The Technology of Catalyst Supports

Structured Catalysts and Reactors

EDITED BY ANDRZEJ CYBULSKI AND JACOB A. MOULIJN, Marcel Dekker, New York, 1998, 670 pages, ISBN 0–8247–9921–6, U.S.$195.00

This book covers the science and technology of structured catalyst supports which exhibit significant improvements in performance compared to conventional fixed bed catalysts. Each chapter is dedicated to a specific topic and written by eminent authorities (thirty-six of them). It is well balanced, with a good combination of fundamental and practical information about areas already penetrated by this technology and also in general catalysis. Many of the applications discussed involve the noble metals.

Structured catalysts are ceramic and metallic configurations, usually prefabricated, which constitute both the catalyst support and the reactor. There are three basic types:

- monoliths, in the form of continuous unitary structures containing small passages with walls loaded with catalytically active agents;
- membrane catalysts – structures with permeable walls between passages, thus allowing selective transport of reactants or products; and
- arranged catalysts, which are either arrays of particles or sheets superimposed, to allow cross-flow. Each type has distinct advantages over beds of packed particles. For example, monoliths have large void fractions (0.7 to more than 0.9) resulting in a very low pressure drop in the structure. Membrane reactors allow selective products to diffuse from the reaction zone, thus driving reversible reactions beyond normal equilibrium conversions and arranged catalysts are characterised by intensive radial mixing. These advantages have led to significant commercial applications.

Chapter 1 begins with an overview of structured catalysts, classifying them in terms of their design, support material, mixing conditions and mode of operation, while emphasising their lack of randomness when functioning as a reactor bed. Much of this chapter is devoted to monoliths used as automotive exhaust converters and stationary devices.

Monoliths, with no convective mass transfer over the reactor cross-section (honeycombs), are treated in Part I, with four chapters dealing comprehensively with automotive exhaust catalysis. There is considerable overlap, but it is refreshing to find similar material treated with a different approach by authors from disparate backgrounds. For example, the emphasis in Chapter 2 is upon ceramic monoliths used in exhaust converters, their structure, properties and fabrication, and attention is paid to materials as viewed by ceramic science. Chapter 3 briefly reviews general industrial applications of metal catalysts and looks at the properties and performance of coated metallic monoliths. Autocatalysts are reviewed from the perspective of catalytic science in Chapter 4. These chapters emphasise the systems approach to optimising these devices. Finally, Chapter 8 looks at the salient features in modelling the performance of converters.

The next largest application for monolithic catalysts – the selective reduction of NOx with ammonia and catalytic combustion or oxidation of fuel – is covered in Chapters 5 and 6. Chapter 5 describes the monolith structures used in stationary devices and how they differ from automotive converters, and then discusses modelling the reactors and the process, with clear descriptions of steady- and unsteady-state operations and reverse flow systems. These devices treat the effluent from combustion processes. Chapter 6 introduces the benefits of using catalytic combustion to reduce emissions. Combustion chemistry is invoked to demonstrate the advantages of monolithic beds loaded with metal catalysts, most of them from the platinum group. In particular, the role of the washcoat and its relationship to performance is thoroughly covered.

Unconventional utilisations of monolithic catalysts are described in the remainder of Part I. Recent literature on partial oxidation reactions,

where the low pressure drop across the monolith allows very fast flow rates and short contact times, is reviewed; this facilitates oxygen insertion reactions without complete combustion. The coverage of monolithic honeycomb catalysts ends with their use for three-phase reactions, involving gas-liquid reactors in different modes. This includes chapters on technical descriptions of the reactors, modelling of gas-liquid flow in the monoliths and applications to gas-liquid counter flows, illustrating how monolith technologies may reach into innovative areas.

Part II considers structured catalysts with convective mass transfer over the cross-section of the reactor. Four chapters occupy just under a hundred pages, which may indicate that this is still an emerging field. Chapter 12 reviews parallel-passage reactors (PPR) and lateral-flow reactors (LFR), which are devices in which flow occurs along catalyst layers instead of through a bed of particles. The chapter ends with a description of a commercial flue gas desulfurisation process utilising these concepts. Chapter 13 introduces the "bead-string reactor", consisting of conventional catalyst particles fixed on arrangements of parallel strings. The potential advantages of the bead-string reactor are explained, but it "is still in an early stage of development". The flow patterns and mass and heat transport in the reactor and modelling techniques are described, but no practical applications.

Open cross-flow-channel catalysts, such as those encountered in catalytic distillation packing, are described in Chapter 14. Washcoated metal, the particle-filled sandwich, and ceramic extrudates are used as examples of these structures. Two-phase operations are discussed.

Part III concentrates on monolithic reactors with permeable walls (or membrane reactors). It includes metal membranes, inorganic membranes, diesel exhaust aftertreatment, zeolitic membranes, and cross-flow reactors with permeable walls. Although these topics are covered in more detail elsewhere, they are a useful extension to the general subject of structured catalysts.

Chapter 16 is predominately concerned with palladium-containing membrane reactors, in which the selective diffusion of hydrogen alleviates thermodynamic equilibrium limitations found in hydrogenation and dehydrogenation processes. The principles are briefly explained, and examples of metallic wall and metal loaded porous ceramic wall reactors are given. Tables give referenced applications, but there are no large-scale operations. Economic processing of the ceramic components will no doubt evolve, leading to greater utilisation of this technology.

Inorganic membrane reactors offer a wide range of molecular and ionic permeability and Chapter 17 gives a very thorough overview. Tables list examples from the literature, but there are as yet no large scale applications.

Ceramic catalytic filters for diesel exhaust aftertreatment are reviewed in Chapter 18. Except for the fact that the device contains micropores which trap and oxidise soot, the material seems strangely out of place in this section and would be better in Part I. However, innovative methods for solving an important problem are addressed.

Zeolitic membranes (Chapter 19) are well referenced, with the fundamentals clearly presented, giving an appreciation of the importance and challenges of this topic. Finally, Chapter 20 reviews cross-flow reactors with permeable walls, such as those in solid oxide fuel cells and electrochemical cell reactors. Design, modelling and scale-up are covered to a limited degree.

Part IV discusses catalyst preparation and characterisation. Chapter 21 gives details, recipes and references for preparing ceramic monoliths, washcoating and dispersing the active species. It is a valuable collection of data for researchers and designers. The last chapter is almost an afterthought, but very necessary to readers using porous structures. Descriptions of models for systems of pores help to clarify an otherwise complex subject.

"Structured Catalysts and Reactors" is a welcome addition to the catalysis bookshelf, adding to our understanding of the functions of these advanced structures, but it is disappointing that ceramic foams in catalysis or recent advances in micro-scale reactor devices were not included. Part I will be particularly useful to readers of this journal, while catalysis practitioners will find all of benefit. JAMES T. RICHARDSON