Handbook of Industrial Catalysts
PREFACE TO THE SERIES

Catalysis is important academically and industrially. It plays an essential role in the manufacture of a wide range of products, from gasoline and plastics to fertilizers and herbicides, which would otherwise be unobtainable or prohibitively expensive. There are few chemical- or oil-based material items in modern society that do not depend in some way on a catalytic stage in their manufacture. Apart from manufacturing processes, catalysis is finding other important and ever increasing uses; for example, successful applications of catalysis in the control of pollution and its use in environmental control are certain to increase in the future.

The commercial importance of catalysis and the diverse intellectual challenges of catalytic phenomena have stimulated study by a broad spectrum of scientists, including chemists, physicists, chemical engineers, and material scientists. Increasing research activity over the years has brought deeper levels of understanding, and these have been associated with a continually growing amount of published material. As recently as sixty years ago, Rideal and Taylor could still treat the subject comprehensively in a single volume, but by the 1950s. Emmett required six volumes, and no conventional multivolume text could now cover the whole of catalysis in any depth. In view of this situation, we felt there was a need for a collection of monographs, each one of which would deal at an advanced level with a selected topic, so as to build a catalysis reference library. This is the aim of the present series, Fundamental and Applied Catalysis.

Some books in the series deal with particular techniques used in the study of catalysts and catalysis: these cover the scientific basis of the technique, details of its practical applications, and examples of its usefulness. An industrial process or a class of catalysts forms the basis of other books, with information on the fundamental science of the topic, the use of the process or catalysts, and engineering aspects. Single topics in catalysis are also treated in the series, with books giving the theory of the underlying science, and relating it to catalytic practice. We believe that this approach provides a collection that is of value to both academic and industrial workers. The series editors welcome comments on the series and suggestions of topics for future volumes.

Martyn Twigg
Michael Spencer
Lawrie Lloyd

Handbook of Industrial Catalysts

Springer
The use of catalysts in chemical and refining processes has increased rapidly since 1945, when oil began to replace coal as the most important industrial raw material. Even after working for more than 35 years with catalysts, I am still surprised to consider the present size of the catalyst business and to see how many specialist companies supply different operators. Now that each segment of the industry is so specialized no single organization is able to make all of the catalyst types that are required. The wide range of catalysts being used also means that it is difficult to keep pace with the details of every process involved. Unfortunately, there are few readily available comprehensive descriptions of individual industrial catalysts and how they are used. This is a pity, since catalysts play such an important part in everyday life.

Modern catalyst use was unimaginable a hundred years ago because catalysts were still chemical curiosities. The use of catalytic processes simply increased with the demand for new products and gradual improvements in engineering technology. Only now is it becoming true to say that catalyst design, which originally relied on luck and the experience of individuals, is becoming a more exact science. New construction materials have made plant operation more efficient and led to the development of better processes and catalysts. It is no coincidence that the two major wars of the twentieth century saw the rapid expansion of a more sophisticated chemical industry. Currently, some new catalysts are evolving from previous experience while others are being specifically designed to satisfy new consumer demands. This is demonstrated by the introduction of catalysts to reduce automobile exhaust emissions in response to environmental regulations. This has been one of the major catalyst growth areas of the past 20 years and the use of catalysts to control various industrial emissions is similarly important.

The demand for catalysts is still increasing particularly in the Far East, as expansion of the chemical and refining industries keeps pace with the increase in world population. As a consequence, the number of catalyst suppliers is still growing. All have the experience needed to produce large volumes of catalysts successfully and can give good advice on process operation, but different catalysts for the same applications are not always identical.

Ownership of key patents for catalysts and catalytic processes has led to licenses being offered by chemical and engineering companies. For this reason precise catalyst compositions are not often published, and while commercial products may seem to differ only in minor details, in a particularly efficient manufacturing process these can certainly improve performance. There are no catalyst recipe books, and details regarded as company secrets are hidden in the vague descriptions of a patent specification.
Competition among suppliers in a market where customers may only place large orders every few years has encouraged overcapacity in order to meet emergency requirements. At the same time, low selling prices and the high costs of introducing new products have reduced profitability. The recent spate of catalyst joint ventures reflects this.

Availability of reliable products must be guaranteed so that a customer’s expensive plant will not have to close down or operate at a loss. Security of supply is clearly a major factor in catalyst selection. Indeed, for many years it was a strategic or political necessity as well as being of commercial importance. For instance, during the Cold War era, most of Eastern Europe and China had to rely on their own domestic production capacity. At the same time, the big chemical companies in the United States and Europe, which had traditionally produced their own catalysts, began to buy the best available commercial products.

Since Sabatier published Catalysis in Organic Chemistry in 1918 many process reviews have been written on the industrial applications of catalysts and they provide a good deal of historical background. Lack of detail has meant, however, that catalyst compositions are not often included. In any case, earlier reviews are usually out of print and can only be found with difficulty from old library stock. Up-to-date information is badly needed.

Catalysts could, by definition, operate continuously, but those used industrially may lose activity very quickly. Some catalysts can then be regenerated at regular intervals by burning of carbon deposited during operation. Others have to be replaced following permanent poisoning by impurities present in the reacting gases. To avoid the necessity for parallel reactors or unscheduled interruptions to replace spent catalyst, efficient operating procedures have had to be devised for online regeneration or the removal of poisons from feedstock. The use of additional catalysts or absorbents to protect the actual process catalysts has become an important feature of operation. Catalysts are also deactivated by overheating. This sinters either the active catalyst or the support and occurs if the operating temperature is at the limit of catalyst stability, particularly in the presence of trace impurities in feedstock. Other problems can result from increasing pressure drop through the catalyst bed, if dust is entrained with process gas or if the catalyst itself slowly disintegrates.

It may therefore be necessary to replace catalysts many times during the life of plant equipment. Stability despite the presence of poisons becomes an important feature of the selection procedure to avoid unscheduled plant closures. Proper catalyst reduction may also be a critical step prior to operation to ensure optimum performance in the shortest possible time. This is not always easy and efforts have therefore been made to use prereduced catalysts and even to regenerate spent catalysts externally to restore as much of the original activity as possible. It should never be assumed that catalyst operation is straightforward. It
is often a nightmare. And effort spent in solving problems or making improvements is time consuming. The provision of an efficient technical service has thus become an indispensable element of the catalyst business.

It is hoped that this extensive survey of industrial catalysis will stimulate a wider general interest in the subject.

The author thanks J.R. Jennings, M. S. Spencer, and M.V. Twigg for much help in bringing this book to publication.

Lawrence Lloyd
Bath, England
## Chapter 1

### Industrial Catalysts

1.1 Introduction .............................................. 1  
1.2 What is a Catalyst? ...................................... 5  
  1.2.1 Activity ........................................... 6  
  1.2.2 Selectivity and Yield ............................. 7  
  1.2.3 Stability ......................................... 7  
  1.2.4 Strength .......................................... 8  
1.3 Catalyst Production ..................................... 8  
  1.3.1 Precipitation .................................... 12  
  1.3.2 Impregnation .................................... 13  
  1.3.3 Other Production Methods ....................... 13  
1.4 Catalyst Testing ......................................... 14  
  1.4.1 Physical Tests ................................... 14  
  1.4.2 Chemical Composition ........................... 14  
  1.4.3 Activity Testing .................................. 15  
1.5 Catalyst Operation ...................................... 18  
  1.5.1 Reactor Design ................................... 18  
  1.5.2 Catalytic Reactors ............................... 18  
  1.5.3 Catalyst Operating Conditions .................. 20  
1.6 Conclusion ............................................... 21  
References .................................................. 22

## Chapter 2

### The First Catalysts

2.1 Sulfuric Acid .......................................... 23  
  2.1.1 The Lead Chamber Process ....................... 24  
    2.1.1.1 Chemistry of the Lead Chamber Process .. 26
2.1.1.2 The Continuing Use of the Lead Chamber Process 27
2.1.1.3 Raw Material for Sulfuric Acid Production 28
2.1.2 Contact Process Development 29
2.1.3 Modern Sulfuric Acid Processes 35
  2.1.3.1 Catalyst Preparation 36
  2.1.3.2 Sulfuric Acid Plant Design 37
  2.1.3.3 Cesium-Promoted Catalysts 38
  2.1.3.4 Sulfuric Acid Plant Operation 39
  2.1.3.5 Improved Catalyst Shapes 39
2.2 The Deacon Process 39
  2.2.1 The Process 40
  2.2.2 Operation 40
  2.2.3 Catalyst Preparation 41
  2.2.4 Development 41
2.3 Claus Sulfur Recovery Process 41
  2.3.1 The Claus Process 42
  2.3.2 Claus Plant Operation 42
  2.3.3 Claus Process Catalysts 45
  2.3.4 Catalyst Operation 46
2.4 Ammonia Synthesis 48
  2.4.1 Sir William Crookes 49
  2.4.2 Development of the Ammonia Synthesis Process 51
  2.4.3 Commercial Application of Ammonia Synthesis Catalysts 52
  2.4.4 The Haber–Bosch Synthesis Reactor 53
  2.4.5 Conclusions 54
2.5 Coal Hydrogenation 55
  2.5.1 The Bergius Process 55
  2.5.2 Commercial Development by I. G. Farben 56
  2.5.3 Cooperation between I. G. Farben and Standard Oil 56
  2.5.4 Commercial Developments by ICI 56
  2.5.5 International Cooperation 57
  2.5.6 Coal Hydrogenation Processes 57
    2.5.6.1 The I. G. Farben Process 58
    2.5.6.2 The ICI Process 59
  2.5.7 Catalysts for Coal Hydrogenation 60
  2.5.8 Creosote and Other Feeds 61
2.6 The Fischer-Tropsch Process 63
  2.6.1 Postwar Development of the Synthol Process by Sasol 65
  2.6.2 The Importance of Gas-to-Liquids as Gasoline Prices Increase 68
References 69
Chapter 3
Hydrogenation Catalysts

3.1 The Development of Hydrogenation Catalysts
   3.1.1 Sabatier and Senderens 73
   3.1.2 The First Industrial Application of Nickel Catalysts 75
   3.1.3 Ipatieff and High-Pressure Hydrogenation of Liquids 75
   3.1.4 Colloidal Platinum and Palladium Catalysts by Paal 76
   3.1.5 Platinum and Palladium Black Catalysts by Willstatter 76
   3.1.6 Adams’ Platinum Oxide 78
   3.1.7 Raney Nickel Catalysts 78
   3.1.8 Nickel Oxide/Kieselguhr Catalysts 80
   3.1.9 Nickel Oxide-Alumina Catalysts 83
   3.1.10 Copper Chromite Catalysts 85
   3.1.11 Copper Oxide/Zinc Oxide Catalysts 86

3.2 Hydrogenation of Fats and Oils
   3.2.1 Process Development 89
   3.2.2 Oil Hydrogenation 90
   3.2.3 Fat Hardening Catalysts 91
   3.2.4 Catalyst Selectivity 93
   3.2.5 Feed Pretreatment 94
   3.2.6 Catalyst Operation 94
   3.2.7 Catalyst Poisons 96

3.3 Fatty Acid Hydrogenation

3.4 The Production of Fatty Alcohols
   3.4.1 Natural Fatty Alcohols 97
   3.4.2 Catalyst Operation 98
   3.4.3 Reaction of Fatty Alcohols 98

3.5 Some Industrial Hydrogenation Processes
   3.5.1 Nitrobenzene Reduction 99
   3.5.2 Benzene Hydrogenation 100
      3.5.2.1 Removal of Aromatics 101
   3.5.3 Hydrogenation of Phenol 101

3.6 Selective Hydrogenation of Acetylenes and Dienes
   3.6.1 Acetylene Hydrogenation Process Design 104
   3.6.2 Early Acetylene Hydrogenation Catalysts 105
      3.6.2.1 Sulfided Cobalt Molybdate 105
      3.6.2.2 Sulfided Nickel Oxide 105
      3.6.2.3 Fused Iron Oxide 106
      3.6.2.4 Palladium Catalyst Guard Beds 106
Chapter 4

Oxidation Catalysts

4.1 Nitric Acid
   4.1.1 The Ammonia Oxidation Process 124
   4.1.2 Catalyst Operation 128
   4.1.3 Platinum Recovery 130

4.2 Formaldehyde
   4.2.1 Silver Catalyst Operation 131
   4.2.2 Mixed Oxide Catalyst Operation 136

4.3 Andrussov Synthesis of Hydrogen Cyanide 137

4.4 Hopcalite Catalysts For Carbon Monoxide Oxidation 139

4.5 Phthalic Anhydride
   4.5.1 Naphthalene Oxidation 141
   4.5.2 Orthoxylene Oxidation 142

4.6 Maleic Anhydride 144
   4.6.1 Benzene Feedstock 144
   4.6.2 n-Butene Feedstock 144
   4.6.3 n-Butane Feedstock 148
   4.6.4 n-Butane Oxidation in a Circulating Fluidized Bed 149

4.7 Ethylene Oxide
   4.7.1 Catalyst 150
   4.7.2 Operation and Reaction Mechanism 153
   4.7.3 Applications of Ethylene Oxide 154

4.8 A Redox Oxidation Mechanism: Mars and Van Krevelen 155

4.9 Acrolein and Acrylonitrile 156
Chapter 5

Catalytic Cracking Catalysts

5.1 Introduction

5.2 Process Development
   5.2.1 Fixed Beds
   5.2.2 Moving and Fluidized Beds
   5.2.3 Catalyst Regeneration and Carbon Monoxide Combustion
      5.2.3.1 Catalyst Regeneration
      5.2.3.2 Carbon Monoxide Combustion Promoter
   5.2.4 Equilibrium Catalyst
   5.2.5 Reaction Mechanism of Catalytic Cracking Reactions

5.3 Catalyst Development
   5.3.1 Natural Clay Catalysts
   5.3.2 Synthetic Silica Alumina Catalysts
   5.3.3 Preparation of Synthetic Catalysts

5.4 Zeolite Catalysts
   5.4.1 Commercial Zeolites
   5.4.2 Production of Zeolites
   5.4.3 Formation of Active Sites by Ion Exchange
   5.4.4 Use of Zeolites in Catalytic Cracking
   5.4.5 The Catalyst Matrix

5.5 Octane Catalysts (Catalysts to Increase Octane Rating)
   5.5.1 Hydrothermal Dealumination of Y-Zeolites
   5.5.2 Chemical Dealumination of Y-Zeolites
   5.5.3 Increasing Octane Number
   5.5.4 Shape Selective Cracking

5.6 Residue Cracking Catalysts
   5.6.1 Residual Feeds


5.6.2 Residue Catalyst Formulation 199
5.6.3 Coke Formation 199
5.7 Residue Catalyst Additives 201
  5.7.1 Nickel Additives 201
  5.7.2 Vanadium Additives 202
  5.7.3 Sulfur Oxides Transfer Additives 203
  5.7.4 Bottoms Cracking Additive 206
5.8 Reformulated Gasoline 206
References 209

Chapter 6

Refinery Catalysts

6.1 The Development of Catalytic Refinery Processes 211
6.2 Polymer Gasoline 213
6.3 Alkylation 217
  6.3.1 Liquid Acid Processes 219
  6.3.2 The Mechanism of Alkylation with an Acid Catalyst 219
  6.3.3 Liquid Acid Operating Conditions 220
  6.3.4 Processes Using Solid-State Acid Catalysts 221
6.4 Hydrotreating 221
  6.4.1 What Is Hydrotreating? 223
  6.4.2 Hydrotreating Processes 223
    6.4.2.1 Catalyst Production and Operation 224
    6.4.2.2 Catalyst Handling 225
    6.4.2.3 Activating the Catalyst 227
    6.4.2.4 Catalyst Operation 229
    6.4.2.5 Catalyst Regeneration 229
6.5 Hydrocracking 231
  6.5.1 Hydrocracking Processes 232
    6.5.1.1 Single-Stage Processes 233
    6.5.1.2 Two-Stage Processes 234
    6.5.1.3 Once-Through Process 234
  6.5.2 Hydrocracking Catalysts 235
    6.5.2.1 Acid Supports 235
    6.5.2.2 Hydrogenation Catalysts 236
    6.5.2.3 Catalyst Preparation 236
    6.5.2.4 Catalyst Activity 237
    6.5.2.5 Catalyst Reactivation 237
Chapter 6

6.6 Catalytic Reforming
   6.6.1 Naphtha Reforming Reactions
       6.6.1.1 Reformer Operation
       6.6.1.2 Coke Formation
   6.6.2 Reforming Catalysts
       6.6.2.1 Bimetallic Catalysts
       6.6.2.2 Catalyst Preparation
   6.6.3 Catalyst Regeneration
       6.6.3.1 Carbon Burn
       6.6.3.2 Oxychlorination
       6.6.3.3 Platinum Re-Dispersal
       6.6.3.4 Catalyst Reduction
   6.6.4 Catalyst Life
   6.7 Octane Boosting
       6.7.1 Selectoforming
       6.7.2 M-Forming
   6.8 Aromatics Production
       6.8.1 Aromatics Process
       6.8.2 Cyclar Process
       6.8.3 M2-Forming Process
   6.9 Catalytic Dewaxing
   6.10 Isomerization
       6.10.1 Isomerization Catalysts
       6.10.2 Reaction Mechanism
References

Chapter 7

Petrochemical Catalysts

7.1 The Development of Petrochemicals
   7.1.1 Isopropyl Alcohol
       7.1.1.1 Acetone
       7.1.1.2 Bisphenol-A
       7.1.1.3 Cumene
   7.1.2 Vinyl Chloride
       7.1.2.1 The Oxychlorination Reaction
       7.1.2.2 Oxychlorination Catalyst
       7.1.2.3 Catalyst Operation
   7.2 Synthetic Rubber From Butadiene and Styrene
Chapter 8
Olefin Polymerization Catalysts

8.1 Low-Pressure Polyethylene
8.1.1 Polyethylene Process Development 313
8.1.2 The Development of Polypropylene Catalysts 314

8.2 Ziegler–Natta Catalysts 314
8.2.1 Early Polyolefin Catalysts 314
8.2.2 Ziegler’s Brown Titanium Trichloride 315
8.2.3 Natta’s Violet Titanium Trichloride 316
8.2.4 Second-Generation Propylene Polymerization Catalysts 317
8.2.5 Supported Polyethylene Catalysts 319
8.2.6 Supported Polypropylene Catalysts 320
8.2.6.1 Third-Generation Catalysts 320
8.2.6.2 Fourth-Generation Catalysts 321

8.3 Phillips Polyethylene Catalysts 322
8.3.1 Catalyst Production 323
8.3.2 Catalyst Reduction 324
8.3.4 Catalyst Operation 324
8.3.5 Catalyst Modifiers 325
8.3.5.1 Titanium 326
8.3.5.2 Alumina and Zirconia 327
8.3.5.3 Fluorides 327
8.3.6 Use of Co-catalysts 327
8.3.7 Organo-chromium Catalysts 328

8.4 Other Catalysts 329

8.5 Polymerization Processes 329
8.5.1 Slurry Processes 332
8.5.2 Solution Processes 332
8.5.3 Gas Phase Process 333

8.6 Metallocene/Single-Site Catalysts 334
8.6.1 Early Development 335
8.6.2 Early Development 336
8.6.3 Industrial Operation 338
8.6.4 Catalyst Activators 338
8.6.5 Molecular Weight Control 339
8.6.7 New Catalyst Developments 340

8.7 The Molecular Structure of Polyolefins 341
8.7.1 Formation of Polymer Chains 341
8.7.2 Polymer Chain Termination 342
8.7.3 Molecular Weight 344
References 345

Chapter 9

Synthesis Gas

9.1 Ammonia Synthesis Gas 352
  9.1.1 Process Developments 353
  9.1.2 Increased Ammonia Production by Steam Reforming 354
9.2 Modern Ammonia Plants 355
9.3 Feedstock Purification 357
  9.3.1 Activated Carbon 358
  9.3.2 Hydrodesulfurization 358
  9.3.3 Chlorine Removal 360
  9.3.4 Sulfur Absorption 360
    9.3.4.1 Operation with Zinc Oxide 361
    9.3.4.2 Preparation of Zinc Oxide 363
    9.3.4.3 Desulfurization of Other Gases 363
9.4 Steam Reforming 363
  9.4.1 Reformer Design 365
  9.4.2 Reforming Catalysts 369
  9.4.3 Reformer Operation 371
  9.4.4 Secondary Reforming 374
9.5 Carbon Monoxide Removal 375
  9.5.1 High Temperature Carbon Monoxide Conversion 376
  9.5.2 High Temperature Conversion Catalysts 377
    9.5.2.1 Operating Conditions 378
  9.5.3 Low Temperature Carbon Monoxide Conversion 379
    9.5.3.1 Operation 381
    9.5.3.2 Catalyst 384
9.6 Methanation 385
  9.6.1 Operation 386
  9.6.2 Catalyst 387
  9.6.3 Other Methanation Processes 388
9.7 Other Applications of Steam Reforming 389
  9.7.1 Methanol Synthesis Gas 389
  9.7.2 OXO Synthesis Gas 390
  9.7.3 Hydrogen Production 390
  9.7.4 Reducing Gas 391
Chapter 10

Ammonia and Methanol Synthesis

10.1 Ammonia Synthesis 397
   10.1.1 Process Development from 1920 399
      10.1.1.1 Haber-Bosch Process 399
      10.1.1.2 Claude Process 400
      10.1.1.3 Casale Process 401
      10.1.1.4 United States of America 402
      10.1.1.5 Mont Cenis/Uhde Process 403
      10.1.1.6 United Kingdom 403
   10.1.2 Ammonia Synthesis Catalysts 405
      10.1.2.1 Catalyst Production 405
      10.1.2.2 Pre-reduced Catalysts 407
      10.1.2.3 Loading Catalyst to Converter 408
      10.1.2.4 Catalyst Discharge from the Converter 409
   10.1.3 Catalyst Reduction 409
      10.1.3.1 Reduction of Oxidized Catalyst 409
      10.1.3.2 Reduction of Pre-reduced Catalyst 410
      10.1.3.3 Mechanism of Catalyst Reduction 410
   10.1.4 The Ammonia Synthesis Process 412
      10.1.4.1 The Ammonia Synthesis Loop 412
      10.1.4.2 Converter Design 414
   10.1.5 New Catalyst Developments 417
      10.1.5.1 Magnetite Catalyst Containing Cobalt 418
      10.1.5.2 Ruthenium Catalyst 419
      10.1.5.3 Catalyst Preparation 419
      10.1.5.4 Full-scale Operation with Ruthenium Catalyst 420

10.2 Methanol Synthesis 421
   10.2.1 High-pressure Synthesis 421
      10.2.1.1 Zinc Oxide-Chromium Oxide Catalysts 421
      10.2.1.2 High-Pressure Operation 423
   10.2.2 Low-pressure Synthesis 425
      10.2.2.1 Copper Oxide Catalysts 426
      10.2.2.2 Copper Catalyst Production 426
10.2.2.3 Precipitates Forming During Production 430
10.2.2.4 Operation with Copper Catalysts 431
10.2.2.5 Reaction Mechanism with Copper Catalysts 432
10.2.2.6 Selectivity 432
10.2.2.7 Low-pressure Methanol Reactor Types 433
10.2.2.8 Catalyst Reduction 433
10.3 Novel Catalysts 434
References 435

Chapter 11

Environmental Catalysts

11.1 Stationary Sources 441
11.1.1 Selective Catalytic Reduction 443
11.1.2 Selective Catalytic Reduction Catalysts 445
11.1.2.1 Catalyst Composition 446
11.1.2.2 Catalyst Operation 447
11.1.2.3 Reaction Mechanism 447
11.1.2.4 Removal of Sulfur Dioxide as Sulfuric Acid 448
11.1.3 Gas Turbine Exhausts 449
11.1.3.1 Low Temperature Vanadium Pentoxide Catalysts 449
11.1.3.2 Catalytic Combustion Processes 449
11.1.4 Nitric Acid Plant Exhaust Gas 450
11.1.5 Ion-exchanged ZSM-5 Zeolites 451
11.2 Mobile Sources 452
11.2.1 Automobile Emission Control 452
11.2.2 Automobile Emission Control Catalysts 455
11.2.2.1 Bead Catalysts 456
11.2.2.2 Monolith Catalysts 456
11.2.2.3 Washcoat Composition 457
11.2.2.4 Platinum Group Metal Catalysts 458
11.2.2.5 Catalyst Poisons 459
11.2.3 Platinum Metal Group Availability 460
11.2.4 Catalyst Operation 460
11.2.5 Nitrogen Oxide Removal in Lean-Burn Engines 463
11.2.6 Diesel Engines 464
11.3 Volatile Organic Compounds 465
11.3.1 VOC Removal Processes 466
11.3.2 VOC Oxidation Catalysts 468
Reference 469
Index 471