

0053499

CATALYSIS

Science and Technology

Edited by

John R. Anderson and Michel Boudart

Volume 11

With 124 Figures and 20 Tables



Springer

Editors

Professor Dr. J.R. Anderson

Chemistry Department
Monash University
Clayton, Victoria 3168
Australia

Professor Dr. M. Boudart

Department of Chemical Engineering
Stanford University
Stanford, CA 94305-5025
USA

ISBN 3-540-60380-8 Springer-Verlag Berlin Heidelberg New York

ISBN 3-540-60440-5 (Set Vols. 1 – 11)

This work is subject to copyright. All rights are reserved whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1996
Printed in Germany

The use of registered names, trademarks, 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.

Typesetting: Fotosatz-Service Köhler OHG, Würzburg
Production: PRODUserv Springer Produktions-Gesellschaft, Berlin

SPIN: 10509268

51/3020 – 5 4 3 2 1 0 – Printed on acid-free paper

CATALYSIS – Science and Technology

Springer

Berlin

Heidelberg

New York

Barcelona

Budapest

Hong Kong

London

Milan

Paris

Santa Clara

Singapore

Tokyo

Editorial

Our series of books on *Catalysis: Science and Technology* is by now complete. Its purpose has been to collect authoritative and, if possible, definitive chapters on the main areas of contemporary pure and applied catalysis. Its style is not that of an Advances series, nor is it meant to be a collection of up-to-date reviews. If the chapters and the volumes were following each other in a neat, logical order, our series might be considered as trying to emulate the original *Handbuch der Katalyse*, pioneered by Professor G.M. Schwab in the 1940's, or be a new version of *Catalysis*, the series edited by Professor P.H. Emmett in the 1950's. As a matter of expediency, to avoid the delays involved in assembling a complete volume of related chapters, we decided at the outset to publish the chapters as received from our authors.

We are most thankful to all our contributors for their co-operation. The Science and the Technology of Catalysis will prosper as a result of their hard work.

General Preface to Series

In one form or another catalytic science reaches across almost the entire field of reaction chemistry, while catalytic technology is a cornerstone of much of modern chemical industry. The field of catalysis is now so wide and detailed, and its ramifications are so numerous, that the production of a thorough treatment of the entire subject is well beyond the capability of any single author. Nevertheless, the need is obvious for a comprehensive reference work on catalysis which is thoroughly up-to-date, and which covers the subject in depth at both a scientific and at a technological level. In these circumstances, a multi-author approach, despite its well-known drawback, seem to be the only one available.

In general terms, the scope of *Catalysis: Science and Technology* is limited to topics which are, to some extent at least, relevant to industrial processes. The whole of heterogeneous catalysis falls within its scope, but only biocatalytic processes which have significance outside of biology are included. Ancillary subjects such as surface science, materials properties, and other fields of catalysis are given adequate treatment, but not to the extent of obscuring the central theme.

Catalysis: Science and Technology thus has a rather different emphasis from normal review publications in the field of catalysis: here we concentrate more on important established material, although at the same time providing a systematic presentation of relevant data. The opportunity is also taken, where possible, to relate specific details of a particular topic in catalysis to established principles in chemistry, physics, and engineering, and to place some of the more important features into a historical perspective.

Because the field of catalysis is one where current activity is enormous and because various topics in catalysis reach a degree of maturity at different points in time, it is not expedient to impose a preconceived ordered structure upon *Catalysis: Science and Technology* with each volume devoted to a particular subject area. Instead, each topic is dealt with when it is most appropriate to do so. It will be sufficient if the entire subject has been properly covered by the time the last volume in the series appears. Nevertheless, the Editors will try to organize the subject matter so as to minimize unnecessary duplication between chapters, and to impose a reasonable uniformity of style and approach. Ultimately, these aspects of the presentation of this work must remain the responsibility of the Editors, rather than of individual authors.

The Editors would like to take this opportunity to give their sincere thanks to all the authors whose labors made this reference work possible. However, we all stand in debt to the numerous scientists and engineers whose efforts have built the discipline of catalysis into what it is today: we can do no more than dedicate these volumes to them.

Preface

Hydrotreating processes in petroleum refining technology have a long history, having been first introduced prior to World War 2 for the removal of sulfur and nitrogen. In fact, the sulfided cobalt-molybdenum catalyst which, together with its near relatives is still widely used, was adapted for this purpose from its previous use in coal hydrogenation/liquefaction.

Removal of sulfur and nitrogen during the processing of quality liquid transport fuels became a technical imperative with the introduction of noble metal catalysts for catalytic conversion technology. However, it was the two "petroleum shocks" of the early 1970's and early 1980's which, among other things, focused attention on the fact that liquid hydrocarbon fuels come from a global reservoir of large but limited size, so that with the passage of time liquid fuels will necessarily come from technically less satisfactory sources, with increasing sulfur and nitrogen levels making hydrotreating of increasing importance.

The present volume consists of a single Chapter by Dr. Henrik Topsøe and his collaborators dealing with the science of Hydrotreating Catalysis. The removal of sulfur and nitrogen by hydrotreating is, of course, a major industrial process world-wide, and it would be both impossible and inappropriate for the present purpose to enter into the fields of plant design or process engineering. The present volume therefore concentrates on the catalytic chemistry of the processes, and in particular deals in some detail with the structure of the most important types of catalysts which are used, and the relationship between structure and activity. With a process which has a history of 60 years or so, one might perhaps be excused for wondering if the details of

process chemistry and catalyst structure were not well understood long before now: the truth is that, in these respects, hydrotreating catalysis has proven to be a particularly refractory subject, and a detailed understanding has only been arrived at relatively recently by the application of modern analytical techniques. We believe that in this respect the present review is particularly timely.

The present Volume is the last in the series *Catalysis: Science and Technology*. The editors would like to take this opportunity to thank all of the authors whose hard work has made the series a success.

List of Contributors

Dr. Bjerne S. Clausen
Dr. Henrik Topsøe
Haldor Topsøe Research Laboratories
Nymollevvej 55
2800 Lyngby
Denmark

Dr. Franklin E. Massoth
University of Utah
Dept. of Chemical and Fuels Engineering
Salt Lake City
84112 Utah
USA

Contents

Hydrotreating Catalysis

1. Introduction	1
2. Technological Aspects	4
A. Crude and Feed Characteristics	5
B. Hydrotreating Reactions	11
C. Hydrotreating in Refining	12
D. Hydrotreating Processes	18
E. Catalyst Selection	22
F. Activation, Deactivation and Regeneration	24
3. Catalyst Characterization	29
A. Structural Models	29
1. Monolayer Model	29
2. Intercalation Model	30
3. Contact Synergy Model	31
4. Co-Mo-S Model	31
5. Other Models	33
B. Characterization Studies	35
1. Structure of Alumina-supported Mo and W Catalysts	36
a. Unpromoted Catalysts	36
i. Calcined Catalysts	36
ii. Sulfided State	38
b. Promoted Catalysts	53
i. Calcined State	53
ii. Sulfided State	55
2. Other Supports	65
3. Sulfiding Reactions	69
4. Effect of Preparation and Activation	73
a. Impregnation Procedure	73
b. Metal Loading	76

c. Calcination Temperature	79
d. Activation	80
e. Additives	83
5. Dispersion and Morphology	88
6. Aged Catalysts	97
7. Unsupported Catalysts	102
8. New Types of Hydrotreating Catalysts	107
9. Model Systems	110
4. Kinetics and Mechanisms of Model Compound Reactions	111
A. Hydrodesulfurization (HDS)	114
1. Reactivities	114
2. Reaction Pathways	116
3. Kinetics	118
4. Poisoning/Coke	118
5. Adsorption/Reaction Sites	120
6. Mechanisms	121
7. Implications from Organometallic and Computational Chemistry	124
B. Hydrogenation (HYD)	128
1. Reactivities	128
2. Reaction Pathways and Kinetics	129
3. Adsorption/Reaction Sites	131
C. Hydrodenitrogenation (HDN)	133
1. Reactivities	133
2. Reaction Pathways and Kinetics	134
3. Promotion/Poisoning/Coke	137
4. Adsorption/Reaction Sites	138
5. Mechanisms	139
D. Hydrodeoxygenation (HDO)	141
1. Reactivities	141
2. Reaction Pathways and Kinetics	141
3. Poisons/Coke	143
4. Adsorption/Reaction Sites	144
E. Cracking (CKG)/Hydrocracking	144
F. Hydrometallation (HDM)	145
G. Mixed Feeds	147
1. Reactivities	148
2. Kinetics	148
H. Role of Hydrogen	150
I. On Active Sites	152
J. Summary	155
5. Structure-Activity Correlations	155
A. Unpromoted Mo and W Catalysts	156
B. Promoted Mo and W Catalysts	162

1. Models for Promotion	162
2. Mössbauer Spectroscopy Studies	165
3. Chemisorption of Probe Molecules and Infrared Spectroscopy Studies	168
a. O ₂	169
b. NO	171
c. CO	172
d. H ₂ , H ₂ S and basic molecules	174
4. EXAFS Studies	175
5. XPS, ISS and Microscopy Studies	176
6. Magnetic Susceptibility, NMR, and ESR Studies	179
7. TPR	181
8. Other Studies	182
C. Correlations with Properties of Calcined Catalysts	183
D. Preparation Parameters	186
1. Metal Loading	188
2. Impregnation procedure	189
3. Calcination temperature	190
E. Additive Effects	191
F. Periodic Trends in Promotion	193
G. Activation Procedures	197
H. Deactivation Phenomena	199
I. Unsupported Catalysts and Support Effects	203
J. Transition Metal Sulfides: Periodic Trends	208
K. Unconventional Catalysts and Model Systems	215
6. Active Sites and Reaction Mechanisms	217
A. Unpromoted Mo and W Catalysts	218
B. Periodic Trends	224
C. Promoted Mo and W Catalysts	226
7. Concluding Remarks	231
8. References	232
References Author Index	271
Subject Index	303
Author Index Volumes 1 – 11	311

Hydrotreating Catalysis*

Henrik Topsøe, Bjerne S. Clausen and Franklin E. Massoth

1. Introduction

Hydrotreating or hydroprocessing refers to a variety of catalytic hydrogenation processes which saturate unsaturated hydrocarbons and remove S, N, O and metals from different petroleum streams in a refinery. These processes represent some of the most important catalytic processes and the annual sales of hydrotreating catalysts represent close to 10% of the total world market for catalysts.

Hydrotreatment usually implies only small changes in overall molecular structure but hydrocracking (HCR) reactions often occur simultaneously and may in fact be desired. Today hydrotreating is used extensively both for conversion of heavy feedstocks and for improving the quality of final products. Hydrotreating also plays an essential role in pretreating streams for other refinery processes such as catalytic reforming, fluid catalytic cracking (FCC), and HCR. More severe environmental legislation with respect to harmful emissions has triggered an increased interest in both basic and applied research within hydrotreating catalysis. These efforts have already led to new technological developments.

Historically, hydrotreating processes have developed from the cracking and hydrogenation processes introduced in the 1930s [1]. For a long time, the most important hydrotreating reaction has been the removal of sulfur from various fuel fractions. Consequently, hydrotreating catalysts are also commonly referred to as hydrodesulfurization (HDS) catalysts. Typical hydrodesulfurization catalysts consist of molybdenum supported on an alumina carrier with either cobalt or nickel added as promoters for improving the catalytic activity. Industrial applications of such alumina-supported “cobalt-moly” catalysts were reported already in 1943 [2].

Many new challenges continue to arise in hydrotreating. In particular, these have been the result of the dramatic worldwide decline in the demand

* Dedicated to Dr. Haldor Topsøe on the occasion of his 80th birthday.

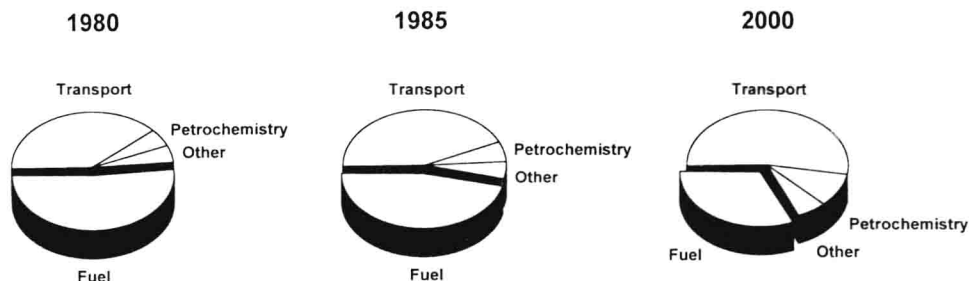


Fig. 1.1. Changes in demand for various oil products

for fuel oil and the resulting need for conversion of heavier fractions into light distillates for transportation use (Fig. 1.1). The oil crisis in 1978 also contributed to the de-emphasis in the use of valuable crude oil for producing heavy fuel oil, reserving its use for making products where no easy substitutes exist. These changes in the demands for different oil products have required more emphasis on hydrotreating in connection with processes for conversion of the heavier fractions.

Other challenges to hydrotreating come from environmental legislation which places increasingly severe restrictions on the gaseous and particulate emissions arising both from the refinery itself as well as from the use of heating and transportation fuels. Table 1.1 gives some examples of present and possible future environmental specifications of different refinery products. Although there are significant variations from region to region (and even within a given country), it is clear that the environmental regulations, which hardly existed twenty years ago, will pose a major driving force for introducing more hydrotreating in refineries. Deep desulfurization and aromatic reduction are examples of hydrotreating reactions which will become increasingly important in order to provide environmentally more acceptable reformulated fuels (Table 1.1). The oil crisis also increased the interest in hydrotreating in connection with the use of heavier feedstocks, including synfuels derived from coal, shale oil or tar sands. Application of such feedstocks requires, in addition to hydrodesulfurization, conversion of large molecules to smaller ones, the removal of metals [by hydrodemetallization (HDM)], nitrogen [by hydrodenitrogenation (HDN)], and in some cases also oxygen [by hydrodeoxygenation (HDO)]. As a result of this increased role of hydrotreating, more than 50 % of all refinery streams undergo hydrotreating today. In 1980, the number was less than 40 % [3].

In the past, due to lack of adequate analytical tools, a detailed fundamental understanding of hydrotreating catalysts and hydrotreating reactions was not available. Consequently, catalyst developments were to a large extent based on trial-and-error experimentation. More recently, the situation has improved with significant progress in the understanding of the active structures, the reaction mechanisms, the origin of catalyst deactivation and the important relations between preparation parameters and catalyst performance. Hence, it appears that “science is catching up with technology” and this review will

Table 1.1. Some present environmental product specifications and likely trends

	Present specifications (< 1993)				Expected future (1993–2000)				
	Europe	Sweden	Japan	US	California	Europe	Japan	US	California
<i>Gasoline</i> (unleaded)									
Max. S (wt %)	0.05–0.1	0.1		0.1		0.01		0.04	0.003
Max. aromatics (vol %)								25	22
Max. benzene (vol %)	5			5	5	1–3		1	0.8
<i>Diesel</i>									
Min. cetane No.	45–50	45–50 ^a	45	40	40	50	50	45	50
Max. S (wt %)	0.2–0.3	0.001–0.20 ^a	0.2	0.3–0.5	0.05	0.05	0.05	0.05	0.05
Max. aromatics (vol %)		5–25 ^a							10
<i>Heavy fuel oil</i> (No. 6)									
Max. S (wt %)	3,5					0.25–1	1	1	1

^a Lower and higher values represent Class I and Class III diesel, respectively.