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Diffusion in nanoporous materials as rate-limiting step in gas separation: Membrane permeation and pressure swing adsorption

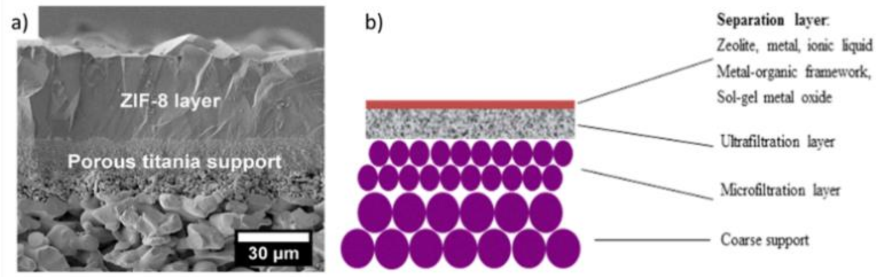
Juergen Caro

Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Germany

Nanoporous materials like zeolites are widely used for industrial gas separation through pressure swing adsorption (psa), new disruptive materials like metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are under evaluation. First LTA zeolite membranes are used in about 500 plants worldwide for the de-watering of solvents, especially bio-ethanol. MOF membranes are tested for their unique ability to separate short chain olefin/paraffin mixtures.

Industrial adsorbents and membranes usually show a hierarchical transport-optimized structure. Such hierarchical structure as shown in the figure allows an effective interplay of nanopore diffusion [1] in the separation layer with fluid flow through the macroporous support [2] to minimize the overall transport resistance [3].

Typical planar ceramic membrane obtained by sequential tape casting with a gas selective layer on top.



a) A metal-organic framework (MOF) type ZIF-8 layer on an asymmetric graded titania support [4], b) Principle of a supported membrane: The µm-thick separation layer is deposited on a macroporous ceramic or metallic support. To reduce the pressure drop across the support, i.e. to minimize the flow resistance, usually asymmetric (graded) supports with hierarchical cross section are used. As a rough estimate, mass transport through a membrane can be described using 1st Fickian Law. The flux density of component A through the membrane is described by $j_A = -D_{TA}\frac{\partial c}{\partial x}$ with j_A as the flux density in mol of A per time and area. D_{TA} is the transport diffusivity of A, and $\partial c/\partial x$ is the concentration gradient of component A across the membrane. Exact knowledge of the transport diffusivity is thus an important prerequisite for a knowledge-based optimization of separation devices [5]. A discussion of the challenges and traps of such measurement is the focus of the Conference Workshop on “Diffusion in Nanoporous Materials” and part of an IUPAC initiative (https://iupac.org/project/2015-002-2-100).

Adsorbents for rapid cycle pressure swing adsorption (psa) processes must allow a quick fluid flow of the feed into the nanopores of a zeolite or coal, where a diffusion-limited adsorption into the micropore system takes place. The shaped zeolite or carbon powders should show transport path like a human lung. For a short cycle time, however, the pressure drop in a packed adsorbent bed becomes a problem. The choice of an appropriate model accounting for intra-particle diffusional limitations is essential to simulate accurately the pressurization and blowdown steps of a psa processes [6].

[1] A. Bunde, J. Caro, J. Kärger, G. Vogel (eds.): *Diffusive spreading in nature, technology and society*, Springer, (2018).
[2] J. Caro: Fluid Flow, in: F. Schüth, K.S.W. Sing, J. Weitkamp (eds.), Handbook of Porous Solids, Wiley-VCH, pp 352-370 (2002).
[3] J. Caro: Diffusion coefficients in nanoporous solids derived from membrane permeation measurements, *Adsorption* **27,** 283-293 (2021).
[4] J. Caro: Hierarchy in inorganic membranes, *Chem. Soc. Rev*. **45,** 3468-3478 (2016). https://doi.org/10.1039/C5CS00597C
[5] J. Kärger, D.M. Ruthven, R. Valiullin (Eds.): Diffusion in Nanoporous Solids, Thematic Issue of the Adsorption Journal **27** (2021).
[6] S. Farooq, D.M. Ruthven: Numerical simulation of a kinetically controlled pressure swing adsorption bulk sepa-ration process based on a diffusion model, *Chemical Engineering Science* **46**, 2213-2224 (1991).

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