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Shifting boundaries – From intra- to interparticle diffusion and surface barriers for transport in hierarchically structured nanoporous materials

Marc-Olivier Coppens

UCL (University College London), London, UK
m.coppens@ucl.ac.uk

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Diffusion in nanoporous materials is a fascinating topic of great industrial relevance, for example, for catalytic and molecular separation processes. Despite decades of intensive experimental and theoretical work, there are still gaps in our understanding of diffusion fundamentals [1, 2]. Crucially, recent insights into which processes limit the overall transport in porous materials could influence the design criteria and the operation of important processes that apply nanoporous materials. Such insights result from more sophisticated experimental characterization tools and molecular simulations, but also progress in materials synthesis.

Here, I will focus on insights obtained from the optimization of hierarchically structured zeolites and other nanoporous media. Large pellets, particles or films are often needed in practical processes, e.g., for mechanical reasons or to avoid large pressure drops in reactor or adsorbent beds of particles. When nanoporous materials like zeolites are used, intracrystalline diffusion often becomes the limiting factor for catalytic reactions, and it affects transport rates in membranes and adsorbents. A nature-inspired chemical engineering (NICE) approach has allowed us first to provide design criteria for macro- and mesoporosity ("highway networks") in nanoporous materials, like zeolites, to alleviate transport limitations and optimize the pore network architecture [3]. Such design rules have become easier to apply, thanks to progress in synthesis. Multiscale computational assistance is especially relevant, as synthesis has tended to either ignore or use hand-waving arguments for what this porosity should be, and how pores should be distributed (in size and spatially) [4]. The overall porosity, their connectivity, and the average macropore size in between microparticles or grains of an optimal size matter most. These values can and should be quantified for a given process to achieve desired effects.

Major improvements in overall yields, product selectivity and catalyst stability against deactivation can be obtained by optimization of the pore network architecture, and I will illustrate this with a few examples related to zeolites and alumina-supported catalysts. Despite low intraparticle diffusivities in micro- or narrow mesopores, the overall transport becomes controlled by the wide channels, i.e., the highway network of broad meso- or macropores, which allows us to better control product distributions. However, this is not always the case: surprises come when careful optimization is carried out for systems with low intrinsic, intracrystalline or intraparticle diffusivity. When very small crystals or polycrystalline materials are used, interfaces and surface barriers could start to dominate the overall transport. Finite surface permeability and the importance of surface barriers had been anticipated since the 1980s by Barrer, Kärger and colleagues, and there was indirect evidence from the comparison of molecular uptake rates with microscopic PFG NMR measurements [1]; however, it was only recently that interference and infrared microscopy demonstrated the dominance of surface barriers in practical zeolites unequivocally, further confirming molecular simulations [5].

Inclusion of the effect of surface barriers to transport across the external zeolite crystal surface proved essential to show agreement between experimental and multiscale simulation results for the ethylation of benzene in hierarchically structured, ZSM-5 zeolite composites. Since, many other examples have been found, including in other industrially important reactions, such as the conversion of methanol to olefins, and hydro-isomerization of paraffins.

This means that the boundary of hierarchically structured nanoporous material optimization has – literally! – shifted. As in nature, not only the hierarchical transport network of channels matters, but the interfaces: thin skins and membranes around grains or cells [3, 4]. This opens tremendous opportunities as, once the pore network is optimized, we can turn our attention to controlling those interfaces as a new handle to increase overall rates, but, especially, selectivity towards the desired components. Our focus should thus turn to controlling not only the internal structures of zeolites and other nanoporous materials, or the pore network, but also the structure of the interfaces and whether to reduce barriers or use them as a tool for selectivity. A schematic of transport in nanoporous materials, shown in Fig.1, is more involved than the one usually presented in textbooks.

To explore this exciting frontier, materials, and experimental transport characterization, as well as advances in molecular simulations and an appreciation for a more holistic, multi-scale view on the design of materials and processes will be essential. In my presentation, I will illustrate this shift, and readers are referred to a recent review by Xu et al. [5] for a recent discussion and perspective on surface barriers.

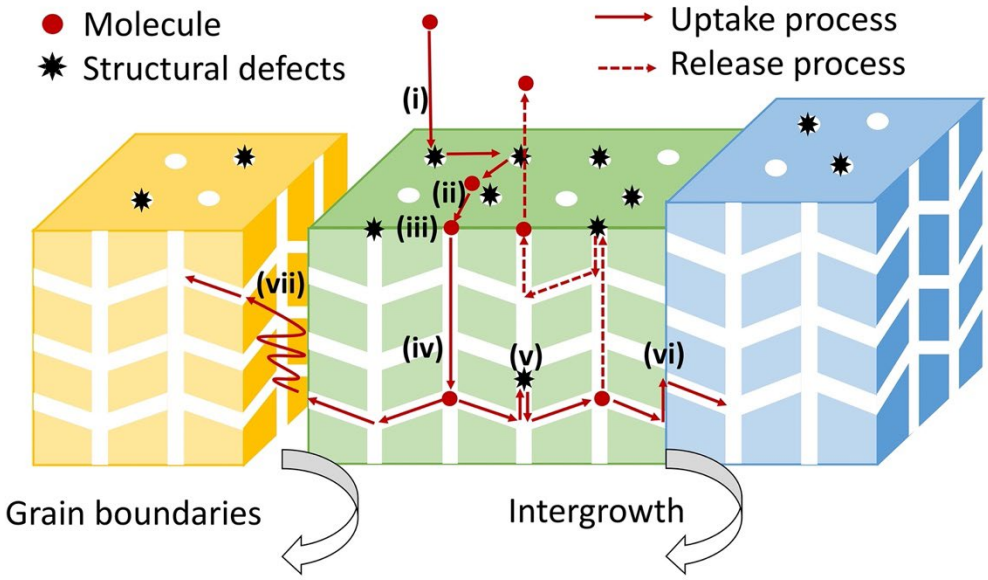

Fig. 1. Illustration of the transport process from the bulk phase into the interior of nanoporous materials. From Xu et al. [5]

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