

## Increasing Robustness of Deactivating Nanoporous Catalysts by Optimizing the Pore Network—Application to Hydrodemetalation

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### 1. Introduction

Diffusion limitations and catalyst deactivation severely limit the performance of industrial nanoporous catalysts. Diffusion limitations result in underutilization of catalytic material, while catalyst deactivation by pore blockage can prevent access to active sites located deep within the catalyst. By introducing an optimized broad pore network, which functions as a “molecular highway” network [1], it is possible to significantly enhance the catalytic activity, relative to a catalyst without broad pores, in industrially important reactions not affected by catalyst deactivation [2]. It is found that such a hierarchically structured catalyst having an optimized distribution in macroporosities and broad pore sizes does not produce a substantially higher activity than a hierarchically structured catalyst with a uniform, optimized macroporosity and a uniform, optimized broad pore size [3].

An optimized broad pore network functions in a similar manner as described above, when catalyst deactivation affects only the micro/mesopores [4]. It is of interest then, to determine the nature of the optimal pore network when catalyst deactivation affects both the micro/mesopores, as well as the broad pores (large mesopores-macropores). Can the optimal broad pore network significantly enhance activity as well as extend the useful lifetime of the catalyst? Secondly, is it sufficient to optimize only the purely mesoporous catalyst itself in order to increase activity and lifetime? The performance of the optimized hierarchically structured catalyst and the optimized purely mesoporous catalyst is compared to address the above question. The problem of catalyst deactivation in the hydrodemetalation of crude oil is employed as a case study to illustrate the optimization approach.

### 2. Mathematical Model and Simulation

The pore space of both the hierarchically structured catalyst and the purely mesoporous catalyst was modeled using the Random Spheres Model [4]. The effect of catalyst deactivation by poisoning and pore blockage on the diffusion-reaction process within a single catalyst pellet was accounted for in a one-dimensional continuum model. The pore network was optimized to maximize the reaction yield over a given time on stream. Optimizations were performed in COMSOL Multiphysics 3.5a in conjunction with MATLAB 2009b.

Figure 1 illustrates the volume integrated reaction rate for a base case purely mesoporous catalyst, an optimized purely mesoporous catalyst, and an optimized

hierarchically structured catalyst. The base case catalyst has a mesopore diameter of 20 nm while the hierarchically structured catalyst has a macroporosity of 29% and a broad pore size of 215 nm. The hierarchically structured catalyst has the same mesopore properties as the base case structure. In contrast, the optimized purely mesoporous catalyst has a mesopore diameter of 27 nm.

The optimized hierarchically structured catalyst has the lowest initial catalytic activity compared to the other two structures; surprisingly, it is also able to retain its activity for a longer time on stream, as evidenced by the benchmark shown in fig. 1. The optimized hierarchical structure has a higher volume averaged diffusivity than the purely mesoporous structures, because of transport primarily through the broad pores. Moreover, the broad pores do not get plugged as quickly as the mesopores, and allow reactant molecules to access the active sites located deep within the catalyst pellet, even after long times on stream. It must be pointed out that diffusion limitations still exist within the optimized hierarchical structure, because the time and length scales associated with transport through the broad pores are large; the broad pores span the entire length of the catalyst pellet.

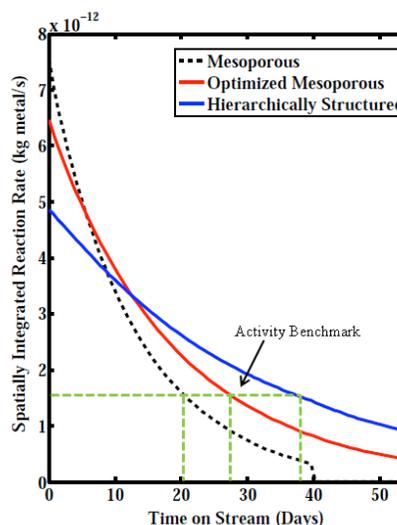


Fig. 1: Catalytic activity as a function of time on stream.

### 3. Conclusions

Optimizing the pore network of nanoporous catalysts can result in substantial savings at the catalyst pellet level, because less volume of active material is required in an optimized structure, while maintaining a high level of catalytic activity and robustness against deactivation. It is expected that such methods of rational design can better guide the synthesis of active and stable nanoporous catalysts.

### References

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