Design of Hierarchically Structured Porous Catalysts with Optimized Yield and Selectivity - Application to Autothermal Reforming for Fuel Cells

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Porous catalysts are widely used in applications ranging from petroleum refining to the production of chemicals, fuel cells and emission control. Nanoporous catalysts like zeolites have an extremely large internal surface area (e.g., 1000 m^2/g), which is beneficial because catalytic reactions occur on the surface. However, their small pore size leads to slow molecular transport and pore blocking, limiting the efficient use of the catalytic material. This indicates that, apart from the nanopores where reactions actually occur, a "distribution" network of macropores is needed for molecules to quickly move in and out of the catalyst. The question is what the optimal pore size distribution is for a desired objective, such as a maximum yield or selectivity toward a particular product, under certain constraints, such as a given catalyst particle size and intrinsic kinetics in the nanopores?

Both explicit pore network based optimization methods, and continuum methods treating the porous catalyst as a pseudo-continuum, defined by a matrix of local porosities and pore diameters, were used. Optimization problems such as these involve the solution of sets of partial differential equations (PDE) over different domains, and are often encountered in the context of optimal design, optimal control and parameter estimation. Based on the reduced gradient method, a general strategy was proposed to solve these problems, building upon existing software (Wang et al., 2008). This strategy was implemented in Fortran, combining a freely available gradient-based optimization package, NLPQL, a multigrid solver, MGD9V, and in-house coding. The value and gradient of the objective function were computed by solving the discretized PDE and another system of linear equations using MGD9V, and fed into NLPQL. The PDE was discretized in terms of a finite volume method on a matrix of computational cells. The number of cells ranged from 129x129 to 513x513, and the number of optimization variables ranged from 41 to 201. Numerical tests were carried out on a Dell laptop with a 2.16 GHz Intel Core2 Duo processor. The results showed that the optimization typically converged within a limited number (i.e., 9-48) of iterations. CPU times varied from a few seconds to about 200 s. The PDE was solved 36-201 times in each of the numerical tests.

Using this methodology, for a single, isothermal reaction, the distribution network that maximizes the conversion corresponds to one where the large pore channels are of the

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same size, and the nanoporous walls (i.e., the nanoporous catalytic material between two neighboring large pore channels) are sufficiently thin so that diffusion limitations vanish inside them (Wang et al., 2007; Johannessen et al., 2007; Wang and Coppens, 2008). It was also found that the performance of the optimal catalyst is dictated by the generalized distributor Thiele modulus, which is defined in a way analogous to the generalized Thiele modulus, but using the molecular diffusivity in the macropores, rather than the effective diffusivity in the nanopores.

These theoretical insights were extended to design a catalyst for autothermal reforming for fuel cells, a non-isothermal problem. Fuel cells are considered for the clean generation of energy. However, the production, transportation and storage of hydrogen are major concerns limiting the use of fuel cells in commercial applications. One possible way to circumvent these difficulties is to produce hydrogen on-board through catalytic reforming of natural gas, methanol or other hydrocarbons. Autothermal reforming of natural gas is a promising option, because it combines an endothermic reaction, steam reforming, and an exothermic reaction, total/partial oxidation. Nevertheless, serious diffusion limitations exist for existing reformers because of very fast intrinsic kinetics of these reactions.

It is shown that the performance of a commercial, meso-macroporous catalyst for the autothermal reforming of methane on Ni/Al_2O_3 could be improved significantly, when macropores are introduced in an optimized way. The commercial catalyst, taken as a base case, has macropores with an average diameter of 2 μ m and mesopores with a n average diameter of 20 nm. The kinetics of Xu and Froment (1989) for steam reforming and the water gas shift reaction were employed, in combination with kinetics for the total oxidation of methane. Transport in the macropores was modeled using the dusty gas equations, including multicomponent molecular diffusion, Knudsen diffusion and viscous flow. At typical reaction conditions, Knudsen diffusion dominates transport in the mesopores; the effect of pore surface roughness was included in the simulations. Both the macropore size and the macroporosity influence the overall conversion; increases of up to 50-80% with respect to a commercial catalyst are possible. A larger macroporosity typically favors a lower CO/H_2 ratio (more hydrogen). Temperature gradients in the catalyst increase with macroporosity, as a result of the lower thermal conductivity of the solid porous material, but the maximum temperature in the catalyst was never more than ten degrees above that at the outer surface at the investigated operating conditions.

References

1. Wang, G.; Coppens, M.-O., Kleijn, C.R. A tailored strategy for PDE-based design of hierarchically structured porous catalysts. *Int. J. Multiscale Comp. Eng.* **2008**, *6*, 179-190.
2. Wang, G.; Johannessen, E.; Kleijn, C. R.; de Leeuw, S. W.; Coppens, M.-O. Optimizing transport in nanostructured catalysts: a computational study. *Chem. Eng. Sci.* **2007**, *62*, 5110-5116.
3. Johannessen, E.; Wang, G.; Coppens, M.-O. Optimal distributor networks in porous catalyst pellets. I. molecular diffusion. *Ind. Eng. Chem. Res.* **2007**, *46*, 4245-4256.

4. Wang, G.; Coppens, M.-O. Calculation of the optimal macropore size in nanoporous catalysts and its application to deNOx catalysis. *Ind. Eng. Chem. Res.* **2008**, *47*, 3847-3855.

5. Xu, J.G.; Froment, G.F. Methane steam reforming, methanation and water-gas shift .1. Intrinsic kinetics. *AIChE J.* **1989**, *35*, 88-96.