

# MITIGATING DEACTIVATION EFFECTS THROUGH RATIONAL DESIGN OF HIERARCHICALLY STRUCTURED CATALYSTS

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## Summary

Industrial catalysts are plagued by deactivation, which reduces their lifetime and hampers their functionality. Optimally designed hierarchically structured catalysts are capable of improvements in yield over conventional nanoporous catalysts. We discuss the rational design of such hierarchically structured catalysts in tackling deactivation due to pore blockage and loss of active sites by deposits. Hydrodemetalation is employed as a case study to demonstrate our approach. The results of this study are useful in guiding the synthesis of improved catalysts with longer lifetimes, or improved yields.

## Keywords

Rational design of catalysts, Computational catalysis, Clean coal/heavy oil/frontier resources/biomass processing technologies.

## Introduction

Deactivation is an inherent problem in many industrial processes, most commonly in oil refining and the synthesis of petrochemicals. Solid byproducts of catalytic cracking reactions, denoted as “coke”, or other undesired products from competing side reactions deposit on the catalyst pore walls, causing loss of active surface area, and, over a longer time period, pore blockage. Deactivation can also be caused by deposition of metal sulfides during hydrodemetalation reactions. Pore blockage is the more severe problem because blocked pores cut off access to active sites located deep inside the catalyst. In many cases, the deactivation is irreversible, leading to substantial catalyst loss, and, thus, increased production costs. Therefore, it is imperative to design catalysts that can withstand deactivation for longer times on stream without substantial loss in activity, or produce a higher yield during the time on stream. To this end, we aim to optimize the pore network structure of porous catalysts, a problem that is of increasing relevance thanks to new ways to synthesize hierarchically structured catalysts with a controlled structure at all length scales, as well as the need to convert heavier feeds.

The introduction of an optimal network of broad pore channels, consisting of uniformly distributed and optimally sized macropores or mesopores, in a nanoporous catalyst can increase the yield

significantly, by alleviating transport limitations to the nanopores for arbitrary kinetics in the nanoporous catalyst<sup>1,2,3</sup>. In the absence of boundary effects and deactivation, such an optimized bidisperse pore size distribution (unique broad pore channel size) does not lead to a lower yield than an optimized bimodal pore size distribution, in which the broad pore channel size and macroporosity are allowed to vary spatially. The question remains, however, whether the same structures are optimal from the point of view of deactivation resistance as well. Both bidisperse and bimodal pore size distributions are considered. Using a model with spatially stepwise continuous variables, the broad pore channel network of bimodal and bidisperse catalysts is optimized with the objective to maximize the integrated yield over a given time period. The design variables in the optimization are the macroporosity (i.e., the fraction of catalyst volume occupied by large pore channels) and the width of the large pore channels. Optimizations are performed combining COMSOL Multiphysics, which is a finite element PDE solver package, with MATLAB, which provides the optimization toolbox.

## Optimization and Results

To demonstrate this approach, deactivation of hydrodemetalation catalysts is studied. Deactivation results from deposition of sulfides of vanadium and nickel, formed due to hydrogenation of metalloporphyrins that are present in crude feedstock or petroleum residue. These deposits cause pore blockage and reduce the active surface area. Previous

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modeling efforts directed towards hydrodemetalation have shown that a bimodal catalyst has a higher initial activity and longevity compared to a unimodal catalyst<sup>4</sup>, and that optimization of the micropore radius and volume can result in an increased conversion<sup>5</sup>. The optimizations in the present work assume that deactivation is limited to the nanopores, because the large pores provide much less surface area for reaction. The Random Spheres Model (RSM) of Wei and co-workers<sup>6,7</sup> is used to represent the nanoporous catalyst and the metal sulfide deposits as an ensemble of Poisson-distributed small spheres. A pseudo-homogeneous model with effective, local diffusivities and kinetic parameters, calculated on the basis of the RSM with an additional broad pore network, is used to solve diffusion and reaction in a bimodal porous catalyst. Optimization of the broad pore network is carried out to maximize the scaled, overall yield or conversion defined as:

$$\text{Scaled Yield} = \frac{\int_t \left[ \int_x \int_y \int_z k_E S_{HS} c \rho_{cat,HS} dx dy dz \right] dt}{\int_t \left[ \int_x \int_y \int_z k S c \rho_{cat} dx dy dz \right] dt}$$

where  $c(x, y, z, t)$  is the local concentration of metalloporphyrins in the catalyst. In this equation,  $k_E$  represents the effective rate constant,  $S_{HS}$  represents the surface area per unit mass of fresh catalyst, and  $\rho_{cat,HS}$  represents the density of the hierarchically structured catalyst. The notations  $k, S, \rho_{cat}$  represent the corresponding parameters for the purely nanoporous monodisperse catalyst, without macroporosity. The spatially integrated yields are integrated over time to obtain the scaled yields.

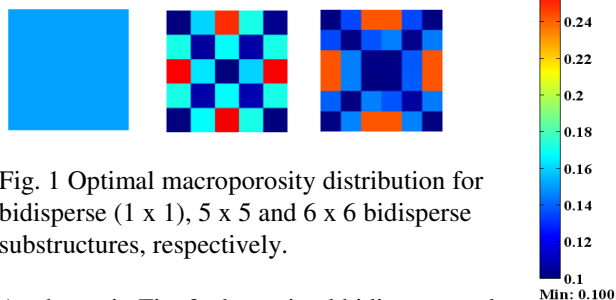


Fig. 1 Optimal macroporosity distribution for bidisperse (1 x 1), 5 x 5 and 6 x 6 bidisperse substructures, respectively.

As shown in Fig. 2, the optimal bidisperse and bimodal catalysts perform equally well, but up to an order of magnitude better than the original monodisperse catalyst, without macropores. Moreover, the optimal macroporosity in the bimodal catalyst fluctuates spatially around the optimal bidisperse value (Fig. 1). Hence, a bidisperse structure is sufficient, and it is typically easier to synthesize.

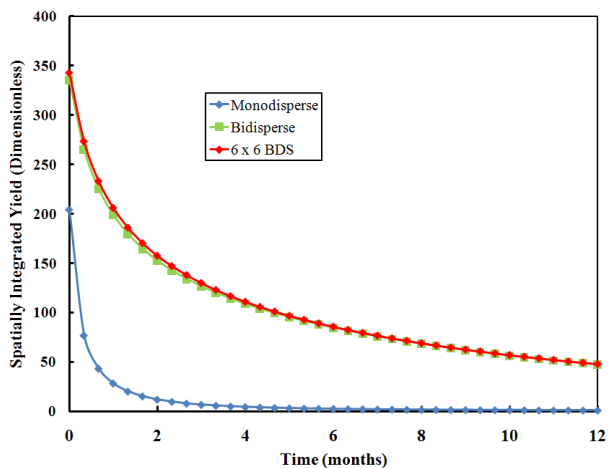


Fig. 2 Spatially integrated, normalized yield vs. time

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