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A highly permeable and selective zeolitic imidazolate framework ZIF-95 membrane for H₂/CO₂ separation†

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Making use of the preferred adsorption affinity and capacity to CO₂ as well as the highly porous structure with huge cavities of 2.4 nm, a highly permeable and selective ZIF-95 molecular sieve membrane was developed for the separation of H₂ from CO₂.

As a clean and efficient energy source related to global climate change, energy security, and reduction of local air pollution, the demand for hydrogen has been increasingly growing in recent years.¹ The majority of hydrogen is produced *via* steam-methane reforming (SMR) followed by water-gas shift (WGS). The resulting gas mixture is mainly composed of H₂ and CO₂ which are principally separated by pressure swing adsorption (PSA).² In comparison with conventional separation methods like PSA, membrane-based separation has been considered to be the most promising alternative because of its low energy consumption, ease of operation, and cost effectiveness.³ Since organic polymer membranes suffer from instability problems in contact with solvents or at high temperatures, inorganic membranes are more promising under harsh separation conditions.⁴ So far, H₂-permselective inorganic membranes, typically dense Pd-based metal membranes,⁵ microporous silica membranes,⁶ carbon membranes,⁷ and zeolite membranes^{8–11} have been developed for the separation of H₂ from CO₂. The Pd membranes display high H₂ selectivity and H₂ permeance at high temperature, but they easily degrade in contact with CO or H₂S.⁶ In addition, the high Pd cost is another bottleneck for the wide application of Pd-based membranes. The microporous silica membranes have amazing H₂ selectivity over other small molecular gases,⁷ but suffer from instability if traces of steam are present.¹² Carbon membranes are too fragile to be used in practice.¹³ Due to intercrystalline defects and relatively large pore sizes in comparison with the kinetic

diameters of H₂ (0.29 nm) and CO₂ (0.33 nm), the zeolite membranes usually show low H₂/CO₂ selectivity.^{8–11} Therefore, the development of thermally and hydrothermally stable microporous membranes with high H₂ permselectivity is highly desired.

Microporous metal–organic frameworks (MOFs) have attracted intense attention as fascinating candidates for the fabrication of membranes/films due to their highly diversified pore structures and pore sizes as well as specific adsorption affinities.^{14–17} In particular, zeolitic imidazolate frameworks (ZIFs) have emerged as a novel type of crystalline porous material for the preparation of superior molecular sieve membranes attributed to their zeolite-like properties such as permanent porosity, uniform pore sizes, and exceptional thermal and chemical stability.^{18,19} Very recently, we have developed a series of supported ZIF membranes, including SOD-type ZIF-7,²⁰ ZIF-8²¹ and ZIF-90^{22,23} as well as LTA-type ZIF-22.²⁴ These ZIF membranes have shown promising separation selectivities, but the permeances are relatively low for practical applications. Therefore, the challenge is to prepare ZIF membranes with high permeance, while maintaining their high separation selectivity. So far, there have been only a few reports on highly permeable ZIF membranes.²⁵

Recently, Yaghi and co-workers have developed a novel POZ topology porous ZIF called ZIF-95 with an unprecedented structural complexity through solvothermal reaction of zinc(II) salt and 5-chlorobenzimidazole (cbIM).²⁶ It is reported that ZIF-95 is not only highly thermally stable up to 500 °C but also shows permanent microporosity with constricted windows (~0.37 nm) and huge cavities (2.4 nm). Especially, ZIF-95 shows a high affinity and capacity for CO₂ adsorption, which can be promising for CO₂ capture.²⁶ Actually, various MOFs have been proposed as promising candidates for CO₂ adsorption, capture and storage.^{27–30} To the best of our knowledge, there is no report on the fabrication of a CO₂ captive MOF membrane for the separation of H₂–CO₂ mixtures. In the present work, we report synthesis and gas separation performance of a highly permeable and selective ZIF-95 molecular sieve membrane as a CO₂ captor for the separation of H₂/CO₂ at high temperatures. For ZIF structures with huge cavities interconnected by small windows, the strongly adsorbed component is immobilized in the big cavities and permeation becomes diffusion-controlled in favor of the highly mobile component.

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It can be expected, therefore, that a ZIF-95 can be fabricated as a membrane for the separation of H₂-CO₂ mixtures since CO₂ is preferentially adsorbed, and H₂ can pass through the membrane, as shown in Fig. S1 (ESI†).

After solvothermal reaction for 3 days at 120 °C, the surface of an APTES-modified asymmetric macroporous α -Al₂O₃ disk has been completely covered by typically tetragon-shaped ZIF-95 crystals (Fig. S2a-c, ESI†).²⁶ Unlike the conventional MOF or zeolite membranes growth, the tetragonal plates do not grow layer-by-layer, but interlock to form a novel membrane structure like folded filters (circle in Fig. S2c, ESI†). Such a large corrugation of the membrane layer can increase the effective surface for permeation and hence promote a high gas permeance. From the cross-sectional view shown in Fig. S2d (ESI†), it can be seen that the ZIF-95 layer is well intergrown as a continuous membrane with a thickness of about 30 μ m. Similar to our previous reports,^{22,24} APTES modification of alumina supports before solvothermal synthesis is helpful in forming a continuous layer. No continuous ZIF-95 layer can be formed on the non-APTES-modified α -Al₂O₃ disk by *in situ* growth (Fig. S3, ESI†).

After on-stream activation at 325 °C using an equimolar H₂-CO₂ mixture in the Wicke-Kallenbach permeation apparatus (Fig. S4, ESI†), the volumetric flow rates of the single gases H₂, CO₂, N₂, CH₄ and C₃H₈ as well as the equimolar binary mixtures of H₂ with CO₂, N₂, CH₄ and C₃H₈ were measured through the activated ZIF-95 membrane by using the Wicke-Kallenbach technique. The permeances and separation factors are summarized in Table S1 (ESI†). Fig. 1 shows the permeances of the single gases through the activated ZIF-95 membrane as a function of the kinetic diameters of the permeating molecules. As shown in Fig. 1 and Table S1 (ESI†), H₂ has the highest permeance of 2.46×10^{-6} mol m⁻² s⁻¹ Pa⁻¹ due to its small kinetic diameter of 0.29 nm. The single gas permeances through the ZIF-95 membrane follow the order: H₂ > N₂ > CH₄ > CO₂ > C₃H₈, which mainly corresponds to their kinetic diameters with the exception of CO₂. As reported previously,²⁶ ZIF-95 has a high affinity and capacity for CO₂ adsorption due to strong quadrupolar interactions of carbon with nitrogen atoms present in the linkers of ZIF-95, leading to a strong adsorption interaction but lowering the diffusional mobility, which results in the end in a lower CO₂ permeance

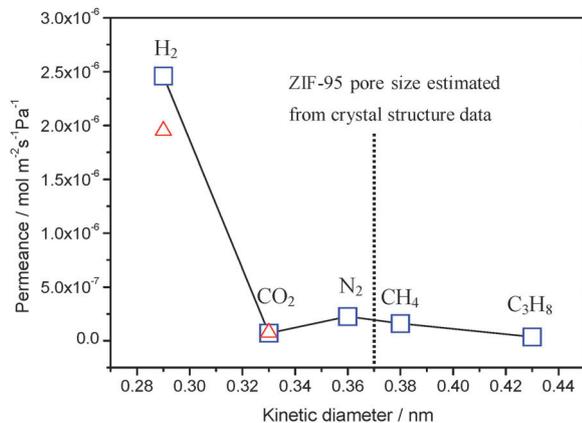


Fig. 1 Single gas permeances of the ZIF-95 membrane as a function of the kinetic diameter at 325 °C. The triangles show the permeances of H₂ and CO₂ in an equivalent binary mixture.

than found for other small molecules like N₂ and CH₄. The strong adsorption affinity of ZIF-95 to CO₂ is also confirmed by a simulation study of the gas adsorption isotherms which coincide with the measured ones (Fig. S5, ESI†). It should be noted that similar to the reported MOF membranes²⁰⁻²⁴ or MOF crystals,^{31,32} molecules like CH₄ and C₃H₈ with a kinetic diameter larger than the crystallographic pore size of ZIF-95 can pass through the membrane due to the well-known lattice flexibility of MOFs. The ideal separation factors of H₂ from CO₂, N₂, CH₄ and C₃H₈ are 34.9, 10.8, 15.3 and 66.8, respectively, suggesting that the ZIF-95 membrane displays a high hydrogen permselectivity.

The performance of the ZIF-95 membrane was confirmed by the separation of equimolar gas mixtures at 325 °C and 1 bar. For the 1 : 1 binary mixtures, the mixture separation factor for H₂/CO₂ is 25.7, which by far exceeds the corresponding Knudsen coefficient (4.7). According to the simulated adsorption isotherms of the equimolar H₂-CO₂ mixture in ZIF-95 at 25 °C (Fig. S6, ESI†), CO₂ is predominantly adsorbed over H₂ in the entire pressure range because CO₂ has a far stronger interaction with ZIF-95 than H₂ (Fig. 2), which is helpful in trapping CO₂, and therefore, enhances the H₂/CO₂ selectivity. Compared with the H₂ single gas permeance, the H₂ permeance from H₂-CO₂ mixtures shows a slight reduction, with H₂ permeances of 1.95×10^{-6} mol m⁻² s⁻¹ Pa⁻¹, indicating that the faster diffusing H₂ molecules are inhibited by the stronger adsorbed CO₂ molecules. For the 1 : 1 binary mixtures, the mixture separation factors of H₂/N₂, H₂/CH₄ and H₂/C₃H₈ are 10.2, 11.0 and 59.7, which again exceed the corresponding Knudsen coefficients (3.7, 2.8 and 4.7). To the best of our knowledge, our ZIF-95 membrane shows by far the highest H₂/CO₂ selectivity for MOF and zeolite membranes (Table S2, ESI†). Further, compared with literature data of H₂ permeances on MOF membranes, the ZIF-95 membrane developed in this study shows a superior H₂ permeance, and also exceeds the Robeson “upper-bound” for polymeric membranes (Fig. 3). The obtained high H₂ permeance of the ZIF-95 membrane is attributed not only to its highly porous structure with huge cavities (2.4 nm) and large windows (0.37 nm), but also to the novel “folded filters” membrane structure

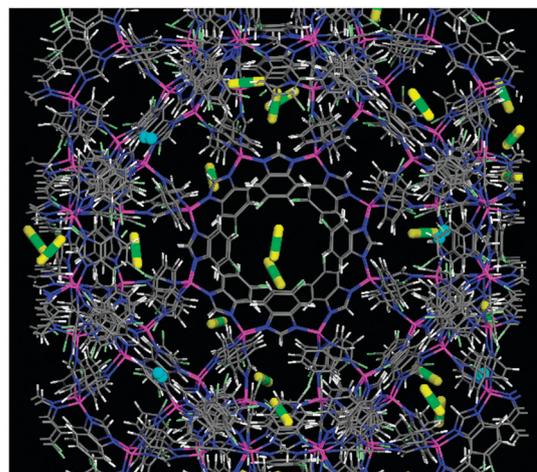


Fig. 2 Snapshot of adsorbed CO₂ and H₂ molecules in the ZIF-95 cages at 25 °C and 100 kPa. CO₂: yellow-green and H₂: cyan.

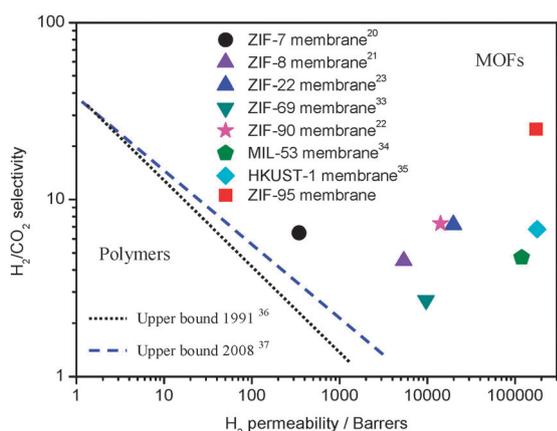


Fig. 3 H_2/CO_2 selectivity versus H_2 permeability for polymeric membranes and MOF membranes. The upper bound lines for polymeric membranes are drawn based on ref. 36 and 37.

which is helpful in reducing the flow resistance of gas transport. It is found that APTES-modification of the supports is helpful in eliminating the influence of the surface chemistry and thus enhances the reproducibility of the membrane preparation (Table S3, ESI†).

Fig. S7 (ESI†) shows mixed gas permeances and the H_2/CO_2 selectivity of the ZIF-95 membrane as a function of the operating temperatures at 1 bar. When the temperature is increased from 25 to 325 °C, the H_2 permeance increases from 5.00×10^{-7} to $1.96 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and the CO_2 permeance slightly increases from 5.91×10^{-8} to $7.64 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, resulting in an observable increase in the $\text{H}_2\text{-CO}_2$ mixture separation factor from 8.5 to 25.7. This phenomenon can be explained by the adsorption–diffusion model. As mentioned above, ZIF-95 has a high affinity and capacity for CO_2 adsorption. Therefore, at low temperature mainly CO_2 is adsorbed in the ZIF-95 pores (Fig. S8, ESI†), thus blocking the diffusion of the rarely adsorbed and highly mobile H_2 (Fig. 2). As the temperature increases, less CO_2 becomes adsorbed and thus more H_2 can diffuse in the resulting free volume, leading to a large enhancement of the H_2 permeance, and consequently selectivity. The ZIF-95 membrane has been tested at 325 °C for 24 h, and it still retains its high separation performances with a H_2 permeance of about $1.94 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and a H_2/CO_2 selectivity of 25.6 (Fig. S9, ESI†). XRD analysis shows that all peaks of the spent ZIF-95 membrane match well with those of the as-prepared ZIF-95 membrane (Fig. S10, ESI†), indicating that the ZIF-95 membrane has a high thermal stability. Further, the ZIF-95 membranes show a very good stability in the presence of steam, and both the H_2 permeance and the H_2/CO_2 selectivity are unchanged for 24 h (Fig. S11, ESI†). This hydrothermal stability combined with a high thermal stability indicates that the permselective ZIF-95 membrane is of promising importance for hydrogen production.

In conclusion, in the present work we have designed and prepared a highly permselective ZIF-95 molecular sieve membrane for the separation of H_2 from CO_2 . For binary mixtures at 325 °C and 1 bar, the mixture separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 and $\text{H}_2/\text{C}_3\text{H}_8$ were 25.7, 10.2, 11.0 and 59.7, respectively, which by far exceed the corresponding Knudsen coefficients. The ZIF-95 membrane also displayed high H_2 permeances of about

$1.9 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ due to its highly porous structure with huge cavities as well as a novel “folded filters” membrane structure. Further, the ZIF-95 membrane shows a high thermal stability up to at least 325 °C and hydrothermal stability in steam, thus offering a potential application in hydrogen production.

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