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Highly permeable and selective amino-functionalized MOF CAU-1 membrane for CO_2/N_2 separation

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A thin tubular CAU-1 membrane of 2-3 μm exhibiting high CO_2 permeance up to 1.34×10^{-6} mol m^{-2} s^{-1} Pa^{-1} and CO_2/N_2 selectivity of 17.4-22.8 for CO_2/N_2 mixtures was achieved, demonstrating for the first time amino-functionalized MOFs membranes can provide high CO_2/N_2 selectivity and posses potential for CO_2 capture from flue gas.

The capture of CO_2 from fossil fuel combustion flue gas is of great significance to our sustainable civilization.[1] Membrane separation is considered as alternative technology to current amino absorption for CO_2 capture due to the low energy requirements. More recently, it is demonstrated that metal-organic frameworks are appealing candidates for molecular separation particularly for CO_2 capture as highlighted in several reviews.[2] Because of the strong interaction of CO_2 with the metal open centres or the ligand of the MOFs remarkably high CO_2 adsorption capacity/selectivity over the non-polar gases such as CH_4 and N_2 were reported for MOFs materials such as HKUST-1,[3] Al containing MOFs,[4] and the series of isostructural framework M2 (dhtp) (CPO-27 or MOF-74)[5] and zeolitic frameworks ZIFs.[6] Among MOFs materials, amino-functionalized MOFs are particularly interesting for CO_2 capture due to the favorable acid-basic interaction between CO_2 and amino group that can largely promote the CO_2 adsorption. Extremely high even unprecedented high CO_2 adsorption capacity/selectivity was reported for amino functionalized MOFs of bio-MOF-11[7], NH_2-MIL-53[8] and CAU-1[9] etc. In the form of powders, MOFs materials as adsorbents have shown high CO_2 adsorptive separation efficiency from N_2 and CH_4. The unique adsorption properties and structures make MOFs exciting fillers for development of mixed matrix membranes with highly enhanced selectivity and permeability for CO_2 capture[10] and other gas separation.[11] The excellent preferential CO_2 adsorption ability is expected to lead to high CO_2 perm-selectivity over N_2 for MOFs membrane particularly for the amino group containing MOFs membrane. However, so far only the MOF-5 membrane showed efficient separation for CO_2/N_2 mixtures under high pressure and CO_2 content conditions[12] and ZIF-69 membrane exhibited CO_2/N_2 selectivity of 6.3.[13] Instead, other reported MOFs membranes including small and large pore size have shown a poor CO_2/N_2 separation selectivity around 1 for either single gas or mixture system despite of their high adsorption selectivity.[14]

For the membrane separation, the permeation selectivity is governed by a combination of adsorption and diffusion selectivity. The strong interaction of CO_2 with MOFs can largely enhance the CO_2 adsorption capacity but probably reduced the mobility of CO_2.[14b, 15] This has ramifications for membrane separation. On the other hand, there is increasing evidence that for the small pore size MOFs with the flexible framework and apertures result in reversible diffusivity selectivity of CO_2 over N_2 that is against the molecular sieving mechanism.[14b, 14d] The interaction affinity and pore structure properties play intricate roles in the separation efficiency of MOFs membrane.

The amino-decorated 12-connected $[Al_4(OH)_2(OCH_3)_4(H_2N\text{-}BDC)_3]\cdot xH_2O$ CAU-1 reported by Stock's group[16] is an appealing membrane candidate for molecular gas applications. CAU-1 is built from unprecedented aluminium-based octameric building units, which are connected through twelve aminoterephthalate linkers to form a three-dimensional microporous framework that involves distorted octahedral and tetrahedral cages as shown in Fig. S2. (ESI†) Access to the cages is only possible through small triangular windows with a free aperture of 0.3-0.4 nm. In addition, CAU-1 shows relatively rigid framework and high thermal stability up to 573 K[16]. The framework functionality with unprecedented high CO_2 adsorption capacity[9] in combination with the small pore aperture and rigid framework prompted us to study the CAU-1 membrane for CO_2 separation from flue gas.

Herein, we reported the successful synthesis and high separation performance of the CAU-1 membrane supported on the asymmetric α-Al_2O_3 tube for CO_2/N_2 mixtures at flue gas conditions by seeded growth method. Zhou et al. synthesized CAU-1 membrane (denoted as CAU-1-Z) but did not obtain the desired CO_2/N_2 selectivity due to activation problem.[17] To the best of our knowledge, it is the first amino-functionalized MOFs membrane exhibiting a high CO_2 selectivity over N_2 with high CO_2 permeance for separation of CO_2/N_2 mixtures.

Asymmetric porous α-Al_2O_3 tubes with α-Al_2O_3 buffer layers of a nominal pore size of 200 nm were used as supports. The uniform rice-body-like CAU-1 crystal seeds of 200-300 nm as shown by the XRD patterns (Fig. S3b, ESI†) and SEM images (Fig. S4a, ESI†) were prepared according to the literature recipe[16] (for details see ESI†). The crystal seed size matched with the pore size of the asymmetric α-Al_2O_3 support (Fig. S4, ESI†). The weak XRD pattern (Fig. S3c, ESI†), the SEM images (Fig. S4b, c, ESI†) and the optical pictures (Fig. S5, ESI†) revealed the formation of a very thin and continuous CAU-1 seed layer. The CAU-1 membrane M1 was grown from a concentrated synthesis solution using mixture solvents of ethanol and methanol[18] by much shorter time of crystallization reaction (for details see ESI†) compared with those of CAU-1-Z membranes.[17]

The XRD pattern of the CAU-1 membrane M1 represented the characteristic peaks of CAU-1 and α-Al_2O_3 (Fig. S3d, ESI†), confirming the formation of pure CAU-1 layer on the α-Al_2O_3 support without the presence of other impure phase. SEM images of the M1 (Fig. 1) revealed that the support surface was fully covered by compact and well inter-grown cube-shaped crystals.

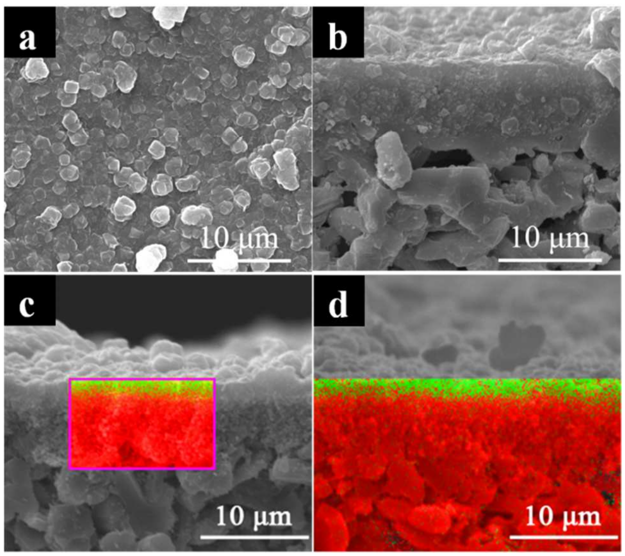

Fig. 1 SEM image of the surface and cross-section of CAU-1 membrane (a, b) and EDS mapping of CAU-1 membrane: green C; red Al(c, d).

EDS analysis further revealed that there was a softly transition of C and Al signals between the CAU-1 layer and the alumina support (Fig. 1c, d and Fig. S6, ESI†) indicating the formation of CAU-1 within the particles of α-Al_2O_3 buffer. The α-Al_2O_3 buffer can act as the secondary aluminum source to react with 2-amino-1, 4-benzenedicarboxylic acid forming CAU-1 crystals as found by Zhou et al.[17]. This explained the excellent adhesion strength between the CAU-1 membrane and the support as SEM images revealed. As evidenced by the profile of EDS carbon content, the thickness of the membrane M1 was thin, about 2-3 µm.

Fig. 2 shows the permeance of single gas as a function of kinetic diameter at room temperature and a pressure difference of 0.1 Mpa. CO_2 had the highest permeance, as high as 1.32×10^{-6} mol m^{-2} s^{-1} Pa^{-1} though H_2 is the smallest molecule. The ideal selectivity of CO_2/H_2, CO_2/N_2, CO_2/CH_4, CO_2/SF_6 system was 2.6, 26.2, 14.8 and 79.3, indicating the permeation of CO_2 through the CAU-1 membrane was governed by the preferential adsorption. On the other hand, the ideal selectivity of H_2/N_2, H_2/CH_4 and H_2/SF_6 system was 9.7, 5.4 and 29.2, respectively, suggesting the molecular sieving mechanism for these non-adsorbable gases. The high CO_2 permeance and selectivity resulted from the high adsorption uptake of CO_2 promoted by the strong interaction of acid-basic interaction between CO_2 and amino group in the framework of the MOFs as supported by the adsorption isotherms (Fig. S7, ESI†). The CAU-1 powders collected from the bottom of the membrane autoclave exhibited unprecedented high CO_2 adsorption capacities of 6.79 mmol g^{-1} and 3.29 mmol g^{-1} at 1 atm and at 273 K and 298 K, respectively, consistent with those reported by Si et al.[9] Besides, the thin membrane thickness contributed to the high gas permeance as well.

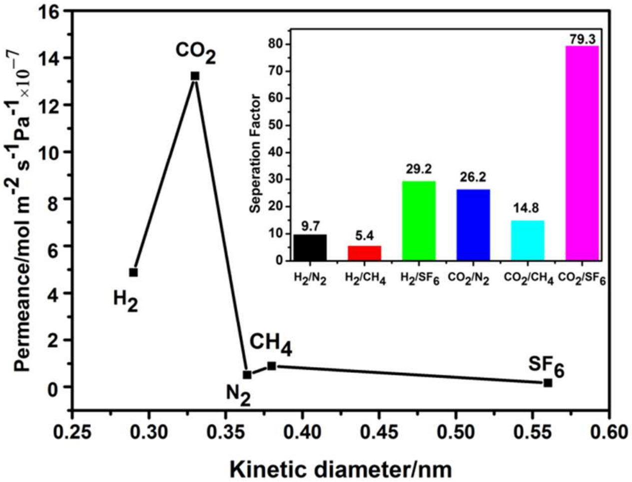

Fig. 2 Single gas permeances of H_2, N_2, CH_4, CO_2 and SF_6 through the CAU-1 membrane and the ideal separation factors for the corresponding gas pairs

The separation performance of the membrane M1 was further evaluated using the CO_2/N_2 mixtures with various CO_2 concentration at 298 K keeping the feed gas mixture under atmosphere pressure and permeate side sweeping with Ar (for details see ESI†). As shown in Fig.3, the CO_2 permeance increased largely with increasing CO_2 content in the feed, particularly at CO_2 content of 0.7 while N_2 increased slightly with increasing feed CO_2 content. Consequently separation factor of CO_2/N_2 increased slightly from 17.4 to 22.8. At CO_2 molar fraction of 0.1-0.2 that is flue gas composition, CO_2 permeance was 5.0-5.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with CO_2/N_2 separation factor of about 17.4. At high CO_2 molar fraction of 0.9, CO_2 permeance of 1.34×10^{-6} mol m^{-2} s^{-1} $Pa^{-1}$and CO_2/N_2 separation factor of 22.8 were obtained. As a result, the separation indexes of the CAU-1 membrane for the CO_2/N_2 mixtures are advantageous over most of the reported zeolite and all the MOFs membranes except MOF-5 membrane as shown in Table S1 (ESI†).

The CO_2 permeance trend through the CAU-1 membrane on the CO_2 feed content is similar to that of the MOF-5 membrane[12], but opposite to that of zeolite membrane[19]. This is because the adsorption isotherm for CO_2 on CAU-1 within the pressure of 700 mmHg is fairly linear, the effect of increasing feed CO_2 pressure on the CO_2 solubility (the slope of the adsorption isotherm) should be negligible[12] while zeolite membranes generally shows a negative effect of increasing feed CO_2 content on the solubility[19].

The MOF-5 membrane can preferentially permeate CO_2 over N_2 with the separation factor up to 60 only at high CO_2 feed molar fraction above 0.65 and high feed pressure above 335 KPa, otherwise, the separation factors were around 1 due to the lower adsorption uptake of CO_2 at low pressure. In contrast, the CAU-1 membrane can efficiently separate CO_2 from N_2 over wide CO_2 composition range at room temperature and at atmosphere pressure, providing high potential for CO_2 capture from flue gas.

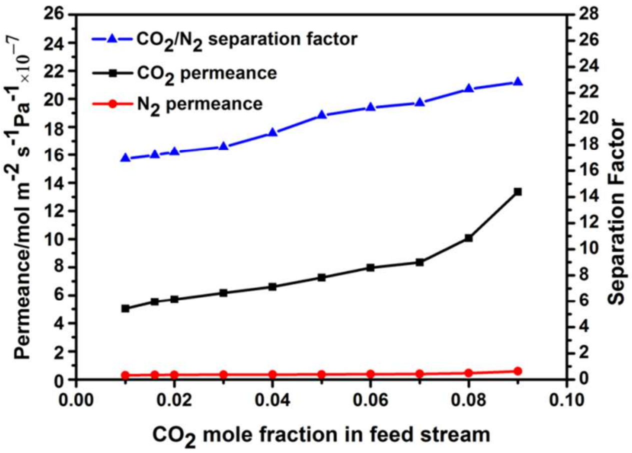

Fig. 3 Effect of the CO_2 feed composition on the permeance and separation factor for CO_2/N_2 binary mixture through the CAU-1 membrane at 298 K with a feed pressure of 0.1MPa.

The reproducibility of our CAU-1 membrane was good as shown in Table S2 (ESI†). Astonishingly, the CAU-1-Z membrane preferentially permeated N_2 over CO_2 with N_2/CO_2 selectivity of 1.38, opposite to our results. Note that the CO_2 uptake of CAU-1-Z powder was 75 cm^{-3} g^{-1} and 40 cm^{-3} g^{-1} at 273 K and 298 K, respectively, only about 60% that of our CAU-1 powder at the same pressure, indicating the incomplete activation of CAU-1-Z that was involved with washing using water (our membrane M1 was washed with methanol instead of water) and vacuuming at 393 K. Compared to methanol, empting the water molecules interacted with amino group required much higher temperature such as at 523 K as reported by Si et al.[9] The reduced CO_2 adsorption uptakes largely influence the CO_2 permeation through the membrane.

In summary, a thin tubular CAU-1 membrane of 2-3 µm supported on the asymmetric α-Al_2O_3 tube was rapidly synthesized from a relatively concentrated solution. In a wide range of CO_2 content the CAU-1 membrane showed high CO_2/N_2 selectivity and high CO_2 permeance for CO_2/N_2 mixtures at atmosphere pressure and room temperature. To the best of our knowledge, the CAU-1 membrane is the first reported amino-functionalized MOFs membrane exhibiting high CO_2 permeance and efficient separation ability for CO_2 capture, demonstrating the potential of amino-MOFs membranes in CO_2 capture from flue gas.

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Notes and references

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