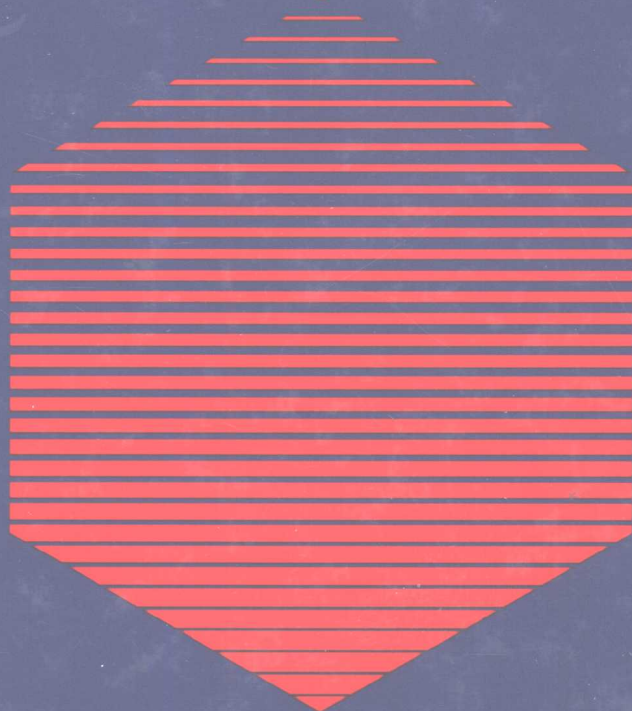


CAMBRIDGE SERIES IN CHEMICAL ENGINEERING

Catalyst Design

**Optimal Distribution of Catalyst in
Pellets, Reactors, and Membranes**



**Massimo Morbidelli,
Asterios Gavriilidis, and Arvind Varma**

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OPTIMAL DISTRIBUTION OF CATALYST IN PELLETS, REACTORS, AND MEMBRANES

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To our teachers and students

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Catalyst Design

Heterogeneous catalysis is widely used in chemical, refinery, and pollution-control processes. For this reason, achieving optimal performance of catalysts is a significant issue for chemical engineers and chemists. This book addresses the question of how catalytic material should be distributed inside a porous support in order to obtain optimal performance. It treats single- and multiple-reaction systems, isothermal and nonisothermal conditions, pellets, monoliths, fixed-bed reactors, and membrane reactors. The effects of physicochemical and operating parameters are analyzed to gain insight into the underlying phenomena governing the performance of optimally designed catalysts. Throughout, the authors offer a balanced treatment of theory and experiment. Particular attention is given to problems of commercial importance. With its thorough treatment of the design, preparation, and utilization of supported catalysts, this book will be a useful resource for graduate students, researchers, and practicing engineers and chemists.

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Preface

Heterogeneous catalysis is used widely in chemical, refinery and pollution-control processes. Current worldwide catalyst usage is about 10 billion dollars annually, with ca. 3% annual growth rates. While these numbers are impressive, the economic importance of catalysis is far greater since about \$200–\$1,000 worth of products are manufactured for every \$1 worth of catalyst consumed. Further, a vast majority of pollution-control devices, such as catalytic converters for automobiles, are based on catalysis. Thus, heterogeneous catalysis is critically important for the economic and environmental welfare of society.

In most applications, the catalyst is deposited on a high surface area support of pellet or monolith form. The reactants diffuse from the bulk fluid, within the porous network of the support, react at the active catalytic site, and the products diffuse out. The transport resistance of the porous support alters the concentrations of chemical species at the catalyst site, as compared to the bulk fluid. Similarly, owing to heat effects of reaction, temperature gradients also develop between the bulk fluid and the catalyst. The consequence of these concentration and temperature gradients is that reactions occur at different rates, depending on position of the catalyst site within the porous support. In this context, since the catalytic material is often the most expensive component of the catalyst-support structure, the question naturally arises as to how should it be distributed within the support so that the catalyst performance is optimized? This book addresses this question, both theoretically and experimentally, for supported catalysts used in pellets, reactors and membranes.

In Chapter 2, optimization of catalyst distribution in a single pellet is considered, under both isothermal and nonisothermal conditions. Both single and multiple reaction systems following arbitrary kinetics are discussed. Chapter 3 deals with optimization of catalyst distribution in pellets comprising a fixed-bed reactor, while systems involving catalyst deactivation are addressed in Chapter 4. In Chapter 5, the effect of catalyst distribution on the performance of inorganic membrane reactors is presented, where the catalyst is located either in pellets packed inside an inert tubular membrane or within the membrane itself. Issues related to catalysts of significant commercial importance, including automotive, hydrotreating,

composite zeolite, biological, and functionalized polymer resin types, are addressed in Chapter 6. The final Chapter 7 considers catalyst preparation by impregnation techniques, where the effects of adsorption, diffusion and drying on obtaining desired nonuniform catalyst distributions within supports are discussed. This book should appeal to all those who are interested in design, preparation and utilization of supported catalysts, including chemical and environmental engineers and chemists. It should also provide a rich source of interesting mathematical problems for applied mathematicians. Finally, we hope that industrial practitioners will find the concepts and results described in this book to be useful for their work.

This book can be used either as text for a senior-graduate level specialized course, or as a supplementary text for existing courses in reaction engineering, industrial chemistry or applied mathematics. It can also be used as a reference for industrial applications.

We thank our departmental colleagues for maintaining an atmosphere conducive to learning. We also thank our families for their encouragement and support, which made this writing possible.

Massimo Morbidelli
Asterios Gavrilidis
Arvind Varma

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Introduction

1.1 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).

1.2 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

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 subsurface-impregnated Pt/Al₂O₃ 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 negative-order 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 SO₂ oxidation in an adiabatic fixed-bed reactor. Smith and Carberry (1975) investigated the production of phthalic anhydride from naphthalene in a nonisothermal nonadiabatic

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

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.

1.3 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

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.

Optimization of the Catalyst Distribution in a Single Pellet

Among 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 η is shown as a function of the Thiele modulus ϕ . It may be seen that among these specific distributions, for small values of ϕ (i.e. kinetic control) the inner

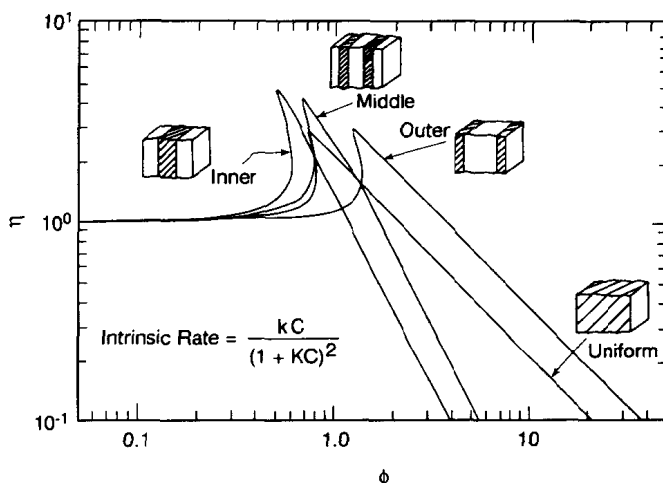


Figure 2.1. Isothermal effectiveness factor η as a function of Thiele modulus ϕ for bimolecular Langmuir-Hinshelwood kinetics in nonuniformly distributed flat-plate catalysts; dimensionless adsorption constant $\sigma = 20$. (From Becker and Wei, 1977a.)

is best, while for large values of ϕ (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 ϕ , 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



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

$$D_e \frac{1}{x^n} \frac{d}{dx} \left(x^n \frac{dC}{dx} \right) = a(x) r(C) \quad (2.2)$$

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:

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