Saha**, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India
- Robert W. J. Scott**, Department of Chemistry, University of Saskatchewan, Saskatoon, SK, Canada
- K. K. Sharma**, Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, NJ, USA
- Wenjie Shen**, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
- Peter S. Shuttleworth**, Departamento de Física de Polímeros, Elastómeros y Aplicaciones Energéticas, Instituto de Ciencia y Tecnología de Polímeros, CSIC, Madrid, Spain
- R. Silva**, Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, NJ, USA
- Lianzhou Wang**, ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering and AIBN, The University of Queensland, Qld, Australia
- Xianqin Wang**, Department of Chemical, Biological and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, NJ, USA
- Zhi-Kang Xu**, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China
- Xu Zong**, ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering and AIBN, The University of Queensland, Qld, Australia

CONTENTS

Foreword	vii
<i>Graham Hutchings</i>	
Preface	ix
List of Contributors	xiii
1 INTRODUCTION TO NANOCATALYSIS	1
<i>Vivek Polshettiwar and Tewodros Asefa</i>	
2 NANOCATALYSTS FOR THE HECK COUPLING REACTIONS	11
<i>T. Asefa, A. V. Biradar, S. Das, K. K. Sharma, and R. Silva</i>	
3 NANOCATALYSTS FOR THE SUZUKI COUPLING REACTIONS	51
<i>Liane M. Rossi, Natalia J. S. Costa, Jones Limberger, and Adriano L. Monteiro</i>	
4 SONOGASHIRA REACTIONS USING NANOCATALYSTS	89
<i>Rafael Chinchilla and Carmen Nájera</i>	
5 NANOCATALYSTS FOR HIYAMA, STILLE, KUMADA, AND NEGISHI C–C COUPLING REACTIONS	133
<i>Abhinandan Banerjee and Robert W. J. Scott</i>	
6 ARYL CARBON–HETEROATOM COUPLING REACTIONS USING NANOMETAL CATALYST	189
<i>Brindaban C. Ranu, Debasree Saha, Debasish Kundu, and Nirmalya Mukherjee</i>	
7 NANOSTRUCTURED CATALYSTS FOR THE ALDOL, KNOEVENAGEL, AND HENRY REACTIONS	221
<i>T. Asefa, A. V. Biradar, S. Das, and R. Silva</i>	
8 NANOCATALYSTS FOR REARRANGEMENT REACTIONS	251
<i>Joaquín García-Álvarez, Sergio E. García-Garrido, and Victorio Cadierno</i>	
9 OXIDATION OF ALCOHOLS USING NANOCATALYSTS	287
<i>Takato Mitsudome and Kiyotomi Kaneda</i>	
10 TUNING THE MORPHOLOGY OF METAL OXIDES FOR CATALYTIC APPLICATIONS	333
<i>Yong Li and Wenjie Shen</i>	

11	NANOCATALYSTS FOR HYDROGENATION REACTIONS	405
	<i>Radha Narayanan</i>	
12	HYDROGENOLYSIS REACTIONS USING NANOCATALYSTS	443
	<i>Aziz Fihri and Vivek Polshettiwar</i>	
13	NANOMATERIAL-BASED PHOTOCATALYSTS	469
	<i>Biswajit Mishra and Deepa Khushalani</i>	
14	NANOCATALYSTS FOR WATER SPLITTING	495
	<i>Xu Zong, Gaoqing Lu, and Lianzhou Wang</i>	
15	PROPERTIES OF NANOCATALYTIC MATERIALS FOR HYDROGEN PRODUCTION FROM RENEWABLE RESOURCES	561
	<i>Zhong He and Xianqin Wang</i>	
16	NANOCATALYSTS FOR BIOFUELS	595
	<i>Vitaliy Budarin, Peter S. Shuttleworth, Brigid Lanigan, and James H. Clark</i>	
17	NANOMATERIAL-BASED BIOCATALYST	615
	<i>Jin Hyung Lee, Soo Youn Lee, Zhi-Kang Xu, and Jeong Ho Chang</i>	
18	ROLE OF NANOCATALYSIS IN CHEMICAL INDUSTRY	643
	<i>Anirban Ghosh, K. S. Nagabhushana, Debabrata Rautaray, and Rajiv Kumar</i>	
19	NANOCATALYSIS: ACTIVATION OF SMALL MOLECULES AND CONVERSION INTO USEFUL FEEDSTOCK	679
	<i>Suresh Babu Kalidindi and Balaji R. Jagirdar</i>	
	Index	713