Supported Membranes

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Metal-Organic Framework Membranes—High Potential, Bright Future?

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The separation of mixtures through the use of membranes is much more energy efficient than distillation and crystallization. These separations are usually based on size and shape of the molecules to be separated or on their interaction with the membrane material. Ideally a well-defined pore size and shape is desired. Zeolites satisfy this requirement as they can be considered porous crystalline materials, having a uniform pore structure. Furthermore, crystalline structures are usually more stable than their amorphous counterparts. Since the early 1990s membranes of various zeolite topologies have been developed and their permeation and separation performance determined. In spite of their potential the implementation in practice proceeds very slowly. The few membrane types (LTA, FAU) that have been applied on the industrial scale serve mainly for the removal of water from organic mixtures, breaking the azeotropes.[1]

Various reasons can be put forward to explain this slow implementation. A membrane layer must be supported (on porous ceramics or metal) to provide strength to the thin zeolite layer that is a few micrometers thick. This layer consists of an intergrowth of small crystals, and grain boundaries may be the cause of reduced separation performance. Practical applications require high fluxes and selectivities, which can be achieved by thin layers and perfect intergrowths. The trade-off is the possibility of defects and the lower stability of the selective zeolite layer. Moreover, more often than not, zeolite membranes are synthesized using trial-and-error procedures. No "universal" method is known and reproducibility is still a major issue.[2]

Applications of zeolite membranes are further hampered by various aspects of the hydrothermal synthesis of many zeolite topologies. Organic template molecules are often used, around which the inorganic structure is assembled and condensed to form large crystalline units. Good interaction between the nuclei and the support, and intergrowth between the growing crystals are required, but surface charging in the often strongly basic environments may counteract this process.[3] Application of ionic polymers as primers,[4] nanocrystals as seeds,[1,5] or synthesis at lower pH[6] may alleviate this issue.

Removal of the template to open up the pore structure requires heating in an oxidative atmosphere to decompose and burn out these organics. Differences in thermal expansion between support and zeolite layer, and changes in unit cell size may induce cracks and loss of performance.[7] Sometimes milder conditions can be applied, for example, the use of ozone.[8]

In the last decade a new class of porous crystalline materials has made clear advances, the so-called metal-organic frameworks (MOFs), and more generally, hybrid organic–inorganic frameworks (HOIFs) or porous coordination polymers (PCPs), to which also the zeolite imidazolate frameworks (ZIFs) belong. These materials cover a much wider range of pore sizes than zeolites, even bridging micro- and mesoporous materials. The combination of organic and inorganic building blocks offers an almost infinite number of variations, enormous flexibility in pore size, shape, and structure, and myriad opportunities for functionalization and grafting. These materials have set world records in adsorption capacities, specific surface areas, and pore volumes. Their porosity is much higher than that of their inorganic counterpart zeolites (up to 0.9), justifying the designation "framework". Their thermostability is sometimes unexpectedly high, reaching temperatures above 400 °C. Obviously, there is tremendous interest in these new materials, but the major studies deal with synthesis,[9] while the majority of applications focus on adsorption/separation[10] and storage.[11] In analogy to zeolites, the fine-tuning of the dimensions and composition of the crystal networks would pave the way to many other applications based on the recognition and binding of specific molecules, for example in catalysis, in substrate-selective membranes, and in chemical, magnetic, and optical sensors, to name but a few. A few materials are already commercially available.[12]

The analogy with zeolites is obvious, but there are also some clear differences. If one thinks in terms of membranes, the highly accessible porosity infers high fluxes, while the wide range of pore sizes (into the mesopore range) would make it possible to tackle classical, extremely important separations such as the separation of hydrogen from other gases, the removal of CO_2, the separation of alkanes from alkenes, linear from branched alkanes, and mixtures of

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aromatic isomers, as well as the separation of larger molecular isomers.

The development of MOF-based membranes was challenged, and recently the first gas-mixture separations were achieved.[13,14] In a recent issue of *Angewandte Chemie* the group of Caro describes the successful preparation of a roughly 2 μm thick ZIF-7 membrane on an α-alumina support.[15] They applied this in the separation of hydrogen from carbon dioxide with a selectivity factor approximately 6.5, above the Knudsen selectivity. In view of the molecular dimensions (pore size ca. 0.30 nm) this selectivity should be a result of molecular sieving.[15]

Two major hurdles were overcome: even coverage and interaction of the seed crystals on the porous α-alumina support, and their intergrowth. Modification of the interaction with the support surface was achieved with an ionic polymer that improved the wetting of the surface with the synthesis fluid and resulted in even coverage of the seed crystals. Seeding had been demonstrated before as a viable technique to obtain a high coverage.[16] A good intergrowth was obtained under microwave irradiation, an effective technique in zeolite synthesis.[17] It goes without saying that both the nanocrystal seeds and membrane synthesis conditions had to be optimized. Without seeding these authors also recently succeeded in manufacturing a ZIF-8 membrane on titania,[13] but the membrane was much thicker (ca. 30 μm) and separated hydrogen from methane with a selectivity greater than 10.

The authors successfully applied their expertise from the field of zeolite membrane synthesis to the work in the present study, although fundamental aspects of the nucleation and crystalline growth may be quite different. Insight into the growth fundamentals may further accelerate and allow better direction of these developments.[18] Guo et al.[14] produced an HKUST-1 membrane by hydrothermally oxidizing part of a copper wire mesh, creating a local supersaturation under formation of the much more voluminous MOF material. This filling up of the space in between the mesh wires resulted in a kind of reinforced self-supported membrane. Also this material showed selectivity for hydrogen over other permanent gases, although this was not anticipated based on the pore size of the MOF structure. ZIF structures are generally much more thermostable. Caro et al.[15] demonstrated application of their MOF membrane at temperatures up to 200 °C, but we anticipate potential operation of covalent organic frameworks (COFs) at much higher temperatures and under harsh conditions. The recent application of such a material (CTF-1), modified to obtain the Pt-based Periana catalyst structure, in the catalyzed oxidation of methane to methanol in fumic sulfuric acid speaks for itself.[19]

The reported membranes confirm the anticipated high fluxes in view of their large porosity. These first MOF membranes are already of the order of magnitude of the best silicalite-1 and DDR membranes.[20] The next steps in improving selectivity are not known. Are smaller pores than those of the currently used ZIFs necessary? What is the effect of the flexibility of many MOF structures? Too much flexibility will impose limits on the molecular sieving, but, on the other hand, may be more forgiving towards differences in thermal expansion between support and selective layer, thus precluding crack formation at elevated temperatures.

If one speculates on the further potential of these materials as membranes, the flexibility could be employed, even with multilayers,[21] to create membranes responsive to specific components or external stimuli ("intelligent" membranes). The use of enantiomeric organic linkers or functional groups may introduce molecular recognition in separation.[22] Even catalytic functionalization[23] or catalyst encapsulation[24] would permit the formation of catalytic membranes.

Future applications of MOF membranes will also depend on the reproducibility of the synthesis and on the applicability of the conditions to the preparation of other MOF topologies. If robust synthetic strategies can be developed that allow the facile synthesis of MOF membranes, we foresee a bright future. In this sense, we believe, new synthetic avenues like the electrochemical route, uncommon for zeolites, will play an important role.[25]

There is still a long road ahead, but the work of Caro's group provides an outlook on a plethora of potential applications of metal-organic frameworks, not only as membranes, but also as protective, catalytic, or responsive coatings.

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[1] J. Caro, M. Noack, P. Kölsch, R. Schäfer, *Microporous Mesoporous Mater.* **2000**, *38*, 3.
[2] J. Coronas, J. Santamaria, *Sep. Purif. Methods* **1999**, *28*, 127.
[3] M. Noack, P. Kölsch, A. Dittmar, M. Stöhr, G. Georgi, R. Eckelt, J. Caro, *Microporous Mesoporous Mater.* **2006**, *97*, 88.
[4] M. Noack, P. Kölsch, A. Dittmar, M. Stöhr, G. Georgi, M. Schneider, U. Dingerdissen, A. Feldhoff, J. Caro, *Microporous Mesoporous Mater.* **2007**, *102*, 1.
[5] M. A. Snyder, M. Tsapatsis, *Angew. Chem.* **2007**, *119*, 7704; *Angew. Chem. Int. Ed.* **2007**, *46*, 7560.
[6] A. Corma, M. J. Diaz-Cabanas, M. Moliner, G. Rodriguez, *Chem. Commun.* **2006**, 3137.
[7] M. J. den Exter, H. van Bekkum, C. J. M. Rijn, F. Kapteijn, J. A. Moulijn, H. Schellevis, C. I. N. Beenakker, *Zeolites* **1997**, *19*, 13.
[8] J. Kuhn, J. Gascon, J. Gross, F. Kapteijn, *Microporous Mesoporous Mater.* **2009**, *120*, 12.
[9] D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257.
[10] J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477; S. Couck, J. F. M. Denayer, G. V. Baron, T. Remy, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.* **2009**, *131*, 6326.
[11] L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294.
[12] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, *J. Mater. Chem.* **2006**, *16*, 626.
[13] H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.* **2009**, *131*, 16000.
[14] H. Guo, G. Zhu, I. J. Hewitt, S. Qiu, *J. Am. Chem. Soc.* **2009**, *131*, 1646.
[15] Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang, J. Caro, *Angew. Chem.* **2009**, *122*, 558–561; *Angew. Chem. Int. Ed.* **2009**, *49*, 548–551.
[16] J. Gascon, S. Aguado, F. Kapteijn, *Microporous Mesoporous Mater.* **2008**, *113*, 132.
[17] C. S. Cundy, P. A. Cox, *Microporous Mesoporous Mater.* **2005**, *82*, 1.

[18] R. Ranjan, M. Tsapatsis, *Chem. Mater.* **2009**, *21*, 4920; T. M. Davis, T. O. Drews, H. Ramanan, C. He, J. Dong, H. Schnablegger, M. A. Katsoulakis, E. Kokkoli, A. V. McCormick, R. L. Penn, M. Tsapatsis, *Nat. Mater.* **2006**, *5*, 400.

[19] R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas, F. Schüth, *Angew. Chem.* **2009**, *121*, 7042; *Angew. Chem. Int. Ed.* **2009**, *48*, 6909.

[20] W. J. W. Bakker, F. Kapteijn, J. Poppe, J. A. Moulijn, *J. Membr. Sci.* **1996**, *117*, 57; J. van den Bergh, W. Zhu, J. Gascon, J. A. Moulijn, F. Kapteijn, *J. Membr. Sci.* **2008**, *316*, 35.

[21] J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau, S. Kitagawa, *J. Am. Chem. Soc.* **2009**, *131*, 12792.

[22] L. Q. Ma, C. Abney, W. B. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248.

[23] J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink, F. Kapteijn, *J. Catal.* **2009**, *261*, 75; D.-Y. Hong, Y. K. Hwang, C. Serre, G. Ferey, J.-S. Chang, *Adv. Funct. Mater.* **2009**, *19*, 1537; D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem.* **2009**, *121*, 7638; *Angew. Chem. Int. Ed.* **2009**, *48*, 7502.

[24] J. Juan-Alcañiz, E. V. Ramos-Fernandez, U. Lafont, J. Gascon, F. Kapteijn, *J. Catal.* **2010**, *269*, 229.

[25] R. Ameloot, L. Stappers, J. Fransaer, L. Alaerts, B. F. Sels, D. E. De Vos, *Chem. Mater.* **2009**, *21*, 2580.