Metal-Organic Framework Membranes for Gas Separation

An aluminium-carboxylate-based metal-organic framework (MOF), CAU-10-H, was utilized to fabricate a dense MOF membrane for CO_2 capture. The pore aperture size of this MOF is identified as 3.2 Å, which is ideal to separate CO_2 from N_2 and CH_4.

Metal-organic frameworks (MOF) possess adjustable pore topologies and interior functionality, and MOF membranes are known to have a great potential in gas separations. A molecular-sieving effect is the principal mechanism for gas separations with membranes. MOF with a controllable pore-limiting diameter (PLD) can be engineered to achieve high performance for such membrane gas separation. This work led by Dun-Yen Kang (National Taiwan University) aimed to fabricate MOF membranes with excellent gas-permeative selectivity. They focused on an aluminium hydroxide isophthalate MOF, CAU-10-H, with a rigid pore structure (PLD = 3.2 Å) for the adsorption of various gas molecules. This MOF was comprised of aluminium as metal cluster and isophthalic acid as organic linker (**Fig. 1**). The chemical formula of this compound is $Al(OH)(C_8H_4O_4)$.

Kang's group conducted time-resolved powder X-ray diffraction (XRD) measurements for various gases to investigate a possible structural change of CAU-10-H using the facilities at **TPS 09A**. These XRD patterns were obtained *in situ* with an X-ray source of synchrotron radiation, which allows for a direct comparison of the signal intensities and positions between the patterns. The results from the measurements under CO_2, N_2 and CH_4 are summarized in **Fig. 2**. They noticed a significantly decreased signal intensity in time-resolved patterns of CAU-10-H with partial pressure of CO_2 increasing from 0.005 to 3 bar (**Fig. 2(a)**, see next page); this substantial drop in intensity indicated the adsorption of CO_2 in CAU-10-H. The adsorption of gas molecules in the cage of MOF decreased the contrast of electron density inside the microporous materials, resulting in a diminished intensity of the powder XRD patterns. They further identified the structure of CAU-10-H after exposure to CO_2 for 30 minutes using Rietveld refinement. The result showed that the crystal structure of CAU-10-H remained nearly unchanged after exposure to CO_2 even though the signal intensity decreased (**Fig. 2(b)**). The rigid pore structure of CAU-10-H makes it an ideal material for CO_2 separation because of a molecular-sieving effect. In contrast to CO_2 measurements, there was no considerable difference in signal intensity for XRD patterns under N_2 and CH_4 (**Figs. 2(c) and 2(d)**). This condition indicates that the uptakes of N_2 and CH_4 in CAU-10-H were smaller than the uptake of CO_2.

The permeation measurements on a CAU-10-H membrane of single gases for H_2, CO_2, N_2 and CH_4 and mixed gas for CO_2 and CH_4 are summarized in **Fig. 3** (see next page). These gas-permeance results indicated that there was a permeation cutoff between CO_2 and N_2 (**Fig. 3(a)**). The ideal selectivity, defined as the permeance ratio between two gases, of CAU-10-H for every gas pair (H_2/CH_4, CO_2/N_2, CO_2/CH_4 and N_2/CH_4) considerably deviated from the Knudsen selectivity (**Fig. 3(b)**), indicating that the formation of pinholes in a CAU-10-H membrane was successfully suppressed; the transport of gases inside CAU-10-H was properly controlled by the intrinsic property of the rigid pore structure of CAU-10-H.

In summary, Kang's group proposed that utilizing the rigid pore structure of MOF under a varied gas atmosphere

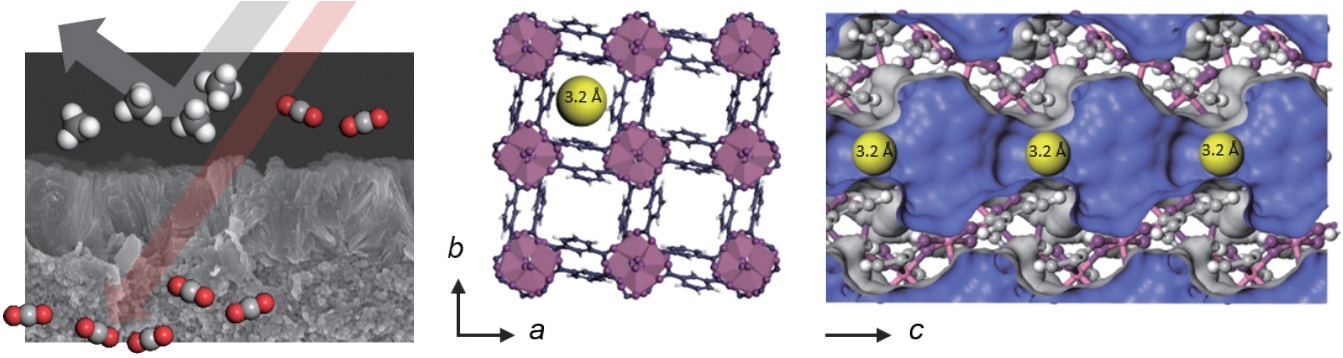

Fig. 1: Aluminium hydroxide isophthalate MOF for membrane separation. [Reproduced from Ref. 1]

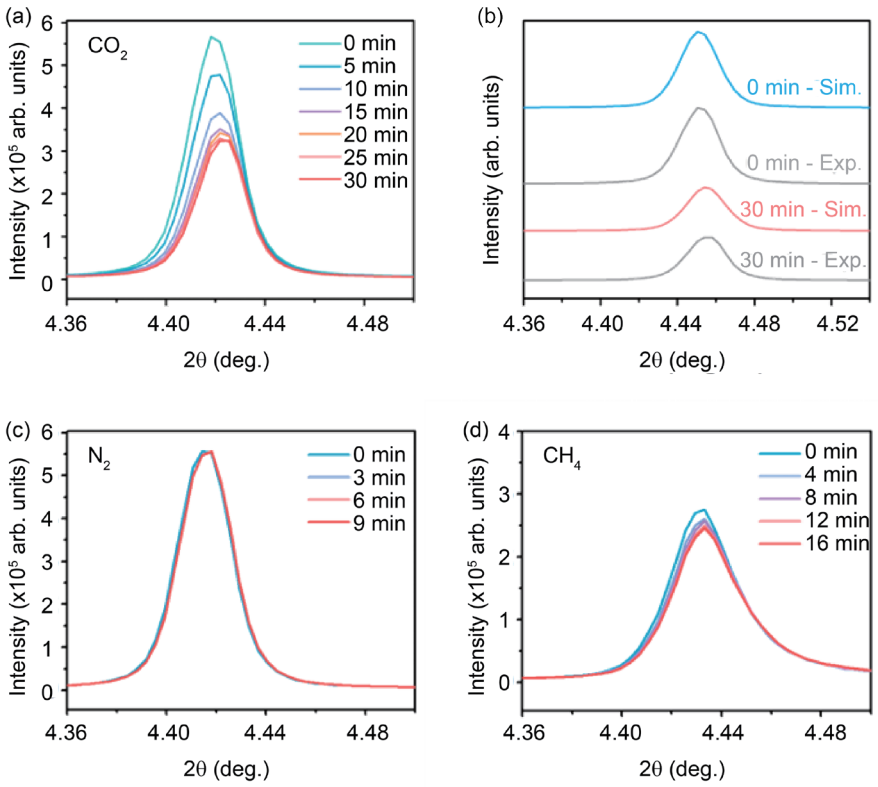

Fig. 2: (a) Time-resolved powder XRD patterns of CAU-10-H exposed to CO_2 under 3 bar. (b) Experimental and simulated XRD patterns of CAU-10-H before and after exposure to CO_2 under 3 bar for 30 minutes. (c,d) Time-resolved powder XRD patterns of CAU-10-H exposed to N_2 and CH_4 under 3 bar. [Reproduced from Ref. 1]

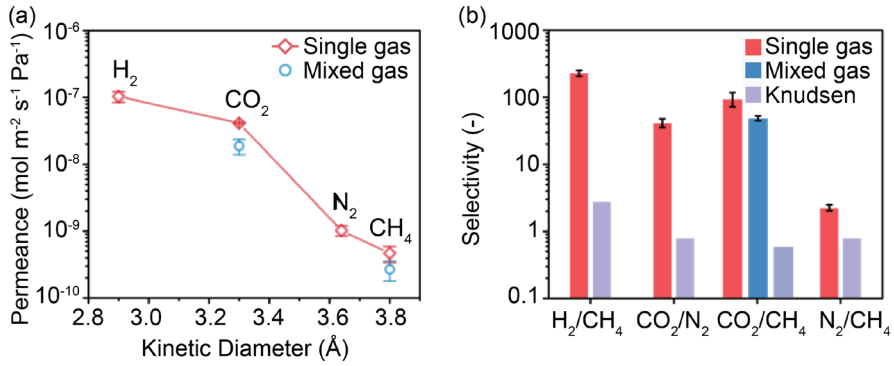

Fig. 3: Single-gas and mixed-gas permeation test on CAU-10-H. (a) Gas permeance of H_2, CO_2, N_2 and CH_4 and (b) selectivity of gas pairs. [Reproduced from Ref. 1]

can achieve a high gas separation performance. These observations were also identified with the molecular simulation results in this work. The strategy of using rigid MOF with an ideal size of pore aperture could open possibilities to advance new MOF materials for membrane separations. (Reported by Da-Shiuan Chiou, National Taiwan University)

This report features the work of Dun-Yen Kang and his collaborators published in Adv. Funct. Mater. ***31****, 2006924 (2021).*

TPS 09A Temporally Coherent X-ray Diffraction

- XRD
- Materials Science, Chemical Engineering, Membrane Gas Separation

Reference

1. D. S. Chiou, H. J. Yu, T. H. Hung, Q. Lyu, Chang, C. K., J. S. Lee, L. C. Lin, D. Y. Kang, Adv. Funct. Mater. **31**, 2006924 (2021).