# Introduction

# I.I Importance of Catalysis

A large fraction of chemical, refinery, and pollution-control processes involve catalysis. Its importance can be demonstrated by referring to the catalyst market. In 1993 the worldwide catalyst usage was \$8.7 billion, comprising \$3.1 billion for chemicals, \$3 billion for environmental applications, \$1.8 billion for petroleum refining, and \$0.8 billion for industrial biocatalysts (Schilling, 1994; Thayer, 1994). The total market for chemical catalysts is expected to grow by approximately 20% between 1997 and 2003, primarily through growths in environmental and polymer applications (McCoy, 1999). For the U.S., the total catalyst demand was \$2.4 billion in 1995 and is expected to rise to \$2.9 billion by the year 2000 (Shelley, 1997). While these figures are impressive, the economic importance of catalysis is even greater when considered in terms of the volume and value of goods produced through catalytic processes. Catalysis is critical in the production of 30 of the top 50 commodity chemicals produced in the U.S., and many of the remaining ones are produced from chemical feedstocks based on catalytic processes. In broader terms, nearly 90% of all U.S. chemical manufacturing processes involve catalysis (Schilling, 1994). Although difficult to estimate, approximately \$200-\$1000 (Hegedus and Pereira, 1990; Cusumano, 1991) worth of products are manufactured for every \$1 worth of catalyst consumed. The value of U.S. goods produced using catalytic processes is estimated to be between 17% and 30% of the U.S. gross national product (Schilling, 1994). In addition, there is the societal benefit of environmental protection, since emission control catalysts are a significant sector of the market (McCoy, 1999).

# I.2 Nonuniform Catalyst Distributions

The active materials used as catalysts are often expensive metals, and in order to be utilized effectively, they are dispersed on large-surface-area supports. This approach in many cases introduces intrapellet catalyst concentration gradients during the preparation process, which were initially thought to be detrimental

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to catalyst performance. The effects of deliberate nonuniform distribution of the catalytic material within the support started receiving attention in the 1960s.

Early publications which demonstrated the superiority of nonuniform catalysts include those of Mars and Gorgels (1964), Michalko (1966a,b), and Kasaoka and Sakata (1968). Mars and Gorgels (1964) showed that catalyst pellets with an inert core can offer superior selectivity during selective hydrogenation of acetylene in the presence of a large excess of ethylene. Michalko (1966a,b) used subsurfaceimpregnated Pt/Al<sub>2</sub>O<sub>3</sub> catalyst pellets for automotive exhaust gas treatment and found that they exhibited better long-term stability than surface-impregnated pellets. Kasaoka and Sakata (1968) derived analytical expressions for the effectiveness factor for an isothermal, first-order reaction with various catalyst activity distributions and showed that those declining towards the slab center gave higher effectiveness factors. A number of publications have dealt with analytical calculations of the effectiveness factor for a variety of catalyst activity distributions. These include papers by Kehoe (1974), Nyström (1978), Ernst and Daugherty (1978), Gottifredi et al. (1981), Lee (1981), Do and Bailey (1982), Do (1984), and Papa and Shah (1992). Some researchers have focused on the issue of shape and activity distribution normalization, where the objective is to provide generalized expressions for the catalytic effectiveness (Wang and Varma, 1978; Yortsos and Tsotsis, 1981, 1982a,b; Morbidelli and Varma, 1983).

Pellets with larger catalyst activity in the interior than on the surface can result in higher effectiveness factors in the case of reactions which behave as negativeorder at large reactant concentrations, such as those with bimolecular Langmuir-Hinshelwood kinetics (Villadsen 1976; Becker and Wei, 1977a). Nonuniform catalyst distributions can also improve catalyst performance for reactions following complex kinetics (Juang and Weng, 1983; Johnson and Verykios, 1983, 1984). For example, in multiple-reaction systems, catalyst activity distribution affects selectivity. Shadman-Yazdi and Petersen (1972) and Corbett and Luss (1974) studied an irreversible isothermal first-order consecutive reaction system for a variety of activity profiles. Selectivity to the intermediate species was favored by distributions concentrated towards the external surface of the pellet. Juang and Weng (1983) studied parallel and consecutive reaction systems under nonisothermal conditions. Which catalyst profile amongst those considered gave the best selectivity depended on the characteristics of the particular reaction system. Johnson and Verykios (1983, 1984) and Hanika and Ehlova (1989) studied parallel reaction networks and showed that nonuniform activity distributions can enhance selectivity. Similar improvements were also demonstrated by Cukierman et al. (1983) for the van de Vusse reaction network. Ardiles et al. (1985) considered a bifunctional reacting network representative of hydrocarbon reforming, and showed that selectivity to intermediate products was influenced by the distribution of the two catalytic functions.

The effects of nonuniform activity in catalyst pellets have also been studied in the context of fixed-bed reactors. Minhas and Carberry (1969) studied numerically the advantages of partially impregnated catalysts for  $SO_2$  oxidation in an adiabatic fixed-bed reactor. Smith and Carberry (1975) investigated the production of phthalic anhydride from naphthalene in a nonisothermal nonadiabatic

# I.2 Nonuniform Catalyst Distributions

fixed-bed reactor. This is a parallel–consecutive reaction system for which the intermediate product yield is benefited by a pellet with an inert core. Verykios et al. (1983) modeled ethylene epoxidation in a nonisothermal nonadiabatic fixed-bed reactor with nonuniform catalysts. They showed that improved reactor stability against runaway could be obtained, along with higher reactor selectivity and yield, as compared to uniform catalysts.

Rutkin and Petersen (1979) and Ardiles (1986) studied the effect of activity distributions for bifunctional catalysts in fixed-bed reactors, for the case of multiple reaction schemes. Each reaction was assumed to require only one type of catalyst. It was shown that catalyst activity distributions had a strong influence on reactant conversion and product selectivities.

Nonuniform activity distribution for catalysts experiencing deactivation has been studied by a number of investigators (DeLancey, 1973; Shadman-Yazdi and Petersen, 1972; Corbett and Luss, 1974; Becker and Wei, 1977b; Juang and Weng, 1983; Hegedus and McCabe, 1984). If deactivation occurs by sintering, it is minimized by decreasing the local catalyst concentration, i.e., a uniform catalyst offers the best resistance to sintering (Komiyama and Muraki, 1990).

In all cases considered above, catalyst performance was assessed utilizing appropriate indexes. The most common ones include effectiveness, selectivity, yield, and lifetime. Effectiveness factor relates primarily to the reactant conversion that can be achieved by a certain amount of catalyst, while selectivity and yield relate to the production of the desired species in multiple reaction systems. In the case of membrane reactors additional performance indexes (e.g. product purity) become of interest. In deactivating systems, other indexes incorporating the deactivation rate can be utilized apart from catalyst lifetime. Another index, which has not been employed in optimization studies because it is difficult to express in quantitative terms, is attrition. Catalyst pellets with an outer protective layer of support are beneficial in applications where attrition due to abrasion or vibration occurs, since only the inert and inexpensive support is worn off and the precious active materials are retained.

The key parameters which control the effect of nonuniform distribution on the above performance indexes are reaction kinetics, transport properties, operating variables, deactivation mechanism, and catalyst cost. All the early studies discussed above demonstrated that nonuniform catalysts can offer superior conversion, selectivity, durability, and thermal sensitivity characteristics to those wherein the activity is uniform. This was done by comparing the performance of catalysts with selected types of activity profiles, which led to the best profile within the class considered, but not to the optimal one. Morbidelli et al. (1982) first showed that under the constraint of a fixed total amount of active material, the *optimal* catalyst distribution is an appropriately chosen *Dirac-delta function*; i.e., all the active catalyst should be located at a specific position within the pellet. This distribution remains optimal even for the most general case of an arbitrary number of reactions with arbitrary kinetics, occurring in a nonisothermal pellet with finite external heat and mass transfer resistances (Wu et al., 1990a).

It is worth noting that optimization of the catalyst activity distribution is carried out assuming that the support has a certain pore structure and hence specific

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effective diffusivities for the various components. Thus for a given pore structure, the catalyst distribution within the support is optimized. An alternative optimization in catalyst design is that of pore structure, while maintaining a uniform catalyst distribution. In this case, the mass transport characteristics of the pellet are optimized. This approach has been followed by various investigators and has been shown to lead to improvements in catalyst performance (cf. Hegedus, 1980; Pereira et al., 1988; Hegedus and Pereira, 1990; Beeckman and Hegedus, 1991; Keil and Rieckmann, 1994).

Much effort has also been invested in the preparation of nonuniformly active catalysts. As insight is gained into the phenomena related to catalyst preparation, scientists are able to prepare specific nonuniform profiles. In this regard, it should be recognized that catalyst *loading* and catalyst activity distributions are in principle different characteristics. In catalyst preparation, the variable that is usually controlled is the local catalyst loading. However, under reaction conditions, the local reaction rate constant is proportional to catalyst activity. The relation between catalyst activity and catalyst loading is not always straightforward. For structure-sensitive reactions, it depends on the particular reaction system, and hence generalizations cannot be made. On the other hand, for structure-insensitive reactions, catalyst activity is proportional to catalyst surface area. Thus, if the latter depends linearly on catalyst loading, then the catalyst activity and loading distributions are equivalent. If the above dependence is not linear, then the two distributions can be quite different. The majority of studies on nonuniform catalyst distributions address catalyst activity optimization, although a few investigators have considered catalyst loading optimization by postulating some type of surface area-catalyst loading dependence (Cervello et al., 1977; Juang et al., 1981). Along these lines, it was shown that when the relation between catalyst activity and loading is linear, and the latter is constrained by an upper bound, the optimal Dirac-delta distribution becomes a step distribution. However, if this dependence is not linear, which physically means that larger catalyst crystallites are produced with increased loading, then the optimal catalyst distribution is no longer a step, but rather a more disperse distribution (Baratti et al., 1993). An important point is that in order to make meaningful comparisons among various distributions, the total amount of catalyst must be kept constant.

Work in the areas of design, performance, and preparation of nonuniform catalysts has been reviewed by various investigators (Lee and Aris 1985; Komiyama 1985; Dougherty and Verykios 1987; Vayenas and Verykios, 1989; Komiyama and Muraki, 1990; Gavriilidis et al., 1993a). In this monograph, these issues are discussed with emphasis placed on optimally distributed nonuniform catalysts. Special attention is given to applications involving reactions of industrial importance.

# I.3 Overview of Book Contents

This book is organized as follows. In Chapter 2, optimization of a single pellet is addressed under isothermal and nonisothermal conditions. Both single and multiple reaction systems are discussed. Starting with simpler cases, the treatment is

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extended to the most general case of an arbitrary number of reactions with arbitrary kinetics under nonisothermal conditions, in the presence of external transport limitations. The analysis includes the effect of catalyst dispersion varying with catalyst loading. Finally, the improved performance of nonuniform catalysts is demonstrated through experimental studies for oxidation, hydrogenation, and Fischer–Tropsch synthesis reactions.

Optimization of catalyst distribution in pellets constituting a fixed-bed reactor requires one to take into account changes in fluid-phase composition and temperature along the reactor. This is discussed in Chapter 3, for single and multiple reactions, under isothermal and nonisothermal conditions. The discussion of experimental work is focused on catalytic oxidations.

Catalyst distribution influences the performance of systems undergoing deactivation, and this issue is addressed in Chapter 4 for selective as well as nonselective poisoning. Experimental work on methanation, hydrogenation, and NO reduction is presented to demonstrate the advantages of nonuniform catalyst distributions.

In Chapter 5, the effect of catalyst distribution on the performance of inorganic membrane reactors is discussed. In such systems, the catalyst can be located either in pellets packed inside a membrane (IMRCF) or in the membrane itself (CMR). Experimental results for an IMRCF are presented, and the preparation of CMRs with controlled catalyst distribution by sequential slip casting is introduced.

In Chapter 6, special topics of particular industrial importance are discussed. These include automotive catalysts, where various concepts of nonuniform distributions have been utilized; hydrotreating catalysts, which is a particular type of deactivating system; composite catalysts, with more than one catalytic function finding applications in refinery processes; biocatalysts; and functionalized polymer resins, which find applications in acid catalysis.

The final Chapter 7 considers issues related to catalyst preparation. The discussion is focused on impregnation methods, since they represent the most mature technique for preparation of nonuniform catalysts. During pellet impregnation, adsorption and diffusion of the various components within the support are important, and can be manipulated to give rise to desired nonuniform distributions. The chapter concludes with studies where experimental results are compared with model calculations.

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> Optimization of the Catalyst Distribution in a Single Pellet

Mong various reaction systems, investigation of optimal catalyst distribution in a *single* pellet has received the most attention. Although the general problem of an arbitrary number of reactions following arbitrary kinetics occurring in a nonisothermal pellet has been solved and will be discussed later in this chapter, it is instructive to first consider simpler cases and proceed gradually to the more complex ones. This allows one to understand the underlying physicochemical principles, without complex mathematical details. Thus, we first treat *single* reactions, under isothermal and nonisothermal conditions, and then analyze *multiple* reactions.

# 2.1 The Case of a Single Reaction

#### 2.1.1 Isothermal Conditions

In early studies, step distributions of catalyst were analyzed for the simple case of a single reaction occurring under isothermal conditions. Researchers often treated bimolecular Langmuir–Hinshelwood kinetics, which exhibits a maximum in the reaction rate as a function of reactant concentration. Thus, there is a range of reactant concentrations where reaction rate increases as reactant concentration decreases. This feature occurs in many reactions; for example, carbon monoxide or hydrocarbon oxidation, in excess oxygen, over noble metal catalysts (cf. Voltz et al., 1973), acetylene and ethylene hydrogenation over palladium (Schbib et al., 1996), methanation of carbon monoxide over nickel (Van Herwijnen et al., 1973), and water-gas shift over iron-oxide-based catalyst (Podolski and Kim, 1974).

Wei and Becker (1975) and Becker and Wei (1977a) numerically analyzed the effects of four different catalyst distributions. In three of these, the catalyst was deposited in only one-third of the pellet: inner, middle, or outer (alternatively called egg-yolk, egg-white, and eggshell, respectively). In the fourth it was uniformly distributed. The results are shown in Figure 2.1, where the effectiveness factor  $\eta$  is shown as a function of the Thiele modulus  $\phi$ . It may be seen that among these specific distributions, for small values of  $\phi$  (i.e. kinetic control) the inner

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#### 2.1 The Case of a Single Reaction



**Figure 2.1.** Isothermal effectiveness factor  $\eta$  as a function of Thiele modulus  $\phi$  for bimolecular Langmuir–Hinshelwood kinetics in nonuniformly distributed flat-plate catalysts; dimensionless adsorption constant  $\sigma = 20$ . (From Becker and Wei, 1977a.)

is best, while for large values of  $\phi$  (i.e. diffusion control) the outer is best. For intermediate values of the Thiele modulus, the middle distribution has the highest effectiveness factor. So the question naturally arises: given a Thiele modulus  $\phi$ , among all possible catalyst distributions, which one is the best? This question can be answered precisely, and is addressed next.

#### Definition of optimization problem

The optimization problem can be stated as follows: given a fixed amount of catalytic material, identify the distribution profile for it within the support which maximizes a given performance index of the catalyst pellet. In order to formulate the problem in mathematical terms, the following equations are required: For a single reaction

$$A \rightarrow \text{products}$$
 (2.1)

the steady-state mass balance for a single pellet is given by

$$D_{\rm e}\frac{1}{x^n}\frac{d}{dx}\left(x^n\frac{dC}{dx}\right) = a(x)r(C) \tag{2.2}$$

where  $D_e$  is the effective diffusivity, x is the space coordinate, C is the reactant concentration, r(C) is the reaction rate, and n is an integer characteristic of the pellet geometry, indicating slab, cylinder, or sphere geometry for n = 0, 1, 2 respectively. The catalyst activity distribution function a(x) is defined as the ratio between the local rate constant and its volume-average value:

$$a(x) = k(x)/\bar{k} \tag{2.3}$$

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# 8 Optimization of the Catalyst Distribution in a Single Pellet

so that by definition

$$\frac{1}{V_{\rm p}} \int_{V_{\rm p}} a(x) \, dV_{\rm p} = 1. \tag{2.4}$$

The boundary conditions (BCs) are

$$x = 0: \qquad \frac{dC}{dx} = 0 \tag{2.5a}$$

$$x = R: \qquad C = C_{\rm f}. \tag{2.5b}$$

The constraint of a fixed total amount of catalyst means that  $\bar{k}V_p$  is constant. In dimensionless form, the above equations become

$$\frac{1}{s^n}\frac{d}{ds}\left(s^n\frac{du}{ds}\right) = \phi^2 a(s)f(u) \tag{2.6}$$

$$s = 0: \qquad \frac{du}{ds} = 0 \tag{2.7a}$$

$$s = 1:$$
  $u = 1$  (2.7b)

$$\int_{0}^{1} a(s)s^{n} ds = \frac{1}{n+1}$$
(2.8)

where the following dimensionless quantities have been introduced:

$$u = C/C_{\rm f}, \qquad s = x/R, \qquad \phi^2 = r(C_{\rm f})R^2/D_{\rm e}C_{\rm f}.$$
  
 $f(u) = r(C)/r(C_{\rm f})$ 
(2.9)

Since we are dealing with a single reaction, the catalyst performance is directly related to the *effectiveness factor*, defined by

$$\eta = \frac{\int_0^1 f(u)a(s)s^n \, ds}{\int_0^1 a(s)s^n \, ds} \tag{2.10}$$

which, using equation (2.8), yields

$$\eta = (n+1) \int_0^1 f(u)a(s)s^n \, ds = \frac{n+1}{\phi^2} \left(\frac{du}{ds}\right)_{s=1}.$$
(2.11)

Thus, the optimization problem consists in evaluating the catalyst distribution a(s) which maximizes the effectiveness factor  $\eta$  under the constraints given by equations (2.6)–(2.8).

#### Shape of optimal catalyst distribution

In order to proceed further, we need to know the specific form for the reaction rate r(C). A variety of expressions can be used for this purpose. However, for illustration we choose the bimolecular Langmuir–Hinshelwood kinetics,

$$r(C) = \bar{k}C/(1 + KC)^2$$
(2.12)

# Birnensionless Concentration, u

2.1 The Case of a Single Reaction

**Figure 2.2.** Shape of the dimensionless bimolecular Langmuir–Hinshelwood rate function  $f(u) = (1 + \sigma)^2 u/(1 + \sigma u)^2$ , for various values of the dimensionless adsorption constant  $\sigma$ . (From Morbidelli et al., 1982.)

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so that

$$f(u) = \frac{r(C)}{r(C_{\rm f})} = \frac{(1+\sigma)^2 u}{(1+\sigma u)^2}$$
(2.13)

where

$$\sigma = KC_{\rm f}.\tag{2.14}$$

The shape of the rate function f(u) depends on the parameter  $\sigma$  and is shown in Figure 2.2. In particular, f(u) has a unique maximum at

$$u_{\rm m} = 1/\sigma. \tag{2.15}$$

The dimensionless reaction rate reaches its maximum value in the range 0 < u < 1 for  $\sigma > 1$ , and at u = 1 for  $\sigma \le 1$ . Thus, summarizing, the Langmuir–Hinshelwood kinetics exhibits a maximum value M at  $u = u_m$ , where

$$u_{\rm m} = 1/\sigma, \quad M = (1+\sigma)^2/4\sigma \quad \text{for} \quad \sigma > 1$$
 (2.16a)

$$u_{\rm m} = 1, \qquad M = 1 \qquad \qquad \text{for} \quad \sigma \le 1 \tag{2.16b}$$

Since  $f(u) \le M$ , from the expression for  $\eta$  given by equation (2.11) it is evident that

$$\eta = (n+1) \int_0^1 f(u)a(s)s^n \, ds \le (n+1)M \int_0^1 a(s)s^n \, ds \tag{2.17}$$

which, using equation (2.8), gives

$$\eta \le M. \tag{2.18}$$

Therefore, for any activity distribution a(s), the effectiveness factor can never be greater than M. It is apparent that if a function a(s) exists for which  $\eta = M$ , this will constitute the solution of the optimization problem.

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This function exists and is given by

$$a(s) = \frac{\delta(s-\bar{s})}{(n+1)\bar{s}^n} \tag{2.19}$$

where  $\delta(s - \bar{s})$  is the Dirac-delta function defined by

$$\delta(s - \bar{s}) = 0 \qquad \text{for all} \quad s \neq \bar{s} \tag{2.20a}$$

and

$$\int_{0}^{1} \delta(s - \bar{s}) \, ds = 1 \tag{2.20b}$$

which physically corresponds to a sharp peak located at  $s = \bar{s}$ . In our optimization problem,  $\bar{s}$  is  $\bar{s}_{opt}$ , the value of s where the rate function f(u) reaches its maximum value; i.e.,  $u(\bar{s}_{opt}) = u_m$ , where  $u_m$  is given by equation (2.16). In practice, this means that all the catalyst should be located at  $s = \bar{s}_{opt}$ . By using the Dirac-delta function property

$$\int_{0}^{1} f(s)\delta(s-\bar{s}) \, ds = f(\bar{s}) \tag{2.21}$$

it can be easily shown that the activity distribution (2.19) is indeed the optimal one. For this, equation (2.19) is substituted into equation (2.11) to give

$$\eta_{\rm opt} = \int_0^1 f(u) \frac{\delta(s - \bar{s}_{\rm opt})}{\bar{s}_{\rm opt}^n} s^n \, ds = f(u_{\rm m}) = M.$$
(2.22)

#### Evaluation of optimal catalyst location

The evaluation of optimal catalyst location  $\bar{s}_{opt}$  must be performed separately for  $\sigma \leq 1$  and  $\sigma > 1$ .

If  $\sigma \le 1$ , then from (2.16b)  $u_{\rm m} = 1$ , which is attained at the particle external surface, and hence  $\bar{s}_{\rm opt} = 1$ . In this case, from equations (2.16) and (2.22), the effectiveness factor is  $\eta_{\rm opt} = 1$ .

If  $\sigma > 1$ , then some more computations are needed to evaluate the optimal catalyst location. The details are available elsewhere (Morbidelli et al., 1982) and lead to

$$\bar{s}_{opt} = 1 - \frac{4(\sigma - 1)}{\phi_0^2}$$
 for  $n = 0$  (2.23a)

$$\bar{s}_{\text{opt}} = \exp\left(\frac{8(1-\sigma)}{\phi_0^2}\right) \quad \text{for} \quad n = 1$$
 (2.23b)

$$\bar{s}_{opt} = \frac{\phi_0^2}{\phi_0^2 + 12(\sigma - 1)}$$
 for  $n = 2$  (2.23c)

where  $\phi_0$  is a "clean" Thiele modulus which does not include the adsorption parameter  $\sigma$  and is defined as

$$\phi_0^2 = \bar{k}R^2/D_e = (1+\sigma)^2\phi^2.$$
(2.24)