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MATERIALS SCIENCE IN ENERGY TECHNOLOGY

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Materials Science in Energy Technology

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Preface

There is an ever-increasing demand for more energy in our society and since the "energy crisis" of 1973, the general public has become aware that our present sources of energy are not limitless. Although there are some disagreements as to the nature and extent of the energy shortages, there is little question that there will be significant changes in our energy technologies in the future. Even if the energy sources remain the same, more efficient means of converting them into useful energy forms will be required. It is not generally realized that in most cases the major hindrances to the development of both present and future energy sources are materials limitations. Therefore, the major purpose of this book is twofold; first, to acquaint those involved in energy technology with the fundamental properties of materials relevant to each form of energy; second, to suggest to materials scientists, including physicists, chemists, and metallurgists, where their areas of expertise may be of value in solving energy related problems.

Each chapter reviews the basic properties of those materials that are important to a particular energy application, and it also attempts to identify the areas of research required for the development of new materials for that application. The first six chapters deal with methods of producing energy, and they are arranged in approximate chronological order as to when the methods were (or will be) first utilized. Fossil fuels have been the major energy source for about a century (wood, before about 1880). Nevertheless, there is still much room for improvement in terms of catalyst materials for production of fuel as discussed in the first chapter, particularly in the area of resid and coal liquids conversion. Nuclear fission has become a significant source of energy in the last decade and the wide scope of materials associated with this technology is reviewed in Chapter 2. Magnetohydrodynamic generators hold out the promise of more efficient production of electricity from fossil fuels; although one such generator has been operated in the USSR using natural gas, there are many high-temperature materials problems that must be solved before they become a feasible source of energy using realistic fuels. Ceramic materials for this application are considered in Chapter 3.

Solar energy has been used for hot water and space heating in individual homes, but its large scale use for electricity production, using photovoltaic cells, awaits the development of new materials that will permit the more economic conversion of this source of energy, as discussed in Chapter 4. Geothermal energy has always been available, but its use has been very limited because of severe corrosion problems, as pointed out in Chapter 5. The maximum utilization of this form of energy depends significantly on materials development. The sixth chapter is concerned with controlled thermonuclear fusion, which is one of the most promising future sources of energy, but also the most difficult to develop because of the very severe materials requirements involved.

The last four chapters cover the materials aspects of energy conversion, storage, and transmission. Fuel cells convert fossil and combustible fuels to electrical energy, while hydrogen energy systems convert electrical or solar energy to a combustible fuel. The latter also provide a means for storing and transmitting energy. Although batteries have been used extensively for storing electrical energy on a small scale in the past, advances in solid state science have provided exciting new concepts for more efficient low-cost batteries. Finally, superconducting materials for electrical energy storage and transmission are reviewed (as well as the use of superconducting magnets to confine plasmas in thermonuclear reactors and MHD generators).

It is apparent that not all of the materials aspects of energy production, conversion, and storage have been covered in this book. For example, important materials for the storage of thermal energy such as low melting eutectic salts, or the high-strength materials required for flywheel storage are only briefly mentioned. In addition, other materials that have not been considered come to mind, such as high-temperature alloys for gas turbines or those used in coal conversion and drilling for oil exploration. Undoubtedly, as new energy sources are developed, new materials problems will come to the fore. Nevertheless, we believe that this book gives sufficiently extensive coverage of the relation between materials science and energy technology to be useful for some time to come to scientists and engineers involved or interested in the various aspects of energy development.

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Chapter 1

Heterogeneous Catalysis in Fossil Fuel Conversion

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I. INTRODUCTION

Heterogeneous catalysis has for many years played a vital role in industrial processes for the manufacture of fuels. This is particularly evident in the petroleum industry, where the demand for high quality gasoline and heating oil has been met very successfully through the application of heterogeneous catalysis. Processes such as catalytic cracking and catalytic reform-

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ing have had an enormous impact for the past several decades. Over the years these processes have improved markedly, as a result of research directed to new or improved catalyst systems. In addition to these major petroleum fuels processes, and such related processes as hydrocracking and isomerization, there are other important applications of heterogeneous catalysis in the fuels area. These include steam reforming of petroleum naphthas to produce methane-rich heating gas and the Fischer–Tropsch process for synthesis of gasoline from carbon monoxide and hydrogen. The former has been of interest for some time because of limitations in availability of natural gas, while the latter was mainly of interest in Germany during World War II. Currently, other applications of heterogeneous catalysis are actively being considered by various groups concerned with extending fuel capabilities through processes such as coal gasification and liquefaction.

The present article begins with a simple discussion of heterogeneous catalysis, which includes some consideration of the nature of catalytic materials and of catalytic processes in general. The bulk of the article is then concerned with specific catalytic processes involved in the manufacture of fuels. The processes are considered primarily with regard to the nature of the reactions and catalysts involved, but some consideration is also given to important technological features of the processes.

II. GENERAL ASPECTS OF HETEROGENEOUS CATALYSIS

A. Nature of Catalytic Materials

In general, catalysts of practical interest have high surface areas. To achieve high surface areas, it is necessary to prepare catalysts in a very finely divided state or in a highly porous form [1]. In the case of nonporous solids, the surface area is confined to the external surface of the particles. The specific surface area (i.e., the surface area per unit weight of material) is then inversely proportional to the particle size, if the particles are perfect spheres or cubes. With porous solids, however, most of the surface area resides in the walls of the pores and is frequently termed the "internal surface" of the solid. In the case of highly porous solids, the internal surface area is commonly several orders of magnitude higher than the external surface area of a particle or granule.

For the classification of various types of catalysts, it is convenient to divide them into two broad categories, metals and nonmetals. In the first category, the most commonly used metals are those in Group VIII and Group IB of the Periodic Table. In the second category, oxides are the most common catalysts. In either of these two categories, the catalyst is often supported on a carrier to achieve higher dispersion and improved resistance

to sintering. For highly dispersed catalysts, the carrier is commonly a high surface area, porous, refractory material such as alumina or silica.

The application of supported metal catalysts in industrial processes is well known. Such catalysts are commonly prepared by impregnation and precipitation methods. In the impregnation method, the carrier is contacted with a solution of a salt of the desired metal. The solute deposits on the carrier, and the resulting material is dried and often calcined at higher temperature. The next step is reduction of the material deposited on the carrier to the metallic form. This is commonly done at elevated temperature in a stream of hydrogen. The final material then consists of an assembly of small metal crystallites dispersed on the surface of the carrier. A typical example would be the preparation of a nickel–silica catalyst, in which an aqueous solution of nickel nitrate would probably be used for the impregnation. The hydrogen reduction step would be conducted at a temperature of about 400°C. Another example would be the preparation of a platinum–alumina catalyst, in which the impregnation would be made with a chloroplatinic acid solution. In this case, the catalyst would usually be calcined in air at about 500–550°C prior to reduction in hydrogen.

In the preparation of supported metals by precipitation methods, a hydroxide or carbonate of a metal may be precipitated from a solution of a metal salt onto a carrier suspended in the solution. Thus, a nickel–silica catalyst could be prepared starting with a nickel nitrate solution in which silica is suspended or slurried. Addition of alkali to the solution causes precipitation of nickel hydroxide onto the silica. The material is then dried and reduced in hydrogen at elevated temperature to form the catalyst. In another procedure, termed "coprecipitation," the carrier is precipitated simultaneously with the active component. Thus, in the preparation of a nickel–alumina catalyst, one may start with an aqueous solution of nickel and aluminum nitrates. On addition of alkali, hydroxides of nickel and aluminum are coprecipitated. The precipitate is then filtered, washed repeatedly, and dried. After calcination at elevated temperature (400–450°C) and subsequent exposure to a stream of hydrogen at about 500°C, the material consists of small nickel crystallites dispersed on alumina.

In the case of nonmetallic catalysts, oxides find the widest application. Such catalysts can be prepared by methods involving precipitation or gel formation. For example, an aluminum oxide catalyst which is highly active for the dehydration of alcohols can be prepared by addition of an aqueous solution of ammonia to an aluminum nitrate solution [2]. This treatment yields a finely divided precipitate of aluminum hydroxide, which is dried and then calcined at elevated temperature (400–600°C) to produce the desired aluminum oxide. An alternate procedure for the formation of the aluminum hydroxide precipitate is the hydrolysis of aluminum isopropoxide [3]. Sur-

face areas of the order of 200 m^2/gm are readily obtained for aluminas prepared by these procedures.

Oxides such as alumina, silica, or chromia are often prepared in the form of gels [4–7]. In the formation of a gel from solution, finely dispersed colloidal particles are generated first. However, instead of remaining in a colloidal suspension as freely moving particles or settling out of solution, the particles are joined together in some form of continuous structure throughout the solution volume. Many gels contain an extremely high fraction of liquid (>99 vol%) within the structure. In such cases, the solid component of the gel is probably fibrillar in form [8]. The formation of a gel, as opposed to a crystalloidal type of precipitate, depends on the detailed conditions of preparation. A classical example of gel formation of interest in catalysis is the preparation of chromia gel by the slow addition of ammonium hydroxide solution to a dilute solution of chromic nitrate [6, 7]. The highly dilute gel which forms is dried to remove most of the water, leaving an amorphous, black solid. Care must be exercised in heating the chromia, since too rapid heating may result in the formation of highly crystalline α–chromia, a bright-green solid. If the chromia is heated slowly through the temperature range 275–375°C, the crystallization can be prevented. Chromia gels heated to temperatures of 300–450°C may give catalysts with surface areas as high as 300 m^2/gm. It has been suggested that the fibrillar structure of chromia gel is due to the formation of a condensation polymer of chromium hydroxide [6, 9, 10].

Like metals, nonmetallic catalyst entities are also frequently deposited on supports to achieve a higher degree of dispersion of the active component. Oxides of metals such as chromium, molybdenum, vanadium, manganese, copper, bismuth, iron, cobalt, and nickel, among others, are commonly supported on refractory oxide carriers in catalytic applications. The catalysts may be prepared by impregnation or coprecipitation techniques. For example, a chromia–alumina catalyst can be prepared by impregnating activated alumina with an aqueous solution of either chromic acid, chromium nitrate, ammonium chromate or ammonium dichromate. The material is then dried at a temperature of 110–150°C and subsequently calcined at temperatures of 350–550°C [11]. Alternatively, a coprecipitated chromia–alumina catalyst can be prepared by adding ammonium hydroxide to a solution of chromic and aluminum nitrates. The material is then dried and calcined in the same manner as impregnated chromia–alumina.

In the foregoing paragraphs, an attempt has been made to describe catalytic materials in a general way, with emphasis on their high surface areas and methods of preparation. The high degree of dispersion is the single most important feature distinguishing catalysts as a class of materials. In addition to their importance as catalysts, highly dispersed solids present some very

challenging questions with regard to the chemistry and physics of the solid state, especially when the degree of dispersion is so high that the surface totally dominates the bulk.

B. Nature of Catalytic Processes

A catalytic process involves a sequence of reaction steps in which active catalytic centers participating in the steps are continually being regenerated, so that many molecules of product are formed per active center. Such a sequence is termed a closed sequence [12]. In heterogeneous catalysis, the active center is a site on the surface of the catalyst or a surface complex of the site with a reactant molecule. In the case of the overall reaction, $A + B \rightarrow C$, the following sequence of steps may be visualized:

$$A + S \rightarrow A\text{–}S$$

$$A\text{–}S + B \rightarrow C + S$$

In this simple sequence the reactant A is adsorbed on an active center S to form the surface complex A–S, which in turn reacts with the reactant B to yield the product C and regenerate S. This sequence illustrates features common to all catalytic processes, namely, the generation of a reactive intermediate, the formation of product from the intermediate, and the regeneration of the active catalyst site. The sequence of steps in a catalytic process is repeated over and over again using the same active centers on the catalyst surface.

For heterogeneous catalysis to occur, chemisorption of at least one reactant is generally required. The reactant molecule is activated in the chemisorption step, and the chemical nature of the surface is an important factor. In general, catalytic activity is related to the strength of adsorption of a reactant on the surface. Maximum catalytic activity results when chemisorption of the reactant is fast but not very strong. If the adsorption bond is too strong, the catalyst will tend to be fully covered by a stable surface compound which does not readily undergo reaction. On the other hand, if chemisorption of the reactant is slow, the reaction may be limited severely by the adsorption step. Optimum catalytic activity corresponds to an intermediate degree of coverage of the surface by the adsorption complex undergoing reaction [13, 14]. In the case of metal catalyzed reactions, this optimum condition is frequently found among the metals of Group VIII, and consequently these metals are particularly important in catalysis.

Perhaps the most intriguing aspect of catalysis is the specificity observed. It has been known for a long time that the chemical nature of a solid surface determines its catalytic properties. If the role of the surface were simply one of concentrating reactants in a physically adsorbed layer, then any high

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