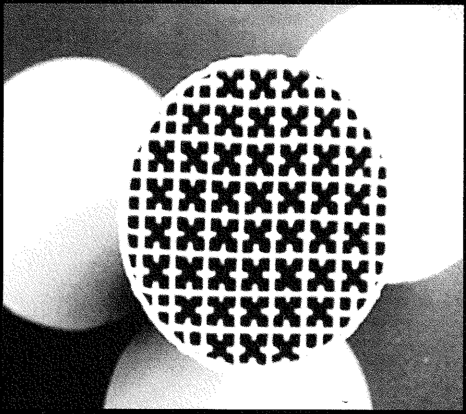
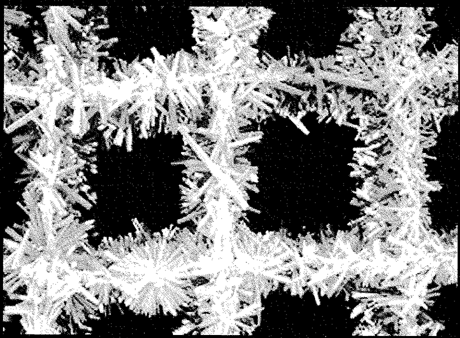
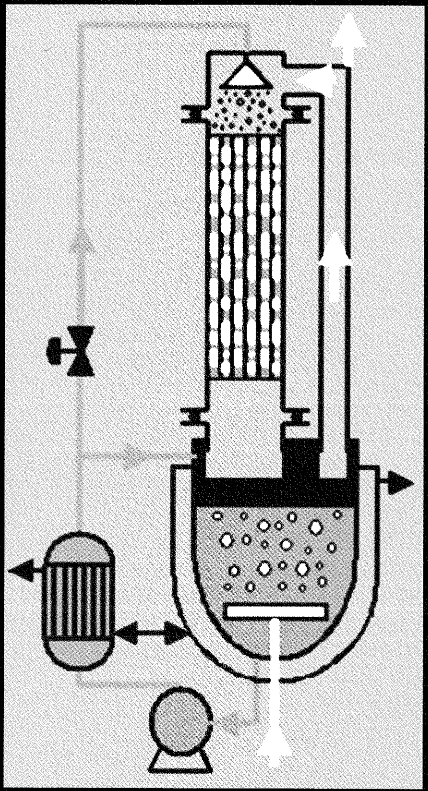
Structured Catalysts and Reactors

Second Edition







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Preface

Heterogeneous catalytic processes are among the main ways to decrease the consumption of raw materials in chemical industries and to decrease the emission of pollutants of all kinds to the environment via an increase in process selectivity. Selectivity can be improved by the modification of catalyst composition and surface structure and/or by the modification of pellet dimensions, shape, and texture, i.e., pore size distribution, pore shape, length, and cross-sectional surface area (distribution). Until recently, the limiting factor in the latter modifications has been the particles' size, to which the length of diffusion in pores is related. The size should not be too small because of the significantly higher pressure drop for such small particles. Shell catalysts, which contain catalytic species concentrated near the outer particles' surface, are a remedy for improving selectivity and keeping pressure drop at a reasonable level. Pressure drop can be the limiting factor even for such catalysts, e.g., when large quantities of raw materials must be processed or when the higher pressure drop results in a significantly higher consumption of raw materials. For instance, converting huge amounts of natural gas in remote areas would require equipment characterized by low pressure drop. Otherwise the cost of processing would be too high to make the process economical. Too high a pressure drop in catalytic car mufflers would result in an increase in fuel consumption by several percent. This would mean a several-percent-higher consumption of crude oil for transportation. An inherent feature of conventional packed-bed reactors is their random and structural maldistributions. A structural maldistribution in fixed-bed reactors originates from the looser packing of particles near the reactor walls. This results in a tendency to bypass the core of the bed, even if the initial distribution of fluid(s) is uniform. The uniformly distributed liquid tends to flow to the walls, and this can drastically alter its residence time from the design value. Random maldistributions result in: (1) a nonuniform access of reactants to the catalytic surface, worsening the overall process performance, and (2) unexpected hot spots and thermal runaways of exothermic reactions (mainly in three-phase reactions).

Structured catalysts (reactors) are promising as far as the elimination of these drawbacks of fixed beds is concerned. Three basic kinds of structured catalysts can be distinguished:

1. *Monolithic catalysts (honeycomb catalysts)*, in the form of continuous unitary structures that contain small passages. The catalytically active material is present on or inside the walls of these passages. In the former case, a ceramic or metallic support is coated with a layer of material in which active ingredients are dispersed.
2. *Membrane catalysts* are structures with permeable walls between passages. The membrane walls exhibit selectivity in transport rates for the various components present. A slow radial mass transport can occur, driven by diffusion or solution/diffusion mechanisms in the permeable walls.
3. *Arranged catalysts.* Particulate catalysts arranged in *arrays* belong to this class of structured catalysts. Another group of arranged catalysts are *structural catalysts*, derived from structural packings for distillation and absorption columns and static mixers. These are structures consisting of superimposed sheets, possibly corrugated before stacking. The sheets are covered by an appropriate catalyst support in which active ingredients are incorporated. The structure is an open cross-flow structure characterized by intensive radial mixing.

Usually, structured catalysts are structures of large void fraction ranging from 0.7 to more than 0.9, compared to 0.5 in packed beds. The path the fluids follow in structured reactors is much less twisted (e.g., straight channels in monoliths) than that in conventional reactors. Finally, structured reactors are operated in a different hydrodynamic regime. For single-phase flow the regime is laminar, and the eddies characteristic of packed beds are absent. For multiphase systems various regimes exist, but here also eddies are absent. For these reasons, the pressure drop in structured catalysts is significantly lower than that in randomly packed beds of particles. Indeed, the pressure drop in monolithic reactors is up to two orders of magnitude lower than that in packed-bed reactors.

Catalytic species are incorporated either into a very thin layer of a porous catalyst support deposited on the structured elements or into the thin elements themselves. The short diffusion distance inside the thin layer of the structured catalysts results in higher catalyst utilization and can contribute to an improvement of selectivity for processes controlled by mass transfer within the catalytic layer. In contrast to conventional packed-bed reactors, the thickness of the catalytic layer in monolithic reactors can be significantly reduced with no penalty paid for the increase in pressure drop. Membrane catalysts provide a unique opportunity to supply reactants to the reaction mixture gradually along the reaction route or to withdraw products from the reaction mixture as they are formed. The former mode of carrying out complex reactions might be very effective in controlling undesired reactions whose rates are strongly dependent on the concentration of the added reactant. The latter mode might result in higher conversions for reversible reactions, which are damped by products. The use of catalytic membranes operated in any of these modes can also contribute to significant improvement in selectivity. The regular structure of the arranged catalysts prevents the formation of the random maldistributions characteristic of beds of randomly packed particles. This reduces the probability of the occurrence of hot spots resulting from flow maldistributions.

Scale-up of monolithic and membrane reactors can be expected to be straightforward, since the conditions within the individual channels are scale invariant.

Finally, structured catalysts and reactors constitute a significant contribution to the search for better catalytic processes via improving mass transfer in the catalytic layer and thus improving activity and selectivity, decreasing operating costs through lowering the pressure drop, and eliminating maldistributions.

Structured catalysts, mainly monolithic ones, are now used predominantly in environmental applications, first of all in the cleaning of automotive exhaust gases. Monolithic reactors have become the most commonly used sort of chemical reactors: nearly a billion small monolithic reactors are moving with our cars! Monolithic cleaners of flue gases are now standard units. Monolithic catalysts are also close to commercialization in the combustion of fuels for gas turbines, boilers, heaters, etc. The catalytic combustion reduces NO_x formation, and the use of low-pressure-drop catalysts makes the process more economical. Some special features of monolithic catalysts make the burning of low-heating-value (LHV) fuels in monolithic units much easier than in packed beds of particulate catalysts. There are some characteristics that make structured catalysts also of interest for three-phase reactions. Several three-phase processes are in the development stage. Catalytic oxidation of organics in wastewater is currently operated in demonstration plants. One process, the hydrogenation step in the production of hydrogen peroxide using the alkylanthraquinone process, has already reached full scale, with several plants in operation.

Interest in structured catalysts is steadily increasing due to the already proven, and potential, advantages of these catalysts. A number of review articles regarding different aspects of structured catalysts have been published in the last decade [see F. Kapteijn, J.J. Heiszwolf, T.A. Nijhuis, and J.A. Moulijn, *Cattech*, 3, 24–41, 1999; A. Cybulski and J.A. Moulijn, *Catal. Rev. Sci. Eng.*, 36, 179–270, 1994; G. Saracco and V. Specchia, *Catal. Rev. Sci. Eng.*, 36, 305–384, 1994; H.P. Hsieh, *Catal. Rev. Sci. Eng.*, 33, 1–70, 1991; S. Irandoust and B. Anderson, *Catal. Rev. Sci. Eng.*, 30, 341–392, 1988; and L.D. Pfefferle and W.C. Pfefferle, *Catal. Rev. Sci. Eng.*, 29, 219–267, 1987].

These articles do not cover the whole area of structured catalysts and reactors. Moreover, the science and applications of structured catalysts and reactors are developing very fast. Therefore, some eight years ago we decided to edit a book on structured catalysts and reactors. In 1998 it was published. The time has now come for an updated version. In this edition an attempt has been made to give detailed information on all structures known to date and on all aspects of structured catalysts and reactors containing them: catalyst preparation and characterization, catalysts and process development, modeling and optimization, and finally reactor design and operation. As such, the book is dedicated to all readers who are involved in the development of catalytic processes, from R&D to process engineering. A very important area of structuring in catalysis is that directed at a catalytic surface, microstructure, and structuring the shape and size of the catalytic bodies. This area is essentially covered by publications concerning a more fundamental approach to heterogeneous catalysis. A lot of the relevant information is scale dependent and, as a consequence, is not unique to structured catalytic reactors. Therefore, these activities are described only briefly in this book.

The book starts with an overview on structured catalysts (Chapter 1). The rest of the book is divided in four parts. The first three parts deal with structures differing from each other significantly in conditions for mass transfer in the reaction zone. The fourth part is dedicated to catalyst design and preparation.

Part I deals with monolithic catalysts. Chapters 2 and 3 deal with the configurations, microstructure, physical properties, and manufacture of ceramic and metallic monoliths. Monolithic catalysts for cleaning the exhaust gas from gasoline-fueled engines are dealt with in Chapter 4, including fundamentals and exploitation experience. Chapters 5 and 6 are devoted to commercial and developmental catalysts for protecting the environment. The subject of Chapter 5 is the treatment of volatile organic carbon (VOC) emissions from stationary sources. In Chapter 6 fundamentals and applications of monoliths for selective catalytic reduction of NO_x are given. Unconventional reactors used in this field (reverse-flow reactors, rotating monoliths) are also discussed. Materials, activity, and stability of catalysts for catalytic combustion and practical applications of monolithic catalysts in this area are discussed in Chapter 7. The use of monolithic catalysts for the synthesis of chemicals is discussed in Chapter 8. Chapter 9 is devoted to the modeling of monolithic catalysts for two-phase processes (gaseous reactants/solid catalyst). Chapters 10–13 deal with three-phase monolithic processes. Both catalytic and engineering aspects of these processes are discussed.

Arranged catalysts allowing for convective mass transfer over the cross section of the reactor are discussed in Part II. Conventional particulate catalysts arranged in arrays are dealt with in Chapter 14. Current and potential applications of ordered structures of different kinds (parallel-passage and lateral-flow reactors) are mentioned. Chapter 15 is devoted to structured packings with respect to reactive distillation with emphasis on Sulzer Katapak-SP packings.

Part III of the book provides information about structured catalysts of the monolithic type with permeable walls, i.e., catalytically active membranes. Chapter 16 deals with catalytic filters for flue gas cleaning.

Catalytic membranes create a unique opportunity to couple processes opposite in character (e.g., hydrogenation/dehydrogenation, endothermic/exothermic) via the combination of reaction and separation. Catalytic membranes can allow for the easy control of reactant addition or product withdrawal along the reaction route. Chapter 17 deals with membrane reactors with metallic walls permeable to some gases. The properties of metallic membranes, permeation mechanisms in metallic membranes, the preparation of membranes, commercial membranes, modeling and design, engineering and operating considerations, and finally current and potential applications of metallic membranes are discussed. Chapter 18 presents inorganic membrane reactors: materials, membrane microstructures, commercial membranes, modeling and design, engineering and operating issues, and current and potential applications. Chapter 19 is dedicated to a special type of catalytic filters used for cleaning exhausts from diesel engines. Recent developments in the field of advanced membranes, in the form of zeolitic membranes are discussed in Chapter 20.

The last part of the book (Part IV) discusses techniques for incorporating catalytic species into the structured catalyst support (Chapter 21) and structuring of catalyst nanoporosity (Chapter 22).

The amount of detail in this book varies, depending on whether the catalyst/reactor is in the developmental stage or already has been commercialized. The know-how gained in process development has commercial value, and this usually inhibits the presentation of the details of the process/reactor/catalyst. Consequently, well-established processes/reactors/catalysts are described more generally. Projects at an earlier stage presented in this book are being developed at universities, which usually reveal more details. Each chapter was designed as a whole that can be read without reference to the others. Therefore, repetitions and overlapping (and sometimes also contradictions) between the chapters of this book are unavoidable.

The authors of individual chapters are top specialists in their areas. They comprise an international group of scientists and practitioners (Great Britain, Italy, The Netherlands, Poland, Russia, Sweden, Switzerland, and the U.S.) from universities and companies that are advanced in the technology of structured catalysts. The editors express their gratitude to all of the contributors for sharing their experience. The editors also appreciate the great help of Annelies van Diepen in shaping the book and its chapters.

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