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MIL-101(Cr) microporous nanocrystals intercalating graphene oxide membrane for efficient hydrogen purification

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Abstract: Graphene oxide (GO) is a promising two-dimensional building block for fabricating high-performance gas separation membrane. Whereas, the tortuous transport pathway may increase the transport distance and lead to low gas permeation rate. Introducing spacers into GO laminates is an effective strategy to enlarge the interlayer channel for enhanced gas permeance. Herein, we proposed to intercalate CO2-phlic MIL-101(Cr) metal-organic framework nanocrystals into the GO laminates to construct 2D/3D hybrid structure for gas separation. The interlayer channels were partially opened up to accelerate gas permeation. Meanwhile, the intrinsic pores of MIL-101 provided additional transport pathways, and the affinity of MIL-101 to CO2 molecules resulted in higher H2/CO2 diffusion selectivity, leading to a simultaneous enhancement in gas permeance and separation selectivity. The MIL-101(Cr)/GO membrane with optimal structures exhibited outstanding and stable mixed-gas separation performance with H2 permeance of 67.5 GPU and H2/CO2 selectivity of 30.3 during the 120-h continuous test, demonstrating its potential in H2 purification application.

Introduction

Membrane-based separation technology, aimed at decreasing energy consumption, equipment size and carbon footprint, is considered as a promising approach for separating gas mixtures compared with conventional distillation and adsorption[1]. The booming of two-dimensional (2D) materials, including graphene and graphene oxide (GO)[2], graphitic carbon nitride (g-C3N4)[3], metal-organic framework (MOF) nanosheets[4], and transition-metal carbides/carbonytrides (MXenes)[5], stimulates development of high-performance separation membranes, owing to the unprecedented mass transport through the assembled nanosheets[5]. Graphene oxide (GO) is the mostly widely investigated 2D material for fabricating separation membranes because of the atomic thinness and rich oxygen-containing groups distributed on the nanosheets. On one hand, the ultrathin GO nanosheet can be assembled into membrane with ultimate thinness for maximizing the mass transfer rate[7]. On the other hand, the interlayer channels of GO laminates can be efficiently tuned by controlling the amount of oxygen-containing groups for precise molecular separation such as gas separation[8]. In 2013, Yu and co-workers reported the fabrication of ultrathin (~1.8 nm) GO membranes for selective hydrogen separation[9]. The as-fabricated GO membranes exhibited excellent H2/CO2 and H2/N2 separation performance, which was attributed to the selective structural defects on the nanosheets. Afterwards, more and more researchers were devoted to the fabrication of GO membranes and the manipulation of gas transport channels for enhanced separation efficiency[10].

The manipulation of the microstructures and chemical properties of transport channels within GO laminates was proven to be critical to the gas separation performance of GO membranes[11]. In the previous work, we employed molecular interaction (e.g., hydrogen bonds) between GO and polymers or the integrated external forces to stimulate the ordered stacking of GO nanosheets and construct subnanometer channels for efficient gas sieving[12]. Jiang and co-workers introduced borate serving as crosslinker and facilitated transport carrier into GO laminates to tune the size of interlayer gallery and enhance the affinity of channels to CO2 molecules, endowing the membrane with excellent CO2/CH4 separation performance[13]. Recently, amino-functionalized polyhedral oligomeric silsesquioxane (POSS-NH2) nanocage was incorporated into GO nanosheets to finely regulate the physico-chemical microenvironment of GO membranes for CO2/CH4 separation[14]. Based on the synergistic intensification of diffusion selective and facilitated transport mechanisms, the resulting membrane showed high CO2/CH4 selectivity of 74.5. Besides the manipulation of interlayer channels, the in-plane pores of GO nanosheets can be controlled to enhance the gas separation performance. Lin and co-workers drilled in-plane nanopores on GO nanosheets via chemical etching and tune the assembly behavior under acidic conditions to improve the gas permeability and the size-sieving ability[15]. Zhao and co-workers reported the intergrowth of ZIF-8 crystals at the in-plane defects of GO membranes, which narrowed the non-selective pores and improved the molecular sieving property[16]. The ZIF-8 modified GO membrane exhibited gas selectivities as high as 406, 155, and 335 for H2/CO2, H2/N2, and H2/CH4 mixtures, respectively.

Although many strategies have been proposed to manipulate the interlayer channels of GO membrane, the tortuous transport pathways usually lead to low gas permeability[17], which could not meet the demand for separation performance. To accelerate the gas permeation through GO membranes, intercalation of nanomaterials, including carbon nanotubes[18] and metal-organic framework (MOF) nanocrystals[19], into GO membrane has been explored to enlarge the interlayer spacing. The size of MOF nanocrystals can be reduced to tens of nanometers, and the porous framework with tunable functional groups can provide gas transport channels and form specific interaction with gas molecules, contributing to enhanced gas separation performance. Wang et al. introduced UiO-66-NH2 into the GO membranes to fabricate the UiO-66-NH2/GO hybrid membrane[19]. Whereas, the...
resulting membrane showed relatively low H$_2$/CO$_2$ ideal selectivity of 6.35. The functionalized pores of MOF nanocrystals were not sufficiently employed for enhancing the gas separation performance of the hybrid membrane. It remains a great challenge of incorporating nanomaterials to enhance gas permeability while preserving the selectivity, because the tiny difference between the kinetic diameters of gas pairs demands for high separation precision and the oversized interlayer channels could lead to a sharp decrease of selectivity.

In this work, we proposed to incorporate porous metal-organic framework (MOF) nanocrystals into GO laminates to partially enlarge the interlayer spacing while retaining some sub-nanometer channels for gas sieving. Specifically, MIL-101(Cr) MOF was selected as a typical spacer embedded in the GO laminates. MIL-101(Cr) possessed a framework of augmented MTN zeotype architecture consisting of chromium(III)-trimers crosslinked by 1,4-benzene dicarboxylate (BDC)$_2$. There are two types of cages with free diameters of 2.9 and 3.4 nm accessible through two micropore windows of 1.2 and 1.6 nm, which are larger than the kinetic diameters of H$_2$ (0.29 nm) and CO$_2$ (0.33 nm) to allow their free permeation. As illustrated in Figure 1, the incorporation of porous MIL-101 nanocrystals partially opened up the original 2D nanochannels and brought additional 3D nanopores for faster gas transport. Moreover, the affinity of MIL-101(Cr) nanocrystals towards CO$_2$ molecules would block their permeation, contributing to the enhanced H$_2$/CO$_2$ selectivity. As a result, the synergistic effect of the gas-sieving channels from 2D laminates and the enhanced affinity from 3D nanopores endowed the MIL-101-embedded GO membranes with outstanding H$_2$/CO$_2$ separation performance that surpassed the upper-bound of polymeric membranes.

**Results and Discussion**

**Morphology and physico-chemical property of MIL-101(Cr)**

MIL-101 was synthesized by a typical hydrothermal method, which was previously reported in literature.$^{[22]}$ SEM and TEM were employed to characterize the morphology of MIL-101. Figure 2a demonstrated that the size of the nanocrystals was uniform and ~200 nm, which could efficiently expand the interlayer spacing when embedded into the GO laminates. TEM image of the MIL-101 showed a well-defined rhombohedra morphology of the nanocrystals, as reported in the literature.$^{[23]}$ (Figure 2b). Moreover, the EDS (energy dispersive X-ray spectroscopy) elemental mapping of the nanocrystals was obtained to confirm the homogeneous distribution of C, O and Cr elements in the nanocrystal resulting from the BDC linker and the metal cluster (Figure 2c). XRD and XPS were employed to confirm the crystal phase and the elemental composition of the synthesized MIL-101. Figure 3a showed the well-resolved diffraction peaks in the XRD pattern of the nanocrystal, which were characteristics of the MIL-101.$^{[24]}$ The XPS spectrum of MIL-101 sample exhibited the peaks corresponding to C1s, O1s and Cr2p orbits (Figure 3b), which was consistent with the EDS mapping result.
The pore structure and the pore distribution of the MIL-101 was evaluated by N$_2$ adsorption-desorption isotherms (Figure 4a). The BET surface area of the MIL-101 was calculated to be 2624 m$^2$/g. The total pore volume of MIL-101 was estimated to be 1.43 cm$^3$/g by a single point adsorption method. The isotherms exhibited secondary uptakes near $P/P_0$ = 0.1 and $P/P_0$ = 0.2, indicating the presence of two nanoporous windows [25]. The pore size distribution profile of MIL-101, calculated by the NLDFT (non-local density functional theory) model [26], indicated the micropore sizes of 1.30 and 1.63 nm, which well agree with the theoretical sizes of the microporous windows (1.2 and 1.6 nm) of MIL-101 to allow the free transport of H$_2$ molecules (0.289 nm). Moreover, the affinity of MIL-101 to H$_2$ and CO$_2$ molecules was compared based on the adsorption isotherms. As shown in Figure 4b, the CO$_2$ adsorption amount of MIL-101 was much higher than the H$_2$ adsorption amount at 100 kPa, indicating the preferential adsorption of MIL-101 to CO$_2$ molecules. On one hand, the carboxyl groups from MIL-101 provided the preferential site for CO$_2$ adsorption, strongly trapping CO$_2$ molecules and retarding their permeation, which was previously reported in literature [26-126]. On the other hand, the absorbed CO$_2$ molecules would partially occupy the micropore windows (1.2 nm and 1.6 nm) of MIL-101 and reduce the window size, which increased the resistance to CO$_2$ diffusion and contributed to enhanced H$_2$/CO$_2$ diffusion selectivity [27]. Based on the trapping and steric hindrance effect, the intercalation of MIL-101 nanocrystals into GO laminates could contribute to enhanced H$_2$/CO$_2$ separation performance.

**Figure 4.** (a) N$_2$ adsorption-desorption isotherms of MIL-101, and the inset represents the pore distribution calculated by the NLDFT model. (b) H$_2$ and CO$_2$ adsorption isotherms of MIL-101 samples at 25 °C.

**Morphology and physico-chemical property of MIL-101(Cr)/GO membrane**

The morphology of MIL-101(Cr)/GO (MCGO) membranes was firstly characterized by SEM. A relatively thick (~1.4 μm) MCGO membrane was fabricated for EDS mapping. As illustrated in Figure 5a, both of the 2D laminar structure of GO nanosheets and the 3D structure of MIL-101 nanocrystals were observed from the cross-section of MCGO membrane. The porous nanocrystals were uniformly intercalated into the interlayer of GO laminates, efficiently opening the transport channels and generating the 2D/3D hybrid nanostructure for the selective permeation of gas molecules. EDS mapping was further employed to demonstrate the elemental distribution inside the membrane structure. Figure 5b-d showed the Cr, O, and C elements were uniformly distributed in the cross-section of MCGO membrane, further confirming the sufficient intercalation of MIL-101 nanocrystals into the GO laminates. Although some voids could be observed from the cross-section of the membrane at the GO deposition of 2 mg, the relatively thick membrane was fabricated merely for the EDS mapping. The MCGO membranes with reduced thickness and dense structure will be fabricated for gas permeation test.

**Figure 5.** (a) Cross-section SEM image of MCGO membrane. The GO deposition is 2 mg, and the MIL-101/GO mass ratio is 0.5:1. (b–d) EDS mapping images of (b) Cr (red), (c) O (green), and (d) C (cyan) of the selected area. The cyan dashed box indicates the area chosen for EDS mapping.

The effect of MIL-101/GO mass ratio on the microstructure of MCGO membranes was investigated. The MCGO membranes with MIL-101/GO mass ratios of 0.25:1, 0.5:1, 1:1, and 2:1 were fabricated and characterized by SEM. At the relative low MIL-101/GO mass ratio of 0.25:1 (Figure 6a), a few MIL-101 nanocrystals were embedded into the GO laminates, and an ultrathin and dense GO layer could be observed. With the gradual increase of the MIL-101/GO mass ratio, more and more MIL-101 nanocrystals were incorporated into the interlayer gallery of GO laminates, which enlarged the gas transport channels of MCGO membrane (Figure 6b-c). Meanwhile, the membrane thickness of MCGO-50 and MCGO-100 increased from 70 nm (MCGO-25) to 409 nm and 488 nm, respectively. Nevertheless, when the MIL-101/GO mass ratio reached 2:1, stacked nanocrystals rather than laminated GO nanosheets dominated the membrane structure (Figure 6d), suggesting that the 2D/3D hybrid structure was destroyed and thus would affect the gas separation performance. Moreover, more islands comprising of lower MOF nanocrystals...
and upper GO layer emerged on the surface of MCGO membrane with adding more nanocrystals (Figure 6e-g), indicating the successful intercalation of MOF nanocrystals into the laminates. Nevertheless, at the MIL-101/GO mass ratio of 2:1, lots of nanocrystals aggregated on the membrane surface, reflecting an excessive introduction of nanocrystals into the membrane layer (Figure 6h).

XRD and XPS were employed to characterize the varying of interlayer spacing and the elemental composition of GO and MCGO membranes, respectively. The characteristic peak in the XRD pattern of GO membranes appeared at $2\theta = 10.6^\circ$ (Figure 7a), corresponding to interlayer spacing of 0.83 nm based on Bragg equation. The patterns of MCGO membranes with different MIL-101/GO mass ratio were obtained to investigate the effect of nanocrystal intercalation on the interlayer spacing of GO laminates. As the MIL-101/GO mass ratio increased, the characteristic peak assigned to GO laminates gradually shifted to the lower degree, indicating the enlargement of interlayer spacing with more embedded nanocrystals. As a result, the MCGO-200 membrane possessed the highest interlayer spacing of 0.87 nm, and the empty space for gas transport was 0.52 nm by subtracting the thickness of single graphene (0.35 nm). Moreover, the characteristic peaks of MIL-101 occurred in the patterns of MCGO-100 and MCGO-200 membranes, confirming the 2D/3D hybrid nanostructure of MCGO membranes. These peaks were not observed in the patterns of MCGO-25 and MCGO-50 membranes due to the relatively low signal at the low MIL-101 loading. Figure 7b showed the XPS spectra of GO and MCGO membranes, both of which possessed the characteristic peaks of O and C elements. Differently, the Cr2p peaks appeared in the spectrum of MIL-101/GO sample, again confirming the incorporation of MIL-101 nanocrystals into the GO laminates and the formation of 2D/3D hybrid structure.

To investigate the functional groups of MCGO membrane, FTIR spectra of MIL-101, GO and MIL-101/GO composite samples were collected (Figure 8). For the spectrum of GO sample, the peak at 1632 cm$^{-1}$ corresponded to C=C vibration from the aromatic ring, and the typical bands at 3437, 1729, 1400 and 1048 cm$^{-1}$ were assigned to hydroxyl groups (-OH), carboxyl groups (C=O), hydroxyl groups (C-OH) and epoxy groups (C-O-C), respectively. The spectrum of MIL-101 exhibited the symmetric (O-C-O) and asymmetric stretching (C=O) vibrations of dicarboxylate at 1400 and 1508 cm$^{-1}$, which were attributed to the existence of BDC linkers within MIL-101. In addition, the C=C stretching vibration was observed at 1618 cm$^{-1}$, corresponding to the benzene ring of the linkers. For comparison, the peaks at 1510 and 1398 cm$^{-1}$ corresponding to C=O and O-C-O vibrations of dicarboxylate occurred in the spectrum of MIL-101/GO sample, indicating the successful intercalation of MIL-101 nanocrystals into the GO laminates and the formation of 2D/3D hybrid structure.
Gas transport property of MIL-101(Cr)/GO membrane

Selective permeation of H$_2$ (0.29 nm) over CO$_2$ (0.33 nm) was conducted to evaluate the gas separation performance of the MCGO membranes. The effect of the GO deposition and the MIL-101/GO mass ratio during the membrane fabrication process on the H$_2$/CO$_2$ separation performance was investigated. As illustrated in Figure 9, when the GO deposition increased from 0.1 to 0.4 mg, the H$_2$ permeance of MCGO membranes sharply dropped at first and then gradually descended. The significant decline was attributed to the elimination of non-selective defects at the GO deposition of 0.2 mg, and the selectivity increasing from 4.4 to 11.4 further verified the formation of integrated membrane structure\[126\]. The gradual decrease of H$_2$ permeance at GO deposition of higher than 0.2 mg was assigned to the thicker separation layer and thus enhanced gas transport resistance\[105\]. When it comes to the relatively higher GO deposition, more MIL-101 nanocrystals can be added into the filtration solution, possibly leading to the easier agglomeration of nanocrystals and lower H$_2$/CO$_2$ selectivity\[23\]. Hence, the GO deposition of 0.2 mg was considered as the optimal deposition for the following investigation.

![Figure 9. Effect of GO deposition on H$_2$/CO$_2$ separation performance of MIL-101/GO membrane. The MIL-101/GO mass ratio of the membranes is controlled at 1:1. The temperature of the gas permeation test is 25 °C.](image)

Furthermore, the effect of MIL-101/GO mass ratio (GO deposition: 0.2 mg) on the H$_2$/CO$_2$ separation performance was explored to optimize the membrane structure (Figure 10). As a control, the pristine GO membrane showed relatively low H$_2$ permeance of 13.3 GPU with H$_2$/CO$_2$ selectivity of 7.1, which was attributed to the tortuous gas transport pathway within the closely stacked GO laminate. When the MIL-101 nanocrystals were introduced at the MIL-101/GO mass ratio of 0.25:1, the as-fabricated MCGO-25 membrane showed enhanced H$_2$ permeance of 20.6 GPU with maintained selectivity of 7.6 because of the additional transport channels from the porous MIL-101 nanocrystals. Increasing MIL-101/GO the mass ratio to 0.5:1 nearly doubled the H$_2$ permeance and prominently enhanced separation selectivity compared with the MCGO-25 membrane. On one hand, the increase of H$_2$ permeance was attributed to the enlarged transport channels for faster gas transport, which was validated by the XRD result (Figure 7a). On the other hand, the enhanced adsorption towards CO$_2$ molecules arising from more embedded MOF nanocrystals would retard the permeation of CO$_2$ molecules through the 2D/3D hybrid nanochannels\[25, 27\], contributing to the elevated H$_2$/CO$_2$ selectivity. Nevertheless, as the MIL-101/GO mass ratio further increased, the H$_2$ permeance gradually increased while the selectivity dropped to 5.0. The phenomenon was assigned to the generation of large voids from the aggregation of MIL-101 nanocrystals (Figure 6c-d). As a result, the membranes fabricated at the MIL-101/GO mass ratio of 0.5:1 (MCGO-50 membrane) exhibited the highest separation performance with H$_2$ permeance of 55.2 GPU and H$_2$/CO$_2$ selectivity of 26.2, which were increased by 314% and 269% compared with the pristine GO membrane.

Moreover, the effects of the transmembrane differential pressure, operation temperature and the humidity of the feed stream on the separation performance of MCGO-50 membrane were investigated in detail (Figure S1-S2, Table S1). As shown in Figure S1, with the increase of transmembrane differential pressure, the H$_2$ permeance and H$_2$/CO$_2$ selectivity could be maintained at first but then gradually dropped when the pressure exceeded 0.2 MPa. The decrease in H$_2$ permeance was attributed to the compacted GO laminates at higher pressure, and the weakened trapping effect towards CO$_2$ molecules led to the decrease in H$_2$/CO$_2$ selectivity. Figure S2 showed the H$_2$ permeance gradually increased while the selectivity sharply dropped as the temperature increased. The affinity of MIL-101 to CO$_2$ molecules would decrease at the elevated temperature\[32\], leading to the permeation of more CO$_2$ molecules and thus reduced selectivity. In addition, the H$_2$/CO$_2$ separation performance of MCGO-50 membranes at the humid state was evaluated (Table S1). When the humidity comes to 85%, the H$_2$ permeance increased from 46.4 to 60.8 GPU because of the expanded interlayer channels with the entrance of water molecules. Meanwhile, the uptake water molecules in GO laminates facilitated the hydration of CO$_2$ and the generation of HCO$_3^-$, which was beneficial to the CO$_2$ permeation and caused the decrease in H$_2$/CO$_2$ selectivity\[13, 34\].

![Figure 10. Effect of MIL-101/GO mass ratio on H$_2$/CO$_2$ separation performance of MIL-101/GO membrane. The GO deposition of the membranes is controlled at 0.2 mg. The temperature of the gas permeation test is 25 °C.](image)

The continuous permeation test of the optimized MCGO membrane was carried out at the feed of equimolar H$_2$/CO$_2$ mixtures. As shown in Figure 11a, the MCGO-50 membrane at the GO deposition of 0.2 mg exhibited excellent separation performance stability during the 120-h continuous test, with the
steady H₂ permeance of 67.5 GPU and H₂/CO₂ selectivity of 30.3. The existence of competitive H₂ molecules partially occupied the transport channels and intensified the size-discrimination property, contributing to the higher mixed-gas selectivity compared with the ideal selectivity of 26.2. In addition, the H₂/CO₂ separation performance of our MCGO membrane was compared with the reported GO[10a, 35] and MOF[36] membranes and the thickness-converted upper-bound of polymeric membranes (Figure 11b). To satisfy the demand for the gas permeance and mechanical strength of membranes used in practical application, the PES-supported composite membranes with relatively thin separation layer (~50~500 nm) were fabricated for the evaluation of gas separation performance in this work. Therefore, the effect of membrane thickness was considered as comparing with the traditional separation performance upper-bound in the literature[25, 10a]. Two lines corresponding to the upper-bound were drawn in Figure 11b. The one at the basis of 500 nm is above the other at the basis of 1 μm. The thinner the membrane is, the higher permeance the membrane is required for reaching the upper-bound with the same selectivity. Compared with the reported GO and MOF membranes, the MCGO-50 and MCGO-100 membranes exhibited competitive H₂/CO₂ separation performance, which surpassed the upper bound and demonstrated the potential in H₂ purification process.

Conclusion

In summary, microporous MIL-101(Cr) MOF nanocrystals were successfully intercalated into the interlayer of GO laminates to construct 2D/3D hybrid nanochannels for H₂/CO₂ separation. By optimizing the GO deposition and MIL-101/GO mass ratio, the interlayer channels of GO laminates were enlarged, facilitating the fast permeation of H₂ molecules. The intercalation of MIL-101 with rich micropores provided additional gas transport pathways, further enhancing the gas permeation rate. Meanwhile, the MIL-101 possessing preferential affinity towards CO₂ molecules blocked their permeation through the 3D channels, contributing to prominently enhanced H₂/CO₂ selectivity. The MCGO membrane exhibited outstanding mixed-gas separation performance with H₂ permeance of 67.5 GPU and H₂/CO₂ selectivity of 30.3. The strategy of intercalating 3D nanocrystals into 2D laminates for constructing 2D/3D hybrid nanochannels can be extended to the advancement of other kinds of 2D-material membranes for molecular separation.

Experimental Section

Materials

GO was synthesized by the typical modified Hummers’ method and provided by Nanjing JCNANO Tech Co., Ltd. Terephthalic acid, chromium nitrate nonahydrate, and sodium acetate were obtained from Sigma-Aldrich. Ethanol was purchased from WuXi City Yasheng Chemical Co., Ltd., and N,N-dimethylformamide (DMF) was obtained from Sinopharm Chemical Reagent Co., Ltd. Acetic acid was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Polyether sulfone (PES) substrates with pore size of 220 nm were purchased from Haining Zhongli Filtration Equipment Co., Ltd. H₂, CO₂ and Ar with purity of 99.99% for gas separation performance test were supplied by Nanjing Special Gases Company. Deionized water was used in all the experiments. All of the materials were used without further purification.

Synthesis of nano-sized MIL-101(Cr)

0.82 g of terephthalic acid, 2.0 g of chromium nitrate nonahydrate, 35 mL of acetic acid and 50 mL deionized water were added into a beaker and stirred for 1 h. After that, it was transferred into a 100 mL Teflon-container autoclave, and the mixture was left in an oven (180 °C) for 12 h. The autoclave was then cooled at ambient temperature, followed by adding 0.3 g of sodium acetate and 10 mL of ethanol into the solution. Afterwards, the mixture was stirred for 1 h and left in an oven (180 °C) for 12 h. The green suspension of the sample was filtered and dried in an oven at 70 °C for 12 h. The filtered MIL-101 was dispersed in DMF at 150 °C overnight and filtrated to remove the excess terephthalic acid. The resulting powder was dispersed in ethanol at 60 °C overnight, filtrated, and placed in an oven at 150 °C for 24 h to remove DMF.

Membrane preparation

MIL-101 at a certain mass ratio to GO was dispersed in deionized water by stirring for 1 h. The resulting solution was added to dilute a certain amount of GO dispersion, which was stirred for 1 h and sonicated for 20 min to ensure the sufficient mixture of GO nanosheets and MIL-101 nanocrystals. The mixed solution was filtrated through the PES substrate to fabricate the MIL-101/GO (MCGO) membrane, which was dried at room temperature for 24 h. The as-prepared membranes were referred as MIL-101-X, where X corresponded to one hundred times the mass ratio of MIL-101/GO during the membrane fabrication process. For instance, the membrane fabricated at the MIL-101/GO mass ratio of 0.25:1 was named

Figure 11. (a) Continuous permeation of H₂-CO₂ mixtures for the MCGO-50 membrane. The temperature of the gas permeation test is 25 °C. (b) Comparison of H₂-CO₂ separation performance of MCGO membranes. The two upper-bound lines for polymeric membranes are drawn based on the literature[25] by converting permeability to permeance assuming a membrane thickness of 1 μm (dash line) and 500 nm (solid line). The H₂-CO₂ separation performance of GO, MOF and MCGO membranes was listed in Table S2.

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as MCGO-25. To investigate the effect of GO deposition on the separation performance of MCGO membranes, the GO deposition was set as 0.1, 0.2, 0.3 and 0.4 mg at the fixed MIL-101 GO mass ratio of 1:1. The MCGO membranes with different loading of MIL-101 was prepared at the MIL-101 GO mass ratio of 0.25:1, 0.5:1, 1:1, 2:1 at the fixed GO deposition of 0.2 mg. For the fabrication of pristine GO membrane, a certain amount of GO was diluted in deionized water, followed by the vacuum filtration to form the GO layer on the PES substrate. In addition, the GO powder and MIL-101/GO composite were obtained from the corresponding aqueous solution via the freeze drying, and employed for the FTIR characterization.

Characterizations

The morphology of MIL-101 nanocrystals and MCGO membranes was observed by field emission scanning electron microscopy (FESEM, S4800, Hitachi Limited, Japan) and transmission electron microscope (TEM, JEM-2100F, Japan Electron Optics Laboratory Co., Ltd., Japan). X-ray diffraction (XRD, Smartlab 3kW, Rigaku, Japan) was employed to characterize the crystal phase of MIL-101 powder and the interlayer heights of membranes. The scan range was set as 2° ≤ 28° ≤ 15° for MIL-101 powder, and 5° ≤ 28° ≤ 40° for membranes with a step of 0.05° and a scan rate of 0.2° s⁻¹ at room temperature. The element compositions of MIL-101 powder, GO and MCGO membranes were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, USA). Fourier transform infrared spectra (FTIR, Thermo, Nicolet Nexus 470 spectrometer, USA) was employed to characterize the functional groups of samples in the range of 500-4000 cm⁻¹. BET surface areas of MIL-101 and the corresponding pore distribution were calculated from N₂ adsorption isotherms (77 K) measured by ASAP 2020 (Micromeritics, USA). Gas adsorption experiments of MIL-101 at 25 °C were measured by BELSORP-HP (Micrometrics Corp., Japan) with H₂ and CO₂.

Gas permeation measurements

During the single and mixed gas permeation tests, a constant pressure/volume variable technique was employed to evaluate the separation performance[24]. The transmembrane differential pressure and temperature were set as 0.1 MPa (absolute pressure) and 25 °C for single gas permeation test. When the system reached steady-state, the gas permeance P was calculated from the average value of at least three results calculated by the following equation[25]:

\[ P = \frac{1}{A} \left( \frac{dV}{dt} \right) \frac{\rho_{atm}}{\Delta P} \tag{1} \]

where P represents the gas permeance (1 GPU = 10⁻¹² cm³(STP) cm⁻² s⁻¹ cmHg), ρₘₐₜ is the atmospheric pressure (atm), ΔP and T refers to the transmembrane pressure (atm) and the testing temperature (°C) respectively, A is the effective area of membrane, and dV/dt corresponds to the volumetric displacement rate in the bubble flow meter. The ideal selectivity α of H₂/CO₂ was calculated by the ratio of the permeance of the individual gases which can be expressed as follows:

\[ \alpha = \frac{P_{H_2}}{P_{CO_2}} \tag{2} \]

During the mixed gas permeation test, the total flux of the gas mixture (H₂ : CO₂, 50 vol% : 50 vol%) was controlled at 60 mL min⁻¹, and Ar was selected as the sweep gas with a flux of 10 mL min⁻¹. The mixed gas permeation test was carried out at the feed stream pressure of one atmosphere (absolute pressure) and 25 °C. When the membranes were tested in a humid state, the feed and sweep gases were both humidified by water bottles. Gas chromatography (Agilent 7820A, USA) was employed to analyze the component of the mixed gas. The selectivity of binary gas mixtures can be calculated as follows:

\[ \alpha_{xy} = \frac{y_x}{y_y} \frac{x_x}{x_y} \]

where x and y represent the volumetric fractions of the one component in the feed and permeate side, respectively.

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Keywords: graphene oxide membrane • MIL-101(Cr) • nanocrystal intercalation • enlarged interlayer channel • H₂/CO₂ separation

Microporous MIL-101(Cr) nanocrystals were embedded into GO laminate to construct 2D/3D hybrid nanochannel for H₂/CO₂ separation. The 2D channels within GO laminates were partially enlarged for faster gas permeation. The intercalation of MIL-101(Cr) nanocrystals provided additional 3D transport pathways for gas molecules, and the affinity of MIL-101(Cr) towards CO₂ molecules would retard the CO₂ permeation, contributing to the simultaneous enhancement in H₂ permeance and H₂/CO₂ selectivity.