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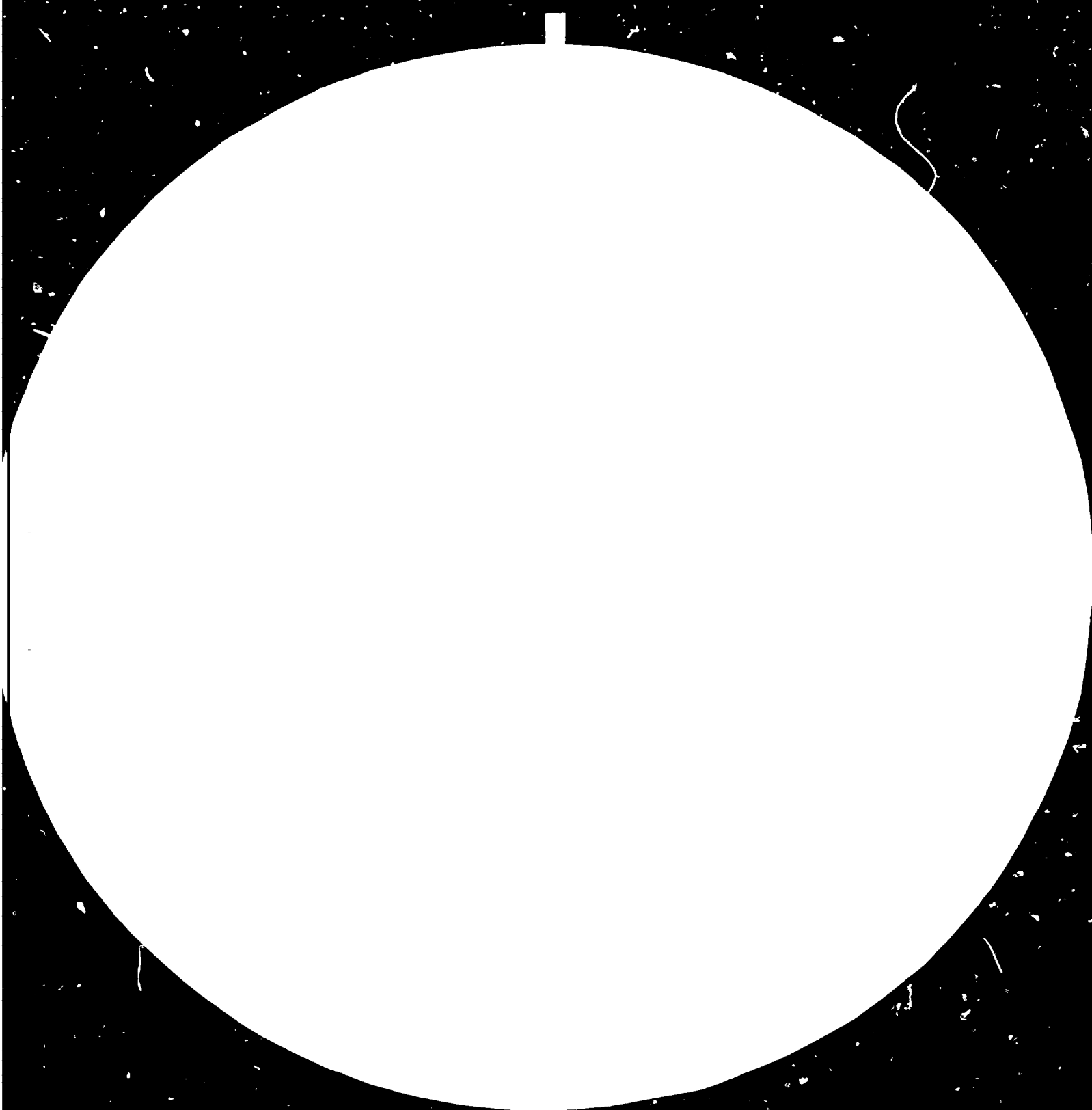
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11339



Distr.  
LIMITED

ID/WG.368/3  
7 April 1982

ENGLISH

**United Nations Industrial Development Organization**

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Petrochemical and Polymer Consultation Week  
Porto Alegre, Brazil, 17 - 21 May 1982

**PROCESSES IN HETEROGENEOUS CATALYSIS\***

by

Sieghard E. Wanke\*\*

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\*\* Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6.

### INTRODUCTION

The objective of this brief overview is to acquaint engineers and scientists, whose specialization is not heterogeneous catalysis, with the main phenomena and techniques encountered in applied and fundamental catalysis. The discussion will be restricted to heterogeneous catalysis, and the emphasis will be on general concepts; detailed discussions of theories and mathematical modelling of reaction kinetics and reactors will not be included. For obvious reasons, no attempt will be made to review the use of catalysts in the various industrial processes, but specific examples of commercial, catalytic processes will be cited for illustrative purposes.

A brief account of the following topics is presented: physical and chemical processes common to most heterogeneously catalyzed reactions, catalyst deactivation, development of catalysts, industrial and laboratory reactors, and catalyst characterization. No extensive reference to the vast scientific and technical literature dealing with heterogeneous catalysis will be made, i.e. this is not a review, but a few pertinent reviews and books will be mentioned. A brief historical synopsis of the use of catalysts in the chemical and petrochemical industries is given at the beginning, and the article concludes with a case study of naphtha reforming catalysts which illustrates various aspects of catalyst development, deactivation and characterization.

BRIEF HISTORICAL PERSPECTIVE OF INDUSTRIAL CATALYSTS

That the presence of certain materials in reaction mixtures affects the rates and the nature of the chemical reactions, without undergoing any apparent chemical changes themselves, has been known for about 150 years (Berzelius and Mitscherlich, ca. 1835). Commercial applications of these catalytic phenomena started about a century ago with the use of supported platinum in the production of oleum from sulfur dioxide, and the production of formaldehyde from methanol over bulk copper or silver catalysts. Since that time a very large number of commercial catalytic processes have come into use. A very brief list of some of these processes is compiled in Table 1.

Table 1. Some milestones in the development of catalytic processes.

Process	Catalysts	Year
oleum from sulfur dioxide	supported platinum	1890
	vanadium oxide	1920s
formaldehyde from methanol	bulk copper or silver	1890
	iron molybdate	1940s
ammonia oxidation for nitric acid	bulk platinum	1906
ammonia from hydrogen and nitrogen	promoted iron oxide	1912
methanol from CO and hydrogen	Zn-Cr oxides	1923
	promoted Cu-Zn oxides	1960s
hydrocarbons from CO and hydrogen (Fischer-Tropsch)	supported cobalt	1920s
	supported iron (SASOL)	1955
ethylene oxide from ethylene	supported silver	1937
catalytic cracking of hydrocarbons	acid clays	1936
	silica-aluminas	1950s
	zeolites	1960s
naphtha reforming	molybdena/alumina	1939
	Pt/alumina	1949
	Pt-Re/alumina	1968
	other bi- and multi-metallic catalysts	1970s
low pressure olefin polymerization	Ziegler-Natta catalysts	1960
	supported chromium oxides	1960
vapor phase production of vinyl acetate	supported and promoted Pd-Au	1968
gasoline from methanol	ZSM5 (a zeolite)	1980s

The entries in Table 1 only represent a minuscule fraction of the industrial processes in past and present use, but they illustrate that catalysts are employed in the production of a wide variety of chemical and petrochemical products. An indication of the evolutionary, and at times revolutionary, development of catalysts is also given in Table 1 (e.g. catalysts for methanol production, catalytic cracking and reforming have undergone dramatic changes since the first commercial catalysts for these processes were developed). Less marked changes in catalyst composition have occurred for other systems (e.g. ammonia synthesis and formaldehyde production), but significant improvements in efficiencies of these processes has also occurred due to catalyst and process modifications. The vapor phase process for vinyl acetate manufacture is included in Table 1, because it is a classic example of the advantages that can be obtained in many industrial processes by the replacement of a homogeneous catalyst by a heterogeneous one.

Many aspects of heterogeneous catalysis, including descriptions of many industrial processes and their development, are discussed in the excellent book by Satterfield (1). This book not only provides a valuable introduction to catalysis for the uninitiated, but also contains much useful information for scientists and engineers actively engaged in catalysis.

#### FUNCTIONS OF CATALYSTS

The objective of the chemical industry is to convert raw materials into consumer products. The conversion of raw materials into finished products usually involves many intermediate steps, and the economic production of many products has only been made possible by the discovery of suitable catalysts. Catalysts play a role in most of the stages of the chemical transformations that are required to convert raw materials to

chemical feedstocks and to final products. At times catalytic processes appear to play a minor, but essential, role in the overall chemical process. For example, most of the ethylene, a very important chemical feedstock, is produced by thermal (non-catalytic) cracking of hydrocarbons, but selective catalytic hydrogenation of the undesired acetylene by-product present in the ethylene is necessary in order to obtain polymer grade ethylene.

The function of a catalyst is to selectively increase the rate of a desired reaction, i.e. two necessary properties of commercial catalysts are activity and selectivity. A catalyst increases the rate of a reaction by providing a pathway, via adsorbed intermediates, which has a lower activation energy than the corresponding non-catalyzed reaction. In many cases non-catalytic reaction for the formation of a desired product are not possible (feasible) because very high temperatures are required to achieve appreciable reaction rates, but thermodynamic equilibrium considerations (for exothermic reactions) can lead to essentially zero conversion at these high temperatures.

A catalyst is a selective catalyst if the intermediates formed on the surface of the catalyst (chemisorbed species) result in the preferential formation of the desired product(s). It is possible, by changing the nature of the catalyst, to obtain completely different products from the same reactants, e.g. alcohols can be selectively converted to olefins or ethers over solid acid catalysts, while aldehydes or ketones can be produced selectively over certain metallic catalysts. Usually specific sites (referred to as active centers or active sites) on the surface of the catalysts are responsible for the catalytic activity. Determination of the nature and concentration of these sites is one of the main goals of catalytic research.

Although the formation of specific adsorbed species is a prerequisite for active and selective catalysts, many other processes (physical and chemical) affect the performance of catalysts. These processes are discussed in the following two sections.



CHEMICAL AND PHYSICAL PROCESSES IN HETEROGENEOUS CATALYSIS

All heterogeneously catalyzed reactions require a chemical interaction of one or more of the reactants with the surface of the catalyst. Reactions may occur solely between adsorbed species (Langmuir-Hinshelwood mechanism) or between adsorbed species and molecules in the adjacent bulk fluid phase (Eley-Rideal mechanism). Reactants have to be transported into the vicinity of an active center before they can be adsorbed; this involves diffusion in small pores since most heterogeneous catalysts are high-surface-area, porous solids with most of the active centers located in the interior of the catalyst particles (pore diameters range from less than 1.0 nm to several hundred nanometers in size, and surface areas range from a few square meters to several hundred square meters per gram). Most reactions and adsorptions also involve significant energy transformations, and heat transfer processes have to be taken into consideration.

The following overall steps are common to most heterogeneously catalyzed reactions:

1. Transfer of reactants from the bulk fluid phase to the external surface of the catalyst particles
2. Transfer of the reactants from the external surface of the catalyst particle into the pores of the catalyst
3. Chemisorption of the reactant(s) on the active sites
4. Surface reaction to form adsorbed product(s)
5. Desorption of product
6. Transfer of product from inside the pores to the external surface of the catalyst pellet
7. Transfer of product from the external surface of catalyst particle to the bulk fluid phase
8. Heat transfer to or from the active sites to the external surface of the catalyst particle
9. Heat transfer from the external surface of the catalyst particle to the bulk fluid phase.

The chemical, mass transfer and heat transfer steps will be discussed

separately. The qualitative influences of mass and energy transfer effect on activity and selectivity will be stressed.

### Chemical Processes

Only three of the above nine steps (Steps 3, 4, and 5) involve chemical changes; the remaining steps are physical processes. The adsorption during catalytic action requires chemical (electronic) interactions between the catalyst and the reactants, and hence is usually referred to as chemisorption or selective adsorption. Physical adsorption, i.e. adsorption due to dispersive forces, is similar to condensation and does not directly participate in the catalytic process. Although all chemisorptions result in the formation and/or breakage of chemical bonds, the nature of the bond formation varies greatly among adsorbate-adsorbent systems. Chemisorption may be dissociative, e.g. the adsorption of hydrogen on many metal catalysts results in the dissociation of gas phase hydrogen molecules, and the adsorbed phase consists of adsorbed hydrogen atoms. Chemisorption of carbon monoxide, on the other hand, is non-dissociative on most of the same metal catalysts, i.e. the carbon-oxygen bond is not broken during the adsorption process. For more complex molecules, such as hydrocarbons, dissociation into many dissimilar fragments may occur during adsorption. The nature of the bonds formed during chemisorption can vary from covalent to ionic.

It is beyond the scope of this brief overview to present a detailed discussion of the adsorption-surface reaction processes, and only a few comments on adsorption and surface reaction will be made. The equilibrium amount of a substance chemisorbed at constant temperature is often well described by a Langmuir adsorption isotherm, e.g. the surface coverage for non-dissociative adsorption of A is given by:

$$\theta_A = U_A/L = \frac{b_A P_A}{1 + b_A P_A} \quad (1)$$

where  $\theta_A$  = fraction of active sites covered by A

$U_A$  = amount of A adsorbed per mass of catalyst

$L$  = concentration of active sites

$b_A$  = adsorption equilibrium constant =  $b_A^0 e^{Q/RT}$

( $Q$  = heat of adsorption)

$P_A$  = partial pressure of A

Extension of Langmuir isotherms to dissociative and competitive adsorption can readily be made. The readers are referred to Thomas and Thomas (2) for a discussion of adsorption isotherms and an excellent presentation of the energetics of adsorption.

The rate of surface reactions is usually assumed to obey the law of mass action, e.g. for the surface reaction



the rate of formation of  $C^*$  is given by

$$r_{C^*} = k_1 \theta_A^a \theta_B^b - k_2 \theta_C^c \quad (3)$$

where  $A^*$ ,  $B^*$  and  $C^*$  represent adsorbed species.

The rate function given by Eq. 3 is not very useful, since surface coverages, i.e. the  $\theta_i$ 's, are not readily measured. If it is assumed that the adsorption of all the components is at equilibrium (i.e. the surface reaction is the rate controlling step), then the surface coverages can be expressed in terms of the partial pressures (which are readily measured) by the use of adsorption isotherms such as Eq. 1. This substitution leads to rate function of the form

$$r = \frac{k \prod_i P_i^{a_i}}{(1 + \sum_i b_i P_i)^c} \quad (4)$$

Equations having a form similar to Eq. 4 are also obtained if steps other than the surface reaction are rate determining. The formulation of rate functions for heterogeneously catalyzed reactions with different rate

controlling steps is discussed in many text books (e.g. 1-3).

It should be pointed out that the general rate behavior of heterogeneously catalyzed reactions can be significantly different than that of homogeneous reactions. Although the rate of heterogeneously catalyzed reactions usually increases with increasing temperature, numerous cases of decreasing reaction rates with increasing temperature are known. This occurs because higher temperatures results in lower surface coverages of adsorbed species, and this decrease in concentrations of adsorbed species can, at times, more than compensate for the increases in surface reaction rate constant. For some reactions decreases in reaction rate with increasing concentrations of reactants have been observed. These abnormal kinetics are due to strong adsorption of one or more of the reactants (3).

In the above treatment it has been assumed that the reaction occurs between adsorbed species. In many partial oxidation reactions, e.g. methanol to formaldehyde over iron molybdate catalysts, reaction between adsorbed hydrocarbons and lattice oxygen of the catalyst occurs. The oxygen removed from the catalyst is replaced by oxygen from the gas phase. This example shows that the mechanism of heterogeneously catalyzed reactions can vary greatly from the usual adsorption-surface reaction processes, and extensive experimental work is usually required to obtain reliable expressions for the rates of the chemical steps in heterogeneously catalyzed reactions. The rates of the chemical steps are often referred to as 'intrinsic rates', i.e. rates in the absence of mass and energy transfer effects.

#### Mass Transfer Steps

The mass transfer steps (Steps 1, 2, 6 and 7; p. 5) can be divided into external mass transfer (Steps 1 and 7) and internal mass transfer (Steps 2 and 6). The external steps involve the transport of reactants and products between the bulk fluid phase and the external surface of the catalyst particles. The external flux is usually modelled by the following equation:

$$F_A = k_m (C_{A,b} - C_{A,so}) \quad (5)$$

where  $F_A$  = flux of A from bulk phase to external surface of catalyst particles

$k_m$  = mass transfer coefficient

$C_{A,b}$  = concentration of A in the bulk fluid phase in the vicinity of the catalyst particle

$C_{A,so}$  = concentration of A at the external surface of the catalyst particle

The mass transfer coefficient,  $k_m$ , depends on the nature of the flow in the reactor, and values of  $k_m$  can be estimated from correlations (1). External mass transfer limitations can usually be eliminated by increasing the velocity in the reactor.

Internal mass transfer involves diffusion in small pores. Molecular diffusion takes place if the mean free path of the diffusing molecules is much less than the pore diameter; Knudsen diffusion occurs if the mean free path is of the order of the pore diameter or larger. These diffusion processes are not affected by variations in the flow of the bulk fluid phase. The reactant molecules adsorb and react as they diffuse in the pores. Large concentration gradients can exist in pores if the reaction rate is large. The Thiele parameter, which is proportional to the square root of the ratio of the chemical reaction rate to the diffusion rate, is a qualitative measure of the influence of internal mass transfer. Numerical values of the Thiele parameter can be calculated from the physical properties of the catalyst (pore and particle sizes), the intrinsic rate function and the effective diffusivity.

The effect of internal mass transfer on the reaction rate is usually expressed in terms of the effectiveness factor,  $\eta$ , which is defined as:

$$\eta = \frac{\text{rate of reaction in the presence of internal mass transfer}}{\text{rate of reaction in the absence of internal mass transfer}} \quad (6)$$

The value of  $\eta$  can be computed from the value of the Thiele modulus. Detailed mathematical treatments of internal and external mass transfer are presented by Carberry (3) and Petersen (4). In these analyses it is shown that mass transfer effects can influence the functional form of the rate expression, as well as alter the activation energy of a reaction. Rates in the presence of transport effects are often referred to a 'global' or 'effective' rates.

Decreases in reaction rates by several orders of magnitude can result from internal concentration gradients. This, usually undesirable effect, can be reduced or eliminated by decreasing the diffusion length in the catalyst particles. This can be accomplished by decreasing the catalyst particle size or by concentrating the active centers close to external surface of the catalyst particles. Increasing the pore size would also decrease the diffusion resistance, but larger pore sizes result in lower surface areas which again produces lower catalytic activity.

Mass transfer limitations can not only lower the activity of a catalyst, but can also influence the selectivity. Internal mass transfer effects always cause reduced selectivity for consecutive reactions in which the intermediate product is the desired one. Mass transfer can also affect the selectivity for parallel reactions. These effects were first analyzed in the classic article by Wheeler (5).

#### Heat Transfer Steps

Adsorption and chemical reaction processes are strongly temperature dependent. In heterogeneously catalyzed reaction the heats of adsorption and surface reaction are released at the active centers inside the catalyst pellets. The thermal energy has to be transferred from the active sites to the fluid phase. Heat transfer through porous solids and convective heat transfer are involved. The convective heat transfer between the external surface of the catalyst particles and the fluid phase is commonly modelled by Newton's Law of Cooling, i.e.

$$q = h (T_{so} - T_b) \quad (7)$$

where  $q$  = heat flux from catalyst particle to fluid phase

$h$  = heat transfer coefficient

$T_{so}$  = temperature of external surface of catalyst particle

$T_b$  = temperature of bulk fluid in the vicinity of the catalyst particle

The heat transfer coefficients, analogous to the mass transfer coefficient in Eq. 5, can be altered by changing the velocity of the fluid in the reactor. External heat transfer effects, i.e. differences between  $T_{so}$  and  $T_b$ , may, however, be significant even at high superficial velocities for very exothermic or endothermic reactions.

Internal heat transfer is usually described by a conduction equation where all internal modes of heat transfer in the porous solid are lumped into an effective thermal conductivity (1). Large temperature gradients can exist inside catalyst pellets, since many catalysts are thermal insulators. High catalyst pellet temperatures, which can be the result of external and/or internal temperature gradients, can often cause rapid catalyst deactivation.

#### CATALYST DEACTIVATION

The activity and/or selectivity of heterogeneous catalysts decreases with increasing length of use. The life-times of catalysts can vary from a few seconds (e.g. cracking catalysts) to several years (e.g. ammonia synthesis catalyst). The life-time of a catalyst is the length of time for which a catalyst, without regeneration, can be used economically to produce the desired product. Deactivated catalysts may still be quite active and selective, but they no longer meet the process specifications.

Deactivation has two general causes; one, phenomena which make active sites inaccessible to reactants, and two, phenomena which decrease the number or alter the nature of the active sites. The first class will be

referred to as 'poisoning' and the second as 'structural or compositional changes'. Poisoning is usually reversible, i.e. poisoned catalyst can often be regenerated, while structural and compositional changes are often irreversible, i.e. catalysts having undergone structural or compositional changes often cannot be regenerated and have to be replaced.

### Poisoning

Poisoning, according to the definition above, encompasses a large number of deactivation processes. The most direct method of poisoning is due to adsorption of impurities from the feed on the active sites. The seriousness of this type of poisoning depends on the strength with which the poison adsorbs on the active sites (i.e. the heat of adsorption of the poison). The stronger the adsorption of the poison, the more serious the problem. Purification of the feed is the usual method of avoiding deactivation by impurity poisoning. Accidental exposure to impurities which poison the catalyst is often reversible, i.e. the catalyst slowly regains its activity when the poison is removed from the feed. Chemical removal of the poison from the catalyst surface may be necessary if the poison adsorbs very strongly. Sulfur, nitrogen and heavy metal containing compounds are common poisons in petrochemical feedstocks, and large purification processes, often catalytic, are needed to reduce the contaminants to acceptable levels.

One of the most common types of deactivation is coking, i.e. carbonaceous materials (called coke) formed during the reactions are deposited on the surface of the catalyst and render the active sites inaccessible. The coke may be a necessary by-product of the catalytic reactions (e.g. in catalytic cracking) or it may be an undesirable by-product (e.g. in reforming). Coked catalysts are regenerated by burning off the coke. The conditions, especially the temperature, have to be controlled carefully during the burn-off, since excessive temperatures can result in permanent deactivation due to structural changes.



### Structural and Compositional Changes

Most catalysts consist of high-surface-area, porous solids, and often contain various catalytically active components and promoters which are dispersed over the surface of the high surface area solid. The resultant structure of the catalyst is almost always thermodynamically unstable. Fortunately, the activation energies for transformation to stabler structures are usually large, and hence the transformations are slow. High temperatures, however, can result in rapid, irreversible structural changes. Some of the structural changes that can result in catalyst deactivation are:

1. Pore collapse: Pore collapse leads to irreversible decreases in total surface area. The presence of impurities, in the catalyst or in the fluid phase, can accelerate pore collapse.
2. Phase transformations: The crystallographic phase of many catalysts is meta-stable (e.g. the transition aluminas), and transformations to stabler phases cause decreases in surface area and destruction of active sites.
3. Segregation of active components: Many catalysts (e.g. mixed oxides, multi-metallic catalysts and promoted catalysts) require intimate contact of the various components in order to be catalytically active. Prolonged use at elevated temperatures or in certain atmospheres can cause segregation of the components which results in the loss of active sites.
4. Agglomeration of dispersed phase: Active sites are lost when the area of the dispersed phase is decreased (e.g. sintering of supported metal catalysts).

Changes in composition of catalysts, which occur with use, can also result in catalyst deactivation. Some processes which cause compositional changes are:

1. Volatilization of active components: Promoters frequently have significant vapor pressures and are lost from the catalyst during use. Deactivation by this process is usually avoided by continuous or intermittent addition of the promoter or promoter precursor to the feed. In other cases, slow sublimation of the catalyst itself (e.g. sublimation of molybdenum oxides from iron molybdate) can result in irreversible deactivation.
2. Changes in oxidation state of catalytically active components: Slow reactions of a catalyst with the reactants or products can result in chemical changes of the catalyst (e.g. reduction of copper chromite in hydrogen atmospheres). Regeneration of catalysts, deactivated in this fashion, is often possible.

3. Formation of volatile compounds: Reactions between the catalyst and compounds in the fluid phase can lead to the formation of volatile materials (e.g. metal carbonyls and certain metal oxides).

Besides the above structural and compositional changes, physical deterioration of the catalyst pellets (formation of fines) can also occur. Although the crumbling of catalyst pellets does not cause a loss of catalytic activity per se, plugging of the reactor by catalyst fines may occur, and reactor shut-down and catalyst replacement may be necessary.

#### DEVELOPMENT OF CATALYSTS

A dramatic increase in research and development of catalysts and catalytic processes has occurred during the past decade. This has been brought about by the decreasing availability of cheap energy and raw materials (i.e. crude oil and natural gas), and by the increased concern with environmental pollution. Catalysis can, and in many cases already has, play a vital role in alleviating problems in these areas. For example, catalytic converters for automobiles have significantly reduced emissions from automobiles, and the Claus process has long been used to decrease sulfur emissions from sour gas plants and oil refineries. Better utilization of raw materials has been achieved through the development of highly selective catalysts, i.e. less of the, now very valuable, raw materials ends up as undesirable by-products. Catalysts also play a key role in the production of liquid fuels and substitute natural gas from coal. The feasibility of converting coal to liquid fuels (Fischer-Tropsch process) was established over 50 years ago, and commercial production by this process is currently occurring in South Africa. However, economic production of liquid fuels and substitute natural gas from coal awaits the development of new, active and poison resistant catalysts.

How are new and improved catalysts discovered? Historically, the discovery and subsequent optimization of a commercial catalyst was a trial-and-error procedure, for example, several thousand catalyst formulations

were tested at the beginning of this century before a commercially acceptable catalyst for the synthesis of ammonia was obtained. Catalyst development at the present still requires extensive, often trial-and-error, experimental efforts, but much empirical and theoretical knowledge, which provides valuable guidelines to the researcher, has been accumulated during the past decades. It is not the objective, nor within the scope, of this paper to discuss the various theories and correlations of catalytic activity and selectivity which are useful in catalyst development. For an extensive discussion of this subject the reader is referred to the recent book on 'Design of Industrial Catalysts' by Trimm (6).

### CATALYTIC REACTORS

#### Industrial Reactors

There are essentially three general types of industrial reactors for solid catalysts; these are fixed bed reactors, fluidized bed reactors, and slurry reactors. There are many sub-classes within each general category, e.g. fixed bed reactors may be adiabatic fixed bed reactors, multi-tubular fixed bed reactors or trickle bed reactors. Variations in reactor geometry, flow patterns, heat exchange facilities and other auxiliary equipment are too numerous to mention; each reactor is tailored to the specific application.

The choice of reactor type for a specific application is influenced by many factors. An adiabatic fixed bed reactor may be suitable if temperature control is not crucial, but for highly exothermic reaction a more expensive multi-tubular fixed bed reactor may be necessary in order to achieve the required temperature control. Excellent temperature control is also obtained in a fluidized bed reactor, but the design of fluidized bed reactors (i.e. scale-up) is still unreliable. Fluidized bed reactors are often used if rapid catalyst deactivation occurs, since continuous removal of catalyst is possible by operating the reactor in the entrainment region. The deactivated catalyst is continuously removed from the reactor and

is regenerated externally before reintroduction into the reactor. Slurry reactors, in which the catalyst is suspended in the liquid phase of the reactants, also allows continuous removal of the catalyst. However, large-scale slurry reactors are less common than fixed bed or fluidized bed reactors.

### Laboratory Reactors

Kinetic studies in heterogeneous catalysis have various objectives; the common objectives in applied catalysis research include:

1. Catalyst screening
2. Determination of intrinsic rate functions
3. Determination of global (effective) rate behavior
4. Determination of catalyst life

Different types of laboratory reactors are used to achieve these objectives.

Catalyst screening studies, i.e. the initial investigations into the possible acceptability, are usually carried out in micro-reactors. A micro-reactor is a small tubular reactor containing small amounts of catalyst powder (fractions of a gram to a few grams). The activity and selectivity are determined under well defined conditions. Micro-reactors can be operated in the continuous or pulse mode. In the pulse mode, a pulse of reactant is injected into a carrier gas stream, and the composition of the product pulse is measured. These reactors are suitable for routine comparisons of performance of different catalysts. Reliable kinetic data can usually not be obtained with these catalyst screening reactors.

Gradientless reactors are best suited for the determination of intrinsic kinetics. A gradientless reactor is the heterogeneous reactor equivalent to the homogeneous continuous stirred tank reactor. The composition and temperature in the fluid phase is kept constant by either circulation of the catalyst phase (Carberry reactor) or by rapid circulation of the fluid phase (by external recycle, or by internal recycle as in the Bertie reactor). External transport effects can be eliminated by these modes of operation,

internal transport effects can, at times, be eliminated by decreasing the catalyst pellet size. Reliable intrinsic rate data can be obtained with these reactors, since large conversions at constant concentrations and temperature are measured. No differentiation of rate data or integral testing of rate functions, as is required for rate data obtained in tubular reactors, is necessary, since numerical values of the rates of reaction as a function of concentrations and temperature are obtained directly.

Determination of global rates, i.e. behavior in the presence of mass and energy transfer effects, for slowly deactivating catalysts, is usually done in tubular reactors having a diameter of a few centimeters. The catalyst is used in pellet form similar to that envisaged for the industrial reactor. The influences of operating conditions and physical properties of the catalyst on activity and selectivity can be obtained in this type of reactor. These fixed bed reactors are also useful for catalyst life studies for slowly deactivating catalysts. Different reactors, such as transported solid reactors, have to be used for more rapidly deactivating catalysts. The suitability of various laboratory reactors for investigating heterogeneous catalysts are compared in a review article by Weekman (7).

#### CATALYST CHARACTERIZATION

Extensive testing of catalysts in laboratory and pilot-scale reactors is expensive and time consuming, and much information useful in the development of catalysts and for the design of catalytic reactors can be obtained by instrumental characterization of catalysts. The objectives of catalyst characterization in applied catalytic research includes determination of the following:

1. mechanical, thermal and physical properties (physical strength, abrasion resistance, effective thermal conductivity, effective diffusivity, total surface area, pore size distribution, crystallinity, etc.)
2. chemical properties (overall composition, surface composition, variations in composition within catalyst pellets and from pellet to pellet, etc.)

3. nature of active sites (surface sites responsible for catalytic activity and selectivity, the concentration of these sites, the distribution of these sites within catalyst pellets, etc.)
4. processes responsible for catalyst deactivation (nature of poisons, types of physical and chemical processes which result in catalyst deactivation, influence of temperature on the rate of deactivation processes, etc.)

A large number of methods have been developed for the characterization of heterogeneous catalysts; a list of some of the techniques used is presented in Table 2. Some of the techniques have been specifically developed for catalyst characterization, while others have found applications in heterogeneous catalysis after extensive use in other areas. The characterization of a given catalyst usually requires the application of a number of techniques, and even with the large arsenal of techniques available today, complete determination of the desired properties is often not possible. Detailed descriptions of many of the experimental methods used in catalyst characterization and research have been reviewed in several recent books (8-11).

In most of the techniques used for catalyst characterization, the catalyst is examined under conditions which are far removed from those existing in industrial reactors. This is a serious limitation of the catalyst characterization methods, since the properties of the catalyst and the nature of the adsorbed species can be significantly affected by the environment. For example, surface compositions determined under high vacuum conditions, which are commonly employed during catalyst characterization, may change drastically in the presence of reacting atmospheres, or the nature of adsorbed species detected at low pressures and temperatures and in clean atmospheres may not reflect the adsorbed species present at reaction conditions (high pressures, high temperatures, and complex and impure atmospheres). Catalytic researchers are well aware of these limitations, and considerable efforts have been, and are being, expended to develop in situ characterization methods, i.e. determination of catalyst properties at conditions which approximate those found in reactors.

Table 2. Techniques for the characterization of commercial catalysts.

Technique	Properties Measured
Crush and abrasion tests	mechanical strength and abrasion resistance
Sieve analyses	catalyst particle (pellet) size distribution
Diffusivity measurements	effective diffusivity in catalyst pellets
Thermal conductivity	effective thermal conductivity of catalyst pellets
Mercury porosimetry	pores size distributions (for pores with diameters larger than about 5 nm)
Physical adsorption (BET)	total surface area and pore size distribution (for pores with diameters of 1 to 50 nm)
Chemisorption	nature and concentration of active sites, isosteric heats of adsorption
Temperature programmed desorption (TPD)	nature and concentration of adsorbed species, heats of adsorption
Calorimetry (many kinds)	heats of adsorption, phase changes
X-ray diffraction (XRD)	
- wide angle	crystal structure, average crystallite size, crystallite size distribution
- small angle	average particle size and particle size distribution
X-ray fluorescence (XRF)	overall elemental composition
Atomic absorption (AAS)	overall elemental composition
Electron microprobe	elemental analysis (resolution about 1000 nm)
Auger electron spectroscopy (AES)	overall surface composition (very useful for detecting poisons)
Electron spectroscopy for chemical analysis (ESCA)	surface composition, oxidation states (nature of active sites and adsorbed species)
Scanning electron microscopy (SEM)	surface morphology, elemental composition (resolution about 50 nm)
Transmission electron microscopy (TEM)	particle size distributions (very useful for supported metal catalysts)
Scanning-transmission electron microscopy (STEM)	particle size distribution, elemental analysis (resolution about 1 nm)
Infrared and Raman spectroscopy	nature and concentration of active sites and adsorbed species
Mössbauer spectroscopy	interactions at the atomic level
Electron spin resonance	detection of paramagnetic species
Nuclear magnetic resonance	relaxation processes of surface species
Extended x-ray absorption fine structure (EXAFS)	atomic structure (number of nearest neighbours and interatomic spacings)

CASE STUDY: NAPHTHA REFORMING

History

Kerosene was the main desired product in the early days of oil refining, and gasoline was a by-product. This, however, changed with the advent of the automobile, and by the 1920's, the amount of straight-run gasoline was insufficient to meet the gasoline demand. Thermal reforming processes were commercialized in the early 1930's to convert naphthas into gasoline. Increases in octane numbers were achieved in thermal reforming by cracking and olefin formation; thermal reforming produced very little of the high octane aromatics and the overall yield of the process was low.

In 1939 a catalytic reforming process, Fixed-Bed Hydroforming, was commercialized. A 9 wt%  $\text{MoO}_3$ /alumina catalyst was used to convert low octane naphthas into high octane reformates. The increase in octane numbers were largely achieved by converting naphthenes into aromatics. The catalyst deactivated rapidly, and had to be regenerated every 4 to 8 hours. This process was, nevertheless, used widely during World War II to produce high octane fuels and aromatics, specifically toluene for the production of explosives. After World War II a temporary decline in the demand for high octane fuels and aromatics occurred, and many Hydroforming units were shut-down, but some remained in operation into the 1960's.

The demise of the Hydroforming process was not only due to the temporary decrease in the demand for the products produced by Hydroforming, but also to the development of a new process, Platforming, which was developed by UOP and commercialized in 1949. The first commercial Platforming unit was a revamped thermal reforming unit. The Platforming process uses a chlorine promoted Pt/alumina catalyst. Many reactions of the complex reaction mixture are catalyzed by this bi-functional catalyst, but the two general classes of reactions which are desired are the dehydrogenation of naphthenes to aromatics (catalyzed by Pt) and the isomerization of normal paraffins (catalyzed by



alumina). Hydrocracking of paraffins (hydrogenolysis) are undesirable side reactions and can be controlled by adjusting the acidic properties of the alumina.

The Pt/alumina reforming catalyst underwent various modifications and improvements in the 1950's and 1960's, but a major change in reforming catalysts did not occur until 1968. In 1968 Standard Oil of California introduced Rheniforming, a process based on a Pt-Re/alumina catalyst. This bi-metallic catalyst could be used at significantly lower hydrogen pressures than the mono-metallic Pt catalyst without increasing deactivation rates due to coking. Low hydrogen pressures are very desirable because increased yields of aromatics can be achieved. Numerous bi- and multi-metallic catalysts have been developed since 1968, and the search for better and more efficient reforming catalysts will continue because the demand for high octane fuels and aromatics will continue to increase.

#### Deactivation and Regeneration of Naphtha Reforming Catalysts

Common causes for the deactivation of reforming catalysts are coking, loss of chlorine, loss of metal surface area and poisoning. Sulfur and sulfur containing compounds poison the dehydrogenation activity (i.e. sulfur occupies active sites on the Pt surface), but only slightly affect the isomerization function. Sulfur poisoning is avoided by feedstock purification, but accidental exposure to sulfur containing feeds is essentially reversible. As a matter of fact, small amounts of sulfur, at the ppm or lower levels, have a beneficial effect since they suppress hydrocracking. Other reversible poisons include nitrogen and oxygen containing compounds; heavy metals, such as arsenic, vanadium, molybdenum and lead, are irreversible poisons. All these poisons are usually removed by an up-stream hydrotreating unit (cobalt-molybdenum catalyst).

The isomerization activity of the catalyst is due to the acid sites on the alumina. The acidity of the alumina is controlled by varying the

chlorine content of the catalyst. With use, chlorine is lost from the catalyst and this alters the isomerization activity. This deactivation problem is overcome by adding chlorine containing compounds to the feed, either intermittently or continuously. The water content of the feed has a significant effect on the rate of chlorine loss.

Coke formation on current reforming catalysts is very slow, but deactivation due to coke deposition still occurs, especially under severe reforming conditions, e.g. low hydrogen pressures. Deactivation also occurs due to decreases in metal surface areas, i.e. sintering. In fresh reforming catalysts, the metal is present as very small metal clusters (less than 1 or 2 nm in size). With use these metal clusters grow, and this results in lower metal surface areas and the concomitant decrease in dehydrogenation activity. Coked and sintered reforming catalysts can be regenerated.

The regeneration procedure for coked and sintered catalysts usually includes the following steps:

1. Removal of hydrogen and hydrocarbons from reactor - This is accomplished by reducing the reactor temperature to about 200°C and flushing the reactor(s) with nitrogen.
2. Coke combustion - After the flushing with nitrogen, the reactor temperature is increased and oxygen is introduced into the nitrogen. The temperature and oxygen content are slowly increased from 380 to about 500°C and from 0.5 to 2%, respectively. The temperature and oxygen content are closely monitored to avoid run-aways. This procedure eliminates coke from the catalyst, and also causes some redispersion of the metal.
3. Redispersion of the metal - This is usually accomplished by treatment at 500 to 550°C in a nitrogen stream containing oxygen (about 10%) and chlorine. The chlorine concentration is adjusted so that the desired chlorine content on the alumina is achieved.
4. Reduction of the catalyst - After all oxygen has been flushed from the reactor, the catalyst is reduced with pure hydrogen. Prior to starting the feed, the catalyst may also be sulfided for the suppression of hydrocracking activity.

Many regenerations may be carried out on the same catalyst charge, and many reforming catalysts have been used for years. Sooner or later, however, all catalysts are irreversibly deactivated and catalyst replacement is necessary.

### Characterization of Reforming Catalysts

Most of the techniques listed in Table 2 have been used to measure various properties of reforming catalysts. However, the most commonly used technique is chemisorption. Chemisorption of hydrogen or carbon monoxide is frequently used for the determination of metal surface areas. Oxygen-hydrogen titrations can also be used for this purpose. Information about metal surface areas can also be obtained by techniques which determine average crystallite sizes or crystallite size distributions (e.g. TEM, XRD line broadening and small angle XRD). These techniques, however, are of limited applicability for fresh reforming catalysts since the average crystallite sizes in these catalysts are below the values which can be measured reliably by TEM or XRD. These characterization methods (TEM and XRD) are very useful for investigating the processes occurring during sintering and redispersion. STEM, with its excellent spatial resolution for compositional analysis, is a valuable tool for investigating microscopic compositions of bi- and multi-metallic clusters.

Many of the spectroscopic methods (e.g. IR, ESCA, AES, EXAFS, etc.) have been used in the characterization of supported metal catalysts. These techniques have provided valuable insight into the nature of active sites, the states of adsorbed species, the nature of poisons, metal-support interactions, and the structure of the metals in reforming catalysts. Thermogravimetric methods are very suitable for studying the rates of coke deposition and coke removal during regeneration.

The activity, selectivity and stability of reforming catalysts has been improved dramatically during the past decades, but even with current catalysts about 10% of the feed is converted to undesirable, low-molecular-weight hydrocarbons. Hence, efforts will continue to develop more selective reforming catalysts. Characterization studies will play an important role in this development by elucidating some of the only partially understood

aspects of reforming catalysis, e.g. the mechanistic role of the additional components in bi- and multi-metallic catalysts, the mechanisms of sintering and redispersion, the nature of metal-support interactions, and the mechanisms of coke formation.

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