



IEAGHG Information Paper; 2012-IP17: Metal-Organic Frameworks

Background: Article in *Chemistry World* (<http://www.rsc.org/chemistryworld/2012/07/mof-gate-opens-selective-carbon-dioxide-gas-storage-door>)

Due to their various tuning possibilities metal-organic frameworks (MOFs) are recently discussed in the literature as promising adsorbents for CO₂ capture and storage. The linked article¹ refers to a publication from researchers of the University of Nottingham² who designed a MOF that selectively adsorbs CO₂ over C₂H₂ and CH₄ through the rotation of pyridyl rings acting as flexible pore gates.

MOFs are hybrid materials that combine complexed metal ions or metal clusters and organic ligands, thus forming a 1D, 2D or 3D coordination network as shown in Figure 1. They have a well-defined crystalline, highly porous structure that leads to superior surface areas compared to other solid adsorbents such as zeolites or activated carbons.

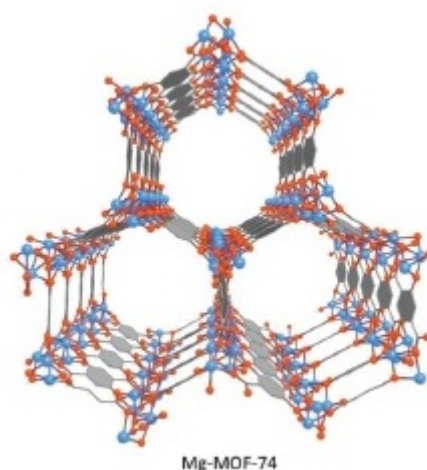


Figure 1 Crystal structure of Mg-MOF-74, one of the most promising MOFs for CO₂ capture, taken from Britt et al.³

Earlier this year two review articles have been published by different research groups discussing the recent advances in MOFs for CO₂ capture^{4,5}.

One of the most important advantages of MOFs is their extraordinary surface area resulting in a large capacity for gas adsorption. The large capacity also allows for an efficient packing. In addition, MOFs show a great structural and chemical tunability so they can be tailored for any type of CO₂ capture technology: post-, pre- or oxyfuel combustion capture. The tuning is usually done through careful selection of the metal ions and the organic linkers. Another option to enhance the selectivity of a MOF is functionalisation with nitrogen bases (e.g. amines), polarising functional groups or open metal cation sites. Finally, MOFs are a promising way to reduce the energy requirement for a CO₂ capture process. Due to their greatly reduced heat capacity compared to aqueous alkanolamine solutions, MOFs can be regenerated by temperature-swing-adsorption (TSA) using low-grade heat.

¹ Gray, *Chemistry World*, September (2012), 25

² Yang et al., *Nature Materials*, 11 (2012), 710-716

³ Britt et al., *Proc Natl Acad Sci USA*, 106 (2009), 20637-20640

⁴ Sumida et al., *Chem. Rev.*, 112 (2012), 724-781

⁵ Liu et al., *Greenhouse Gas Sci Technol.*, 2 (2012), 239-259



Their favourable properties make MOFs a promising performance enhancer for membrane materials as well. However, no mixed-matrix MOF membrane exceeded the best polymer membrane up to date.

Although MOFs show a generally good potential for application in CCS, there are a number of challenges and research gaps that need to be overcome before their widespread, large-scale application. Because the metal-ligand bond is relatively weak the chemical and thermal stability of MOFs is normally lower than that of other solid adsorbents. The mechanical properties are not yet fully explored with respect to CO₂ capture processes.

A huge problem for application in post-combustion capture is the moisture-sensitivity of the majority of the MOFs. In presence of H₂O the metal-ligand bond can hydrolyse and the resulting displacement can lead to a collapse of the whole framework structure. Increased water stability is crucial for application of MOFs in post-combustion capture because prior flue gas drying is costly and usually not feasible.

Synthesising MOFs in high yield and crystallinity remains a great challenge. At the moment most MOFs are synthesised from non-renewable sources with the help of toxic organic solvents like DMF.

It is also crucial that promising MOFs are studied under more realistic working conditions. Most research data in the literature stems from single-component isotherms or breakthrough experiments at temperatures below 298K. CO₂ adsorption capacities relevant for CCS are not directly reported and data for gas mixtures is only simulated from pure-component data.

The effect of impurities which are present in the different CO₂ capture processes (O₂, H₂S, SO₂, NO_x, CO, H₂O ...) is currently not investigated in any of the publications and thus remains unknown.

Apart from this there is the danger of “disimprovement” through over-tuning the MOF: the bond could be designed to strong for capture purposes or the applied functional groups may block the pores. In contrast, a strong irreversible bond is favourable for storage of CO₂. Furukawa et al.⁶ have synthesised MOF-210, which holds the CO₂ storage record at the moment. At room temperature and 50 bar the material showed a CO₂ uptake of 2400 mg/g and the highest reported BET surface area (6240 m²/g) for any crystalline material so far.

In conclusion:

MOFs promising for CO₂ capture have been successfully synthesised and tuned in the lab regarding CO₂ capacity and selectivity. Single-component isotherms, breakthrough experiments and modelling of gas mixtures have been performed, which preliminary recommend MOFs as CO₂ capture materials.

However, neither large-scale production nor tests under realistic CO₂ capture conditions have been demonstrated. Cost data that would allow for a comparison with competing capture technologies is also still missing.

As MOFs show in principal potential for use in CO₂ capture and storage IEAGHG will continue to watch the research and development in this area.

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⁶ Furukawa et al., Science, 329 (2010), 424