Development of Hydrogen-Selective CAU-1 MOF Membranes for Hydrogen Purification by ‘Dual-Metal-Source’ Approach

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Abstract

Hydrogen energy could provide viable, sustainable options for meeting world's energy requirements thanks to its high energy density, abundance, environmental and climatic cleanness. Hydrogen is relevant to all of the energy sectors-transportation, buildings, utilities and industry. In all of these sectors, hydrogen-rich gas streams are needed. Thus, hydrogen-selective membrane technology with superior performances is highly demanded for separation and purification of hydrogen gas mixtures. In this study, novel $[\text{Al}_4(\text{OH})_2(\text{OCH}_3)_4(\text{H}_2\text{N-BDC})_3] \cdot x\text{H}_2\text{O}$ (CAU-1) MOF membranes with accessible pore size of 0.38 nm are evaluated for this goal of hydrogen purification. High-quality CAU-1 membranes have been successfully synthesized on $\alpha\text{-Al}_2\text{O}_3$ hollow ceramic fibers (HCFs) by secondary growth assisted with the homogeneously deposited CAU-1 nanocrystals with a size of 500 nm as seeds. The energy-dispersive X-ray spectroscopy study shows that the HCFs substrates play dual roles in the membrane preparation, namely aluminum source and as a support. The crystals in the membrane are intergrown together to form a continuous and crack-free layer with a thickness of 4 μm . The gas sorption ability of CAU-1 MOF materials is examined by gas adsorption measurement. The isosteric heats of adsorption with average values of 4.52 kJ/mol, 12.90 kJ/mol, 12.82 kJ/mol and 27.99 kJ/mol are observed for H_2 , N_2 , CH_4 , and CO_2 respectively, indicating different interactions between CAU-1 framework and these gases. As-prepared HCF supported CAU-1 membranes are tested by single and binary gas permeation of H_2/CO_2 , H_2/N_2 and H_2/CH_4 at different temperatures, feed pressures and testing time. The permeation results show preferential permeance of H_2 over CO_2 , N_2 , and CH_4 with high separation factors of 12.34, 10.33, and 10.42 for H_2/CO_2 , H_2/N_2 , H_2/CH_4 , respectively. The temperature, pressure and test time dependent studies reveal that HCFs supported CAU-1 membranes possess high stability, resistance to cracking, temperature cycling, high reproducibility, these of which combined with high separation efficiency make this type of MOF membranes are promising for hydrogen recycling from industrial exhausts.

Keywords:

hydrogen recycling; α -Al₂O₃ hollow ceramic fiber; CAU-1 metal organic framework membrane; dual sources; gas separation and purification.

1. Introduction

Nowadays, one of the greatest challenges facing the global society of today and tomorrow's energy involves the production of adequate, clean, and sustainable fuels, which is due to an exhaustion of non-renewable energy resources by the continuing depletion of coal, fossil oil and natural gas. Hydrogen fuel with high energy density represents an alternative renewable and clean energy, which has been witnessed with great progress by the increasing production and purification in the past decade [1-2]. Unfortunately, hydrogen usually coexists with other light gases (CO_2 , CH_4 , N_2 , etc) during the production from industrial processes such as gasification or steam reforming reactions. To better use of these hydrogen-rich streams as fuels, hydrogen separation is required. To achieve this goal of high-purity hydrogen with minimized impurities, it is clear that new technologies are needed to be developed. New technologies also feature in an integration of new materials, simplicity, and economics. Nanoporous membranes, a branch of materials science, are expected to make contributions in the coming transition from energy-cost systems (pressure swing adsorption or cryogenic separation) [3] to a sustainable process. From this point of view, zeolite membranes with well-defined pore structures have been prepared and investigated for the refinery of hydrogen from exhausted gas streams [4]. Recently, metal-organic framework (MOF) membranes as a subclass of zeolitic materials have been proposed and used for gas separation, for example hydrogen recovery [5-13].

MOFs, emerging as a new class of zeolitic materials, are composed of inorganic bricks and organic linking molecules [14-18]. Owing to their intrinsic porosity, highly thermal and chemical stability, and fascinating properties, MOFs have attracted much attention recently and applied in various fields, such as in gas storage, separation, catalysis, optics, drug delivery, ion exchange and so on [19-31]. To be mentioned, the diversified structures and tailored properties of MOFs make them ideal candidates for the preparation of defect-free and continuous membranes for gas separation with excellent performance [32-37]. The copper net supported $\text{Cu}_3(\text{BTC})_2$ membrane was firstly synthesized in Zhu's group and evaluated for the recovery of H_2 [38]. Subsequently, a

microporous MOF membrane was prepared on an alumina support for use in the separation of binary H_2/N_2 gases [39]. Meanwhile, Caro and coworkers have established another milestone of molecular sieving MOF membranes, exemplified by successful preparation of zeolite imidazolate framework (ZIF) membranes for separating H_2 from other common light gases [40-41]. More recently, Zhu et al described the synthesis of NH_2 -MIL-53 MOF membranes with specific adsorption affinity for the separation of hydrogen; and the membrane was exhibiting high permselectivity towards H_2 [42].

In regard to practical applications, gas separating membranes are synthesized on tubular supports and used in tube-type modules, which bear the merits of low packing density (i.e. high area/volume ratio) and flexibility in the membrane scale-up. In this respect, Zhou et al have shown an example in the fabrication of $Cu_3(BTC)_2$ MOF membrane on a hollow ceramic fiber with outer diameter of 3.5 mm and a thickness of 500 μm , and these membranes have been evaluated for hydrogen separation [43]. Additionally, the mechanical strength of membranes is also very important in the operating process. Based on the considerations above, in this study, a “dual-aluminum” method is employed for the fabrication of CAU-1 MOF membranes. In this method, the interaction force between the $\alpha-Al_2O_3$ HCF support and CAU-1 MOF crystals would be strengthened. CAU-1 material is constructed of Al metal centers and 2-amino-1,4-benzenedicarboxylic acid (H_2N - H_2BDC) as ligands to form three-dimensional frameworks with pore size of 0.38 nm estimated from crystallographic data [44]. CAU-1 membranes are appropriate for hydrogen separation through a molecular sieving vs. selective adsorption/diffusion mechanism, however, the molecular sieving plays a lead role if taking accounts of the molecular size of hydrogen (0.29 nm) and pore opening of CAU-1 membrane (0.38 nm).

The homogeneity and good quality of CAU-1 seed crystals in nanoscale, which is prepared according to an original protocol [44], are crucial for growing a high-performance membrane. The size of CAU-1 seed crystals generally should be not too small to block the pore of the support (the HCF outside pore size: 2 μm , inside pore size: 200 nm). Besides, the thickness of $\alpha-Al_2O_3$ HCF

supported CAU-1 membrane could be very thin under special elaboration, which would guarantee a high permeance of the membrane.

2. Experimental

2.1. Chemicals and Materials

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was purchased from Beijing north of fine chemicals Co. Ltd. 2-amino-1, 4-benzenedicarboxylic acid ($\text{H}_2\text{N}-\text{H}_2\text{BDC}$, 99%) was purchased from Alfa Aesar. Methanol and ethanol were used as received. Asymmetric $\alpha\text{-Al}_2\text{O}_3$ hollow ceramic fibers (HCFs: i.d. 2.5 mm, o.d. 3.5 mm and length 30 mm, inside layer pore size: 200 nm, and outside layer pore size: 2 μm , porosity: 30%-40%) were supplied by Hyflux membrane Co..

2.2. Synthesis of CAU-1 Nanocrystals

0.75 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (3.11 mmol) and 0.19 g $\text{H}_2\text{N}-\text{H}_2\text{BDC}$ (1.05 mmol) were dissolved in 10 mL methanol. After $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{H}_2\text{N}-\text{H}_2\text{BDC}$ completely dissolving, the homogeneous solution was transferred into an autoclave and heated to 398 K for 5 hours. Followed by cooling the autoclave down to room temperature, CAU-1 nanocrystals were obtained by subsequent centrifugation. For the complete removal of chloride ion in the product, the nanocrystals were subjected to further repetitive purification (four times). The typical procedure for one cycle included the dispersion of CAU-1 powder in 250 mL distilled water under stirring for one day, and then the centrifugation of formed suspension. The seed solution was prepared by re-dispersing the purified CAU-1 nanocrystals in 15 mL distilled water under ultrasonic vibration for 2 minutes.

2.3. Preparation of CAU-1 Membrane by Secondary Growth

Prior to the membrane synthesis, $\alpha\text{-Al}_2\text{O}_3$ HCFs were calcined in argon atmosphere from room temperature to 873 K with a heating rate of 1.5 K/min. And then, the HCFs were washed with distilled water and ethanol in an ultrasonic bath for several times to remove organic impurities and dried at 348 K for 24 h. Before secondary growth, HCFs after cleaning were seeded with CAU-1 nanocrystals via dip-coating method. Typically, the HCFs were first immersed vertically into the CAU-1 seed suspension with each end of the HCF plugged up with a Teflon tape, and then taken

out slowly (about 5 min). This process was repeated four times to ensure full coverage of the external surface of the HCFs with the CAU-1 seeds.

After seeding, the seeded supports were placed vertically in Teflon-lined autoclaves containing a clear solution: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.25 g, 1.04 mmol), $\text{H}_2\text{N-H}_2\text{BDC}$ (0.06 g, 0.33 mmol) and mixed solvents of ethanol (5mL) and methanol (15mL). A further solvothermal treatment was carried out at 398 K for 4 days. After the secondary growth, the CAU-1 membrane was washed with 250 mL distilled water for four times in order to remove the inorganic residues.

2.4. Characterizations of CAU-1 Nanocrystals and Membrane

The crystalline structures of the CAU-1 nanocrystals and the membrane were determined by the X-ray diffraction (XRD) measurements using a Siemens D5005 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The morphologies and the chemical compositions of the CAU-1 seed layer and membrane were monitored by field-emission scanning electron microscope (FE-SEM: JEOS JSM 6700F) and attached energy-dispersive X-ray spectroscopy (EDS), respectively. Gas adsorption-desorption isotherms of H_2 (99.995%), CO_2 (99.995%), CH_4 (99.95%) and N_2 (99.995%) were measured on a Quantachrome Autosorb iQ2 analyzer. Prior to the measurements, the samples were degassed at 423 K for 24 h, and the measurements were carried out at 273 K and 298 K.

2.5. Gas Separation

In order to evaluate the performance of the CAU-1 membrane, the membrane is further used for the gas separation of H_2 , CO_2 , N_2 and CH_4 . Prior to the measurement, the CAU-1 membrane was pretreated/activated as followed. Firstly, the membrane was solvent-exchanged by soaking into 250 mL methanol for 12 h with repeated six times every 12 h. Secondly, the membrane was activated under vacuum at 393 K for 24 h to remove the solvent. The activated membrane as described above was sealed in a membrane module and the separation tests were performed. The gas penetrating through the membrane was analyzed by an on-line HP6890 gas chromatograph. The permeation setup was described in detail elsewhere [43].

3. Results and Discussion

3.1. Characterizations of CAU-1 Nanocrystals and Membrane

The crystalline structure of as-prepared CAU-1 material is studied by the X-ray diffraction (XRD). Fig. 1 shows XRD patterns of simulated CAU-1 single crystal, seed crystals, α -Al₂O₃ HCF support and the membrane, respectively. As can be seen, the seed crystals are pure CAU-1 nanoparticles, free of impurities and with high crystallinity (Fig. 1b). The XRD pattern of the CAU-1 membrane after secondary growth at 398 K for 4 days (Fig. 1d) is similar to the simulated pattern of CAU-1 single crystal (Fig. 1a), which indicates that highly crystalline and randomly oriented MOF crystals are grown on the HCF substrate.

The optical pictures of HCF, seeded support and the supported membrane are shown in Fig. 2a. The yellow color indicates that the CAU-1 seed crystals are fully covered on the outside surface of the fiber if taking non-treated HCF support as a reference and the CAU-1 membrane is in good quality indicated by the brilliant yellow color, which is due to the further growth of the seeded layer to form continuous layer after four days' solvothermal treatment.

The pore size of HCF support is about 2 μ m (Fig. 2b) and the homogeneous CAU-1 seed crystals around 500 nm are uniformly dispersed on the support (Fig. 2c), which is prerequisite for the preparation of well-grown and crack-free membranes. After four days' solvothermal treatment, the seed crystals have undergone a further growth with particle size to reach about 1 μ m (Fig. 2d) by drawing comparisons with the seed crystals in Fig. 2c. As shown in Fig. 2d, the crystals are compactly packed to form a continuous membrane layer without any visible cracks, which is in consistent with the enlarged top view SEM image of the CAU-1 membrane (Fig. 2e). Viewing from the cross-sectional SEM image, the thickness of the CAU-1 membrane is estimated to be approximately 4 μ m. With a close look, the CAU-1 crystals are tightly anchored to the support.

The role of the HCF support is dual, which is confirmed by the energy-dispersive X-ray spectroscopy (EDS) measurement. As shown in Fig. 3, the signal of aluminum element in the EDS pattern is becoming stronger and stronger from the membrane layer (Fig. 3a) to the HCF support (Fig. 3c). It is worth noting that there exists a transition layer between the top layer of the

membrane and the support (Fig. 3b, d). For a better illustration, the distribution of the aluminum contents is presented in Fig. 3d. Analyzing from the EDS data, Al contents of the CAU-1 membrane, transition layer and α -Al₂O₃ HCF support are 7.31%, 24.49% and 42.89%, respectively, which are marked by different colors in Fig. 3d. The aluminum content (24.49%) in the transition layer is higher than that of the top membrane layer (7.31%) and lower than that of the α -Al₂O₃ HCF support (42.89%). Therefore, it can be concluded that the α -Al₂O₃ HCF support is a bit dissolving to release aluminum source under the solvothermal condition. The released aluminum participates in the formation of CAU-1 crystals. As the crystal growth proceeds, the CAU-1 membrane is formed on the top of the transition layer by absorbing nutrients from the additional aluminum salts in the mother solution and released source from the support. It is worth mentioning that the surface etching favors a strong connection of the membrane to the α -Al₂O₃ HCF support, providing a good robustness of the supported membrane.

3.2. Gas Separation of the CAU-1 Membrane

As shown in Table 1, the single gas permeance of H₂ is similar to its mixture gas permeances, while the permeances of other gases are lowered a lot from H₂, indicating the CAU-1 membrane exhibits permeation priority towards hydrogen. The ideal separation factors of H₂ over CO₂, N₂ and CH₄ are 13.27, 9.60 and 10.84, respectively. These values greatly exceed the Knudsen constants, suggesting that as-prepared CAU-1 membrane displays good quality and is appropriate for gas separation. Meanwhile, the gas separation factors of their binary mixtures are calculated to be 12.34 for H₂/CO₂, 10.33 for H₂/N₂, and 10.42 for H₂/CH₄ (Table 1). The high separation factors in the single and mixture gases provide good evidence that the CAU-1 membranes are excellent candidates for the gas separation. In more details, the separation behaviors have also been investigated. The gas permeance in function of molecular size is plotted in Fig. 4. As shown in Fig. 4, the hydrogen permeances in gas mixtures at 298 K are similar and maintain at high values which is higher than the reported ones[40, 45]. It can be also found that there is a steep decrease in the permeance between H₂ and CO₂. The reduced permeance for the big molecular gas (CO₂, N₂, and

CH₄) can be explained with molecular sieving effect.

For this respect, the CAU-1 MOF structure is drawn for better illustration. As seen in Fig. 5, the CAU-1 MOF material possesses a three-dimensional microporous framework, constructed by two types of cages (distorted octahedral and tetrahedral cages) with effective diameters of approximately 1 nm and 0.5 nm. The accessibility to the cages is mediated by small triangle windows with a free aperture of 0.38 nm determined from the crystallography. This small window plays a great role in the gas permeation (Fig. 4) if taking account of the kinetic diameters of different gases (0.29 nm, 0.33 nm, 0.36 nm and 0.38 nm for H₂, CO₂, N₂ and CH₄ respectively). This phenomenon is quite different from our previously reported HKUST-1 membrane with big pore size of 0.9 nm for hydrogen separation [43]. In this case, the small opening of 0.38 nm does not allow two molecules pass through the membrane simultaneously. Once hydrogen molecules diffuse to the permeate side, other gases (CO₂, N₂ and CH₄) would be excluded in the feed side.

Additionally, the physical adsorption properties of the CAU-1 MOF material towards H₂, CO₂, N₂ and CH₄ gases are examined to study the effect of sorption abilities on the gas permeation. Fig. 6a and b show gas sorption isotherms of H₂, CH₄, N₂ and CO₂ on the CAU-1 material at 273 K and 298 K. Obviously, the adsorption and desorption branches are almost identical, which implies that the four gases can be reversibly adsorbed or desorbed on the CAU-1 material. Further, the uptake for hydrogen is the lowest among the four gases (H₂, CH₄, N₂ and CO₂). The low uptake is ascribed to the weak interaction between hydrogen and the MOF framework, which is confirmed by the results of the isosteric heats of adsorption (the calculated average values are 4.52 kJ/mol, 12.90 kJ/mol, 12.82 kJ/mol and 27.99 kJ/mol for H₂, N₂, CH₄, and CO₂ respectively, see Fig. 6c [46-47]. Owing to the adsorption quantities of H₂ at 273K and 298K are nearly 0 cm³/g, the isosteric heats of adsorption of H₂, calculated from the adsorption isotherms are not accurate. So we test the H₂ sorption isotherms at 77K and 87K to calculate the the isosteric heats of adsorption.) Generally, the low adsorption affinity would result in low separation performance of the membranes [48], which can explain the reason why a bit lower separation factors are observed for the mixtures in comparison to the single gases (Table 1). However, the overall effect on the preferred permeation for hydrogen is due to the molecular sieving effect.

3.3. Stability and Reproducibility of the CAU-1 Membrane

3.3.1. Thermal and Pressure Behaviors of the CAU-1 Membrane

Fig. 7 depicts the dependence of gas permeance and separation factor on the test temperatures in binary gas mixture systems of H_2/CO_2 , H_2/N_2 and H_2/CH_4 using the CAU-1 membrane at a pressure drop of 1 atm. The permeance of H_2 in the gas mixtures of H_2/CO_2 , H_2/N_2 and H_2/CH_4 shows a decreasing trend with elevating the temperature from 298 K to 358 K, which is due to a larger contribution of surface adsorption than diffusion rate [48-51]. However, for CO_2 , N_2 , CH_4 , their permeances increase slightly with temperature, which can be explained by the dominated effect of an increase diffusion rate in the gas permeation [50-51]. The reverse behaviors of H_2 and CO_2 , N_2 , CH_4 lead to a decrease in the observed separation factors in the studied temperature range. To be mentioned, the separation factors are still greatly surpassing their Knudsen constants, which is an indication of high quality of the prepared CAU-1 membrane.

To further address the mechanical stability of the CAU-1 membrane, the pressure-dependent behaviors of the HCF supported CAU-1 membrane are investigated. The permeation tests were carried out at different feed pressures from 1 bar to 2 bars and the results are plotted in Fig. 8. It is found that the permeance of H_2 is decreasing, while the permeances of CO_2 , N_2 and CH_4 remain almost constant in the entire test range, indicating that few defects are present and the CAU-1 membrane is primarily crack-free. The declining permeation behavior of hydrogen with CAU-1 membrane is followed by surface adsorption diffusion mechanism [51-52], which is attributed to selective gas adsorption (Fig. 6). Meanwhile, the nearly unchanged permeances of CO_2 , N_2 and CH_4 validate the molecular sieving effect of the small-pore CAU-1 membrane.

3.3.2. Reproducibility and Robustness of the CAU-1 Membrane

In order to examine the reproducibility and robustness of the HCF supported CAU-1 membrane, the binary gas mixture permeation was conducted by the continuous testing with time. The permeation data for H_2/CO_2 , H_2/N_2 and H_2/CH_4 at 298 K with a pressure drop of 1 atm is presented in Fig. 9. As can be seen, the CAU-1 membrane retains the separation factor and permeance over a 50 h period. The long durability of the membrane with repetitive using (over 2 months) proves that the HCF supported CAU-1 membranes possess high mechanical stability, which makes the CAU-1

MOF membranes promising for hydrogen recycling in industrial applications.

4. Conclusion

In summary, continuous CAU-1 MOF membranes supported on α -Al₂O₃ hollow ceramic fibers have been prepared via secondary growth assisted with CAU-1 nanocrystals of 500 nm in size as seeds. In the membrane synthesis, the HCF substrate plays a dual role of providing additional aluminum source and as a support. The different gas sorption abilities of this MOF material point out lower interaction between H₂ and the framework compared with other tested gases, indicated by its low isosteric heat of adsorption. Furthermore, the pore size of 0.38 nm facilitates hydrogen (0.29 nm) rather than other molecules of CO₂ (0.33 nm), N₂ (0.36 nm) and CH₄ (0.38 nm) penetration into the pores. As-prepared CAU-1 membranes are evaluated for hydrogen separation. The gas permeation studies of single gas and binary mixtures reveal the membrane shows preferential permeation of hydrogen, resulted in high separation factors of 12.34, 10.33 and 10.42 for H₂/CO₂, H₂/N₂ and H₂/CH₄ at 298 K, respectively. The high selectivity towards hydrogen is explained with the molecular sieving effect; and the high permeance (higher than 1.0×10^{-7} mol·m⁻²·s⁻¹·pa⁻¹) is interpreted by its fast diffusion rate in couple with thin thickness of the membrane (4 μ m). The permeation behaviors of H₂, CO₂, N₂ and CH₄ through the membrane are investigated at different temperatures and different feed pressures in details. The retained high performance of the CAU-1 membrane after long-time using validates high robustness and reproducibility of the HCF supported membrane. The hydrogen-selective CAU-1 MOF membranes are demonstrated to be potential interests for applications in the hydrogen gas recycling and recovery.

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Caption to the Table

Table 1 - Single and mixture gas permeances ($\text{mol}/(\text{m}^2 \cdot \text{s} \cdot \text{pa})$) and separation factors for the $\alpha\text{-Al}_2\text{O}_3$ HCFs supported CAU-1 membrane at 298K and with a pressure drop of 1 atm, and the volume ratio for mixture gas systems is 1:1.

<i>Gas</i>	<i>H₂</i>	<i>CO₂</i>	<i>H₂</i>	<i>N₂</i>	<i>H₂</i>	<i>CH₄</i>
Mixture gas permeances	1.08×10^{-7}	8.74×10^{-9}	1.01×10^{-7}	9.80×10^{-9}	0.98×10^{-7}	9.43×10^{-9}
Single gas permeances	1.93×10^{-7}	1.46×10^{-8}	1.93×10^{-7}	2.01×10^{-8}	1.93×10^{-7}	1.78×10^{-8}
Separation factor	12.34		10.33		10.42	
Ideal separation factor	13.27		9.60		10.84	
Knudsen constant	4.69		3.74		2.83	

Caption to the Figures

Fig. 1 - XRD patterns of (a) simulated CAU-1 single crystal, (b) CAU-1 seed powder, (c) α -Al₂O₃ HCFs support, and (d) CAU-1 MOF membrane on α -Al₂O₃ HCFs. (the peaks from α -Al₂O₃ HCFs are marked by ■).

Fig. 2- (a) Optical pictures of α -Al₂O₃ HCF (1), CAU-1 seeded support (2), and the supported membrane on α -Al₂O₃ HCF substrate (3); SEM images of (b) α -Al₂O₃ HCF, (c) CAU-1 seed layer, (d) as-prepared CAU-1 membrane, (e) an enlarged top view of (d), and (f) cross-sectional view of the CAU-1 membrane.

Fig. 3 - EDS patterns of (a) CAU-1 membrane, (b) transition layer, (c) α -Al₂O₃ HCF support; (d) the distribution of Al content in the CAU-1 membrane (orange), transition layer (green) and the support (blue) detected by EDS.

Fig. 4 - Gas permeances of H₂, CO₂, N₂ and CH₄ in the volume ratio 1:1 binary mixtures through the CAU-1 membrane in function of kinetic diameter at 298 K.

Fig. 5 - The distorted octahedral (a) and tetrahedral cage structures (b) of the CAU-1 MOF material, and accessible triangle window of the cages by gas molecules (c).

Fig. 6 - Gas sorption isotherms of H₂, CH₄, N₂, CO₂ on the CAU-1 material at (a) 273 K, (b) 298 K, and (c) the isosteric heats of adsorption of H₂, CH₄, N₂ and CO₂ at different adsorbed amounts.

Fig. 7 - Gas permeances and separation factors of the CAU-1 membrane as a function of temperature (a) H₂/CO₂, (b) H₂/N₂ and (c) H₂/CH₄ in the volume ratio 1:1 binary gas mixtures with a pressure drop of 1 atm.

Fig. 8 - Gas permeances and separation factors of the CAU-1 membrane as a function of feed pressure (a) H_2/CO_2 , (b) H_2/N_2 and (c) H_2/CH_4 in the volume ratio 1:1 binary gas mixtures at 298 K.

Fig. 9 - H_2 permeances and separation factors in the volume ratio 1:1 binary gas mixture H_2/CO_2 , H_2/N_2 and H_2/CH_4 systems for CAU-1 membrane as a function of test time at 298 K with a pressure drop of 1 atm.

Fig. 1 - XRD patterns of (a) simulated CAU-1 single crystal, (b) CAU-1 seed powder, (c) α -Al₂O₃ HCFs support, and (d) CAU-1 MOF membrane on α -Al₂O₃ HCFs. (the peaks from α -Al₂O₃ HCFs are marked by ■).

Fig. 2 - (a) Optical pictures of α - Al_2O_3 HCF (1), CAU-1 seeded support (2), and the supported membrane on α - Al_2O_3 HCF substrate (3); SEM images of (b) α - Al_2O_3 HCF, (c) CAU-1 seed layer, (d) as-prepared CAU-1 membrane, (e) an enlarged top view of (d), and (f) cross-sectional view of the CAU-1 membrane.

Fig. 3 - EDS patterns of (a) CAU-1 membrane, (b) transition layer, (c) α -Al₂O₃ HCF support; (d) the distribution of Al content in the CAU-1 membrane (orange), transition layer (green) and the support (blue) detected by EDS.

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Fig. 5 - The distorted octahedral (a) and tetrahedral cage structures (b) of the CAU-1 MOF material, and accessible triangle window of the cages by gas molecules (c).

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Fig. 7 - Gas permeances and separation factors of the CAU-1 membrane as a function of temperature (a) H_2/CO_2 , (b) H_2/N_2 and (c) H_2/CH_4 in the volume ratio 1:1 binary gas mixtures with a pressure drop of 1 atm.

Fig. 8 - Gas permeances and separation factors of the CAU-1 membrane as a function of feed pressure (a) H_2/CO_2 , (b) H_2/N_2 and (c) H_2/CH_4 in the volume ratio 1:1 binary gas mixtures at 298 K.

Fig. 9 - H₂ permeances and separation factors in the volume ratio 1:1 binary gas mixture H₂/CO₂, H₂/N₂ and H₂/CH₄ systems for CAU-1 membrane as a function of test time at 298 K with a pressure drop of 1 atm.