Diffusion in MOFs: The surface barrier phenomenon

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The loading with guest molecules is the key for most applications of metal-organic frameworks (MOFs). It was found in numerous studies that the rate of the mass transfer into a MOF material may differ by several orders of magnitude for different samples. This phenomenon is commonly attributed to the presence of so-called surface barriers, which are almost omnipresent, but unwanted and poorly understood. Using well-defined and highly crystalline epitaxially grown thin films of type MOF HKUST-1 as model system, we have been able to quantitatively study this phenomenon using a quartz crystal microbalance (QCM). These experiments clearly demonstrate that surface barriers are not an intrinsic feature of MOFs – perfect, pristine films do not show these limitations. Only by destroying the structure at the outer surface of the MOF films, e.g. by exposure to air or water vapor, the molecular uptake is reduced.

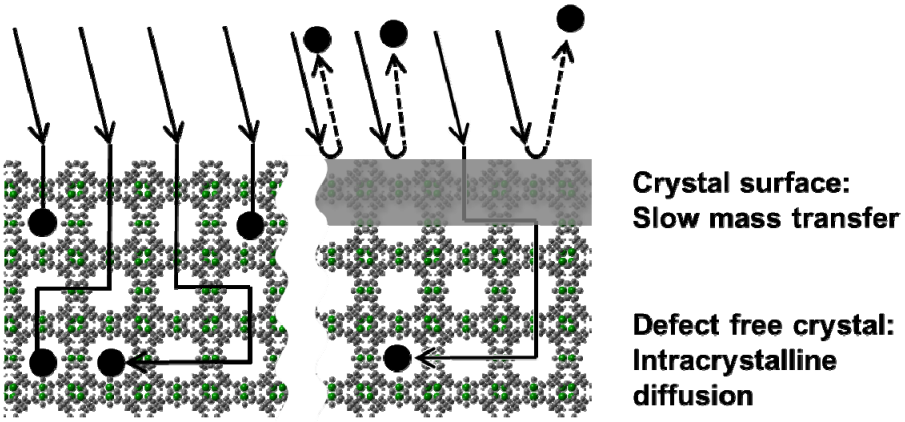

Figure: Model of the mass transfer in MOFs. Left side: unhindered diffusion in the nanoporous crystal. Right side: Surface barriers hinder the guest molecules in entering (and leaving) the pore space and slows down the mass transfer significantly.

Ref.:
L. Heinke*, Z. Gu, C. Wöll *The surface barrier phenomenon at the loading of metal-organic frameworks* Nat. Comm. 5 (2014) 4562.