EFFICIENT OLEFIN/ALKANE SEPARATION VIA IN-SITU CYANO-TRANSFORMED METAL–ORGANIC FRAMEWORKS

Chaohui He[a], Ben Pilgrim[b]

[a]Department of Chemistry, North University of China, Taiyuan, China
[b]School of Chemistry, University of Nottingham, Nottingham, UK

Olefin/alkane separation is among the most energy-intensive yet indispensable processes in the global chemical industry and has been identified as one of the "seven chemical separations to change the world."[1]Herein, we report a versatile in-situ ligand transformation strategy to construct a series of metal–organic frameworks (MOFs) with precisely tailored pore environments for highly efficient C_2 and C_3 hydrocarbon separations. NUC-201 undergoes a site-specific cyano-to-tetrazolyl transformation during synthesis, generating an ultramicroporous framework enriched with nitrogen-active sites. Owing to the synergistic effect of pore confinement and strong host–guest interactions, NUC-201 exhibits an exceptional ethane uptake of 36.4 $cm^3\ g^{-1}$ at 0.01 bar, representing the highest reported low-pressure ethane adsorption capacity to date, surpassing state-of-the-art MOFs including MAF-49, $Fe_2(O_2)$(dobdc), and TYUT-17[2]. In addition, two derivative MOFs (NUC-202 and NUC-203) were obtained via in-situ cyano-to-amide/imidate conversion combined with ligand functionalization. Through precise pore aperture engineering enabled by bromo substitution, NUC-203 achieves effective molecular size-sieving, completely excluding propane while selectively adsorbing propylene, resulting in highly efficient C_3H_6/C_3H_8 separation. This work highlights in-situ ligand transformation as a powerful platform for atomic-level pore regulation, offering new insights into structure–function relationships and opening a promising avenue for next-generation, energy-efficient olefin/alkane separations.

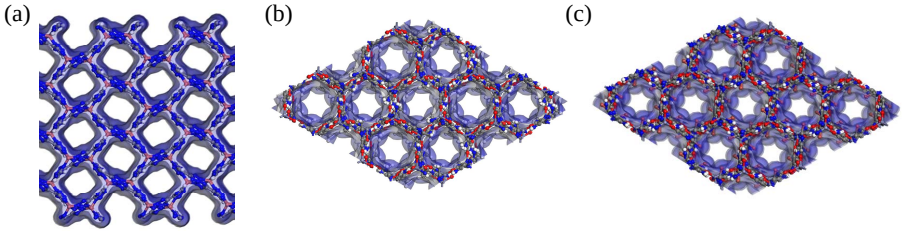

Fig. 1 The crystal structure of (a) NUC-201, (b) NUC-202 and (c) NUC-203.

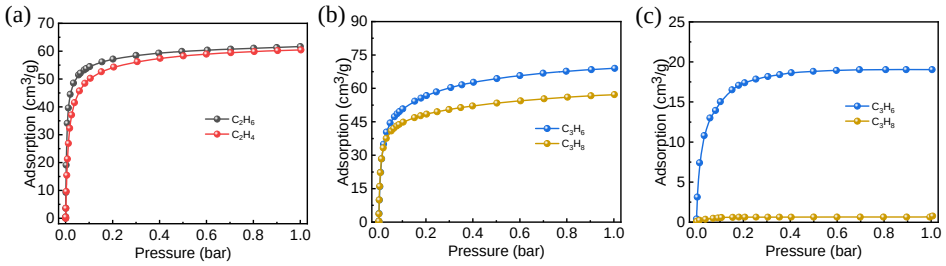

Fig. 2 The single-component adsorption isotherms of (a) NUC-201, (b) NUC-202 and (c) NUC-203 at 298 K.

[1] Sholl, D. S.; Lively, R. P. Nature, 2016, 532, 435-437.

[2] Zhang, L.; Yu, B.; Wang, M.; Chen, Y.; Wang, Y.; Sun, L. B.; Zhang, Y. B.; Zhang, Z.; Li, J.; Li, L. Angewandte Chemie, 2025, 137, e202418853.