Hydrogen Selective NH_2-MIL-53(Al) MOF Membranes with High Permeability

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Hydrogen-based energy is a promising renewable and clean resource. Thus, hydrogen selective microporous membranes with high performance and high stability are demanded. Novel NH_2-MIL-53(Al) membranes are evaluated for hydrogen separation for this goal. Continuous NH_2-MIL-53(Al) membranes have been prepared successfully on macroporous glass frit discs assisted with colloidal seeds. The gas sorption ability of NH_2-MIL-53(Al) materials is studied by gas adsorption measurement. The isosteric heats of adsorption in a sequence of $CO_2 > N_2 > CH_4 \approx H_2$ indicates different interactions between NH_2-MIL-53(Al) framework and these gases. As-prepared membranes are measured by single and binary gas permeation at different temperatures. The results of singe gas permeation show a decreasing permeance in an order of $H_2 > CH_4 > N_2 > CO_2$, suggesting that the diffusion and adsorption properties make significant contributions in the gas permeation through the membrane. In binary gas permeation, the NH_2-MIL-53(Al) membrane shows high selectivity for H_2 with separation factors of 20.7, 23.9 and 30.9 at room temperature (288 K) for H_2 over CH_4, N_2 and CO_2, respectively. In comparison to single gas permeation, a slightly higher separation factor is obtained due to the competitive adsorption effect between the gases in the porous MOF membrane. Additionally, the NH_2-MIL-53(Al) membrane exhibits very high permeance for H_2 in the mixtures separation (above 1.5×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) due to its large cavity, resulting in a very high separation power. The details of the temperature effect on the permeances of H_2 over other gases are investigated from 288 to 353 K. The supported NH_2-MIL-53(Al) membranes with high hydrogen separation power possess high stability, resistance to cracking, temperature cycling and show high reproducibility, necessary for the potential application to hydrogen recycling.

1. Introduction

Hydrogen has been proposed as a promising renewable energy resource due to its elemental abundance and high-energy density by weight. Recently, hydrogen-based energy has attracted tremendous attention as an ideal candidate for fuel energy, driven by the depletion of global fossil fuels and gas reserves.[1] Further, hydrogen fuel is a very clean and green energy resource with less air pollution and no greenhouse gases or toxic emissions; water is the only one product of its combustion.[2] From an environmental perspective, it is compulsory for the purification and recovery of hydrogen from industrial flue gas. Additionally, the industrially produced hydrogen from gasification reaction or steam reforming reaction,[3] contains some other contaminants (impurities) such as CO_2, N_2, CH_4, CO, H_2O and etc.. Thus, upgrading of hydrogen is of great interest because of the versatile demand for high-purity hydrogen in vehicles and high-efficiency fuel cells, and other advanced applications.[4]

Hydrogen selective membranes as an attractive alternative can be of great benefits for the cost-effective H_2 purification using an economical membrane technology.[5] Hydrogen permselective inorganic membranes[6] have paved the way for use in separations due to their high thermal resistance and mechanical strength.[7] In the past decade, intense research efforts have been made in dense metallic Pd-based membranes,[8] which are exclusively permeable for hydrogen at high temperatures. However, the high cost of palladium metals has made it desirable to explore new palladium-free membranes. Subsequently, zeolite and its related molecular sieve membranes materials show excellent thermal stability and chemical resistance and prove their efficiency for hydrogen separation from other light gases.[9] Besides the low-cost merit, the new zeolite membranes also possess comparable or even higher hydrogen purification capacity than Pd-based membranes.

More recently, metal-organic frameworks (MOFs) are novel nanoporous crystalline solids combining metal ions with organic linkers resulting in highly porous frameworks, and are emerging as a new family of molecular sieve materials.[10] Besides the versatile applications in ion-exchange, gas separation and storage, optics, drug delivery and catalysis,[11] their unique properties including uniform pore size, high surface

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areas and specific adsorption affinities make MOFs attractive for assembling into membranes with excellent performance.[12] Very recently, MOF membranes have been evaluated in the separation of hydrogen by several groups.[13] MIL-53(Al) is built of infinite chains of octahedrals formed by coordination of Al(III) by terephthalate and OH groups with pore walls mainly consisting of aromatic rings. The structure of MIL-53(Al) has a remarkable flexibility, adjusting its cell volume in a reversible manner to optimize interactions between the guest molecules and the framework. Based on these merits, this MOF material and its derivates (MIL-53(Fe, Ga)) have been intensively investigated including liquid-liquid separation,[14] gas sorption,[15] thin-film growth,[16] drug delivery[17] and Li-insertion reactions.[18]

Herein, a general and facile route called colloidal assembly of MOF seeds was used to prepare amino-MIL-53(Al) (NH_2-MIL-53(Al)) membranes. The target MOF material NH_2-MIL-53(Al), which is an analogue to MIL-53(Al) and share the same topology of MIL-53, is composed of $AlO_4(OH)_2$ clusters with 2-amino terephthalate as linkers instead of terephthalate.[19] The framework of NH_2-MIL-53(Al) contains 1-D diamond shaped channels with free standing amino groups, having a free diameter close to 7.5 Å. Due to its unique porous framework and sorption ability, this material has shown good properties in CO_2/CH_4 sorption and separation.[20] Also, the large pore would guarantee a high permeance when it is explored as a candidate for composite membrane fabrication.[21]

The NH_2-MIL-53(Al) membranes have been achieved via further solvothermal treatment of assembled colloidal seeds. The sorption abilities of the NH_2-MIL-53(Al) material are studied by gas adsorption of H_2, CH_4, N_2 and CO_2. The obtained membrane is investigated for gas separations. Aiming at the potential application in hydrogen purification, a detailed investigation on both single and binary gas permeations through the NH_2-MIL-53(Al) membrane was performed, including H_2, CH_4, N_2 and CO_2, and their binary mixtures. In addition, the influence of permeation temperature on the separation of hydrogen from binary mixtures was systematically studied.

2. Results and Discussion

2.1. Preparation and Characterization of NH_2-MIL-53(Al) Seeded Layer and Membrane

The crystalline structure of as-synthesized nanocrystals was identified by X-ray diffraction (XRD) and the pattern is shown in **Figure 1**b. As can be seen, the XRD pattern of the seeded layer is similar to the simulated one (Figure 1a), indicating the seeded layer is composed of pure NH_2-MIL-53(Al) crystalline particles without any traces of other crystalline phases. The morphology of the seeded layer was monitored by scanning electron microscope (SEM). SEM images of pure and seeded macroporous glass frits are shown in **Figure 2**. As can be seen, spherical seeds around 600-800 nm in size homogeneously cover the substrate and form a continuous layer (Figure 2b). The uniform distribution of the seeds can promote uniform growth of the entire surface of the support with a continuous membrane.[22]

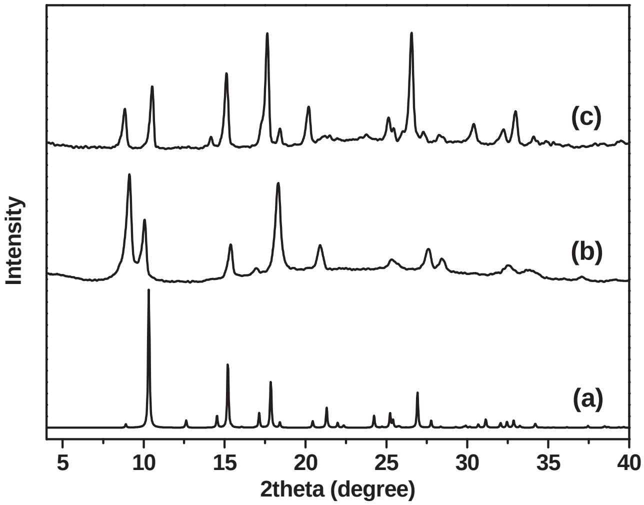

Figure 1. XRD patterns of (a) simulated MIL-53(Al) material, (b) NH_2-MIL-53(Al) seed layer on a macroporous glass frit, and (c) grown NH_2-MIL-53(Al) membrane.

The NH_2-MIL-53(Al) membrane after solvothermal treatment was also characterized by XRD (Figure 1c). The XRD pattern shows that highly crystalline randomly oriented MOF crystals are grown on the substrate indicated by the relative peak intensities. The surface morphology of as-prepared membrane can be seen in **Figure 3**. After three days of further treatment at 423 K, a continuous NH_2-MIL-53(Al) membrane was obtained. An optical image of a large-scale MOF membrane prepared on a 25 mm support is shown in Figure 3a. The yellow color indicates that the support is entirely covered with the MOF crystals. As demonstrated in Figure 3b, the SEM top view shows that the NH_2-MIL-53(Al) membrane consists of an intergrown crystalline layer. This means that a further solvothermal treatment facilitates the healing of the interparticle voids due to the overgrowth of the crystals. The crystals in the top layer of the membrane have random orientation, which is in good agreement with the XRD result. Figure 3c shows the cross section of the membrane from which a thickness of about 15 μm is determined.

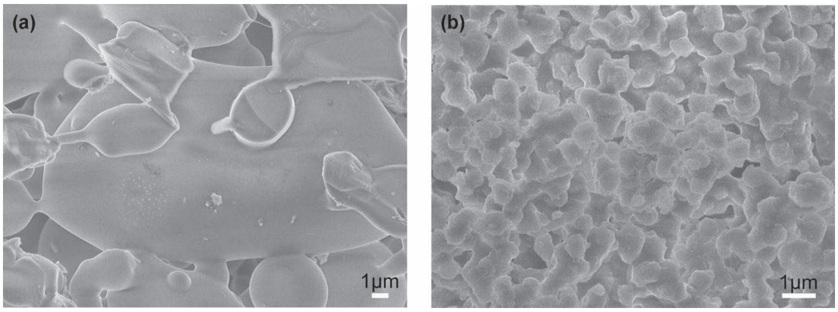

Figure 2. SEM images of (a) the macroporous glass frit support and (b) the NH_2-MIL-53(Al) seeded layer.

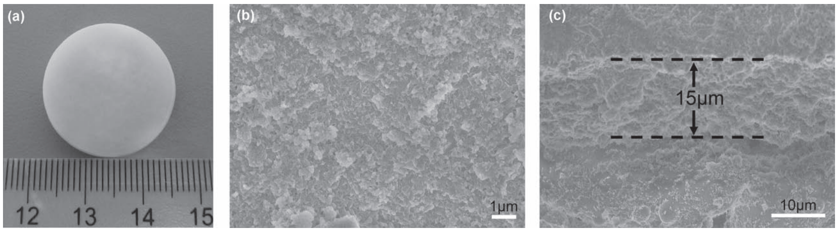

Figure 3. (a) Optical image of a NH_2-MIL-53(Al) membrane grown on a glass frit, (b) Top and (c) side views of SEM images of NH_2-MIL-53(Al) membrane.

2.2. Gas Adsorption

The adsorption isotherms for H_2, CH_4, N_2 and CO_2 are recorded at 273 K and 298 K (**Figure 4**a and 4b). A very high uptake of CO_2 is observed from the adsorption-desorption isotherm at 273 K (Figure 4a). The uptakes of H_2, CH_4 and N_2 are 1.18, 5.86, 1.84 cc g^{-1} at $P/P_0 = 0.95$, which are much less than that of CO_2 (66.47 cc g^{-1}). The adsorption isotherms of H_2, CH_4, N_2 and CO_2 at 298 K are shown in Figure 4b. The isotherms have similar adsorption and desorption curves to those at 273 K. The desorption curve is identical to the adsorption branch, which indicates that these molecules can enter and be released from the pores of NH_2-MIL-53(Al) material reversibly. The adsorbed amount of CO_2 decreases remarkably at 298 K by taking the uptake at 273 K as a reference. Also, the adsorbed amounts of other gases are considerably decreased. This means that elevating temperature would lower down the sorption ability. The NH_2-MIL-53(Al) material has the lowest H_2 uptake in respect to CH_4, N_2 and CO_2 at both 273 K and 298 K. The lower H_2 adsorption ability over other gases (CH_4, N_2 and CO_2) is most probably due to the weaker interaction between the porous MOF material and H_2 molecules. The weak sorption affinity would conversely facilitate mass transport through the membrane; that is to say H_2 molecules could pass through the pores easily. In addition, the isosteric heats of adsorption of H_2, CH_4, N_2 and CO_2 for different adsorbed amounts are calculated using the Clapeyron equation (Figure 4c).[23] The isosteric heats for CH_4, N_2 and CO_2 are 17, 26, 35 kJ·mol^{-1} in average, respectively. In the case of H_2, the isosteric heat is about 17.4 kJ mol^{-1}. The isosteric heat for CH_4 is similar to that of H_2, while those values for N_2 and CO_2 are much higher in comparison to that of H_2. Thus, one can confirm that there are stronger interactions between NH_2-MIL-53(Al) structure and N_2 or CO_2 molecules than that of H_2. This is another proof that the NH_2-MIL-53(Al) MOF material shows a preferred adsorption of some specific gases. Also, the variation in the gas interaction with NH_2-MIL-53(Al) framework would give us some hints on different retention abilities of this MOF material towards flowing gases.[20] Therefore, NH_2-MIL-53(Al) MOF material shows promise for applications in gas separation if it is fabricated into a membrane.

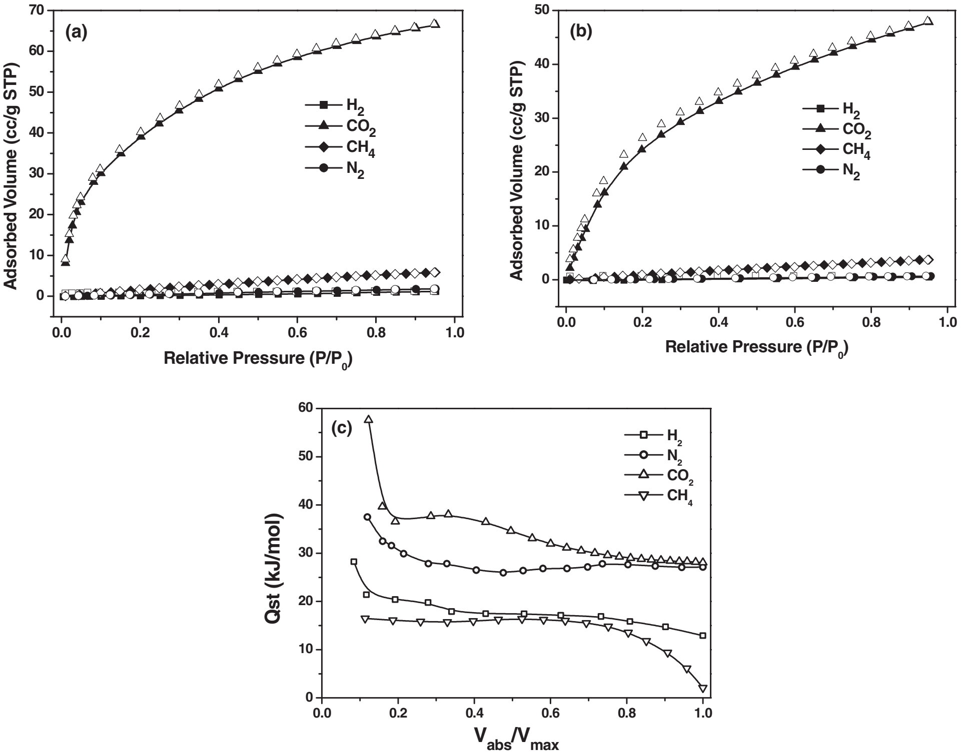

Figure 4. Gas sorption isotherms of H_2, CH_4, N_2, CO_2 on the NH_2-MIL-53(Al) membrane at (a) 273 K, (b) 298 K, and (c) the corresponding isosteric heats of adsorption; adsorption and desorption branches are indicated by filled and open symbols, respectively.

Table 1. Permeances, H_2 permselectivities for single gas at 288 K and 1 atmospheric pressure. The volume ratio for mixture gas systems is 1:1.

Gas	Permeance ($\times10^{-7}$ mol m^{-2} s^{-1} Pa^{-1})	H_2 permselectivity
H_2	26.71	-
CH_4	1.44	18.5
N_2	1.37	19.5
CO_2	0.98	27.3

2.3. Gas Separation of the NH_2-MIL-53(Al) Membrane

2.3.1. Permeation of Single Gas

Encouraged by the successful synthesis of NH_2-MIL-53(Al) membrane and specific sorption affinity towards the gases, we demonstrated the feasibility of the membrane for H_2 recycling through the separation of H_2 from other permanent gases. The NH_2-MIL-53(Al) membranes are tested for permeation using H_2, CH_4, N_2 and CO_2 as single gases. The permeation results at room temperature (288 K) are summarized in **Table 1**. As shown in Table 1, the membrane exhibits high selectivity for H_2 over CH_4, N_2 and CO_2. The ideal selectivity of H_2 over CH_4, N_2 and CO_2 is 18.5, 19.5 and 27.3, respectively.

These values greatly exceed the corresponding Knudsen separation factors (Table 1, **Table 2**), which are probably due to longer retention time of CH_4, N_2 and CO_2 gases in the NH_2-MIL-53(Al) MOF membrane than that of H_2. It is also worth mentioning that the ideal selectivity is close to the highest one in the previous report,[13d] indicating the membrane itself shows good quality and suitable for gas separation. Additionally, improved permeances are obtained among the MOF membranes, which would bring benefits to H_2 recycling. Moreover, it can be found the permeances show a decreasing trend in an order $H_2 > CH_4 > N_2 > CO_2$ with increasing molecular weight of permeating gases rather than molecular size. The dependence of gas permeances on molecular weight is plotted in **Figure 5**. It can be seen that there is a steep drop of permeance between H_2 and other gases (CH_4, N_2 and CO_2). As well known, the permeance is governed by both diffusion and adsorption. Therefore, the discrepancy of the permeances can be explained with the difference of their intrinsic diffusion properties, combined with the effect of adsorption.[24] This interesting phenomenon is contrast to the molecular sieving effect because the pore size of NH_2-MIL-53(Al) is far beyond gas molecules.[13c] Generally, the permeance and selectivity can be influenced by the temperature. **Figure 6**a illustrates the gas permeances through

Table 2. Permeances, H_2 separation factors from equimolar binary mixtures at 288 K and 1 atmospheric pressure. The volume ratio for mixture gas systems is 1:1.

Gas (H_2/j)	Knudsen constant	Permeance (H_2) ($\times10^{-7}$ mol m^{-2} s^{-1} Pa^{-1})	Permeance (j) ($\times10^{-7}$ mol m^{-2} s^{-1} Pa^{-1})	H_2 separation factor
H_2/CH_4	2.8	15.17	0.73	20.7
H_2/N_2	3.7	17.90	0.75	23.9
H_2/CO_2	4.7	19.85	0.64	30.9

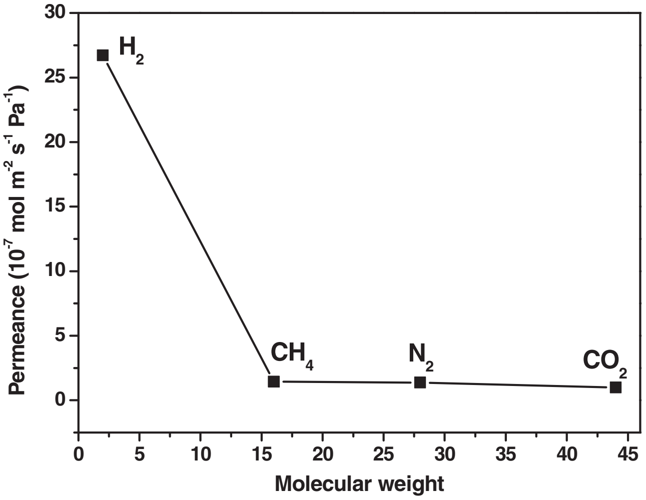

Figure 5. The permeances of single gases through the NH_2-MIL-53(Al) membrane at 288 K as a function of the molecular weight.

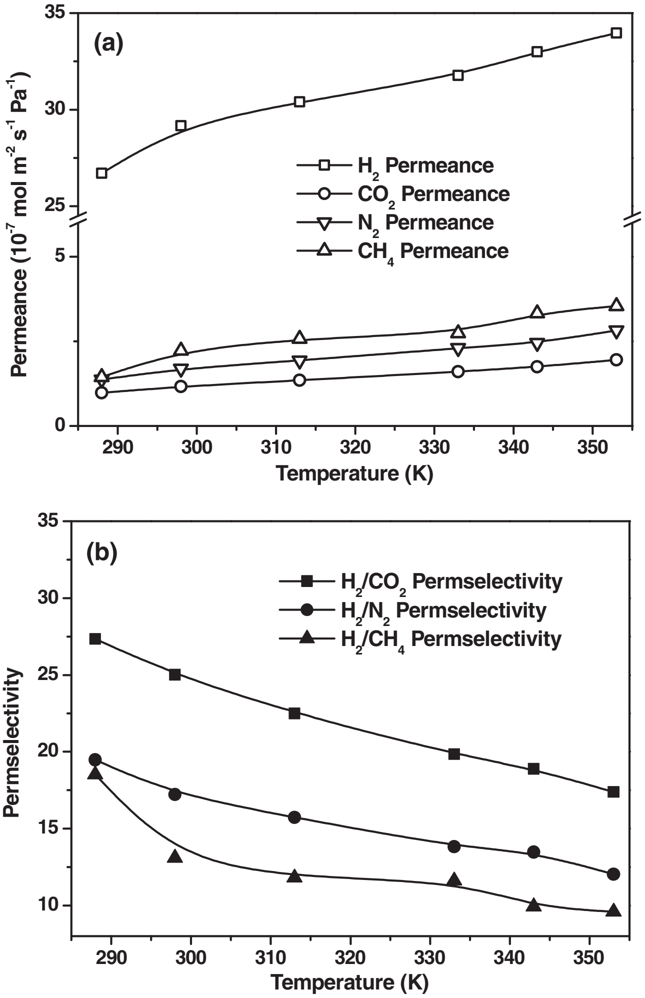

Figure 6. The variations in permeances (a) and permselectivity (b) for single gases as a function of temperature.

NH_2-MIL-53(Al) membranes as a function of temperature. The permeances of H_2 increase quickly with an increased temperature. The permeances of other single components (CH_4, N_2 and CO_2) also show a continuous increasing trend from 288 K to 353 K due to an increase of the fugacity.[25] To be mentioned, the permeances of H_2 in a range of 2.7×10^{-6} to 3.4×10^{-6} mol m^{-2} s^{-1} Pa^{-1} are much higher than those of other gases for all studied temperatures. Therefore, the NH_2-MIL-53(Al) membranes are expected to display hydrogen selectivity in mixed-gas permeations. Figure 6b gives the corresponding permselectivities in the temperature range of 288 K to 353 K. It is found that the permselectivities of NH_2-MIL-53(Al) membrane for H_2 in respect to CH_4, N_2 and CO_2 are decreasing with increasing operated temperatures. For details, the permselectivity of H_2 over CH_4, N_2 and CO_2 is gradually decreasing from 18 to 9, 20 to 12 and 27 to 17 with temperatures from 288 K to 353 K (Figure 6b), respectively. It is worth underlining that the values of permselectivity are still considerably higher than their Knudsen separation factors.

2.3.2. Permeation of Binary Gas Mixture

To evaluate the performance of the NH_2-MIL-53(Al) membranes in the purification and recycling of hydrogen from gas mixtures, gas separation studies of binary gases (H_2/CH_4, H_2/N_2 and H_2/CO_2) with an equal volume ratio are carried out. The permeances and separation factors are summarized in Table 2. As shown in Table 2, the NH_2-MIL-53(Al) membrane shows high efficiency of hydrogen separation from the gas mixtures of H_2/CH_4, H_2/N_2 and H_2/CO_2, including high permeance (above 1.5×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) and high separation factors (above 20). Furthermore, compared with literature data on hydrogen permeation properties of those MOF membranes, the NH_2-MIL-53(Al) membrane exhibits higher permeance than those of ZIF-8 (about 1×10^{-7} mol m^{-2} s^{-1} Pa^{-1} for H_2 over CH_4),[13c] ZIF-22 (1.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1} for H_2 over N_2) and ZIF-90 (2.5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} for H_2 over CH_4) MOF membranes, as shown in Table S1. The NH_2-MIL-53(Al) membrane displays high separation factor of 23.9, 30.9 and 20.7 for H_2/N_2, H_2/CO_2 and H_2/CH_4 respectively, comparable to the best result of 18.9 for H_2/CH_4 by ZIF-90 membranes (Table S1). Comparing Table 1 and 2, it can be observed that the H_2 permeance measured in gas mixtures at 288 K is lower than that of its single gas. Meanwhile, the permeances of CH_4, N_2 and CO_2 are also greatly reduced. This phenomenon can be attributed to a competitive adsorption between the gases towards the membrane. In this way, the diffusion of CH_4, N_2 and CO_2 through the NH_2-MIL-53(Al) membrane is hindered to some extent by H_2 molecules. Thus, intrinsic fast diffusion of H_2 coupled with the large pore (7.5 Å) of the NH_2-MIL-53(Al) material accounts for the high permeance with less influence by other gases. As a result, a slight higher separation factor can be achieved from mixtures due to the competitive adsorption effect.

Based on the observations of single and binary gas permeations, the permeability of the NH_2-MIL-53(Al) membrane for the separation of H_2 from a binary mixture can be correlated with gas adsorption and diffusion in a simple way.[24] Firstly, the intrinsic faster diffusion of H_2 (Knudsen diffusion) favors a higher permeance of H_2 over the gases of CO_2, N_2 and CH_4. Secondly, the weak adsorption ability of H_2 leads to a short retention time in the NH_2-MIL-53(Al) membrane, facilitating H_2 molecules fast penetrating through the membrane. During the binary gas permeations, a competitive adsorption is taking place when two components are passing through the membrane simultaneously. Therefore, the high selectivity for H_2 can be predicted from the product of intrinsic sorption selectivity and diffusion selectivity combined with a competitive adsorption effect. The permeance can be correlated with fast diffusion rate of H_2 (2.9 Å) in the pores with negligible hindering by other gases (3.8 Å, 3.64 Å, and 3.3 Å for CH_4, N_2 and CO_2, respectively), and big enough pores of the NH_2-MIL-53(Al) material (7.5 Å).

2.4. Thermal Stability of the NH_2-MIL-53(Al) Membrane

To address the issue of temperature effect on the permeation behaviors, the permeation tests at different temperatures (288-353 K) are performed. The dependence of the permeances and separation factors on the temperature is exemplified by the separation of H_2/CO_2 mixture in **Figure 7**. It can be found the H_2 and CO_2 permeances are increasing noticeably when the permeation temperature is increased from 288 to 353 K. A declining trend of H_2/CO_2 separation factor is observed accordingly. This finding can be interpreted as follows: the influence of competitive adsorption on the internal or external surface of the NH_2-MIL-53(Al) membrane is reduced, well consistent with sorption data (Figure 4) and the diffusion rates are improved in different magnitudes between H_2 and CO_2 at high temperatures. As a result, a slightly lower separation factor is obtained, which is different from the case of ZIF-7.[13f] Nevertheless, a high permeance (2.3×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) with high separation factor (23.7) is still observed at a relatively high temperature (353 K), which is sound proof that the NH_2-MIL-53(Al) membrane possesses very good reversibility upon temperature cycling and high thermal stability.

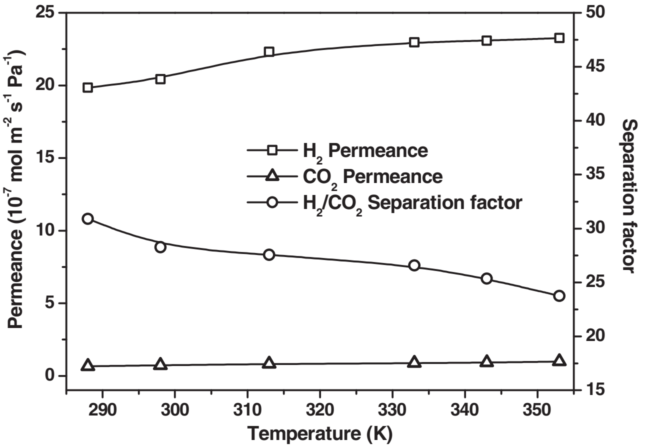

Figure 7. H_2/CO_2 permeances and separation factor of the NH_2-MIL-53(Al) membrane as a function of the permeation temperature.

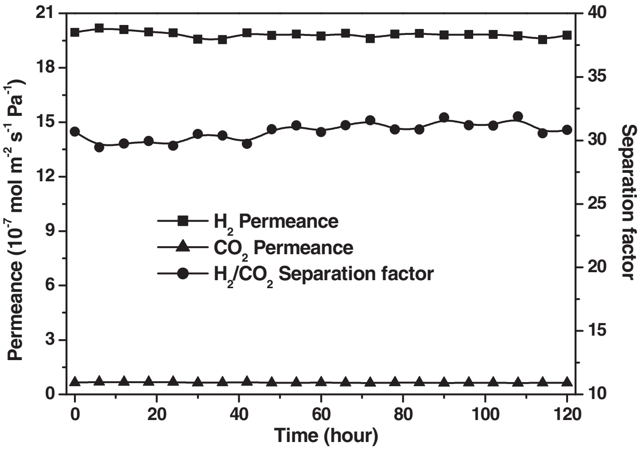

Figure 8. Plot of H_2/CO_2 permeances and separation factor of the NH_2-MIL-53(Al) membrane versus test time.

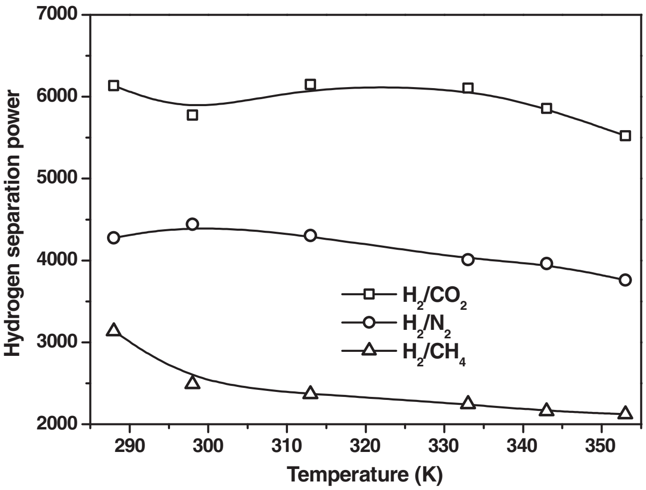

Figure 9. Hydrogen separation power of the NH_2-MIL-53(Al) membrane as a function of the permeation temperature.

2.5. Reproducibility of the NH_2-MIL-53(Al) Membrane

The mechanical stability and robustness of membranes are very important for gas separations. From this point of view, the reproducibility and durability of the NH_2-MIL-53(Al) membrane are also examined. As depicted in **Figure 8**, the NH_2-MIL-53(Al) membrane retains a high separation factor and high permeance with small fluctuation over a 5 days period. The membrane can also be used repeatedly under ambient conditions for more than three months, which shows that the membrane has high mechanical stability. This high robustness recommends the NH_2-MIL-53(Al) membrane for the H_2 recycling from industrial exhausts.

2.6. The Hydrogen Separation Power

The separation power[26] is an index to represent the separation efficiency and usefulness of a membrane for a specific gas. It is defined as the product of permeability by selectivity. Both high selectivity and high permeance are required for membrane separations. Generally, the selectivity of membrane is increasing with a decrease of permeance. Therefore, the term of separation power is another index for the evaluation of a membrane.[27]

Hydrogen separation power of the NH_2-MIL-53(Al) membrane is evaluated by using CH_4, N_2 and CO_2 as a comparative gas. **Figure 9** shows hydrogen separation power of the NH_2-MIL-53(Al) membrane as a function of temperature. As clearly illustrated in Figure 9, separation powers of H_2 over CO_2 and H_2 over N_2 reach maximum values of 6148 and 4442 at 313 K and 298 K respectively, whereas the H_2 separation power over CH_4 decreases with an increase of temperature. By comparing other MOF membranes in gas separation, as-synthesized NH_2-MIL-53(Al) membrane in the present study possesses a good balance between H_2 permeance and selectivity, and exhibits a very high hydrogen separation power (Table S1). From this point of view, the NH_2-MIL-53(Al) membrane shows superior hydrogen separation performance, and would be a good candidate in the hydrogen separation membranes.

3. Conclusions

In summary, NH_2-MIL-53(Al) membranes supported on macroporous glass frits are prepared by a colloidal synthetic route. The different gas sorption abilities of this MOF material show that the membrane exhibits preferential permeation of H_2 compared with other gases, explained by its low isosteric heat of adsorption. As-prepared NH_2-MIL-53(Al) MOF membranes are tested for H_2 separation. The study of the single gas permeation reveals that the permeance of H_2, CH_4, N_2 and CO_2 is dependent on diffusion and adsorption properties. The NH_2-MIL-53(Al) membrane is also evaluated for binary gas permeations of H_2/CH_4, H_2/N_2 and H_2/CO_2. The membrane is demonstrated to be highly selective for H_2 permeation with a separation factor higher than 20 due to its specific sorption affinity and the competitive adsorption effect. The permeation behaviors of H_2, CH_4, N_2 and CO_2 through the membrane are investigated at different temperatures and a possible separation mechanism is discussed on the basis of sorption isotherms in couple with gas permeation measurements. Besides, as-prepared membranes have been proved to exhibit very high permeance for H_2 together with very high hydrogen separation power. The supported NH_2-MIL-53(Al) membranes display high stability and reproducibility, which are of potential interest for applications in the hydrogen gas recycling and recovery.

4. Experimental Section

Materials: 2-amino terephthalic acid (H_2N-H_2BDC, 99%, Aldrich), aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, Co., Ltd, Shanghai, China, AR), and the solvent of *N,N*-dimethylformamide (DMF, Tianjin Guangfu Chemical Research Institute, AR) were used as received without any further purification.

The pretreatment of substrates: The macroporous glass frit support (P4 or G5, 25 mm in diameter, pore size 2-4 µm, Taixing City, Science and Education Equipment Co. Ltd., China) were used as substrates in our experiments. Prior to use, one side of the glass frit was polished with SiC sandpaper (2000 mesh) to obtain a smoother surface. Then, the supports were sequentially treated with piranha solution (H_2SO_4/H_2O_2 =

3/1, v/v) at 363 K for 8 h, followed by ultrasonic treatment in deionized water several times until the pH value of the water was about 7, and then dried at 373 K.

The synthesis of NH_2-MIL-53(Al) colloidal seed crystals: $AlCl_3 \cdot 6H_2O$ (158 mg, 0.525 mmol) was dissolved in DMF (5 mL) under stirring for 20 minutes, followed by an addition of H_2N-H_2BDC (37.5 mL, 1.05 mmol). The resulted precursor was transferred to a Teflon-lined microwave reactor (XT-9900 Intelligent Microwave Digestion System, Xintuo Analytical Instruments Co., LTD, Shanghai, China) and heated at 423 K for 80 seconds at a constant pressure of 2 MPa. The seed powder obtained was purified by ultrasonic vibration and centrifugation (8000 rpm, 3 minutes) with DMF, repeated subsequently three times. The NH_2-MIL-53(Al) seed crystals were re-dispersed in methanol (10 mL) in ultrasonic bath for 5 minutes to obtain a primrose yellow colloidal suspension (20 g L^{-1}).

The preparation of NH_2-MIL-53(Al) membrane: As-prepared colloidal seed suspension was deposited on the pretreated macroporous glass frit support in a drop way, and then dried in air at room temperature overnight to form a seed layer. The seeded supports were placed vertically in Teflon-lined autoclaves containing a mother solution of $AlCl_3 \cdot 6H_2O$ (0.59 mmol), H_2N-H_2BDC (3.86 mmol), and DMF (20 mL), and then subjected to a further solvothermal treatment at 423 K for three days. The NH_2-MIL-53(Al) membrane was activated as previously described in the literature[19] with slight modification. Typically, 2-aminoterephthalic acid in pores was exchanged by DMF at 423 K for 5 h, after the membrane washed with DMF (10 mL) for three times. The membrane was activated under vacuum to remove the solvent at 423 K overnight prior to further characterizations and use.

Characterizations: The crystalline structures of NH_2-MIL-53(Al) seeds and membranes were determined by X-ray Diffraction (XRD) measurements using Riguku D/MAX2550 diffractometer with Cu-Kα radiation (λ = 1.5418 Å) running at a voltage of 50 kV and a current of 200 mA. The morphologies of seed crystals and membranes were also monitored by field emission scanning electron microscope (FE-SEM: JEOS JSM6700F). Gas adsorption-desorption of H_2 (99.995%), CO_2 (99.995%), CH_4 (99.95%) and N_2 (99.995%) measurements on NH_2-MIL-53(Al) were carried out on an Autosorb iQ2 adsorptometer, Quantachrome Instruments and their isotherms were recorded. The sample was degassed at 423 K overnight under vacuum (residual pressures lower than 10 − 6 torr), and the measurements were carried out at 273 K and 298 K.

Gas permeation: In order to evaluate the performance of the NH_2-MIL-53(Al) membrane, the membrane is further used for the separation of H_2 (2.9 Å), CO_2 (3.3 Å), N_2 (3.64 Å) and CH_4 (3.8 Å) gases. The NH_2-MIL-53(Al) membrane pretreated as described above was sealed in a cell and the separation tests were performed. The permeation setup is described in detail elsewhere.[13a] The gas penetrating through the membrane was analyzed by an on-line HP6890 gas chromatograph. The feed side was exposed to single gas or gas mixture while the permeate side of the membrane was swept by argon (Ar). The flow rate of Ar was controlled at 100 ml min^{-1} and the pressures at both sides were maintained at 101 kPa (1 atm) in all experiments. The feed flow rate was set to 50 ml min^{-1} for the single gas measurements. The total volumetric flow in the feed for binary gas measurements was 100 ml min^{-1} with each gas of 50 ml min^{-1} and kept constant. The flux of the gas was measured by a soap-film flow meter.

The permeability is the ability to pass through a membrane and termed as the permeance (P_i (mol m^{-2} s^{-1} Pa^{-1})) for a single gas or a component in a mixture are calculated by **Equation 1**:

$$Pi = \frac{Ni}{\Delta p_i \times A} \tag{1}$$

where N_i (mol s^{-1}) is the permeate flow rate of component i, Δp_i (Pa) is the trans-membrane pressure drop of i, and A (m^2) is the membrane area.

The selectivity of the membrane is defined as separation factor ($\alpha_{i,j}$): the ratio of the molar fractions X of the component i and j in the permeate divided by the ratio of the molar fractions Y of i and j in the feed. Therefore, the separation factor for hydrogen can be calculated according to **Equation 2**:

$$\alpha_{H2,j} = \frac{X_{H2} / X_j}{Y_{H2} / Y_j} \tag{2}$$

The separation power (SP) is defined as the separation efficiency of a membrane for a specific gas (**Equation 3**)

$$SP = P_i \times \alpha \tag{3}$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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