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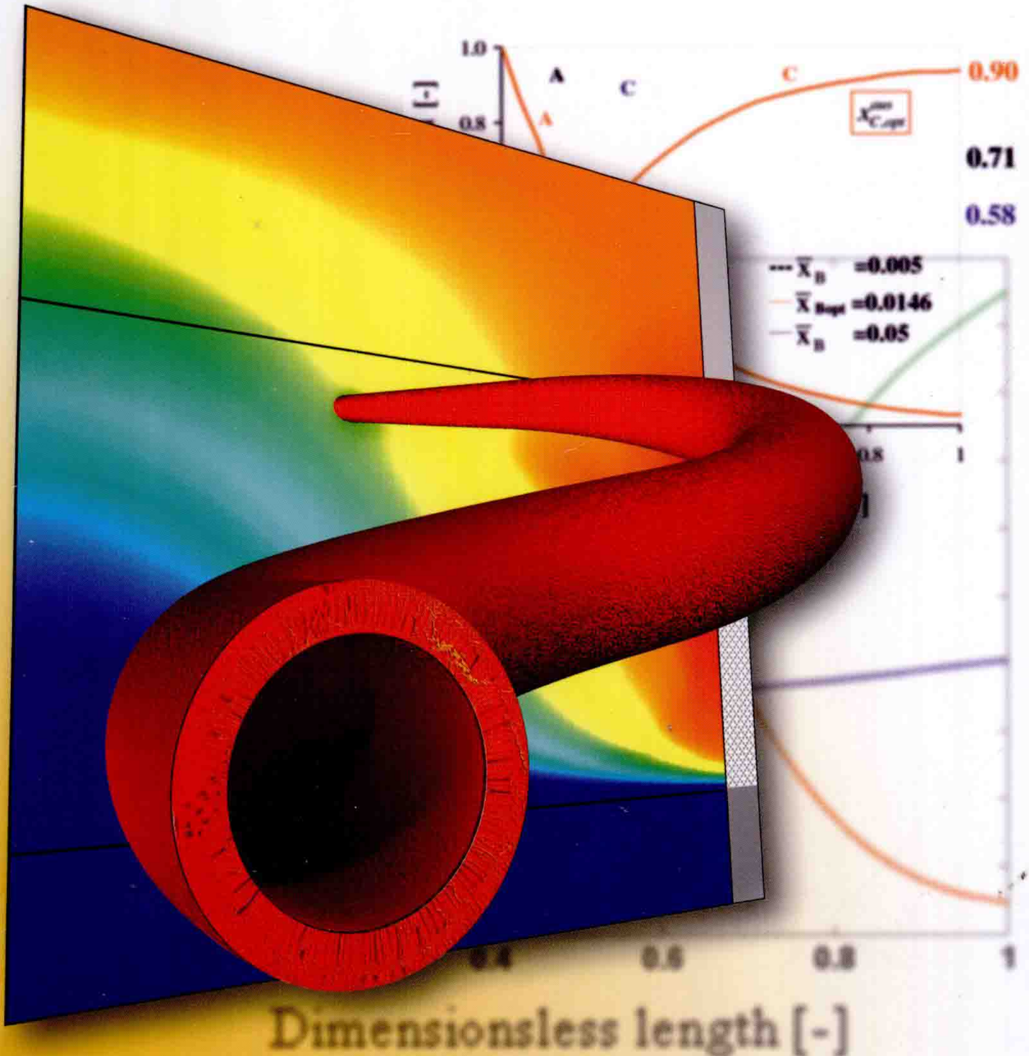
Membrane Reactors

Distributing Reactants to Improve Selectivity and Yield



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Preface

The chemical and pharmaceutical industries are characterized by the fact that a very large spectrum of different target compounds is synthesized. Due to the variety of the physical and chemical properties of the reactants and products involved a wide spectrum of operating conditions and reactor concepts is applied (Moulijn *et al.*, 2001).

Despite the long history of chemical reaction engineering there are still many problems which are not solved in a satisfactory manner (Levenspiel, 1999). One of the most difficult problems motivated the research leading to this book. This problem lies in the fact that during the synthesis of a certain target component typically undesired parallel or consecutive reactions occur which reduce the achievable yields. Formed side products have to be separated from the target product at the reactor outlets, which is a demanding and expensive task. Thus, there is considerable interest in developing technologies which allow increasing the selectivity and yield with which a certain target product can be generated.

It is well known that the selectivity in reaction networks towards a target compound can be increased following various concepts. First, a careful selection of the reaction temperature can be made to favor the formation of the target. A second, more versatile and very important direction is connected with the intensive activities devoted to developing and applying dedicated catalysts which accelerate specifically the desired reaction (Ertl *et al.*, 2008). The third approach, which is studied in this book, exploits the fact that the selectivity with respect to a certain desired product can be increased by properly adjusting the local concentrations of the reactants involved.

Innovative distributing and dosing concepts have for some time been an objective of research in chemical reaction engineering (Levenspiel, 1999). Besides adding certain reactants in a discrete manner into chemical reactors, various possibilities have been suggested for using different porous or non-porous membranes in order to arrange different ways of contacting the reactants (Coronas, Menendez, and Santamaria,1994; Lu *et al.*, 1997; Seidel-Morgenstern, 2005). Although the membrane reactor concept has been identified as interesting and promising, there are still several difficult problems that must be solved prior to an industrial application.

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This book describes results obtained within the research project "Membrane supported reaction engineering", which was funded by the German Research Foundation (DFG) and was carried out between 2001 and 2008 at the Otto von Guericke University and the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg (Germany). Chemists, chemical engineers and mathematicians worked in this project together in order to investigate various options of the so-called distributor type of membrane reactors (Dittmeier and Caro, 2008). The projects focused on a single and important class of reactions, namely the selective oxidations of gaseous alkenes. These reactions require typically elevated temperatures and suffer from severe selectivity limitations (Hodnett, 2000). Different types of membranes and reactor configurations were studied, concentrating on the oxidative dehydrogenation of ethane to ethylene. In order to allow a comparison of the results of different project partners working on packed-bed membrane reactors, fluidized membrane reactors and electrochemical membrane reactors, the same type of vanadia-based catalyst was always used. To implement a range of dosing concepts various high-temperature-resistant membranes were applied. On the one hand, this book was written to summarize the large amount of experimental material generated during the project. On the other hand, it was also the goal of the authors to provide theoretical concepts which allow quantitative descriptions and evaluations of the various types of membrane reactors investigated.

The book starts in Chapter 1 with an introduction into some basics of chemical reaction engineering. The equations presented are helpful to evaluate in a quantitative manner the potential of dosing reactants via reactor walls, as applied in membrane reactors of the distributor type, in order to enhance the selectivity of producing a certain target component in a network of reactions.

Chapter 2 gives a summary of the current state of the art of modeling packed-bed reactors. This chapter serves to introduce the overall notation and provides a frame for modeling mass and heat transfer processes relevant in the different reactors studied. Appropriate model reduction methods, discretization techniques and suitable solvers for the typically large systems of algebraic equations are also discussed in this chapter.

Chapter 3 introduces the heterogeneously catalyzed oxidative dehydrogenation (ODH) of ethane which was studied as a model reaction in various projects. Although this reaction is currently far from a wide industrial application, it was identified to be a suitable object of investigation for the purpose of the overall project. Chapter 3 provides further an important basis for the experimentally oriented projects described later. It summarizes the preparation, characterization and properties of the vanadia catalysts used, the reaction network and a model capable of quantifying the reaction kinetics.

The aim of Chapter 4 is the analysis of the relevant transport phenomena, in particular the superposition of convection and diffusion processes. Another point addressed in this chapter is the experimental and theoretical analysis of transport processes in membranes. Finally, an analysis of the influence of membrane geometry and structural parameters as well as of the operating conditions is performed for reactors with catalytically coated membranes. Hereby, some aspects of the numerical solution of the corresponding differential equations are discussed from a mathematical point of view.

Chapter 5 describes results of a theoretical study of a packed-bed membrane reactor using models of different levels of complexity. Hereby, membrane reactor tubes are filled with particles of the solid catalyst. The chapter further summarizes the results of detailed experimental investigations of single- and multi-stage packed-bed membrane reactors as well as conventional packed-bed reactors carried out in laboratory- and pilot-scale reactor set-ups. Besides the ODH of ethane also the ODH of propane was considered.

Chapter 6 summarizes the results of an extensive experimental and theoretical investigation devoted to evaluating the potential of porous membranes which are dipped into a bed of fluidized catalyst particles and which serve as an oxygen distributor. This chapter also discusses benefits and limitations of this reactor concept compared to the classic co-feed reactant dosing applied in a conventional fluidized bed reactor.

Chapter 7 introduces electrochemical membrane reactors equipped with ion-conducting membranes, which are ideally impermeable for non-charged species. These reactors operate as electrochemical cells in which the oxidation and reduction reactions are carried out separately on catalyst/electrode layers located on opposite sides of the electrolyte. The working principle of a solid electrolyte membrane reactor is introduced. Further, material aspects and the modeling of solid electrolyte membrane reactors are discussed. The synthesis of maleic anhydride and again the oxidative dehydrogenation of ethane are considered as experimental examples.

Chapter 8 provides insight on nonlinear phenomena that may occur in membrane reactors. It is demonstrated that such reactors can become instable, when membranes are used for side-injection of reactants in order to enhance yields. Under certain conditions, spatially homogeneous solutions can give rise to concentration and temperature patterns which may be quite complex.

In the final Chapter 9 the results achieved for the different reactor configurations are compared and a short summary is given to evaluate the current state of membrane reactors of the distributor type.

This book is seen by the authors as a contribution to the actively investigated wider field of integrated chemical processes (Sundmacher *et al.*) and more specifically to membrane reactors combining reaction and separation steps (Sanchez Marcano and Tsotsis, 2002).

The editor is very grateful to all colleagues in Magdeburg who contributed to this book for their inspiring, fruitful and pleasant cooperation during the period of this project.

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Magdeburg, August 2009 *Andreas Seidel-Morgenstern*

References

Coronas, J., Menendez, M., and Santamaria, J. (1994) Methane oxidative coupling using porous ceramic membrane reactors. *Chem. Eng. Sci.*, **49**, 2015–2025.

Dittmeier, R., and Caro, J. (2008) Catalytic membrane reactors, in *Handbook of Heterogeneous Catalysis* (eds G. Ertl, H. Knözinger, F. Schüth, and J. Weitkamp), Wiley-VCH Verlag GmbH, Weinheim, pp. 2198–2248.

Ertl, G., Knözinger, H., Schüth, F., and Weitkamp, J. (eds) (2008) *Handbook of Heterogeneous Catalysis*, vol. 8, Wiley-VCH Verlag GmbH, Weinheim.

Hodnett, B.K. (2000) *Heterogeneous Catalytic Oxidation: Fundamental and Technological Aspects of the Selective and Total Oxidation of Organic Compounds*, John Wiley & Sons, Ltd.

Levenspiel, O. (1999) *Chemical Reaction Engineering*, 3rd edn, John Wiley & Sons, Inc., New York.

Lu, Y.L., Dixon, A.G., Moder, W.R., and Ma, Y.H. (1997) Analysis and optimization of cross-flow reactors with distributed reactant feed and product removal. *Catal. Today*, **35**, 443–450.

Moulijn, J.A., Makkee, M., and van Diepen, A.E. (2001) *Chemical Process Technology*, John Wiley & Sons, Ltd, Chichester.

Sanchez Marcano, J.G., and Tsotsis, T.T. (2002) *Catalytic Membranes and Membrane Reactors*, Wiley-VCH Verlag GmbH, Weinheim.

Seidel-Morgenstern, A. (2005) Analysis and experimental investigation of catalytic membrane reactors, in *Integrated Chemical Processes* (eds K. Sundmacher, A. Kienle, and A. Seidel-Morgenstern), Wiley-VCH Verlag GmbH, Weinheim, pp. 359–389.

Sundmacher, K., Kienle, A., and Seidel-Morgenstern, A. (eds) (2005) *Integrated Chemical Processes*, Wiley-VCH Verlag GmbH, Weinheim.

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