

# APPLIED INDUSTRIAL CATALYSIS

*VOLUME 2*

Edited by

Bruce E. Leach

# Applied Industrial Catalysis

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BRUCE E. LEACH

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## Preface

Catalysts play a major role in the production of chemical intermediates from oil, natural gas, coal, and natural feedstocks. Catalysis represents an active research field with increasing cooperation between academic and industrial scientists. The objective of these volumes is a practical description of catalysis as practiced by industry to explain important aspects of commercial operation with the use of specific examples.

The reader should recognize that the processes discussed are examples of current industrial practice but obviously do not disclose proprietary information. Competitive processes are available for the synthesis of most chemical intermediates. The emphasis is on commercial practice and not on theory, kinetics, and reaction mechanisms. Excellent reference works already exist for these important aspects of catalysis.

This second of three volumes begins with helpful guidance in catalyst selection by A. W. Sleight and U. Chowdhry. Forty catalysts most often cited in the literature are reviewed by F. S. Wagner. Catalytic uses of these forty compounds are reviewed using only the most recent references.

Hydrogenation and dehydrogenation reactions produce a wide variety of chemical intermediates. A. B. Stiles reviews catalyst and reactor selections for these important synthetic reactions.

The synthesis of hydrocarbons from carbon monoxide and hydrogen has recently received renewed attention. M. E. Dry reviews the history and development of Fischer-Tropsch plant technology from the perspective of commercial experience.

The synthesis of methanol from carbon monoxide and hydrogen ranks third in volume behind ammonia and ethylene. The history and development of methanol synthesis catalysts are described by F. Marschner and F. W. Moeller.

Sulfuric acid is the largest volume chemical commodity produced. J. R. Donovan, R. D. Stolk, and M. L. Unland describe the catalysts, reaction equilibria and kinetics, and reaction variables for oxidation of sulfur dioxide to sulfur trioxide.

The editor acknowledges Drs. D. P. Higley and J. B. Winder, who assisted in reviewing the chapters. Dr. C. M. Starks, who encouraged me to edit this work, and Sherry Head, who assisted with communication to authors and typed manuscript revisions, deserve special recognition.

It is the editor's hope that this book will contribute to an understanding of industrial catalysis and industrial processes and further scientific cooperation between academic and industrial scientists.

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# Catalyst Design and Selection

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## I. Introduction

For a catalyst to be useful in a commercial process, it must usually meet certain requirements of activity, selectivity, and lifetime. There are situations in which selectivity might be discounted, for example, in a catalyst for the complete combustion of hydrocarbons to carbon dioxide and water. However, there has generally been increased emphasis on catalyst selectivity in recent years even to the point where activity and lifetime are sometimes sacrificed. Important factors have been the increasing cost of feedstocks, energy, and disposal of undesirable by-products.

There are often compromises to be made with respect to catalyst activity, selectivity, and lifetime. A catalyst with very high activity due to a very high

surface area may possess intrinsic problems involving lifetime and even selectivity. In general, the most active catalysts are amorphous or are very poorly crystalline materials with considerable disorder. Most highly selective catalysts on the other hand tend to be crystalline and present a more uniform distribution of active sites.

In principle, one can quickly screen large numbers of catalysts for activity and selectivity. Evaluation of lifetime is by its very nature time-consuming. Many publications (including patents) present interesting examples of catalyst activity and selectivity with little or no information on catalyst life. In view of the difficulty of evaluating the lifetime for every catalyst with attractive selectivity and activity, an understanding of catalyst design and selection with regard to catalyst life becomes especially desirable.

## II. Principles of Design and Selection

### A. PROPOSED REACTION

Before selection of a catalyst, one must carefully consider the conditions to which the catalyst will be subjected in a reactor. Starting with thermodynamic considerations, appropriate ranges of temperature, pressure, and feed composition must be defined for the desired reactants and products. Competing side reactions and product degradation reactions must also be considered. Usually, there are further practical considerations. In oxidation reactions, explosive mixtures of reactants are generally, but not always, avoided. Corrosion problems in a reactor can influence the selection of reactor conditions.

There are many economic factors to be considered in defining reasonable reactor conditions. Optimum energy utilization is important as well as the cost of the feed material and the reactor itself. Frequently it is desirable that the feed to the reactor contain an amount of the least expensive reactant in excess of that required for a stoichiometric reaction. Desirable reactor conditions may also be influenced by considerations of the value of various by-products or the difficulty of separating the various reaction products.

### B. POSSIBLE CATALYSTS

After deciding upon appropriate reaction conditions, the next phase in catalyst selection might be consideration of what types of materials are likely to survive under what in many cases may be regarded as very hostile



conditions. For hydrogenation reactions, stable materials are generally metals or oxides not reduced by hydrogen, e.g.,  $\text{Cr}_2\text{O}_3$ . For oxidation reactions, stable materials are normally oxides or noble metals.

There is a considerable amount of misleading literature concerning the types of materials considered for various reactions. Frequently, oxide catalysts are reduced to the metal or a metal oxide-metal mixture when used. Indeed, there may be some indication of this in that a pretreatment or activation step is recommended for the catalyst. An oxide catalyst may become a sulfide when used as a hydrodesulfurization catalyst, or it may become a fluoride when used as a fluorination catalyst. In fact, there are situations in which a given oxide catalyst finds application in several different reactions. In one case it may in truth be a sulfide; in another case it may be a mixture of a metal and a metal oxide. If one is interested in the rational design of a catalyst based on the underlying chemistry, it is essential to know the nature of the real working catalyst which in some cases bears little resemblance to the catalyst a manufacturer supplies.

Many catalysts contain metals known to exhibit several different oxidation states. For example, in an oxide catalyst containing iron there may be  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , or both. In fact, there is good reason to believe that this mixed or variable oxidation state directly influences catalytic properties. However, when considering a variable oxidation state catalyst, there should be some appreciation of the plausible oxidation state under a given set of conditions. For example, molybdenum oxides are in a low oxidation state (+4 or lower) under highly reducing conditions but are close to the maximum oxidation state of +6 when used as oxidation catalysts with excess oxygen. Although one might inquire about the catalytic properties of  $\text{MoO}_2$  versus  $\text{MoO}_3$  for a particular reaction, only one of these two compounds can be maintained under a given set of reactor conditions.

A complication in considering the stability of a catalyst in a catalytic reactor is that the conditions inside the reactor usually vary dramatically from one region of the reactor to another. A successful catalyst must then survive these various conditions. In fluid bed or riser reactors, catalyst particles rapidly move through various parts of the reactor where different conditions exist. In a fixed bed reactor, the conditions at the inlet generally are very different than at the outlet. The temperature may be significantly different, and the gas phase composition is definitely different. For example, in an oxidation reaction operated under lean oxygen conditions to avoid the explosive region, there may be no oxygen at the outlet. In this case the catalyst is exposed to significant oxygen pressure at the beginning of the bed but to essentially no oxygen at the end of the bed. If the catalyst is a metal oxide, the oxidation state of the metal, and its catalytic properties, might well differ in various regions of the bed.

### C. PROBABLE CATALYSTS

Having decided which types of materials are likely to be stable under reaction conditions, one must then decide which of these materials might actually be a catalyst for the desired reaction. First, one considers past experience with similar reactions. For example, molybdates and vanadates are good candidates for a wide variety of selective oxidation reactions, and palladium is a good catalyst for a wide variety of hydrogenation reactions.

One can also consider known chemistry: solution chemistry, noncatalytic reaction chemistry, homogeneous catalysis for possible heterogeneous analogs, and surface chemistry. For example, if one is interested in an acid-catalyzed reaction, the literature could be evaluated for solid compounds of high acidity. One should also consider whether or not such candidates will be stable under the reactor conditions. Then candidates should be obtained and screened in a laboratory reactor.

Zeolites present special opportunities for rational catalyst design and selection in view of their unique selectivity capabilities. The pores in zeolites are well-defined and of molecular dimensions. Therefore, one can design catalyst selectivity based on dimensions of products, reactants, or transition state intermediates. Also, one has considerable control over the acidity which can be very high.

In choosing probable catalyst candidates, one must also consider the undesirable side reactions that might be promoted by various catalysts. One must as well examine the known chemistry of the product. Is the product likely to survive reactor conditions in the presence of the candidate catalyst? Some catalysts are more impressive for what they do not catalyze than for what they do catalyze. For example, a good selective oxidation catalyst gives high conversions to the desired product, yet there is very little overoxidation to carbon dioxide and water even in the presence of a great excess of oxygen.

Consideration should be given at this point in catalyst design and selection to whether or not the catalyst will be supported. If a support is desirable for a reason such as dispersion or strength, the support should be carefully chosen. Candidate supports must first be considered from the point of view of stability. Because alumina dissolves in acid, it cannot, for example, be used as a support in a slurry bed reactor run at low pH. Likewise, silica cannot be used as a support for a fluorination reaction since  $\text{SiF}_4$  is volatile. Another aspect of choosing the proper support is the catalytic activity of the support itself. Silica is generally regarded as more inert than alumina; however, the catalytic activity of alumina is sometimes advantageous, for example, in reforming reactions.

Some consideration should also be given to the physical requirements of the catalyst. For example, what are the physical strength requirements? If

the catalyst will be used as pellets, the crush strength may well be important. If the catalyst is to be used in a fluid bed or slurry bed reactor, attrition resistance will be important. The physical form of catalysts used in laboratory reactors should, at least in the later stages of evaluation, closely resemble that anticipated in the application.

#### D. CATALYST SCOUTING

Having decided upon what types of catalysts to obtain or prepare, how should the catalytic properties be evaluated? Two different strategies can be implemented. One is to design a laboratory reactor that can most closely match the envisioned application. However, with such a reactor it may be essentially impossible to obtain intrinsic rate and kinetic data. Usually, it is preferable to start with a laboratory minireactor designed not to simulate a plant reactor but rather to produce intrinsic kinetic and mechanistic information. This affords the possibility of obtaining a better understanding of the reaction at the same time one is scouting for different catalysts.

Frequently in a catalyst scouting program, each catalyst is examined under very few conditions, and the only information obtained is reactant conversion and selectivity at this conversion. There are several problems with this approach. One is that a good catalyst can easily be overlooked, since conditions appropriate for the catalyst may not have been employed. Another problem is that little useful information is obtained that will be of value for the next round of catalyst design and selection. One will have obtained an indication that some catalysts are good and others are not, but there will be little understanding of *why* some are good and others are not. The increasing automation of laboratory reactors for catalyst scouting has led to a situation where the examination of each catalyst under many conditions is feasible. It is, of course, essential that the pattern of conditions used be such that the catalyst is not adversely affected by inappropriate conditions before it has been evaluated under its optimum working conditions. For example, the temperature is normally increased rather than decreased during a set of runs. As a check on changes occurring in the catalyst while in the reactor, the final reactor conditions should be the same as certain prior reactor conditions.

#### E. MECHANISMS

Once leads to a good catalyst for a given reaction have been found, it is desirable to obtain some mechanistic information. Such information can be very useful in optimizing the catalyst and can also influence the optimiza-

tion of reactor operating conditions. Even in the case where a catalyst acceptable for a plant is found through a semiempirical scouting procedure and no further optimization appears worthwhile, one can be confident that there will eventually be problems in the plant reactor. The more one already knows about the mechanism, the more likely one is to find a quick solution.

Mechanistic studies can start simply with rate data obtained for various temperatures and reactant mixtures under differential conditions where heat and mass transfer are under control. One might also consider isotopic labeling and kinetic isotope experiments. A reasonably sound picture of certain critical steps may emerge from such a study. The rate-limiting step may become apparent. When one is attempting to increase the activity of a selective but relatively inactive catalyst, it can be very useful to know what is limiting the rate of the reaction. A comprehensive mechanistic understanding of a reaction carried out over a heterogeneous catalyst is only rarely achieved. However, instrumentation advances in recent years make such a goal much less elusive today than 10 yr ago. Substantial understanding of some aspects of the mechanism may be obtained by combining sophisticated reactor studies with thorough catalyst characterization, chemisorption measurements, temperature-programmed desorption (TPD), and surface spectroscopic studies that examine the catalyst surface and reaction intermediates on the catalyst surface.

### III. Surface Sites

Surface sites are clearly of paramount importance in the design and selection of a catalyst. Frequently, the focus is only on this aspect of a catalyst, and this can be shortsighted. However, it is difficult to overemphasize the requirement that a selective catalyst must have just the right type of surface sites and that it cannot have too many of the wrong type.

Acid and base sites on the surface of a catalyst are important for a wide variety of reactions. They may be either on the Brönsted or the Lewis type. Frequently, dissociative chemisorption requires an adjacent pair of acid and base sites. For example, the dissociative adsorption of methanol on an oxide surface to form methoxy and hydroxyl groups can take place at a Brönsted base site (B) next to a Lewis acid (L) site:



There are many different ways to measure the acid or base properties of a surface [1] and not surprisingly these methods tend to give somewhat different results.

Traditionally, types of surface sites are assessed by a variety of chemisorption experiments. This method becomes even more powerful if it is followed by temperature-programmed desorption or decomposition of the chemisorbed species. Additional assessment of the nature of surface sites is obtained if the chemisorbed species are observed directly by a technique such as infrared spectroscopy.

Chemisorption measurements of the actual reactants and products of the reaction under consideration are desirable. This is sometimes, but not always, possible. If the rate-limiting step in the reaction occurs strictly on the catalyst surface, then chemisorption measurements of a reactant may well yield the number of active sites. However, if the rate-limiting step in the reaction is the chemisorption step itself, and this is often the case, meaningful chemisorption measurements of this reactant may not be possible. In such cases, chemisorption measurements of other molecules may be useful in probing surface sites, and this may ultimately yield the number of active sites.

On oxide catalyst surfaces, the most common chemisorption measurements are those directed at an assessment of the acid-base properties of the surface. On metal catalyst surfaces, the most common chemisorption measurements are of CO and hydrogen. In many situations dissociative hydrogen chemisorption and nondissociative CO chemisorption tend to give a reasonable picture of metal dispersion on a support. If this is coupled with another technique such as TPD, the chemisorption data may give a reliable indication of the number of active sites for a given reaction.

#### IV. Bulk Properties

The bulk properties of a catalyst are sometimes neglected because their importance is less clear than that of surface properties. Indeed, there are probably many cases where the bulk properties of a catalyst play no significant role. However, for very fast and very exothermic reactions, the thermal conductivity of the bulk can be important. If the surface is left in a thermally excited state for too long a time, reactions other than those desired may occur.

Oxidation reactions frequently operate through redox mechanisms whereby the catalyst is continually reduced by hydrocarbon molecules at one set of surface sites and continuously reoxidized by molecular oxygen at another set of surface sites. For such a process to function successfully, there must be good communication between the two sites. Electrons must flow from site to site—thus the electronic structure of the bulk is relevant. Also,

oxygen mobility in the bulk as well as at the surface is important in replacing oxygen at the surface site when it becomes depleted through reaction. Thus, in a typical selective oxidation catalyst, one must consider the proper set of surface sites, the electronic properties of the bulk, and the oxygen mobility in the bulk.

## V. Metal-Support Interactions

Frequently catalyst supports are considered inert materials having the simple role of dispersing the catalyst. In fact, supports very often significantly alter catalytic selectivity. There are many different types of interactions between catalysts and their supports. The effect of these interactions on catalysis is not always well understood.

The reducibility of metals depends on the support used. The best documented case is iron. Although iron is readily reduced completely to the metal on silica and carbon supports, hydrogen treatment generally fails to reduce all iron past the divalent state when it is supported on alumina. Thus, if one desires metallic iron for catalysis, an alumina support might best be avoided. On the other hand, if one is interested in catalysis by divalent iron under highly reducing conditions, alumina might be the preferred support. An analogous metal-support interaction has been observed for other metals, for example, rhodium.

Another type of chemical interaction between a metal and its support has been observed for platinum on alumina under high-temperature reduction with hydrogen. Some alumina is taken into solid solution with platinum. At present it is not clear how widespread or important this effect is. Certainly one might expect that an impurity in a support, such as iron in alumina, would become alloyed with the supported metal. Such alloying could have significant effects on catalytic properties.

The size, shape, and distribution of metal particles can also vary considerably depending on the support used. One critical factor is that metals tend to wet some supports and not others. For example, metal particles that tend toward cubic or octahedral morphology might form rafts instead if the metal tended to wet the support. The size of metal particles can depend on the pore structure of the support and also on the mobility of very small metal particles on the support surface. The actual pattern of metal particles on the support surface may also be governed by the surface and pore structure of the support.

Electronic interactions between a metal and its support can be significant, especially if the metal particles are very small. From work function consider-



ations, one expects that for metals supported on oxides there will generally be a net electron flow from the metal to the oxide. Thus, metal particles tend to take on a small positive charge when supported on an oxide such as silica. However, for a reduced metal oxide such as  $\text{TiO}_{2-x}$ , the reverse electron flow occurs, since the work function of the support is less than that of the metal [2]. Although the direction of electron flow has been confirmed by various experiments, the magnitude of the charge on the metals has not been established. Presumably, the magnitude of the metal charge depends on the size of the metal particles as well as on the particular metal and support. Surface electronic states, essentially what most chemists refer to as Lewis acid or base sites, are also expected to transfer electron charge to or from small metal particles. The relative impact of the bulk and surface electronic structure of a support on the electronic state of supported metals needs considerable further investigation.

Spillover is yet another type of metal-support interaction. The most common and best established example of this is hydrogen spillover. Hydrogen is adsorbed and dissociated on metal particles. Then it may spill over onto the support surface where it reacts with other molecules adsorbed there.

It is also possible that a special situation for catalysis exists at the interface between a metal and its support. For example, a molecule might chemisorb on a support close enough to the metal to interact with it directly. This type of metal-support interaction tends to be important only for highly dispersed metals.

The pore structure of the support can also have considerable influence on catalysis by the metal. This can be a dramatic effect when a metal is supported within the pores of a zeolite structure. The pore structure of amorphous supports can also influence catalytic properties [3].

## VI. Other Multiphase Catalysts

Many catalysts other than supported metals are multiphase systems. For example, catalysts for selective oxidation frequently contain 10 or more elements forming several phases, some crystalline and some not [4]. It can be very difficult to understand the roles of the various phases in such catalysts that were generally arrived at by largely empirical methods. A common mistake made is to assume that all ingredients of such catalysts have some direct catalytic function. This is not generally true. Usually, some components are present for reasons of ease of synthesis and promotion of desired microstructure, catalyst strength, and catalyst life.

The most selective catalyst for the oxidation of methanol to formaldehyde is one based on iron, molybdenum, and oxygen. The catalyst used commercially is simply a physical mixture of ferric molybdate and molybdenum trioxide. These phases are highly crystalline. There is no support, and usually there are no promoters. There has been considerable controversy on the question of why both phases apparently need to be present in a commercially viable catalyst. A typical question involves which phase is really the catalyst. We now know that both ferric molybdate and molybdenum trioxide are excellent catalysts for the oxidation of methanol to formaldehyde [5]. In fact, from the point of view of intrinsic catalytic properties, there are practically no differences between the two phases. However, neither phase by itself can be a practical catalyst. Molybdenum trioxide is too volatile under reactor conditions, and it very readily loses surface area. Iron tends to stabilize molybdenum oxide against volatilization and loss of surface area. However, the surface of ferric molybdate gradually loses some molybdenum through volatilization, and then a loss in selectivity occurs. In the presence of excess molybdenum this surface depletion does not occur. Therefore, the mixing of ferric molybdate and molybdenum trioxide results in a catalyst with a lifetime far in excess of that possessed by either component alone.

## VII. Catalyst Microstructure

An understanding of the fundamental processes that govern the evolution of catalyst microstructure during catalyst processing is essential to rational catalyst design. The phrase "catalyst processing" is chosen to include catalyst synthesis as well as catalyst fabrication (Fig. 1). Some of the critical microstructural features of a catalyst are surface area, pore volume, pore size and distribution, particle size and distribution, arrangement of phases, particle morphology, and degree of agglomeration. These features can affect catalyst activity, selectivity, and lifetime. The important message to be conveyed in this section is that the microstructure of the catalyst should be examined at each step along the catalyst processing route. Control over the evolution of this microstructure can then be systematically attempted. The kinetic processes of nucleation and growth of particles during synthesis, particle morphology change, matter transport, and pore coarsening or shrinkage during fabrication are generally not well understood or controlled. A data bank of carefully documented observations of microstructural evolution during catalyst processing and use would be an invaluable asset in improving our understanding of catalytic phenomena.



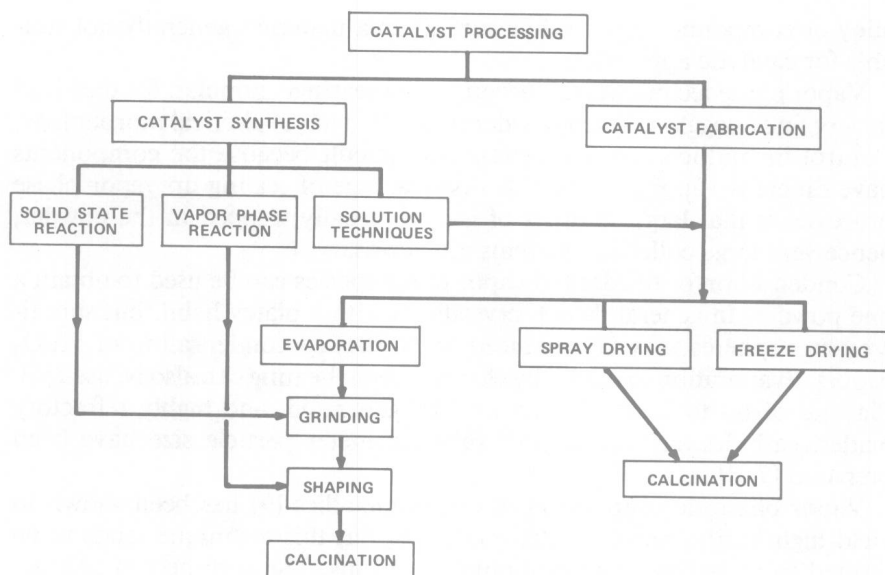


Fig. 1. Steps involved in catalyst processing.

Although catalyst microstructural requirements are dictated by the type of catalytic reaction as well as reactor configuration, it is generally true that catalyst activity increases with surface area. Section VII.A describes some nontraditional techniques for making oxide catalysts with high surface areas. To increase the surface area of the catalytically active phase, some oxides and most metals are supported on porous, refractory supports. A high-surface-area support may, however, be detrimental if undesirable side reactions occur in the pores of the support or on its surface. Techniques must then be sought to obtain a high dispersion of the active phase on a low-surface-area inert support, and this is difficult to achieve in practice. In the final analysis, it is catalyst performance that one is seeking to optimize. Thus, all studies relating to microstructural control must aim at preservation of the microstructural design under catalytic conditions for a reasonable period of time.

### A. SYNTHESIS ROUTES

The range of techniques used for preparing mixed oxide catalysts or supports includes solid state reactions, vapor phase processes, and solution techniques. Traditional solid state approaches of milling metals or oxides together and firing at high temperatures to effect formation of the desired