

Synthesis of metal-organic framework materials for CO₂ capture

Metal-organic frameworks (MOFs) are a fascinating class of crystalline materials consisting of metal ions or clusters coordinated to organic linkers to form one-, two-, or three-dimensional structures. They possess many attributes such as huge and accessible pore volumes (up to 6000 m³/g), ultralow densities, highly tailorable pore functionalities, dynamic and reversible structural properties. These characteristics make them promising absorber materials for the specific adsorption of high concentrations of CO₂. Presently, reducing the concentration of CO₂ in the Earth's atmosphere is one of urgent tasks for stabilizing the global climate change. The challenge facing us is to make improvements for MOFs to selectively catch and concentrate atmospheric CO₂.

Conversion of known MOFs into nano-sizes and hierarchical nanostructures. With excellent gas sorption, separation and storage properties exhibited by the bulk phase MOFs, their nanoscopic counterparts are expected to exhibit interesting, novel and even improved gas sorption properties. As the physical dimension reduces to the nanometer scale (usually less than 100 nm), the material will possess additional properties besides the bulk phase properties. For example, the improved guest molecule diffusion/mass transfer properties as well as high surface energy would benefit their applications in catalysis and gas capture. Nanocrystals are also prerequisites for the construction of hierarchical nanostructures and the further integration of the material into other catalytic supports. However, the research on nano-MOFs is still in its infancy, probably because of the synthetic challenges. In the beginning of this project, we will take some known MOFs with high affinity for CO₂ and stability to water to make nanocrystalline MOFs. MOF thin films with various thicknesses can be prepared a range of supports by dip-coating or an in-situ method. By further introducing physical templates such as colloidal crystals, we are aiming to prepare nano-MOF membranes or films with hierarchical porous structure and good mass transport properties for rapid capture and concentration of CO₂ from low atmosphere concentrations.

Formation of new MOFs for CO₂ capture. Enhancement of the affinity of MOFs for CO₂ can be achieved by functionalisation of either the surfaces of the material, or the internal pore surface. Surface modifications of nanocrystalline MOFs can enhance both stability and selectivity, and also control hydrophobic/hydrophilic properties. Functionalisation of the internal pores can be achieved by using appropriate functional linkers in the synthesis. Inclusion of both amino groups and halides has been shown to increase the affinity of MOFs for CO₂. Other functional chemicals, such as 2-aminopyrazine, 2,5-diaminopyrazine, can be added post-synthetically to coordinate unsaturated metal centers in MOFs. However, this modification often leads to the reduced absorbing capability due to the reduced pore volume in the modified materials. An alternative approach is to grow a functional mono-molecular layer or new MOF layers on the outer surfaces of nanocrystalline MOFs by in-situ or post-synthetic modification. This surface modification is expected to lead to both high selectivity and high capacity.