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Are MOF membranes better than those made of zeolites?

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During the last few years, remarkable progress in the development of zeolite and MOF membranes have been obtained. Examples in the field of zeolite membranes are the development of LTA molecular sieve membranes as cation-containing aluminiumsilicate [1] and cation-free aluminiumphosphate [2] and ITQ-29 silica [3]. Examples in the field of MOF (metal organic framework) membranes are the ZIF (zeolitic imidazolate framework) membranes ZIF-7 [4], 8 [5], 22 [6] and 90 [7], all of them with hydrogen selectivity.

The above addressed progress in the development of zeolite and MOF membranes could be achieved by the rigorous application of sophisticated new and improved synthesis tools:

- Matching of the zeta potential between support and the precursor particles in solution: By docking of modifying molecules or control of the pH, a surface charge which electrostaticall attracts seeds or precursors in a seeding-free synthesis, can be established.

- Application of microwave heating in zeolite and MOF membrane synthesis: In combination with seeding, the quick heating up of the synthesis solution suppresses new nucleation, only the attached to the support seeds grow.

- Development of new seeding techniques using zeolite and MOF nano seeds: By using PEI (polyetherimine), seeds become fixed via H-bridging to the support.

- Covalent bonding between the growing zeolite and MOF layer and the support: By using di-socyanate or APTES (aminopropyltriethoxysilane), first the surface charge can be tuned, and second a covalent bond between the support and the seed/molecular sieve layer can be formed.

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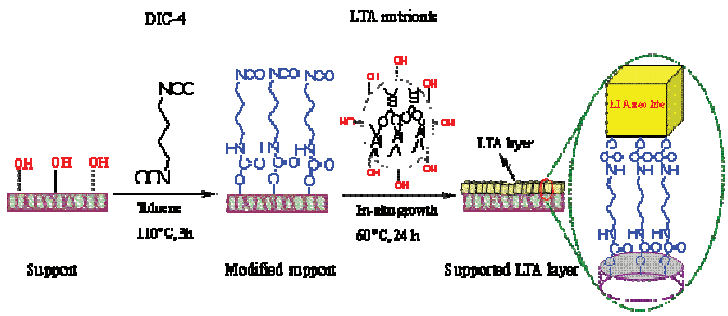
Covalent bonding of LTA seeds to an alumina support by using di-isocyanate as linker



(A. Huang , J. Caro, J. Mater. Chem. 21 (2011) 1142)

Whereas the synthesis tools for zeolite and MOF membranes are very similar, there exist severe differences between them:

- Because of the phenomenon framework flexibility, MOF membranes show no sharp cut-off in molecular sieving. On the other hand, this flexibility is helpful in matching the thermal expansion coefficients between membrane and support.
- The performance of MOF membranes can be predicted and designed by using the rough estimate “membrane selectivity = adsorption selectivity x diffusion selectivity” [8].
- Some MOFs are unstable without solvent, whereas for others – like ZIFs – a permanent porosity at temperatures 300 – 400°C, even in the presence of steam, is reported. When using MOFs as catalyst, oxidative degradation becomes an issue.
- Whereas mixed matrix membranes of zeolites/polymers showed no remarkable progress, MOF based mixed matrix membranes show revolutionary improvements since hydrophobic MOFs can interact perfectly with hydrophobic polymer matrices.

[1] A. Huang, J. Caro, *Facile synthesis of LTA molecular sieve membranes on covalently functionalized supports by using diisocyanates as molecular linkers,* J. Mater. Chem. 21 (2011) 11424-11429

[2] A. Huang, J. Caro, *Highly oriented, neutral and cation-free AlPO LTA: from seed crystal monolayer to a molecular sieve membrane,* ChemComm 47 (2011) 4201.

[3] A. Huang, J. Caro, *Steam-stable hydrophobic ITQ-29 molecular sieve membrane with H_2 selectivity prepared by secondary growth using Kryptofix 222 as SDA,* Chem. Commun. 46 (2010) 7748.

[4] Y. Li, F. Liang, H. Bux, A. Feldhoff, W. Yang, J. Caro, *Molecular Sieve Membrane: Supported Metal-Organic Framework with High Hydrogen selectivity,* Angew. Chem. Int. Ed. 49 (2010) 548.

[5] H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, Zeolitic Imidazolate Framework Membrane with Molecular Sieve Properties by Microwave Assisted Solvothermal Growth, JACS 131 (2009) 16000.

[6] A. Huang, H. Bux, F. Steinbach, J. Caro, *Molecular Sieve Membrane with Hydrogen Permselectivity: ZIF-22 in LTA Topology Prepared with 3-Aminopropyltriethoxysilane as Covalent Linker,* Angew. Chem. Int. Ed. 49 (2010) 4958.

[7] A. Huang, J. Caro, *Steam-stable zeolitic imidazolate framework ZIF-90 membrane with hydrogen selectivity through covalent functionalization,* JACS 132 (2010) 15562.

[8] H. Bux, C. Chmelik, J.M. van Baten, R. Krishna, J. Caro,*Novel MOF-membrane for molecular sieving predicted by IR-diffusion studies and molecular modeling,* Advanced Materials 22 (2010) 4741

Keywords: zeolite membrane, MOF membrane, molecular sieve membrane, gas separation