

**Broad Pore Channels as Molecular Highways in Nanoporous Catalysts:
Multiscale Modeling, Optimization and Applications**

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Abstract

Porous catalysts are widely used in many applications, ranging from petroleum refining to fuel cells and emission control. Nanoporous catalysts like zeolites often have an extremely large internal surface area (e.g., $1000\text{m}^2/\text{g}$), 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 broad pore channels is needed for molecules to quickly move in and out of the catalyst. Despite considerable experimental efforts in the introduction of broad pore channels into nanoporous catalysts in a controllable way, the following generic question remains: which broad pore channel network should be included in a nanoporous catalyst for optimal catalyst performance?

To this end, model-based optimizations were used to optimize hierarchically structured porous catalysts, containing both broad pore channels and nanopores. Extensive optimizations showed that, for a single, isothermal reaction, the nanoporous walls (i.e., the nanoporous catalytic material between two neighboring broad pore channels) should be sufficiently thin so that diffusion limitations vanish inside them. It was found that the optimal catalytic performance 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 broad pore channels, rather than the effective diffusivity in the nanopores.

The use of hierarchically structured porous catalysts was demonstrated for power plant deNO_x catalysis and autothermal reforming of methane. For deNO_x catalysis, overall catalytic activity in a mesoporous deNO_x catalyst with a median pore size of 32.5 nm could be increased by a factor of 1.8-2.8 simply by introducing 8-22 μm broad pore channels (occupying 20-40% of the total volume of the catalyst) and keeping broad pore channel walls (consisting of the same mesoporous catalytic material) 33 μm thick. For autothermal reforming of methane, the gain in overall catalytic activity could be improved by a factor of 1.5-1.8, by the introduction of broad pore channels with a size of

1 μ m, and occupying an optimized fraction of space. The H₂/CO ratio could be tuned as well: a large channel volume fraction generally favors a high H₂/CO ratio.