HETEROGENEOUS CATALYSIS & FINE CHEMICALS IV

Studies in Surface Science and Catalysis

Advisory Editors: B. Delmon and J.T. Yates

Vol. 108

HETEROGENEOUS CATALYSIS AND FINE CHEMICALS IV

Proceedings of the 4th International Symposium on Heterogeneous Catalysis and Fine Chemicals, Basel, Switzerland, September 8-12, 1996

Editors

H.U. Blaser
Ciba-Geigy AG, Basel, Switzerland

A. Baiker
ETH Zürich, Zürich, Switzerland

R. Prins
ETH Zürich, Zürich, Switzerland

1997
ELSEVIER
Amsterdam — Lausanne — New York — Oxford — Shannon — Tokyo

ELSEVIER SCIENCE B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

ISBN 0-444-82390-5

This book is printed on acid-free paper.

Printed in The Netherlands

Studies in Surface Science and Catalysis 108

HETEROGENEOUS CATALYSIS AND FINE CHEMICALS IV

Foreword

After three meetings in Poitiers, France, the *4th International Symposium on Heterogeneous Catalysis and Fine Chemicals* was held under the auspices of the New Swiss Chemical Society in Basel, Switzerland, from September 8 to 12, 1996. 270 scientists attended the meeting, more than a third of them from in industry - reflecting the importance of catalysis not only as an academic but also as a practical science. The focus of the symposium remained unchanged: fundamental as well as applied contributions on the use of heterogeneous catalysis for the preparation of fine chemicals were presented and discussed.

The program consisted of 4 plenary lectures, 28 oral contributions and around 90 posters covering a broad range of reactions and catalytic aspects. 82 of these contributions are collected in the present proceedings, grouped into the following 8 topical areas:

- Industrial and engineering problems (7 contributions)
- Alkylation and acylation reactions (11 contributions)
- Enantio- and diastereoselective hydrogenation reactions (9 contributions)
- Chemoselective hydrogenation reactions (12 contributions)
- Oxidation reactions (14 contributions)
- Immobilized and encapsulated complex catalysts (12 contributions)
- Zeolite and clay catalysts (12 contributions)
- Miscellaneous topics (5 contributions)

Compared to the first three symposia, there are two developments worth mentioning. First, the number of contributions describing stereoselective hydrogenation reactions has increased noticeably, pointing to the growing importance of stereochemically pure active compounds. Second, immobilized and encapsulated complexes are making a comeback. There obviously is still hope that such heterogeneous catalysts can be useful for solving special selectivity problems.

The Organizing Committee would like to acknowledge the efforts of all members of the Scientific Committee who helped to select the oral and poster contributions and in addition reviewed most papers of the present proceedings. We would also like to thank the staff of AKM Congress Services, Basel (Switzerland) and all other persons who helped to organize the symposium.

Scientific Committee

Chairmen
Baiker, ETH Zürich, Switzerland
H.U. Blaser, Ciba-Geigy AG, Switzerland
R. Prins, ETH Zürich, Switzerland

Members
C. Andersson, University of Lund, Sweden
Arntz, Degussa AG, Germany
R. Bader, Ciba-Geigy AG, Switzerland
M. Bartok, József Attila University, Hungary
A. Corma, Universidad Politécnica de Valencia-CSIC, Spain
B. Delmon, Université Catholique de Louvain, Belgium
I. Dodgson, Johnson Matthey Ltd., UK
F. Figueras, IRC Villeurbanne, France
L. Forni, Università di Milano, Italy
P. Fünfschilling, Sandoz AG, Switzerland
P. Gallezot, IRC Villeurbanne, France
E. Gehrer, BASF AG, Germany
P. Gravelle, CNRS-PIRSEM, France
J. Heveling, Lonza AG, Switzerland
W. Hölderich, Technische Hochschule Aachen, Germany
J. Kervennal, Elf Atochem S.A., France
K. Kühlein, Höchst AG, Germany
T. Mallat, ETH Zürich, Switzerland
G. Perot, Université de Poitiers, France
F. Rössler, Hoffmann-La Roche AG, Switzerland
F. Schmidt, Süd-Chemie AG, Germany
R. Sheldon, Delft University of Technology, The Netherlands
K. Smith, University of Wales, UK
M. Spagnol, Rhône-Poulenc, France
M. Studer, Ciba-Geigy AG, Switzerland
H. van Bekkum, Delft University of Technology, The Netherlands
E. Zirngiebl, Bayer AG, Germany

Organizing Committee

R. Bader, Basel (Chairman)
H.U. Blaser, Basel (Secretary)
D. Fritz, Basel (Secretary's office)
A. Baiker, Zürich; W. Graf, Visp; G. Perot, Poitiers; R. Prins, Zürich (Members)

Financial Support

The organizers gratefully acknowledge the financial support of the following sponsors:
Canton and City of Basel
Ciba-Geigy AG, Basel
Degussa AG, Frankfurt a.M./D
Engelhard Corporation, Iselin NJ/USA
Hoechst AG, Frankfurt a.M./D
Hoffmann-La Roche AG, Basel
Johnson Matthey, Royston/UK
Lonza AG, Basel
New Swiss Chemical Society
Novartis AG, Basel
Sandoz AG, Basel
Swiss Federal Institute of Technology (ETH), Zürich

Heterogeneous Catalysis and Fine Chemicals IV
H.U. Blaser, A. Baiker and R. Prins (editors)

Homogeneous Catalysis for Fine Chemical Synthesis - New Trends and Perspectives -

Matthias Beller

Anorganisch-chemisches Institut der TU München, Lichtenbergstr. 4, 85747 Garching, Germany

Abstract

Homogeneous catalysis used for fine chemical synthesis is a success story of both organometallic chemistry and organic synthesis. The wide scope for application of recently developed transition metal catalysts and ligands is illustrated by selected examples. Emphasis is given on efficient catalytic CC-coupling reactions, atom economic processes, and new stereoselective methods. Apart from the synthetic possibilities of homogeneous catalysts trends to overcome the basic problem of catalyst recycling are briefly reviewed. Here, two phase catalysis offers the most elegant solution. Recent achievements, e.g. the use of alternative two phase systems as well as the design of new ligands in this area are reported.

Keywords: Homogeneous catalysis; Organometallic chemistry; Two phase catalysis; CC-coupling reactions, Asymmetric catalysis

1. Introduction

In the area of classical fine chemicals significant changes are taking place worldwide because a number of established productions in the western world e.g. for chlorinated aromatics, ß-naphthol, resorcin, and others, which are characterized by large amounts of unwanted side-products and waste can not compete with productions in industrially developing countries which operate under different conditions. As a consequence the development of profitable production of already established fine chemicals can only be achieved with innovative methods which have ecological and economical benefits. In this regard catalysts in general are of key importance due to their abilities to open up new reaction pathways and to improve all kinds of selectivity (chemo-, regio-, and stereoselectivity) in a given reaction. Consequently it is possible to use cheaper feedstocks and to avoid unwanted side-products.

Compared to heterogeneous catalytic systems homogeneous catalysts often show very attractive selectivities under remarkably mild conditions. Moreover, homogeneous catalysis is generally better understood on a molecular level which leads to a more rational driven design and variation of homogeneous catalysts. However, many published homogeneous systems show only poor activities (turnover frequencies) and lifetime (total turnover numbers). In addition, even with very stable catalysts recycling is often not possible. As a consequence catalyst costs are dominating for certain processes and prevent commercial application.

Contents

Enantio- and Diastereoselective Hydrogenation Reactions

Chemoselective Hydrogenation Reactions

Oxidation Reactions

Immobilized and Encapsulted Complex Catalysts

Zeolite and Clay Catalysts

Miscellaneous Topics

Heterogeneous Catalysis and Fine Chemicals IV
H.U. Blaser, A. Baiker and R. Prins (editors)

Homogeneous Catalysis for Fine Chemical Synthesis - New Trends and Perspectives -

Matthias Beller

Anorganisch-chemisches Institut der TU München, Lichtenbergstr. 4, 85747 Garching, Germany

Abstract

Homogeneous catalysis used for fine chemical synthesis is a success story of both organometallic chemistry and organic synthesis. The wide scope for application of recently developed transition metal catalysts and ligands is illustrated by selected examples. Emphasis is given on efficient catalytic CC-coupling reactions, atom economic processes, and new stereoselective methods. Apart from the synthetic possibilities of homogeneous catalysts trends to overcome the basic problem of catalyst recycling are briefly reviewed. Here, two phase catalysis offers the most elegant solution. Recent achievements, e.g. the use of alternative two phase systems as well as the design of new ligands in this area are reported.

Keywords: Homogeneous catalysis; Organometallic chemistry; Two phase catalysis; CC-coupling reactions; Asymmetric catalysis

1. Introduction

In the area of classical fine chemicals significant changes are taking place worldwide because a number of established productions in the western world e.g. for chlorinated aromatics, ß-naphthol, resorcin, and others, which are characterized by large amounts of unwanted side-products and waste can not compete with productions in industrially developing countries which operate under different conditions. As a consequence the development of profitable production of already established fine chemicals can only be achieved with innovative methods which have ecological and economical benefits. In this regard catalysts in general are of key importance due to their abilities to open up new reaction pathways and to improve all kinds of selectivity (chemo-, regio-, and stereoselectivity) in a given reaction. Consequently it is possible to use cheaper feedstocks and to avoid unwanted side-products.

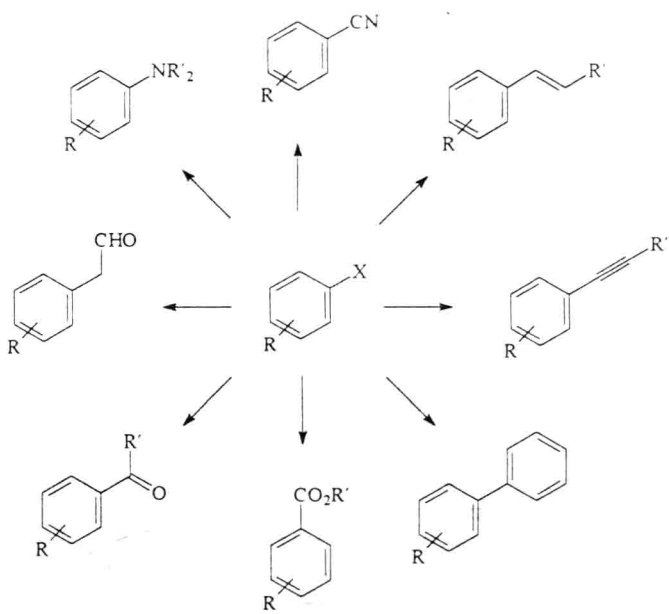
Compared to heterogeneous catalytic systems homogeneous catalysts often show very attractive selectivities under remarkably mild conditions. Moreover, homogeneous catalysis is generally better understood on a molecular level which leads to a more rational driven design and variation of homogeneous catalysts. However, many published homogeneous systems show only poor activities (turnover frequencies) and lifetime (total turnover numbers). In addition, even with very stable catalysts recycling is often not possible. As a consequence catalyst costs are dominating for certain processes and prevent commercial application.

Various strategies have been pursued to overcome these problems. On the one hand the introduction of new ligands has proved to be extremely successful in gaining new reactivity and improved activity and on the other hand the concept of two phase catalysis nowadays allows recycling of highly sophisticated catalysts and ligands even in the synthesis of advanced organic building blocks.

2. New transition metal catalysts and ligands

Traditionally the strength of homogeneous catalysis results from the concept of tuning catalyst properties by changing the electronic and steric environment of a given transition metal center. Here, the ligands play an extremely important role. Thus, the introduction of new types of ligands often parallels breakthroughs in catalytic applications. Selected examples from our own research as well as highlights from the literature in the 90´s will be adressed and discussed:

The palladium-catalyzed activation and subsequent functionalization of aryl halides has received increased attention in the last decade[1]. The enormous synthetic possibilities are demonstrated in Scheme 1 by the synthesis of aromatic intermediates such as cinnamic acid derivatives, styrenes, biaryls, benzoic acids, benzonitriles, or anilines.



Scheme 1: Palladium-catalyzed activation of aryl halides

Until now aromatic fine chemicals are often synthesized using classical stoichiometric organic reactions. In principle, catalytic methodologies based on the pioneering work of Heck[2] offer an interesting alternative for the generation of new carbon-carbon or carbon-heteroatom bonds in a selective and economically feasible manner. However, the reactions