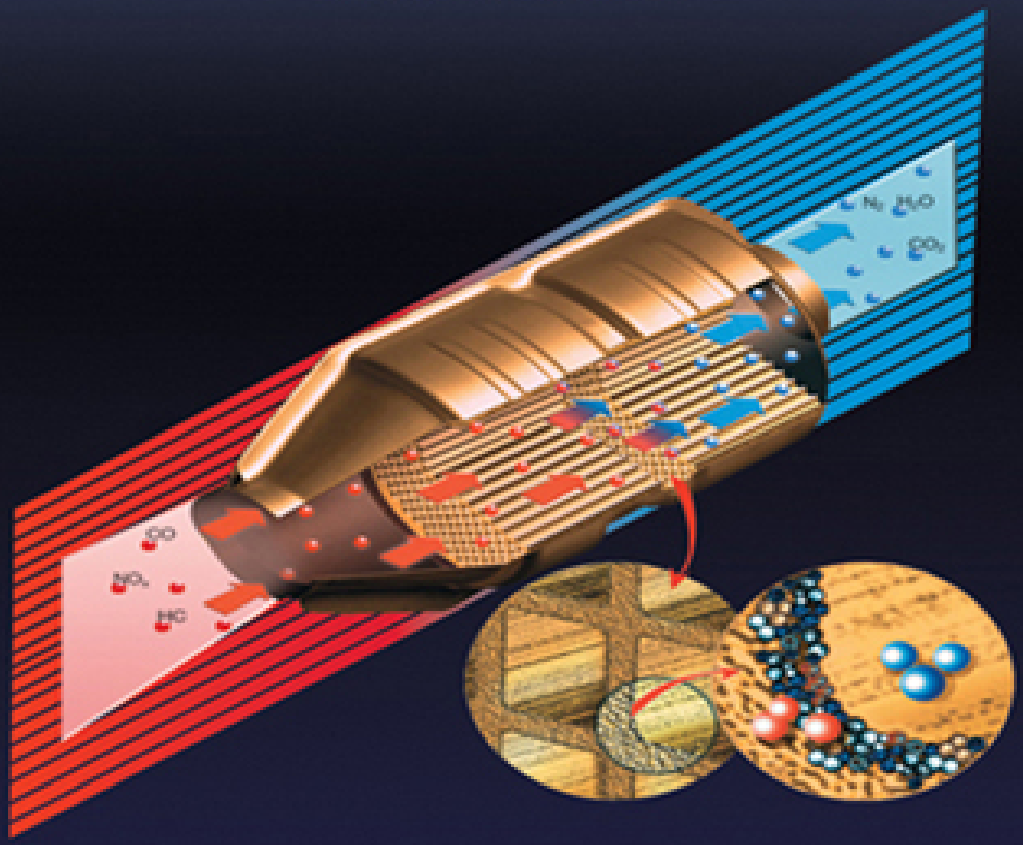
RONALD M. HECK • ROBERT J. FARRAUTO
with SURESH T. GULATI

CATALYTIC AIR POLLUTION CONTROL

COMMERCIAL TECHNOLOGY

THIRD EDITION



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To my wife, Barbara, whose friendship, support, understanding (especially on lost weekends), humor and selflessness made this endeavor much easier. I'm glad I will have more time for her as this project is finished. Unk for always being there for support; and to Merc and Dutch who were overseeing it all.

Ronald M. Heck

To my wife Olga (Olechka) who has given me love, understanding, focus and a new vision of the wonders of life; my loving daughters Jill Marie and Maryellen and their husbands Glenn and Tom. To my grandchildren Nicholas, Matthew, Kevin, Jillian, Owen and Brendan who represent everything that is beautiful in life.

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Suresh T. Gulati

Preface

Environmental quality is certainly a worldwide concern. Air pollution knows no boundaries, and reducing it is of the utmost importance. Countries are now establishing environmental regulations that must be met by mobile as well as by stationary pollution sources. Exhausts containing volatile organic compounds, carbon monoxide, nitric oxides, ozone, and so forth all can be converted to harmless nonpollutants at reasonable temperatures and with cost-effective systems using heterogeneous catalysts. The use of the right catalyst system converts pollutants to nonpollutants at low-energy requirements and at higher rates, resulting in cost-effective pollution control. The use of catalytic systems for pollution abatement was virtually nonexistent before 1976, but now it is a multibillion-dollar worldwide business that addresses gasoline- and diesel-fueled automobiles and trucks, destruction of volatile organic compounds from stationary sources such as chemical processing plants, reduction of nitric oxides from power plants and stationary engines, decomposition of ozone in high-flying commercial aircraft, pollution from small engines, and so on. The utilization of catalysts for future pollution abatement applications promises to grow at a strong pace over the next decade.

This book is designed to be a stand-alone introductory reference or textbook on the commercially available catalytic systems used today for reducing harmful emissions for both mobile and stationary sources. It is like no other book currently available, because it describes modern catalytic air pollution abatement techniques from a practical point of view. The subjects are discussed in clear and succinct language, with emphasis placed on the real-world

catalytic system performance. It is intended to serve as a bridge for academic and industrial catalysis.

Part I has been expanded to include more catalyst fundamentals to give readers a more detailed understanding of kinetics, characterization, and deactivation modes for environmental catalysts. Additionally questions have been added at the end of each chapter to challenge the reader's knowledge of the material presented. In both of these regards, the book now can serve as an introductory text with special emphasis on the applied aspects of environmental catalysis normally not covered in fundamental textbooks. It is especially useful for newcomers as well as for experienced catalyst scientists and engineers.

Part II discusses the application of catalytic systems for mobile source emission control, the automobile catalytic converter, diesel oxidation catalysts, diesel particulate filters (the newest major application of environmental catalysis), and the decomposition of ozone in high-flying aircraft. The sections on both automotive and diesel have been substantially expanded to reflect the opportunities for catalysis with the new emission standards particularly in diesel.

Part III describes the stationary application of catalysts, including volatile organic compounds, reduction of nitric oxides, and oxidation of gaseous carbon monoxide and hydrocarbons. A new section has been added to small-engine applications as this is a new developing field of catalytic applications.

Finally, Part IV presents new and emerging applications that, if developed, will dramatically change current catalytic technology for environmental control. For this reason, materials for the hydrogen economy including fuel cells have been updated.

* * *

Dr. Ron Heck is president of RMH Consulting where he specializes in consultation on environmental catalysis for auto, diesel, and stationary source; general catalysis; fuel cells; reaction engineering; combustion technology; chemical engineering; and expert witness. He retired as a principal scientist and research manager from Engelhard Corporation in 2003 where he was responsible for developing new catalyst technology for Engelhard Corporation's worldwide customers in environmental catalysis. He was responsible for developing the PremAir® family of catalysts technologies for removing pollutants from the ambient air and the close-coupled catalyst technology that allowed commercial development of ultra-low-emission systems. Ron was with Engelhard for 31 years and worked on development of catalytic processes for Engelhard in SCR NO_X, NSCR NO_X, automotive catalyst, diesel catalyst, PremAir® catalyst systems, hydrogenation technology, ozone abatement, volatile organic compound abatement, ammonia oxidation, chemical feedstock purification, and chemical synthesis.

Ron is a member of American Men and Women of Science and Who's Who in Technology Today. He is a recipient of the Forest R. McFarland Award from the Society of Automotive Engineers for outstanding contributions to this professional society. Ron is an SAE Fellow in recognition of engineering creativity and contributions to the profession and the public at large. With Dr. Gulati, Ron teaches a 2-day course on automotive emission control catalysis and diesel emission control catalysis organized by the Society of Automobile Engineers.

He is the co-author of the book with Dr. Farrauto entitled *Catalytic Air Pollution Control: Commercial Technology*. Ron was a co-editor of the "News-Brief" section of *Applied Catalysis B: Environmental* and was a member of the Scientific Advisory Board (SAB) for environmental studies for

the Strategic Environmental Research & Development Program (SERDP).

Ron and his former research team from Engelhard received the 2004 Thomas Alva Edison Patent Award from the R&D Council of New Jersey for the invention of close-coupled catalyst technology for ultra-low-emission gasoline vehicles.

Ron has been involved in over 80 publications in commercial applications of catalysts and holds 36 U.S. patents on catalytic processes.

Ron received his B.S. in chemical engineering and his Ph.D. from the University of Maryland and his M.A. in theology from the College of Saint Elizabeth.

Dr. Farrauto is a research fellow at the Corporate Research Laboratories of BASF Catalysts LLC (formerly Engelhard) in Iselin, New Jersey. He has worked extensively in the development of catalysts for the environmental, chemical, and alternative energy industries. His major responsibilities have included the development of advanced automobile emission control catalysts for passenger cars. He was technical leader of the Engelhard team that developed diesel oxidation catalysts now commercialized in the United States and Europe for trucks and passenger cars. Currently he is managing a research team investigating hydrogen production for fuel cells to be used for stationary, portable, and vehicular applications.

In addition to the third edition of *Catalytic Air Pollution Control: Commercial Technology*, he is the co author of *Fundamentals of Industrial Catalytic Processes*, second edition, published by Wiley. Dr. Farrauto is the author of 85 publications, and 50 U.S. patents, and he served as the North and South American Editor of *Applied Catalysis B: Environmental*. He is the recipient of the 2008 Ciapetta Lectureship Award sponsored by the North American Catalysis Society and in 2005 received the Catalysis and Reaction Engineering Practice Award in sponsored by the

American Institute of Chemical Engineering. He is the recipient of the Canadian Catalysis Foundation (Year 2000–2001) Cross Canada Lectureship Award and in 2001 received the Henry Albert Award for excellence in precious metal catalysis sponsored by the International Precious Metal Institutes. He is an adjunct professor in the Earth and Environmental Engineering Department of Columbia University in New York City where he teaches catalysis courses and supervises graduate students.

He received his B.S. in chemistry from Manhattan College in New York City and a Ph.D. from Rensselaer Polytechnic Institute in Troy, New York.

Dr. Suresh Gulati is a former corporate fellow of Corning Inc. and currently is a consultant to Corning. He has spent 33 years helping Corning develop and optimize ceramic catalyst supports and particulate filters for gasoline- and diesel-powered vehicles. Prior to retiring in 2000, he applied his mechanical engineering background to ensure long-term reliability of glass and ceramic products like space windows, CRT, fiber optics, and liquid crystal displays. He has published extensively in refereed journals, holds 15 U.S. patents, and continues to give talks at conferences organized by the SAE, ASME, and ACerS. He is a fellow of these professional societies. In addition, he is a recipient of two SAE awards: the Lloyd L. Withrow Distinguished Speaker Award in 2000 and the Forest R. McFarland Award in 2003. Both Drs. Gulati and Heck teach a 2-day course on catalytic converters that is organized by the Society of Automobile Engineers.

Dr. Gulati holds a B.S. from the University of Bombay, an M.S. from the Illinois Institute of Technology, and a Ph.D. from the University of Colorado—all in mechanical engineering.

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Acknowledgments, First Edition

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Finally, they would like to acknowledge Engelhard Corporation and many of its employees, past and present, who pioneered in the development of processes and catalysts for treating environmental problems, and who will continue to do so in the future.

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PART I

Fundamentals

Chapter 1

Catalyst Fundamentals

1.1 INTRODUCTION

Chemical reactions occur by breaking chemical bonds of reactants and by forming new bonds and new compounds. Breaking stable bonds requires the absorption of energy, whereas making new bonds results in the liberation of energy. The combination of these energies results in either an exothermic reaction in which the conversion of reactants to products liberates energy or an endothermic process in which the conversion process requires energy. In the former case, the energy of the product is lower than that of the reactants, with the difference being the heat liberated. In the latter case, the product energy is greater by the amount that must be added to conserve the total energy of the system. Under the same reaction conditions, the heat of reaction (ΔH) being a thermodynamic function does not depend on the path or the rate by which reactants are converted to products. Similarly, the free energy of reaction (ΔG) of the reaction is not dependent on the reaction path because it too is a thermodynamic state function. This will be emphasized once we discuss catalytic reactions. The rate of reaction is determined by the slowest step in a conversion process independent of the energy content of the reactants or products.

1.2 CATALYZED VERSUS NONCATALYZED REACTIONS

A few decades ago, chlorofluorocarbons (i.e., CF_2Cl_2), emitted primarily from refrigerants, were found to catalyze the destruction of the ozone (O_3) layer in the stratosphere necessary to protect us from harmful ultraviolet (UV) radiation and its skin cancer consequences. Fortunately alternative chemicals are now used, and this problem is no longer of great concern. It does, however, serve as an excellent example of a homogeneous gas phase catalytic reaction. First let us consider the very slow noncatalytic reaction between gaseous O_3 and O atoms produced by dissociation of O_2 by solar radiation in the upper atmosphere:

(1.1) $O_3 + O \rightarrow 2O_2$

Chlorine atoms, produced by solar radiation of chlorofluorohydrocarbons, catalyze the decomposition of ozone by reacting with it to form ClO and O_2 (1.2). The ClO then reacts with the O atoms regenerating Cl and producing more O_2 (1.3).

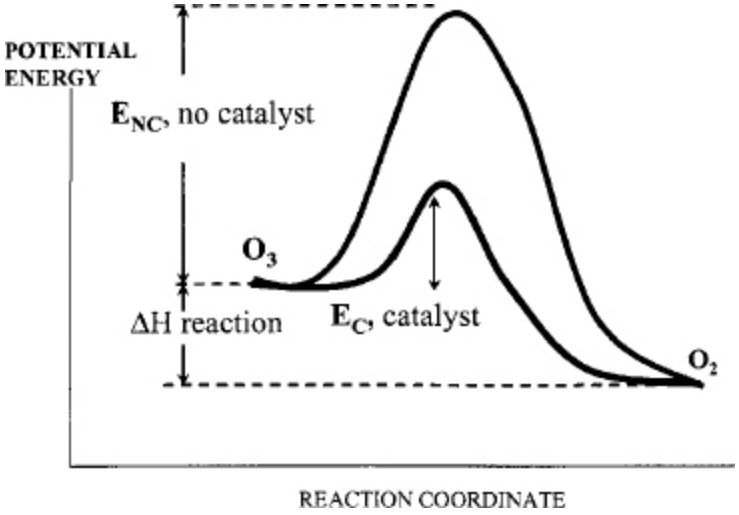
(1.2) $Cl + O_3 \rightarrow ClO + O_2$

(1.3) $ClO + O \rightarrow Cl + O_2$

Adding both reactions results in Eq. (1.1) and completes the catalytic cycle since the Cl and ClO are both consumed and regenerated in the two reactions. Thus, Cl is a homogeneous catalyst for the destruction of O_3. The uncatalyzed reaction is very slow, and its reaction profile can be described kinetically by the Arrhenius profile in which reactants convert to products by surmounting the noncatalytic

activation energy barrier (E_{NC}) as shown in Figure 1.1. The rate constant k of the reaction is inversely related to the exponential of the activation energy, where T is the absolute temperature, R is the universal gas constant, and k_o is the preexponential constant. The Arrhenius equation (1.4) indicates that the rate constant k decreases the higher the activation energy (E).

FIGURE 1.1. Catalyzed and uncatalyzed reaction energy paths for O_3 decomposition to O_2. Activation energy for catalyzed reaction E_C is lower, and the reaction is faster than the noncatalyzed E_{NC}.



(1.4) $k = k_o \mathrm{Exp}(-E/RT)$

Since the catalyzed reaction has a lower activation energy (E_C), its reaction rate is greater. The barrier was lowered by the Cl catalyst providing a chemical shortcut to products. Although the rate is greater for the catalyzed reaction, the enthalpy (ΔH) and free energy (ΔG) are not changed. Similarly the equilibrium constant for both catalyzed and noncatalyzed reactions is not changed since both operate under the same reaction conditions in the stratosphere. The catalyst can only influence the rate of which reactants are converted to products in accordance to the equilibrium constant and cannot make thermodynamically unfavorable

reactions occur. In industrial practice, reactions conditions, such as temperature and pressure, are varied to bring the free energy to a desirable value to permit the reaction to occur.

Now we will consider the conversion of carbon monoxide (CO), a known human poison, to CO_2, a reaction of great importance to the quality of air we breathe daily. The overall rate of the noncatalytic reaction is controlled by the dissociation of the O_2 molecule to O atoms (rate-limiting step), which rapidly react with CO forming CO_2. The temperature required to initiate the dissociation of O_2 is greater than 700°C, and once provided, the reaction rapidly goes to completion with a net liberation of energy (the heat of reaction is exothermic). The requirement to bring about the O_2 dissociation and ultimately the conversion of CO to CO_2 has an activation energy (E_{NC}). Reaction occurs when a sufficient number of molecules (O_2) possess the energy necessary (as determined by the Boltzmann distribution) to surmount the activation energy barrier (E_{NC}) shown in Figure 1.2a). The rate of reaction is expressed in accordance with the Arrhenius equation (1.4). Typically the activation energy for the noncatalytic or thermal conversion of CO to CO_2 is about 40 Kcal/mole.

FIGURE 1.2. Activation energy diagram for a) thermal reaction of CO and O_2 and b) the same reaction in the presence of Pt. Activation energy for the noncatalyzed reaction is E_{NC}. The Pt catalyzed reaction activation energy is designated E_c. Note that the heat of reaction ΔH_R is the same for both reactions. ΔH_a = heat of adsorption; ΔH_D = heat of desorption.