CO_2 capture with mixed matrix membranes containing (per-)fluorinated metal-organic framework fillers

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Mixed matrix membranes, constituted of a polymeric matrix and a filler material, are a promising technology for the energy efficient separation of CO_2 from either post-combustion flue gases or biogas. Among the various candidates as fillers, metal—organic frameworks (MOFs), crystalline and porous materials composed of metal ions and organic linkers, are emerging thanks to their hybrid inorgano-organic nature, which can guarantee good compatibility with the matrix, leading to improved permeability and selectivity.

The doMino project, funded by the Italian Government under the PRIN scheme, involves the National Research Council and the Universities of Pisa, Perugia and Torino. The aim of the project is to develop mixed matrix membranes containing (per-)fluorinated MOFs, which display improved affinity for CO_2 and resistance towards humidity. The project encompasses the synthesis of novel MOFs, the characterisation of their crystal structure and adsorption properties, the fabrication of mixed-matrix membranes and the investigation of their transport properties.

This contribution will focus on one of the sorbents investigated within the doMino project, namely F4_MIL-140A(Ce), a MOF based on Ce^{IV} as the metal and tetrafluoroterephthalic acid as the organic linker. The synthesis of this MOF was optimised to conveniently prepare multigram quantities starting from commercially available reagents in aqueous medium and mild conditions. F4_MIL-140A(Ce) displays a peculiar "phase change" CO_2 adsorption behaviour, as evidenced by its step-shaped adsorption isotherm, which endows it with an exceptional selectivity for CO_2 over N_2 and CH_4. The origin of this behaviour was investigated with a combination of advanced characterisation methods, finding that it is due to a cooperative rearrangement of the perfluorinated aromatic rings when a threshold pressure of CO_2 is reached. Mixed matrix membranes containing F4_MIL-140A(Ce) as the filler were prepared using the fluorinated polymer Hyflon, demonstrating that the "phase change" behaviour of the MOF is preserved in the membrane and observing an improvement in both CO_2/N_2 and CO_2/CH_4 selectivity. Current efforts are aimed at optimising the morphology and surface chemistry of F4_MIL-140A(Ce) to maximise its dispersibility within the polymeric matrix and further improve the separation performance.