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HETEROGENEOUS CATALYSIS IN PRACTICE

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HETEROGENEOUS CATALYSIS IN PRACTICE

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To Anne
Mark and Karen
Joye and Thomas

PREFACE

Studies of solid catalysts and reactions catalyzed by solids have burgeoned in recent years, stimulated by an increasing number and variety of applications in industry. Significant contributions have come from individuals or groups whose formal academic education was in one or more of a wide variety of disciplines: these have ranged over the entire field of chemistry (including organic chemistry, inorganic chemistry, physical chemistry, chemical kinetics, and surface chemistry) to solid-state and surface physics, ceramics, physical metallurgy, and chemical reaction engineering.

One's first impression, which may be reinforced by further study, is apt to be that it is a vast and confusing field replete with an enormous quantity of perhaps significant but empirical facts intermixed with perhaps useful theories. The situation is not surprising when one reflects that heterogeneous catalysis in practice is concerned with controlling the rate and direction of a chemical reaction, whose basic mechanism is frequently understood only in broad outline; by means of a complex solid substance selected typically rather poorly characterized, from one or more of the many elements of the periodic table.

In such a situation there is the need for an overview of the landscape to identify features that provide orientation. This book has been written for chemists, chemical engineers, and others who seek such an overview, and especially for those who have had little previous exposure to heterogeneous catalysis and would like an introduction to the subject. The term "practice" in the title is to warn the reader that attention is devoted primarily to catalysts and reactions that are of industrial significance for large-scale operations and utilized under practicable conditions of pressure, temperature, and contact time, often processing impure reactants or mixtures. At present, theoretical concepts are the most successful in interpretation of the reactions of small molecules such as hydrogen, carbon monoxide, oxygen, and nitrogen on well-characterized surfaces. In the present volume, theory has not been neglected, but the attention devoted to various theoretical concepts is in some proportion to those that have stood the test of time and also seem to be of present practical importance or of some value for prediction for those reactions of industrial interest. Properly applied and with appreciation for their limitations, these various correlations, hypotheses, and theories can be a useful guide for effectively employing knowledge, past experience, and intuition.

This book is intended to provide a comprehensive introduction to the kinds of information that one needs to know in order to work with solid catalysts in the laboratory, pilot plant, or commercial installations. For those concerned with chemical reaction engineering it may provide some perspective on the chemical aspects that must be considered in reactor design in addition to the mathematical aspects treated in numerous texts. In this respect the present volume can be useful as a text or reference.

To some degree,thevalue of an introductory treatment such as this may be inversely prrportional to its size,and therefore it has been attempted, at the risk of oversimplification,to reduce each topic to its essentials. It is hoped that readers may find the balance appropriate anduseful for their needs. Appendix A provides an annotated guide to the vast literature Because of their rather specialized nature, polymerization reactions, photocatalysis, and electrocatalysis have not been considered. Experience has shown that many laboratory studies of practical catalysts are vitiated by inadequate experimental procedures, and especially by lack of recognition of the possible effects of mass- and heat-transfer gradients. Some suggestions on design of experiments and warning signals to look for in analyzing data are made in Chapter 11.

A number of problems are given in Appendix B with which the reader, whether a student or practicing scientist or engineer, can test his or her mastery of the material. Most of these deal with experimental data or are drawn from situations that have occurred in practice. Most real problems do not arrive conveniently packaged to fit within the neat framework of a textbook, and some of those included here likewise do not correspond specifically to the subject matter taken up in any one chapter. Therefore the problems are deliberately grouped together, but the order in which they appear corresponds approximately, where appropriate, to the order in which topics are taken up in the book. As a further challenge to the reader, a few problems are included that may or may not involve catalysis as such, and they require for their solution more of a general knowledge of chemistry.

An author is indebted to countless individuals in ways that are frequently difficult to recognize and to acknowledge explicitly. This book is the outgrowth of class notes that I first began to write more than 15 years ago for use in a course in catalysis, directed primarily to seniors and first-year graduate students in chemical engineering. Expanded and revised versions have also been further tested by recent use in intensive courses in industry, and I have profited from innumerable comments and suggestions from neophyte students and experienced practitioners alike. Among the many who have contributed valuable advice and criticisms are: George A. Huff, Jr., William J. Linn, John P. Longwell, William H. Manogue, Michael A. Serio, John H. Sinfelt, Preetinder S. Virk, James Wei, and James F. Weiher. I am also indebted to Craig Abernethy for his careful typing of the manuscript and I wish to express my especial gratitude to my wife, Anne, for help in a variety of ways.

Charles N. Satterfield

CONTENTS

CHAPTER

ONE

INTRODUCTION AND BASIC CONCEPTS

1.1 INTRODUCTION

The concept of catalysis as a method of controlling the rate and direction of a chemical reaction has captured the imagination of scientists and technologists since Berzelius in 1835 coordinated a number of disparate observations on chemical transformations by attributing them to a "catalytic force" and coined the term *catalysis* to refer to the "decomposition of bodies" by this force. At about the same time Mitscherlich introduced the term *contact action* for a similar group of phenomena. Ideas of what constitutes a catalyst and the mechanism of catalytic activity have undergone continuous refinement since, spurred by the enormous industrial importance of catalysts as illustrated by the variety of catalytic processes characteristic of modern petroleum refineries and of the chemical industries. Most of these processes involve solid catalysts, and an understanding of catalysis from both the theoretical and practical point of view is essential to chemists and chemical engineers.

In practice catalysis is primarily a technology which draws on many fields such as organic chemistry, surface chemistry, chemical kinetics, thermodynamics, solid-state physics, ceramics, and physical metallurgy. No unified theory of catalysis exists, and there are frequently several alternative, and not necessarily mutually exclusive, theoretical "explanations" for any given set of facts.

A basic concept is that a catalyzed reaction involves the transitory adsorption (almost always chemisorption) of one or more of the reactants onto the surface of the catalyst, rearrangement of the bonding, and desorption of the products. This leads to three groups of theories of catalysis:

1. The *geometrical theories* emphasize the importance of the correspondence between the geometrical configuration of the active atoms at the surface of the catalyst

and the arrangement of the atoms in the portion of the reacting molecule that adsorbs on the catalyst, this portion sometimes being called the *index group*. In one sense the usefulness of this approach is limited in that seldom can one change the geometrical arrangement of atoms in the catalyst surface without changing something else. Studies of reaction rates on different crystal faces of a metal have shown that the rates indeed may change with geometry, and it is found that the introduction of defects by cold rolling of a sheet of metal, by grinding, or by radioactive bombardment may substantially change the rate of a reaction if the reaction temperature is sufficiently low that the defects do not rapidly anneal or that the structure does not assume a more stable configuration.

An aspect of the geometrical approach of great usefulness is the observation that reaction selectivity may be markedly altered by the number and arrangement of sites required for competing reactions, which leads to the concepts of the importance of "ensembles" or specific grouping of atoms at the catalyst surface and *structure sensitivity* as affected by particle size, alloying, and other variables (Chap. 6).

2. The *electronic theories* proceed from the fact that chemisorption involves the distortion or displacement of electron clouds, and they attempt to relate activity to the electronic properties of the catalyst. This may be in terms of the electronic structure of the solid as a whole, or in terms of the orbitals around individual atoms. In the charge-transfer theory of catalysis (see, e.g., Volkenstein, 1963) it is postulated that the reaction rate is controlled by the availability of charge carriers—electrons or holes—in the catalyst. These are visualized as being nonlocalized; i.e., a sea of electrons or holes is available. Chemisorption is then related to the electronic properties of the catalyst—for example, the ease or difficulty of removal or donation of an electron to or from the lattice—as predicted by applying band theory as developed for metals and semiconductors.

   This approach, of considerable interest in the 1950s, is now seen to be too broad and is inadequate or inapplicable for most cases. More recently attention has been directed to the properties of atoms as individual entities and to the electronic effects caused by the nearest neighbors in the solid rather than by the solid as a whole. In many cases it is difficult to separate geometrical effects from localized electronic effects; the relative importance of the two probably varies greatly from case to case.

3. The above two theories represent primarily a physical approach in that the catalyst is regarded as essentially a static material having the property of converting reactant to product. The *chemical approach* on the other hand regards the catalyst as a chemical intermediate that forms an unstable, surface, transitory complex with the reactants. This decomposes into the final products, returning the catalyst to its initial state. The rates of these processes and the structures formed are assumed to obey chemical principles. If the energy of formation of the unstable intermediate is low, the affinity between catalyst and reactants will be weak and the overall rate is limited by the rate of formation of the intermediate. If the energy of formation is high, the intermediate compound will be stable and the rate is limited by the rate of breakup of this intermediate.