Heterogeneous Catalytic Oxidation

Heterogeneous Catalytic Oxidation

Fundamental and Technological Aspects of the Selective and Total Oxidation of Organic Compounds

B.K. HODNETT

Department of Chemical and Environmental Sciences
and
The Materials and Surface Science Institute
University of Limerick, Ireland

JOHN WILEY & SONS, LTD
Chichester • New York • Weinham • Brisbane • Singapore • Toronto

Baffins Lane, Chichester,
West Sussex PO19 1UD, England
National 01243 779777
International (+44) 1243 779777
e-mail (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on http://www.wiley.co.uk
or http://www.wiley.com

Other Wiley Editorial Offices

John Wiley & Sons, Inc., 605 Third Avenue,
New York, NY 10158-0012, USA

WILEY-VCH Verlag GmbH, Pappelallee 3,
D-69469 Weinheim, Germany

Jacaranda Wiley Ltd, 33 Park Road, Milton,
Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01,
Jin Xing Distripark, Singapore 129809

John Wiley & Sons (Canada) Ltd, 22 Worcester Road,
Rexdale, Ontario M9W 1L1, Canada

Library of Congress Cataloging-in-Publication Data

Hodnett, BK
Heterogeneous catalytic oxidation: fundamental and technological aspects of the selective and total oxidation of organic compounds/B.K. Hodnett.
p. cm.
Includes bibliographical references and index.
ISBN 0-471-48996-8 (alk. paper)
1. Oxidation. 2. Heterogeneous catalysis. I. Title.

QD281.O9 H63 2000
541.3'93–dc21

99-052447

British Library Cataloguing in Publication Data

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

ISBN 0 471 48994 8

Typeset in 10/12pt Times by Keytec Typesetting Ltd, Bridport, Dorset
Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham Wiltshire
This book is printed on acid-free paper responsibly manufactured from sustainable forestry, in which at least two trees are planted for each one used for paper production.

To Eveline

Preface

Heterogeneous catalytic oxidation is an important technological area which lies at the heart of a multitude of processes for the production of bulk chemicals, for pollution abatement and, increasingly, for the production of fine chemicals. In recent years this field has progressed sufficiently to allow a molecular level understanding of oxidation phenomena at catalyst surfaces. Hence, the modern researcher in this area must have a thorough understanding of fundamental chemical and engineering phenomana that range in scale from a typical reactor, constructed on the 1–10 m scale, to events occurring on active sites on the catalyst surface, constructed on the nanometre scale.

Over the years many superb experiments have been designed to probe the macroscopic and microscopic structure of heterogeneous oxidation catalysts and to investigate the mechanism of interaction with and transformation of hydrocarbons on these catalysts. This book attempts to describe some of these experiments and illustrates how the resultant data and its interpretation has led to our current understanding of heterogeneous catalytic oxidation.

The main body of the book centres around seven case studies (Chapters 4–10) each dealing with an important commercial process involving heterogeneous catalytic oxidation. Each study touches on a small number of generic features of oxidation catalysis and focuses in detail on a different fundamental or engineering aspect for each process. The choice of case studies was based on the author's own experience in this field. Other areas could equally validly have been included, but those offered are sufficient to illustrate all the major generic aspects of heterogeneous catalytic oxidation, which are introuced in Chapter 3.

The greatest benefit of presenting a detailed account of seven separate case studies in catalytic oxidation is that, taken together, they allow a clear overview of the entire field of heterogeneous catalytic oxidation. This overview in turn points to a small number of features common to all heterogeneous catalytic oxidation processes. Identification of these generic features lifts a lot of the mystery surrounding heterogeneous catalysis and enables researchers to view their field from a more logical and scientific perspective.

The book is written from the perspective that the newcomer to the field of heterogeneous catalysis is best introduced to the subject through an in-depth presentation and analysis of a very specific subsection of the field. Heterogeneous catalytic oxidation serves this purpose very well, with its wealth of classical experimentation, clear-cut experimental results and treatment of all chemical engineering and fundamental aspects of catalysis. Chapter 2 of this book has been written with the newcomer in mind. It is intended to be an introduction to the essential concepts and techniques of heterogeneous catalysis. This aspect of the book is not intended to be exhaustive and other texts, especially those dealing with characterization techniques, should be read in association with this chapter.

I wish to express my gratitude to a number of people who helped at various stages during the preparation of this book. A large part was written during a sabbatical leave with the group of Prof. RA van Santen at Eindhoven University of Technology, The Netherlands and I am particularly grateful to Pieter Stobbelaar for many discussions and for his patience in helping me with my basic computing skills. I also wish to thank my colleagues at the University of Limerick, in particular Seamus McMonagle, Tom O'Dwyer, Teresa Curtin, Finbar O'Regan and Aidan Doyle for reading and offering critical feedback on various parts of the book.

Most especially I wish to thank my wife Eveline and children, Anneke and Lieneke for their unending support and for putting up with my many absences from normal family life for the 18 months that this book was in preparation.

Contents

1

General Introduction

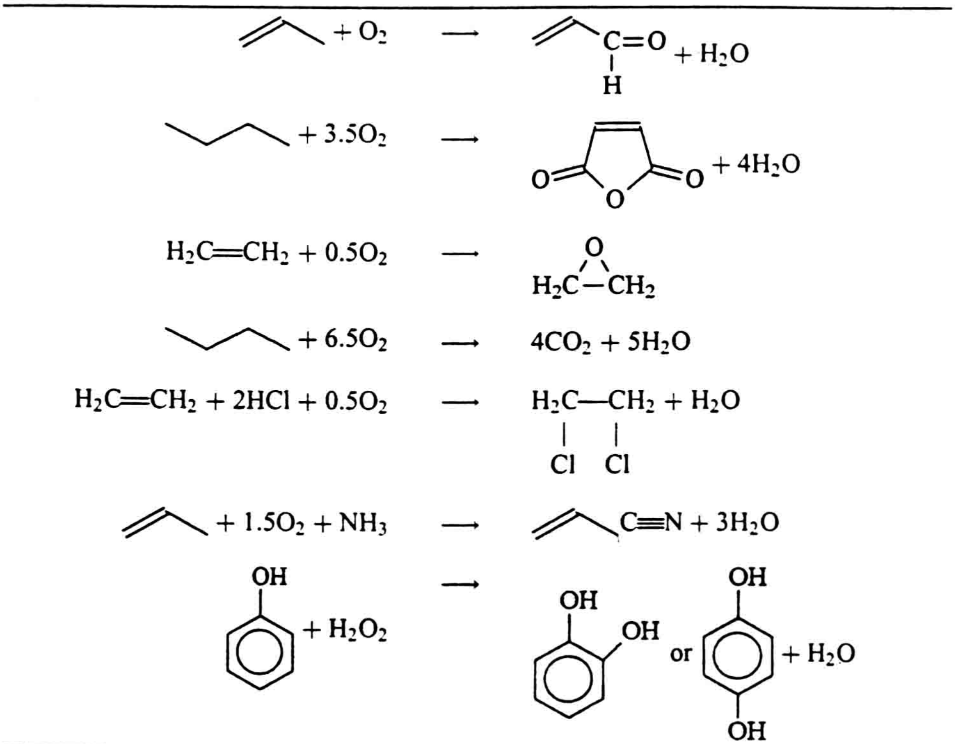
This book concentrates on those chemical processes in which an organic substrate is oxidized over a heterogeneous catalyst. It covers areas such as the production of bulk organic chemicals, the production of fine chemicals and environmental applications. For each of these areas the fundamental chemistry is explored as well as aspects of the industrial processes which they drive.

Selective oxidation and ammoxidation reactions and processes form a large part of the commercial processes covered here. These are reactions in which C—H bonds in the organic substrate are ruptured and oxygen or nitrogen is inserted to yield the corresponding aldehyde, ketone, carboxylic acid or nitrile. A large part of the technology currently used for the functionalization of hydrocarbons which in turn serve as feedstocks for plastic and polymer production is driven by these reactions. Acrolein, maleic anhydride and acrylonitrile production are examples of chemicals produced using technologies based on heterogeneous catalysts capable of rupturing a specific C—H bond in an organic substrate and assisting in the insertion of oxygen or nitrogen into the product. Some examples of these reactions are listed in Table 1.1.

A second class of oxidation reaction important in the production of bulk organic chemicals by heterogeneous catalysis are those in which a functional group is inserted into the molecule without rupture of a C—H bond. Reactions covered here include epoxidation of alkenes where an oxygen species is added across the double bond of an ethylene molecule and oxychlorination reactions, which involves the addition of chlorine to ethylene. This book explores fundamental and applied aspects of the epoxidation of ethylene over silver/alumina catalysts and the oxychlorination of ethylene over copper chloride/alumina catalysts.

Heterogeneous catalysts, very often in the form of zeolites and mesoporous materials, are now finding new applications for the production of fine

Table 1.1 Typical oxidation, ammoxidation and oxychlorination reactions catalysed by heterogeneous catalysts



chemicals through oxidation reactions. This development is explored here with a review of the new materials that have been developed, principally transition metal substituted zeolites, zeotypes and mesoporous materials. An example of a reaction catalysed by one such material, namely titanium substituted into a form of silicalite, is the hydroxylation of phenol, shown in Table 1.1.

Finally applications of heterogeneous oxidation catalysts for the abatement of environmental problems will be explored. These include the introduction of catalyst based technologies for the modification of combustion processes so that less pollution is produced (for example low temperature catalytic combustion of natural gas below the threshold temperature for NOx production) or applications to situations where waste streams must be treated prior to discharge into the environment (for example the catalytic oxidation of a gaseous waste streams containing less than 1 vol% of a hydrocarbon, i.e. at a concentration that is too low to sustain normal thermal combustion). One aspect of the use of heterogeneous oxidation or redox catalysis not covered here is the so called deNOx problem, wherein a catalyst is used to reduce oxides of nitrogen (NOx) into nitrogen (N_2) through the reducing action of ammonia or a hydrocarbon. In that process the emphasis is on the reduction part of the redox cycle, namely the reduction of NOx, rather than the oxidation of the reductant, and for that reason deNOx chemistry and processes are not covered in this book.

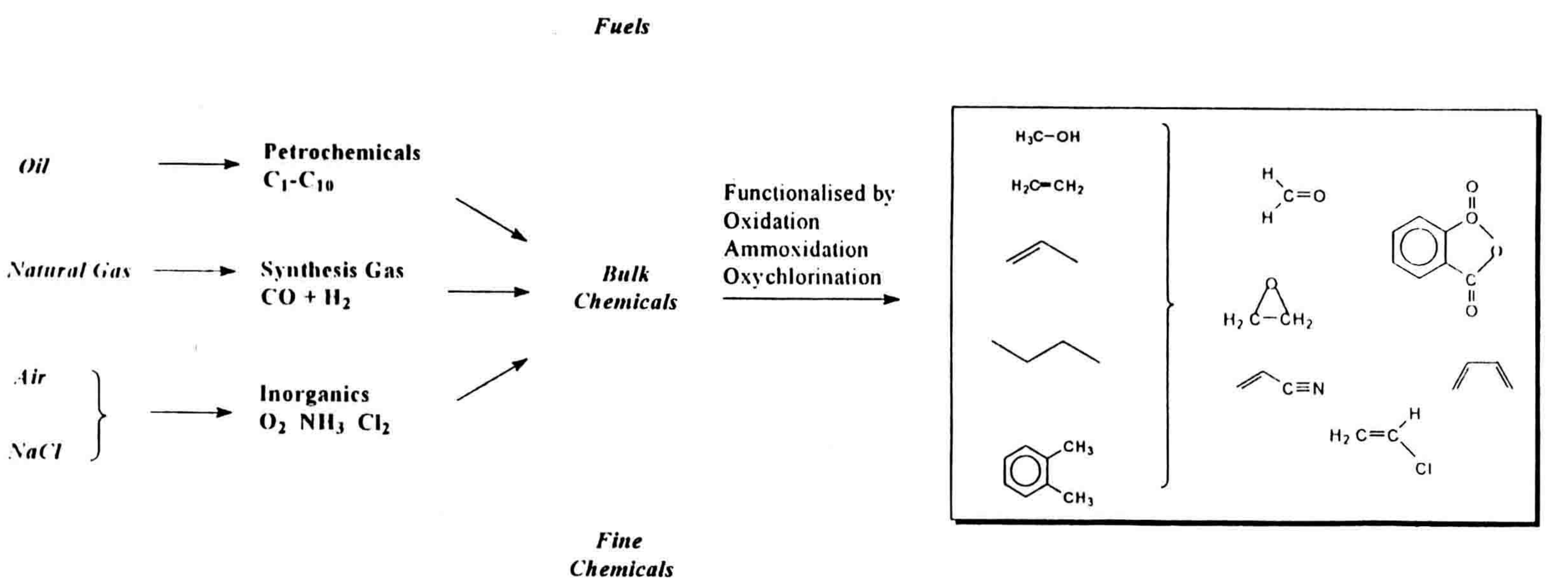
1.1 PRESENTATION OF MATERIAL

This book is intended to cover the basics of heterogeneous catalytic oxidation as well as applied aspects of individual processes. Accordingly, this chapter serves as an introduction to the role of oxidation catalysis within the framework of the overall chemical industry. Fundamentals of heterogeneous catalysis, with a particular emphasis on the elementary processes and the most basic characterization methods important in oxidation catalysis, are covered in Chapter 2. Hence, mechanical aspects of heterogeneous catalysts, diffusional processes, adsorption of oxygen and hydrocarbon species on catalyst surfaces, the nature of these adsorbed species and kinetic models useful in describing catalytic oxidation processes will be explored. Methods for the testing and physicochemical analyses of catalyst materials will also be presented, although it should be pointed out that there will not be an elaborate presentation of surface analytical methods. The emphasis throughout this chapter is on those fundamental principles and basic characterization techniques essential for a full understanding of oxidation catalysis. Where a more detailed elaboration of a special characterization topic, beyond that presented in Chapter 2, is required, this will be presented within the relevant chapter. For a more general introduction to heterogeneous catalysis, the reader is referred to recent publications that cover in more detail fundamental principles of heterogeneous catalysis and modern characterization techniques (Thomas and Thomas, 1997; Niemantsverdriet, 1997; Farrauto and Bartholomew, 1997).

Chapter 3 serves as a general introduction to the topic of heterogeneous catalytic oxidation, and covers generic features of oxidation reactions. The reader is introduced to the concept of active sites, the nature and reactivity of oxygen species on heterogeneous oxidation catalysts, the concept of kinetic control of oxidation reactions, the mechanism of activation of hydrocarbons and the origins of selectivity in selective oxidation and ammoxidation reactions.

Chapters 4–10 are case studies of aspects of individual selective and total oxidation reactions, including the oxidation of propene to acrolein (Chapter 4), the oxidation of *n*-butane to maleic anhydride (Chapter 5), the epoxidation of ethylene (Chapter 6), catalytic combustion (Chapter 7), the ammoxidation of propene to acrylonitrile (Chapter 8), the oxychlorination of ethylene and the combustion of chlorinated volatile organic compounds (Chapter 9) and the application of heterogeneous oxidation catalysts for the production of fine chemicals (Chapter 10). It is not the intention to cover all commercial oxidation reactions that involve heterogeneous catalysts. Sufficient material is

Overview of The Chemical Industry



Scheme 1.1 An overview of the role of oxidation processes in the chemical and petrochemicals industries.

presented in these chapters to elucidate the nature of heterogeneous oxidation catalysis and the general principles developed through these case studies can be applied throughout the field.

1.2 THE ROLE AND IMPORTANCE OF HETEROGENEOUS CATALYTIC OXIDATION PROCESSES IN THE CHEMICAL INDUSTRY

Oxidation processes that are driven by the heterogeneous catalysts can be divided into two groups, namely selective oxidation, ammoxidation and oxychlorination where the desired reaction product is not the most thermodynamically stable, and total oxidation reactions where the desired reaction products (simply carbon dioxide and water in the case of hydrocarbons) are the most stable thermodynamically. In general, the former type of reaction is practised for the production of bulk organic chemicals whereas the latter is practised for energy conversion or for pollution abatement.

Scheme 1.1 presents an overview of the chemical industry and the place therein of bulk organic chemicals produced by heterogeneous oxidation, ammoxidation and oxychlorination.

All major components for the chemical industry originate from a limited number of starting materials. Oil is the principle source of organics with natural gas as a source of synthesis gas (CO and H_2) becoming increasingly

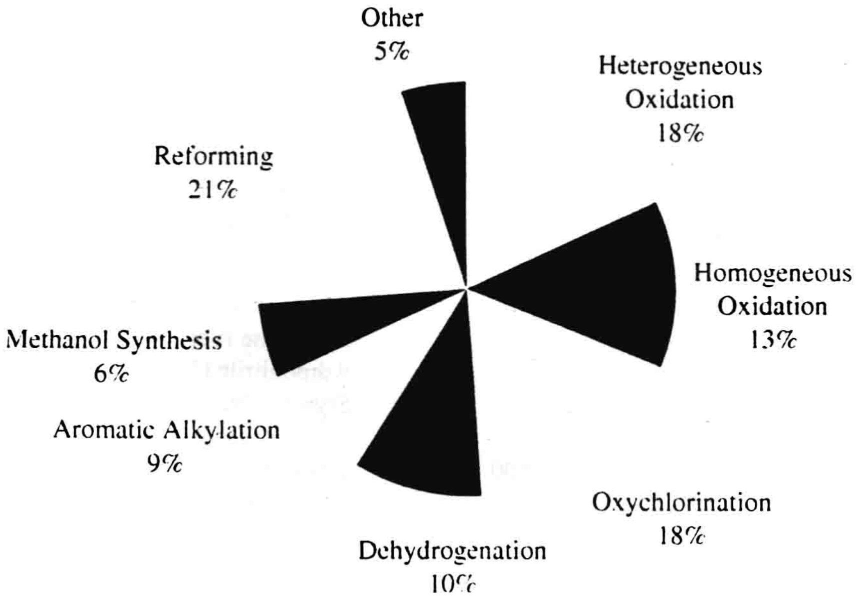


Figure 1.1 Catalytic production of bulk organic chemicals in the United States in 1991 (Oyama *et al.*, 1993) (reproduced by permission of the American Chemical Society).

important. Ammonia is produced through the Haber process, from the hydrogen component of synthesis gas and atmospheric nitrogen. Chlorine is sourced from the electrolysis of aqueous sodium chloride. Specifically, heterogeneous catalytic oxidation, ammoxidation and oxychlorination is concerned with those processes which add oxygen, nitrogen or chlorine or which remove hydrogen from C_1-C_{10} hydrocarbons. Almost all the output from these processes is used as feedstock for polymer and plastics production.

About 66 % of organic chemicals production in the United States is carried out by catalytic means. Figure 1.1 presents a profile of the catalytic production of bulk organic chemicals in the United States for 1991. Heterogeneous oxidation, ammoxidation and oxychlorination forms nearly 40 %. In fact,

Table 1.2 Production capacity and principal uses of the products of selective oxidation ammoxidation and oxychlorination processes
(Chemweek, 1997)

Chemical	*World production / ktonnes yr^{-1}*	*Principal uses*
Formaldehyde	18 000	Urea resins (50 %) Phenolic resins (10 %) Polyacetal resins (10 %)
Ethylene oxide	10 600	Ethylene glycol (58 %) Ethololates (18 %) Diethylene, triethylene glycol (7 %) Ethanolamines (6 %)
Vinyl chloride monomer	19 900	Polyvinylchloride
Acrylonitrile	4600	Acrylic fibre (53 %) ABS/SAN (30 %)
1,3-Butadiene	5700	Styrene–butadiene rubber (29 %) Butadiene rubber (27 %) Adiponitrile (14 %) Styrene–butadiene latex (12 %)
Maleic anhydride	600	Unsaturated polyester resins (63 %) Lube oil additives (12 %) Copolymers (6 %)
Phthalic anhydride	2300	Plasticizers (53 %) Unsaturated polyester (26 %) Alkyd resins (10 %)

worldwide the catalytic oxidation, ammoxidation and oxychlorination business has a turnover of about 50 billion dollars per year (1998) and is fairly evenly distributed between America, Europe and Asia. The core of this technology is catalytic oxidation in which a hydrocarbon gas is mixed with air or oxygen (and with ammonia or hydrochloric acid for ammoxidation and oxychlorination, respectively) and passed over a solid catalyst usually at temperatures in the range 600–900 K.

There are about 15 specific selective oxidation, ammoxidation and oxychlorination reactions practiced commercially in about 1000 chemical plants globally. Some of the major commodity chemicals (average price of 0.6–1.0 $ per kilogram in 1997) produced by heterogeneous oxidation, ammoxidation and oxychlorination are presented in Table 1.2, with an indication of their main uses.

REFERENCES TO CHAPTER 1

Chemweek, 1997, Product Focus Reports (http://www.chemweek.com/marketplace/prod_focus.html).

Farrauto RJ and Bartholomew CH (1997) *Fundamental of Industrial Catalytic Processes*. Blackie, London.

Niemantsverdriet JW (1997) *Spectroscopy in Catalysis. An Introduction*. VCH, Weinheim.

Oyama ST, Desikan AN and Hightower JW (1993) Research challenges in selective oxidation. *ACS Symposium Series 523, Catalytic Selective Oxidation*, Oyama ST and Hightower JW (Eds). American Chemical Society, Washington, pp. 1–14.

Thomas JM and Thomas WJ (1997) *Principles and Practice of Heterogeneous Catalysis*. VCH, Weinheim.

2

Introduction to Heterogeneous Catalysis

Summary

Heterogeneous catalysis lies at the heart of many technologies for the production of petrochemicals, bulk chemicals and for pollution abatement. In this a chapter the newcomer to the field is introduced to the main macroscopic and microscopic structural features of heterogeneous cata-