There is an increasing need to find cost-effective and environmentally sound methods of converting natural resources into fuels, chemicals and energy; catalysts are pivotal to such processes. **Catalysis** highlights major developments in this area. Coverage of this Specialist Periodical Report includes all major areas of heterogeneous catalysis. In each volume, specific areas of current interest are reviewed. Examples of topics include experimental methods, acid/base catalysis, materials synthesis, environmental catalysis, and syngas conversion.

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ISBN 978-0-85404-249-4

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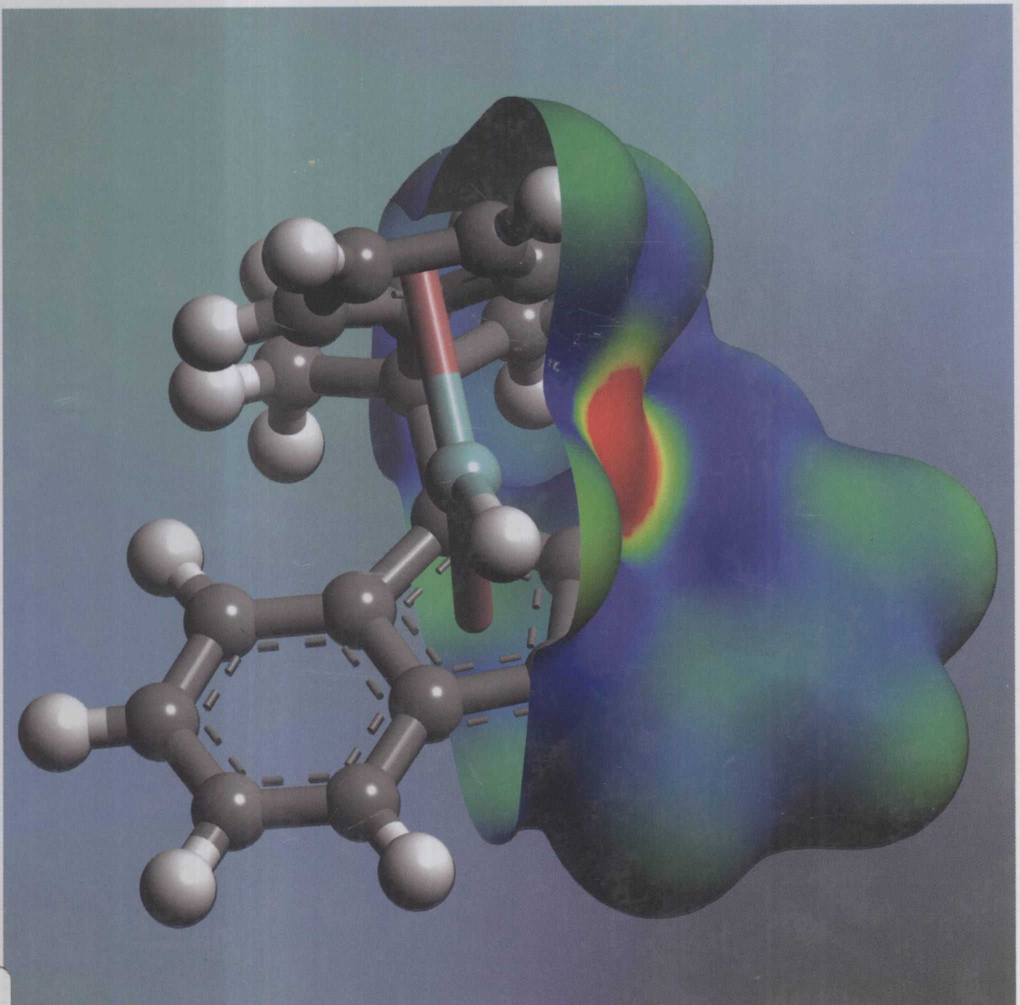
Specialist Periodical Reports

Edited by J J Spivey and K M Dooley

Catalysis

Volume 21



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A Specialist Periodical Report

Catalysis
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A Review of Recent Literature

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ISBN 978-0-85404-249-4
ISSN 0140-0568

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Typeset by Macmillan India Ltd, Bangalore, India
Printed and bound by Lings, Dorchester, Dorset, UK

Preface

James J. Spivey* and Kerry M. Dooley*
DOI: 10.1039/b820546a

The field of catalysis enjoys significant scientific prominence due to its importance in areas that affect the general public—clean energy, environmental protection, and conversion of sustainable feedstocks, for example. These driving forces, among others, will guide research efforts in our field for the foreseeable future. This volume of the Royal Society of Chemistry's Specialist Periodical Reports: Catalysis book series addresses these issues directly, providing up-to-date reviews on subjects of current interest.

First, Claus Christensen and colleagues Kresten Egeblad, Jeppe Rass-Hansen, Charlotte Marsden, and Esben Taarning (Technical University of Denmark, Lyngby) review the production of high-value chemicals and intermediates from biomass. This is important because a wide range of biomass feedstocks have the potential to replace fossil-based raw materials to produce these end products. Among other challenges, heterogeneous catalysts with extremely high activities and selectivities must be developed to compete with current processes.

James Anderson and M. F. Garcia (Univ. Aberdeen, UK) show that the significant challenges in developing processes for water purification can be addressed using photocatalytic reactions to remove both organic and inorganic pollutants. They point out the difficulties in studying the fundamentals of catalytic reactions in an aqueous medium, and the need to improve the typically low quantum yield in the processes—*e.g.*, by the addition of noble metals to titania.

Gabriele Centi and Siglinda Perathoner (Univ. Messina, Italy), report on approaches to the synthesis of titania catalysts, particularly ways to control the structure at the nanometer scale. They show approaches to develop specific active sites, and to direct the synthesis in a way that also produces a local 3-D environment around the active site with desired properties.

Computational catalysis has enjoyed rapid progress as computer speed and available codes have allowed more realistic catalytic cycles to be studied. Ye Xu (Oak Ridge National Lab, USA) shows that the transition in heterogeneous catalysis from a primarily empirical science to one that is based on first principles will provide new materials for experimental research. Coupled with new imaging methods with greatly improved spatial resolution, and atomically precise synthesis methods, computational approaches hold great promise for the development of catalysts with unprecedented levels of activity and selectivity.

In addition to their use as solvents, surfactants, and biocides, ionic liquids are attractive for use in catalytic reactions due to their ability to activate reactant molecules, the ease of separation from final products, thermal stability, solubility of gaseous reactants, among other properties. Amit Gujar and Mark White (Mississippi State Univ., USA) show, for example,

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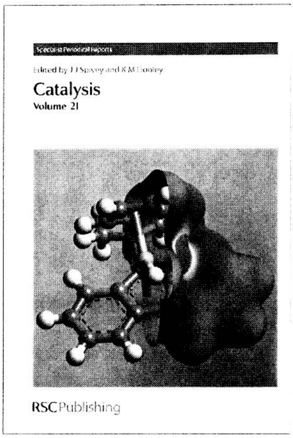
how these liquids can be used in a number of different catalyst-liquid systems, *e.g.*, monophasic systems in which the catalyst and substrate are dissolved in the ionic liquid, or monophasic systems in which the ionic liquid acts as both the solvent and the catalyst.

Finally, Nora McLaughlin and Marco Castaldi (Columbia University, USA) provide a review of *in situ* techniques to study catalytic reaction mechanisms. Because the catalyst is not static but can change during a reaction, it is important to be able to characterize the surface at reaction conditions. In addition, identification of reaction intermediates can help us understand the reaction mechanism. The authors review surface measurement techniques and recent developments in spectroscopy that can help us examine these catalytic properties.

We greatly appreciate the efforts of the authors who have contributed to this volume. We thank the Royal Society of Chemistry for their support of this series. Comments are welcome.



Cover

Image provided courtesy of computational science company Accelrys (www.accelrys.com). An electron density isosurface mapped with the electrostatic potential for an organometallic molecule. This shows the charge distribution across the surface of the molecule with the red area showing the positive charge associated with the central metal atom. Research carried out using Accelrys' Materials Studio®.

Heterogeneous catalysis for production of value-added chemicals from biomass

Kresten Egeblad, Jeppe Rass-Hansen, Charlotte C. Marsden, Esben Taarning and Claus Hviid Christensen*
DOI: 10.1039/b712664f

1. Introduction

Almost everything around us is in some way a product of controlled chemical processes. That is either chemical processes conducted in Nature or chemical processes conducted in the chemical industry. In the most developed parts of the World, it is in fact products from the chemical industry that completely dominate our everyday lives. These products range from fuels and fertilizers to plastics and pharmaceuticals.[1] To make these products widely available, a huge amount of resources have been invested during the last century to develop the chemical industry to its current level where it is the largest industry worldwide, a cornerstone of contemporary society, and also a platform for further global economic growth.[2,3] It can be argued that the enormous success of the chemical industry can be attributed to the almost unlimited availability of inexpensive fossil resources, and to a continuously increasing number of catalysts and catalytic processes that make it possible to efficiently transform the fossil resources into all the required compounds and materials. Accordingly, more than 95% of the fuels and chemicals produced worldwide are derived from fossil resources, and more than 60% of the processes and 90% of the products in chemical industry somehow rely on catalysis. It has been estimated that 20–30% of the production in the industrialized world is directly dependent on catalytic technology.[4] Therefore, it is not surprising that we are continuously expanding our already vast empirical knowledge about catalysis to further improve the efficiency of existing catalysts and processes, to discover entirely new ways of valorizing available resources, and to lower the environmental impact of human activities.[5] Due to the overwhelming importance of fossil resources during the 20th century, most catalysis research efforts have, so far, concerned the conversion of these resources into value-added fuels and chemicals. There are, however, indications that the era of easy access to inexpensive fossil resources, especially crude oil, is coming to an end. The resources are certainly limited and the demand from everywhere in the world is growing rapidly. At the same time, it is becoming increasingly clear that the emission of CO_2 that follows the use of fossil resources is threatening the climate of the Earth. Together this makes the development of a chemical industry based on renewable resources one of the most important challenges of the 21th century.

This challenge has two different facets. One is the discovery and development of methods to use renewable resources to supply suitable energy carriers, in sufficient quantities at acceptable costs, and with minimal impact

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on the environment. The other is the discovery and development of new ways to provide all the chemicals needed to sustain a modern society. Whereas there are several possible energy scenarios that do not involve carbon-containing energy currencies, it is in fact impossible to envisage how it should be possible to provide the required chemicals and materials without relying extensively on carbon-containing compounds. Thus, to develop a chemical industry that does not depend on fossil resources, there are only two alternative carbon sources and that is CO_2 and biomass. Since transformation of CO_2 into useful chemicals always requires a significant energy input and since it is usually only available in minute concentrations, it appears attractive to instead utilize biomass as the dominant feedstock for chemical industry. In this way, it is possible to harvest the energy input from the Sun that is stored by photosynthesis in the C–C, C–H, C–O, and O–H bonds of the biomass. Clearly, a shift from fossil resources to renewable resources as the preferred feedstock in chemical industry is a formidable challenge. However, it is worth pointing out that during the early part of the 20th century, before fossil resources became widely available, biomass was the preferred feedstock for the emerging chemical industry, and today, biomass still finds use as a feedstock for a range of very important chemicals.[6] Interestingly, these processes often rely mostly on the availability of biological catalysts whereas the processes for conversion of hydrocarbons use mostly heterogeneous catalysts. However, to explore the full potential of biomass as a feedstock in chemical industry, it appears necessary to integrate processes that rely on biological catalysts with processes that use heterogeneous or homogeneous catalysts to develop new, cost-competitive and environmentally friendly technologies.[7] Here, we will survey the possibilities for producing value-added chemicals from biomass using heterogeneous catalytic processes.

2. Setting a new scene

2.1 Biomass for production of fuels and chemicals

Currently, there exists a strong focus on the manufacture of transportation fuels from biomass.[8,9] Clearly, this can be attributed to a desire to relinquish our dependence on fossil fuels, in particular crude oil, and also to significantly lower the emission of greenhouse gasses to minimize global warming. In some regions of the world, it seems that production of bio-ethanol is indeed already cost-competitive with gasoline[8] and this demonstrates the potential of biomass as a renewable raw material. However, it is also clear that widespread use of biomass as a raw material for biofuel production remains controversial from both an economical and an ecological perspective. These issues must, of course, be resolved soon in a fully transparent way to identify sustainable paths forward. However, it is undisputable that we will eventually need alternatives to the fossil resources for producing chemicals and materials.[9–11] It can be argued that if the amount of biomass available is too limited to substitute fossil resources in all its applications and if sufficiently efficient methods for transforming biomass into value-added chemical can be developed, this will represent the optimal use of biomass.[7] There are two reasons for this. First of all, most chemicals, even most of the simple petrochemical building blocks, are significantly more valuable than transportation fuels. This can be illustrated in a semi-quantitative way by comparing the value chains in a chemical industry based on fossil and renewable resources, respectively.[7] In this context, it is instructive to compare the cost of renewable resources to fossil resources over time. It is noteworthy that today, the cost of glucose is comparable to the cost of crude oil (on a mass-to-mass basis). Secondly, it is clear that by use of renewable resources as a feedstock for the chemical industry, significantly higher reductions in the emissions of green-house gases can be achieved than what is possible by production of biofuels. This can be attributed to the fact that production of many large-scale commodity chemicals from fossil resources is associated with a substantial co-production of CO_2 as expressed *e.g.*, by the C-factor (kg CO_2 produced by kg of desirable product).[7] This can often be attributed to the high temperature required to transform hydrocarbons. To illustrate this, the C-factor for industrial production of hydrogen from natural gas is about 9 and for ethylene from naphtha it is 0.65. If hydrogen or ethylene was produced efficiently from biomass, the C-factor would approximately express the amount of CO_2 emission that would be saved compared to what would be possible by production of biofuels instead. Since ethylene alone is currently produced in an annual amount close to 100 mill. tonnes, it is obvious that this would have a substantial impact on the total emission of green-house gases.

2.2 Biomass in chemical industry

There are many ways in which biomass can be envisaged to become an increasingly important feedstock for the chemical industry, and this has already been the topic of numerous studies.[10–22] The most comprehensive study was published recently by Corma *et al.*[10] and it contains a very detailed review of possible routes to produce chemicals from biomass.

In Fig. 1, we illustrate schematically how selected commodity chemicals could be produced using abundant bio-resources, *i.e.*, carbohydrates (starch, cellulose, hemi-cellulose, sucrose), lipids and oils (rapeseed oil, soy oil, *etc.*), and lignin as the sole raw materials. From these bio-resources, it is possible to directly obtain all the compounds classified in Fig. 1 as primary renewable building blocks (of which only selected examples are given) with only one purification step. For example, ethanol can be obtained by fermentation of sucrose, glucose by hydrolysis of starch, glycerol by transesterification of triglycerides (or by fermentation of glucose), xylose by hydrolysis of hemi-cellulose, fructose by hydrolysis of sucrose (and by isomerization of glucose), and finally synthesis gas can be obtained directly by gasification of most bio-resources or by steam-reforming of the other primary renewable building blocks. From the primary renewable building blocks a wide range of possible commodity chemicals can be produced in a single step, and again examples of selected transformations are shown in Fig. 1. For instance, acetic acid can be produced by fermentation of glucose or by selective oxidation of ethanol. Lactic acid is available by fermentation of glucose, and 5-hydroxymethyl furfural can be obtained by dehydration of fructose. These compounds can again be starting materials for other desirable products and so forth. Some of the commodity chemicals shown are already produced on a large scale from fossil resources, *e.g.*, ethylene,

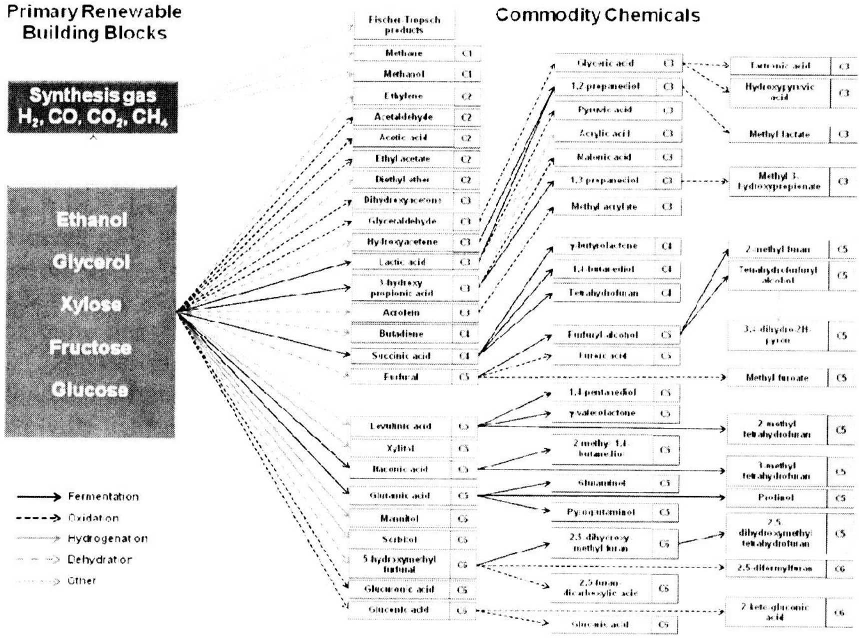

Fig. 1 Overview of how selected commodity chemicals could be produced from primary renewable building blocks.

acetic acid, acrolein and butadiene. Others are envisaged to become important large-scale commodity chemicals in the future when biomass gradually becomes a more important feedstock.[14] The different commodity chemicals are labeled to categorize them according to their number of carbon atoms. It is seen that a wide range of C_1 to C_6 compounds can be made available by quite simple means. Moreover, the chemical transformations in Fig. 1 are labeled with different arrows to illustrate specific ways to convert one building block into another. As it is apparent, the reactions all require a suitable catalyst, and this can be either a biological catalyst or a heterogeneous/homogeneous catalyst. Most of the primary renewable building blocks are produced today from bio-resources using mainly biocatalytic processes, and similarly several of the proposed commodity chemicals can also be produced from the primary renewable building blocks using biological catalysts. On the other hand, it is also clear that a very substantial number of the desirable transformations rely on the availability of suitable heterogeneous or homogeneous catalysts. Thus, it appears likely that a chemical industry based on renewable resources as the dominant feedstock will feature biological and chemical processes intimately integrated to efficiently produce all the desired chemicals and materials.

2.3 Heterogeneous catalysis and biomass

Often, it appears that the possible role of heterogeneous catalysis in this scenario is not receiving sufficient attention in comparison with that of the biocatalytic methods. Therefore, in the present chapter we will highlight some of the existing possibilities for converting bio-resources, primary