Crystal engineered hybrid ultramicroporous materials for single-step ethylene purification from C_2-CO_2 ternary mixture

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Mankind is now in the "*age of gas*"[1] and there are urgent needs in gas purification that will likely only be solved by a new generation of physisorbent porous materials that offer reduced cost and superior performance. Engaging the principles of crystal engineering, hybrid ultramicroporous materials, HUMs (pore size < 0.7 nm) [2], by means of combining small pores (< 0.7 nm) with strong electrostatics offer an ideal sorbent platform suited for tight-fit of the target sorbate, resulting in performance benchmarks over the recent years [3, 4]. However, due to narrow pore networks imposing steric restrictions, crystal engineering of modular HUMs on account of organic ligand functionalisation has remained largely elusive.

Moving one step ahead of the synergistic sorbent separation technology [5], herein we address single-step purification of ethylene (C_2H_4), the highest volume product of the chemical industry, by crystal engineering of two HUMs of formula $[Ni(pyz\text{-}NH_2)_2(MF_6)]_n$ (pyz-NH_2 = aminopyrazine, 17; M = Si, Ti), **MFSIX-17-Ni** [6]. Isostructural pyrazine analogues (**SIFSIX-3-Zn** [7], **SIFSIX-3-Ni** [8]) are the benchmark physisorbents for trace carbon capture but are unsuited for acetylene capture. No single physisorbent has the requisite selectivity to purify C_2H_4 from ternary C_2-CO_2 mixtures (C_2H_4/C_2H_2/CO_2) under ambient conditions until now. Indeed, both **MFSIX-17-Ni** sorbents produce polymer grade ethylene (> 99.95% purity) from a 1:1:1 ternary mixture (**Figure 1**). Regarding insights for the future, we attribute the observed properties to the unusual binding sites in **MFSIX-17-Ni** that offer comparable affinity to both CO_2 and C_2H_2, thereby enabling coadsorption of C_2H_2 and CO_2. *In situ* synchrotron x-ray diffraction, *in situ* IR spectroscopy and molecular modelling provide insight into these binding sites and why they differ from those of the pyrazine-linked materials.

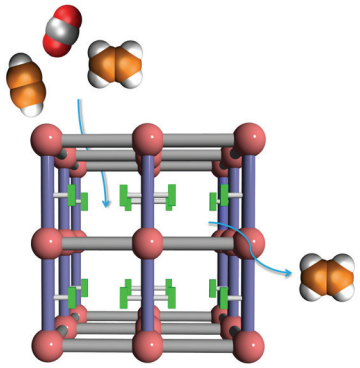

Figure 1. Schematic illustration of **MFSIX-17-Ni** that exhibits single-step C_2H_4 purification by simulatneous CO_2 and C_2H_2 removal.

Keywords: porous materials; crystal engineering; coordination networks; physisorption; ethylene purification

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