Catalysis for Alternative Energy Generation

László Guczi • András Erdőhelyi Editors

# Catalysis for Alternative Energy Generation



*Editors* László Guczi Department of Surface and Chemistry and Catalysis Institute of Isotopes Hungarian Academy of Sciences Budapest, Hungary

András Erdőhelyi Department of Solid State and Radiochemistry University of Szeged Szeged, Hungary

ISBN 978-1-4614-0343-2 ISBN 978-1-4614-0344-9 (eBook) DOI 10.1007/978-1-4614-0344-9 Springer New York Heidelberg Dordrecht London

Library of Congress Control Number: 2012935430

#### © Springer Science+Business Media New York 2012

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

#### Preface

Chemistry without catalysis is like a bell without sound, or a warrior without blade.

Alwin Mittasch

In the twenty-first century, human beings face the exhaustion of fossil energy feedstock. The amount of high quality and easily accessible feedstocks is decreasing, hence the use of heavy and dirty feedstocks must perforce be explored. Poisoned crudes need to be treated in order to remove contaminants such as Nitrogen- and Sulfur-containing molecules and metals. Thus it is imperative to consider alternative sources of energy – such as biomass – for chemicals and for transportation fuels. To underline its importance let me refer to President Bush: *President Bush launches the Hydrogen Fuel Initiative. "Tonight I am proposing \$1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free."* 

Alternative feedstocks, such as biomass and renewables, are being investigated in biorefineries for the production of biofuels and (bio)chemicals. These feedstocks contain many oxygen-containing molecules, hence they are more or less polar. This poses special problems for the development of catalytic technology to treat such new feedstocks.

Very pure and simple natural feedstocks, such as methane and light alkanes, can also be used as the basis for production of fuels and chemicals. The fundamental problems here are the selective activation of the C–H bond without the formation of excessive amounts of  $CO_2$ , hydrogenation of  $CO_2$ , or its conversion into other useful materials.

Looking through the possible technologies, it becomes clear that catalysis is the key technology to help solve the problems associated with the use of alternative feedstocks. Traditional catalysts are extremely efficient for pure, apolar oil feedstocks. Heavy and dirty feedstocks require catalysts for removal and decomposition of poisonous molecules and for removal of heavy metals. Can these processes be combined in one catalyst? This "ideal" catalyst fixes the heavy metals in such a way that they serve as catalytic sites for decomposition and removal of the poisonous molecules. In addition, the catalyst contains the acid sites necessary for cracking and isomerization of long-chain hydrocarbons.

In the case of biomass and renewables, poisoning of the catalyst surface by polar molecules must be avoided. The "ideal" catalyst takes oxygen atoms out of the polar molecules and stores them in its structure in such a way that the catalyst becomes ready to do its job, the conversion of biomass into fuels and basic chemicals.

For methane conversion, catalytic research boils down to "selectivity": selective activation of the C–H bond while avoiding complete burning of methane into carbon dioxide and water.

The ideal catalysts, as described above, do not exist, except for the enzymes that activate methane by insertion of an oxygen atom in the C–H bond. We must rely on

- 1. The design and construction of improved catalyst materials, which are designed by either combinatorial methods or rational catalyst design, based on theory and advanced characterization methods
- 2. The intelligent combination of different types of catalysts, making use of the respective strengths of these catalytic materials; all combinations should be allowed: enzyme plus heterogeneous catalyst, homogeneous plus heterogeneous catalyst; and so on;. In this respect, photocatalysis also comes into the picture; and
- 3. Alternative reaction media in which catalytic and separation technologies are combined. Examples include catalysis in ionic liquids, supercritical conditions. In this way, nonreactive aggregates of molecules can be disentangled into monomolecular entities, which are more susceptible to catalytic attack.

Finally, irrespective of the catalytic process developed, questions will be raised about the sustainability of the catalyst, its impact on the environment, and its impact on climate. The economic, environmental, and social impacts of a process must be evaluated before production can start. Scientists must take these considerations into account in multidisciplinary studies.

Readers of this book will learn about the importance of catalysis in these processes. Introductory chapters discuss catalysis and catalytic processes to handle the broad variety of alternative feedstocks (biomass, methane, very heavy crude, and bitumen) that one can use for the production of transportation fuels and chemicals. The start of the discussion is knowledge of the performance of the catalysts currently on the market and the performance of catalysts in development. Further chapters explore the effect of impurities and poisons in these alternative feedstocks on the performance of existing catalyst materials and propose new challenges for improving these materials. In addition, several routes are designed to approach the "ideal" multifunctional catalyst or the "most appropriate" combination of "ideal" catalytic materials to handle these new feedstocks.

Preface

The role of new tools of investigation, in situ spectroscopic observation of catalysts in action, and theory in this process of catalyst development is highlighted. Finally, the socioeconomic implications in using these alternative feedstocks are briefly covered.

Budapest, Hungary Szeged, Hungary László Guczi András Erdőhelyi

## Contents

1	Introduction and General Overview Gabriele Centi, Paola Lanzafame, and Siglinda Perathoner	1
2	Catalytic Production of Liquid Hydrocarbon Transportation Fuels Juan Carlos Serrano-Ruiz and James A. Dumesic	29
3	Utilization of Biogas as a Renewable Carbon Source: Dry Reforming of Methane Christina Papadopoulou, Haris Matralis, and Xenophon Verykios	57
4	<b>Reforming of Ethanol</b> András Erdőhelyi	129
5	Methanol Steam Reforming Malte Behrens and Marc Armbrüster	175
6	Biodiesel Production Using Homogeneous and Heterogeneous Catalysts: A Review	237
	Ajay K. Dalai, Titipong Issariyakul, and Chinmoy Baroi	
7	Ajay K. Dalai, Titipong Issariyakul, and Chinmoy BaroiHeterogeneous Catalysts for Converting RenewableFeedstocks to Fuels and Chemicals.Karen Wilson, Adam F. Lee, and Jean-Philippe Dacquin	263
7 8	Heterogeneous Catalysts for Converting Renewable Feedstocks to Fuels and Chemicals	263 305
-	Heterogeneous Catalysts for Converting RenewableFeedstocks to Fuels and Chemicals.Karen Wilson, Adam F. Lee, and Jean-Philippe DacquinCatalytic Combustion of Methane.	

х

11	Some Colloidal Routes to Synthesize Metal Nanoparticle-Based Catalysts Szilvia Papp, László Kőrösi, Rita Patakfalvi, and Imre Dékány	413
12	Synthesis, Structure, and Photocatalytic Activity of Titanium Dioxide and Some of Its Surface-Modified Derivatives László Kőrösi, Szilvia Papp, and Imre Dékány	459
13	<b>Photocatalysis: Toward Solar Fuels and Chemicals</b>	491
14	<b>Concluding Remarks and Future Perspectives</b> András Tompos	513
Ind	ex	525

### Contributors

Marc Armbrüster Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

Chinmoy Baroi Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, Canada

Malte Behrens Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

**Christina Bock** Institute for Chemical Processes and Environmental Technologies, National Research Council of Canada, Ottawa, ON, Canada

**Gabriele Centi** Department of Industrial Chemistry and Engineering of Materials and CASPE (INSTM Laboratory of Catalysis for Sustainable Production and Energy), University of Messina, Messina, Italy

Jean-Philippe Dacquin Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK

Ajay K. Dalai Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, Canada

**Imre Dékány** Supramolecular and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, University of Szeged, Szeged, Hungary

Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary

James A. Dumesic Department of Chemical and Biological Engineering, University of Wisconsin—Madison, Madison, WI, USA

András Erdőhelyi Department of Solid State and Radiochemistry, University of Szeged, Szeged, Hungary

Koichi Eguchi Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, Japan

**Titipong Issariyakul** Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, Canada

Naoto Kamiuchi Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, Japan

László Kőrösi Supramolecular and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, University of Szeged, Szeged, Hungary

**Paola Lanzafame** Department of Industrial Chemistry and Engineering of Materials and CASPE (INSTM Laboratory of Catalysis for Sustainable Production and Energy), University of Messina, Messina, Italy

Adam F. Lee Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK

Haris Matralis Department of Chemistry, University of Patras, Patras, Greece

**Barry MacDougall** Institute for Chemical Processes and Environmental Technologies, National Research Council of Canada, Ottawa, ON, Canada

**Guido Mul** Photocatalytic Synthesis Group, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands

Christina Papadopoulou Department of Chemistry, University of Patras, Patras, Greece

**Rita Patakfalvi** Supramolecular and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, University of Szeged, Szeged, Hungary

**Szilvia Papp** Supramolecular and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, University of Szeged, Szeged, Hungary

**Siglinda Perathoner** Department of Industrial Chemistry and Engineering of Materials and CASPE (INSTM Laboratory of Catalysis for Sustainable Production and Energy), University of Messina, Messina, Italy

Juan Carlos Serrano-Ruiz Department of Chemical and Biological Engineering, University of Wisconsin—Madison, Madison, WI, USA

**M. Aulice Scibioh** NASA-URC Centre for Advanced Nanoscale Materials, University of Puerto Rico-Rio Piedras, San Juan, PR, USA

National Centre for Catalysis Research (NCCR), Indian Institute of Technology Madras (IITM), Chennai, India

C.-L. Sun Department of Chemical and Materials Engineering, Chang Gung University, TaoYuan, Taiwan

András Tompos Research Center for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

Xenophon Verykios Department of Chemical Engineering, University of Patras, Patras, Greece

**B. Viswanathan** National Centre for Catalysis Research (NCCR), Indian Institute of Technology Madras (IITM), Chennai, India

Karen Wilson Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK