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BOOK REVIEW

Industrial Catalysis, Optimizing Catalysts and Processes. R. J. Wijngaarden, A. Kronberg, and K. R. Westerterp. Wiley–VCH, Weinheim, 1998. 286 pp., $165.00.

This book focuses on heterogeneous catalysts rather than homogeneous catalysts. The design of a heterogeneous catalyst for commercial application includes a consideration of not only the intrinsic chemistry of the reaction but also the proper accounting of the relevant transport processes. In some instances unfavorable conditions for transport of heat and mass into the porous catalyst may compromise the favorable activity and selectivity intrinsic to the catalytic agents. Thus, it is appropriate and necessary to consider the effects of pore structure upon the apparent performance of the porous catalyst. Moreover, it is desirable to optimize the design of a porous catalyst in order to realize the full benefits of the intrinsic chemistry.

"Industrial Catalysis: Optimizing Catalysts and Processes" is 268 pages in length with 17 pages of preface, table of contents, and nomenclature. The text is organized into 9 chapters with 6 appendix sections. Citations to the literature appear at the end of each chapter. The authors describe the purpose of their text as "to teach the mathematical tools that are available for calculating interaction between transport phenomena and true chemical kinetics, allowing optimization of catalyst performance." They continue with the statements: "Simple rules are set forth to aid in making optimum choices to obtain fully effective catalyst particles, which give the best performance from an economic point of view. The discussed theories are elucidated with examples to provide training for application of the mathematics." The following is a brief review of the chapters.

Chapter 1 begins with a description of the basic ideas of catalyst porosity and its effects on reactivity, selectivity, and catalyst life. The characteristics of reactor performance are related to the reaction rate, conversion, selectivity, and yields.

Chapter 2 describes reaction kinetics. The chapter leads off with a discussion of activated processes, elementary reactions, the Arrhenius rule, reaction orders, and phenomenological rate expressions. The discussion switches to heterogeneously catalyzed reactions with a description of the microkinetic steps of adsorption to surface sites, reaction at these sites, and desorption from surface site. Langmuir–Hinshelwood kinetics are described for the classical cases. The concept of catalyst deactivation is described for reversible and irreversible reactions. Reaction selectivity is described for parallel and series reactions and for the combination of these reaction networks. The chapter ends with a discussion of kinetics in practice. The difficulties often encountered in practice are reviewed: (1) variable catalyst reactivity from one catalyst lot to another; (2) nonuniqueness in assigning rate equations to a system; and (3) uncertainty in measuring the reaction temperature for heterogeneous catalysts.

Chapter 3 discusses the production and physical characterization of solid catalysts. The tools and procedures are described for measuring pore volume and surface area. The physical forms of common catalysts are discussed. Common techniques for the manufacture of catalysts are described next. This discussion includes the materials used in the manufacture (active catalyst agent, support, promoters, and binders). Examples are given for unsupported catalysts, supported catalysts, impregnated catalysts and precipitated catalysts. Additional examples are given for Raney-type catalysts as well as fused and molten catalysts, such as the ammonia synthesis catalyst. Detailed discussion follows for the physical characterization of the catalysts for porosity, surface area, and pore size distribution. Whereas 16 pages were devoted to the aforementioned topics, 18 pages were required to describe these effects of heat and mass transport in porous catalysts. This lengthy discussion includes the common transport models as well as the more complicated models such as the "Dusty Gas Model." The chapter ends with some practical suggestions for determining the effective diffusivity.

Chapter 4 begins with a discussion of external mass transport in heterogeneous systems. The emphasis of this discussion is the coupling of external heat and mass transport between the fluid phase and the catalytic interface. Examples are described for the following systems: gas/solid and gas/liquid/solid where the catalytic reaction occurs on the solid phase. These examples include first-order kinetics and Langmuir–Hinshelwood kinetics for only one reactant. Asymptotic solutions are shown for the limiting cases. Caveats are given when the concentration of the reactant in the bulk phase approaches zero. This methodology is extended to bimolecular processes where one must develop balances for the second component. Heat and mass transport coefficients are described for flow around catalyst particles in two-phase flow. The correlations are described for single particles in laminar and turbulent flow. Additional correlations are shown for particles in packed beds and these equations are related to the correlations for single particles. Correlations for suspended particle reactors are also described. The thermal behavior of catalyst particles is discussed as well as the behavior known as "pellet runaway." The balances are shown for heat production rate and heat removal rate from a pellet. The conditions for "runaway" are given and the criteria for the absence of external transport limitations are described.

Chapter 5 describes the experimental methods used to determine the diffusion in porous solids and to measure reaction rates. The diffusion cell method is described using the Wicke–Kallenbach cell as well as the procedures for determining the diffusivity from steady-state and unsteady-state methods. The advantages of each method are discussed. Chromatographic techniques are reviewed for determining effective diffusivity in porous catalysts. Data of first and second moments are used to determine the second central moment. The measurement of reaction rates is considered next. Laboratory scale reactions are described to include the differential and integral fixed-bed reactors, the recycle reactors either with external or internal recycle (e.g., the Berty-type reactors). Under the general aspects of kinetic studies, the authors describe the criteria to confirm complete mixing in recycle reactors and the errors associated with determining the kinetic parameters.

Chapter 6 is concerned with the calculation of effectiveness factors in *isothermal* porous catalysts. The chapter begins with a survey of the literature in which the well-known models are given for both isothermal and nonisothermal pellets. Less-well-known cases are described next to include bimolecular reactions with nonisothermal effects. Other phenomena are described that include the impact of bimodal pore size distributions (e.g., zeolite in an amorphous binder), the pore shape, and inhomogeneities of the catalyst surface upon the effectiveness factor. This survey of the literature suggested that shortcomings existed in the body of knowledge on this subject. These shortcomings include (1) the use narrowly defined definitions of parameters, such as the Thiele modulus for which it is claimed that 20 different definitions are reported in the literature, and (2) some of the formulae are reported to contradict each other. In response to this situation reported by the present authors, they described a general method to calculate the effectiveness factor for arbitrary shape and for arbitrary kinetics. This theory seeks to bring the effectiveness factor curves

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together at the two extrema: $\eta \to 1$ and $\eta \to 0$ for all geometries and for all kinetics. The method begins by defining two dimensionless numbers: the zeroth Aris number (A_{N0}) and the first Aris number (A_{N1}). These new numbers replace the well-known Thiele modulus and can be calculated knowing (1) the volume/surface ratio of the catalyst pellet; (2) the effective diffusivity; and (3) the kinetic rate expression. The advantages of the new method are described in detail and it is claimed that the new methodology overcomes some of the problems associated with defining the Thiele modulus for negative-order reactions. Examples are described for the following reaction orders: −2, −1, −1/2, 0, 1, and 2-order kinetics. Where possible, comparisons are shown with cases published in the open literature. An interesting result of multiplicity of operating states is described for the case of −1-order kinetics and the isothermal pellet. For complicated cases, generalized approximations to the exact solutions are given in the limits of $\eta \to 1$ and $\eta \to 0$. The error is shown for using these approximations in place of the exact functions.

Chapter 7 describes the more complicated case of calculating the effectiveness factors for nonisothermal porous pellets. The Aris number method is modified to account for the effect of heat transfer within the pellet using either two or three parameters. The relative error is shown associated with using the two-parameter model instead of the three-parameter model for some typical oxidation and hydrogenation reactions. The authors demonstrate how the two-parameter, Aris numbers method is used to simplify the calculation of nonisothermal effectiveness numbers. Criteria are described for which one may neglect the effects of heat transport within the pellet. This method was illustrated for zero-, first-order, and bimolecular reactions. The method can be extended to account for intraparticle pressure gradients and to address anisotropy in effective diffusion.

Chapter 8 is concerned with the elements of catalyst pellet design and how one improves catalyst performance through pellet design. The elements of pellet design are the physical properties of the catalyst rather than the chemical properties. Cases are elaborated to show the effect of pore structure upon catalyst activity. Examples are described for the cases of control by kinetics or by diffusion. The effect of pore diffusion upon reactivity is demonstrated for bidisperse pore systems. The influence of mass transfer upon selectivity is discussed for the series reaction $A \to B \to C$ under the kinetics of a first-order, irreversible reaction. Optimal particle size and shape is described for minimizing pressure drop through a packed bed of catalysts. The chapter ends with a discussion of the optimal placement of catalyst agents in a nonuniformly active catalyst. Two examples are described that illustrate such design method: (1) butene dehydrogenation to butadiene and (2) automotive emission control catalysts. The butene example suggests that greater yields of butadiene are possible when only a thin layer of catalytic agent is placed near the external part of the porous solid. The auto exhaust catalyst example shows that the Pt component is placed on the external part of the support as a thin band, the Rh component should be placed just inside the Pt component, and the Pd component is placed inside the Rh catalyst.

Chapter 9 contains 22 examples that are worked out in some detail. These examples include calculation of kinetics, diffusion coefficients, Aris numbers, and effectiveness factors for specific cases.

Appendixes A–C show derivations of the Aris numbers and calculation of effectiveness factors for specific cases. Appendixes D–F work out the details of intrapellet pressure gradients, effective diffusion coefficients in simple gas reactions, and the first Aris number for concentration dependent effective diffusion in simple reactions.

The authors do fulfill the promise “to teach the mathematical tools that are available . . .” as they stated in the preface. Much of the first three chapters of this text (60 pp.) and Chap. 5 (31 pp.) are written for the general reader in catalysis literature and could be used as source material for teaching the principles of heterogeneous catalysis to scientists and engineers. Beginning with Chaps. 4 and 6 and continuing to the end of the book (148 pp.), the subject matter becomes increasingly more detailed and suitable for the specialist and practitioner who, out of necessity, must be concerned with the effects of transport processes upon the catalysis. Thus, the authors also fulfilled the promise made on the outside back cover jacket: “This is a book for developers of catalysts and for practitioners . . . .” The use of mathematics increases dramatically in these chapters so as to describe the phenomena. More than half of the text is devoted to a detailed description of the effects of transport processes upon catalyst performance. A significant portion of Chaps. 6–9 and the appendixes are devoted to describing a new method for calculating effectiveness factors. This new method combines the shape generalization and generalization for arbitrary kinetics described by L. K. Doraiswamy and M. M. Sharma (“Heterogeneous Reactions: Analysis, Examples and Reactor Design,” Vol. 1, Wiley, New York, 1984). This book mentions the shape generalization for first-order kinetics by Aris (*Chem. Eng. Sci.* **6**, 262 (1957)) and the generalization for arbitrary kinetics for a slab by Bischoff (*Chem. Eng. Sci.* **29**, 1384 (1974)). The current theory combines these two generalizations to arrive at definitions that are generalized both for shape and kinetics.

None of this theory is referenced to citations in the open literature. This statement is important since peer review is the mechanism by which new theories and technologies are tested. When new theories are published without the benefit of peer review, then the reader is warned to use the information with caution. Much of the information in this text should be of interest to the specialist in reaction and diffusion through porous catalysts.

Mark G. White

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332