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Communication

# Efficient $CO_2/N_2$ separation by mixed matrix membrane with amide functionalized porous coordination polymer filler

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ABSTRACT

Mixed matrix membrane used to selective removal of $CO_2$ was considered as an efficient solution to energy and environmental sustainability. In this study, a MMM that consists of amide functionalized porous coordination polymer filler (MIL-53-$NH_2$) was successfully prepared, which sharply promotes the $CO_2/N_2$ selectivity from 44 (neat polymeric membrane) to 75. Remarkably, the positive effect of amide group and nanochannel of MIL-53-$NH_2$ filler was illustrated by decreased selectivity of the MMM with formic acid modified MIL-53-$NH_2$ filler (MIL-53-NHCOH).



As the main greenhouse gas, $CO_2$ is considered to be a threat in the context of global warming. The development of efficient technology for selective $CO_2$ capture is a scientific challenge in a highest order [1]. Traditionally, the strategies of chemisorption by amide solvent and physical adsorption by porous absorbents have been widely investigated [2,3]. However, due to the group of benefits in lower energy consumption, ease operation, environmental friendliness and mechanical simplicity, membrane process was believed as one of the most attractive strategies for continuous and efficient $CO_2$ capture [4,5].

Generally, membrane material played crucial roles in final separation performance [6–8]. For example, since the first report of organic polymer membrane in 2002 [9], various polymeric membranes have drawn widespread attention for gas separations [10–12]. However, the common problem of trade-off between permeability and selectivity of organic membranes limited their further development [11]. In parallel to the development of polymeric membrane, much research effort has been devoted to establish inorganic membranes [13]. Inorganic membranes with good separation performance are expensive, brittle and difficult to upscale. Thus, in order to overcome the above limitations, mixed matrix membrane (MMM) with combined advantages of good separation performance of inorganic materials and mechanical stability of organic polymers provides an alternation to go beyond the limitations of organic and inorganic membranes [14].

To date, a group of inorganic particles, such as carbon nanotubes [15], zeolites [16], silica [17] and attapulgite [17] have been employed as functional filler for MMM preparation. Indeed, each filler has its own advantages for the formation of MMM with controlled free volume or/and improved gas permeation, which are of great importance and considered to be the key factors in optimizing the performance in MMMs. In recent years, porous coordination polymer (PCP) materials, featuring well-defined pores, high crystalline and labile surface chemistry, exhibited intriguing advantages in gas storage and separation [18–23]. Therefore, the involved PCP filler with pre-designed function site will lead to bright future for rapid MMMs development and efficient $CO_2$ selective capture.

Inspired by enhanced capability of $CO_2$ capture by PCPs, herein, MIL-53-$NH_2$, one of the water stable PCPs with accessible amide group and one dimensional (1D) channel, was selected as filler for MMM fabrication (Fig. 1). As expected, the MMM (15 wt% loading) showed sharply improved $CO_2/N_2$ selectivity from 44 (neat polymeric membrane) to 75. Furthermore, by changing the MIL-53-$NH_2$ particles to formic acid modified MIL-53-$NH_2$ filler (MIL-53-NHCOH), the decreased selectivity (from 75 to 65) of the MMM reflects the positive effect of amide group and assessable 1D channel in MIL-53-$NH_2$ filler for faster $CO_2$ permeation.

MIL-53-$NH_2$ was synthesized according to previous literatures [24,25]. The crystalline structure and phase purity of as-synthesized MIL-53-$NH_2$ were confirmed by powder X-ray diffraction (XRD) (Fig. S1 in Supporting information). Transmission electron microscopy (TEM) image showed that the average size of MIL-53-$NH_2$ nanoparticles is around 150 nm (Fig. S2 in Supporting information). Further gas adsorption isotherms showed that

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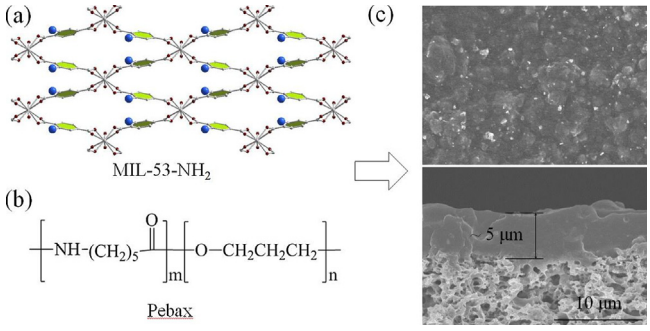


**Fig. 1.** (a) View of 1D channel with rich amide groups (blue ball) in MIL-53-$NH_2$; (b) Structure of Pebax; (c) Top and cross-sectional view of MIL-53-$NH_2$@Pebax membrane (15 wt%).

MIL-53-$NH_2$ has significant higher $CO_2$ gas uptake (50 $cm^3$/g) than that of $N_2$ (7 $cm^3$/g) at 1 bar, 298 K (Fig. S3a in Supporting information). The predicted gas selectivity by ideal adsorbed solution theory (IAST) is as high as 135 at low pressure range, similar as the result in previous report [26]. In other words, the amide groups in the channel of MIL-53-$NH_2$ work well for selective $CO_2$ capture (Fig. S4 in Supporting information).

Poly(vinylidene fluoride) (PVDF) ultrafiltration membrane was selected as support (average pore size: 450 nm) to prepare MMMs by a method of solution casting [27]. With varied filler loading, four MIL-53-$NH_2$@Pebax MMMs (named as MMM-5-$NH_2$, MMM-10-$NH_2$, MMM-15-$NH_2$ and MMM-20-$NH_2$) were prepared. PXRD of them showed that the characteristic diffraction peaks are same as that of as-synthesized MIL-53-$NH_2$, indicating good chemical stability of MIL-53-$NH_2$ filler (Fig. 2). Evidenced by SEM images and EDX mapping, the membrane thickness is around 5 μm, while the fillers distributed uniformly (Fig. 3 and S5 in Supporting information). The results of thermal gravimetric (TG) analysis confirmed high thermal stability of these MMMs, up to 350 °C (Fig. S6 in Supporting information) [24,28].

After activation, the MMMs were sealed into the sample cell. Then, binary gas permeation experiments were performed on each of them by method of Wicke-Kallen bach at 10 °C. In order to avoid machine error, each measurement was repeated three times. The flow rate of binary gas feed was consistent with a volumetric flow rate of 100 mL/min (each gas of 50 mL/min). For these MMMs, $CO_2$/$N_2$ selectivity increases with filler loading, and reaches to 75 at the loading of 15 wt%, which is 70% improvement than that of pure Pebax membrane (44). This is because the loaded MIL-53-$NH_2$ filler exhibits not only the enhanced affinity towards selective $CO_2$ capture, but also the regular 1D channel for $CO_2$ permeation. However, when the filler loading reached to 20 wt%, the gradually increased non-selective interface defect within the MMM body results in decreased gas selectivity (58) (Fig. 4a), similar as other PCP-based MMMs [29,30]. The non-selective interface defect here

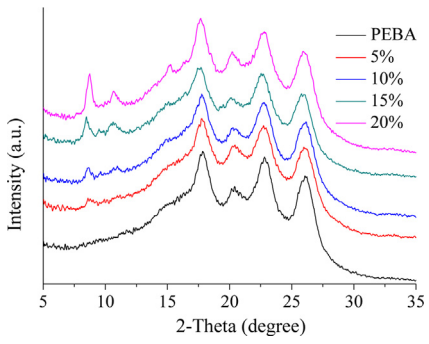


**Fig. 2.** PXRD of series MMMs with varied MIL-53-$NH_2$ loading.

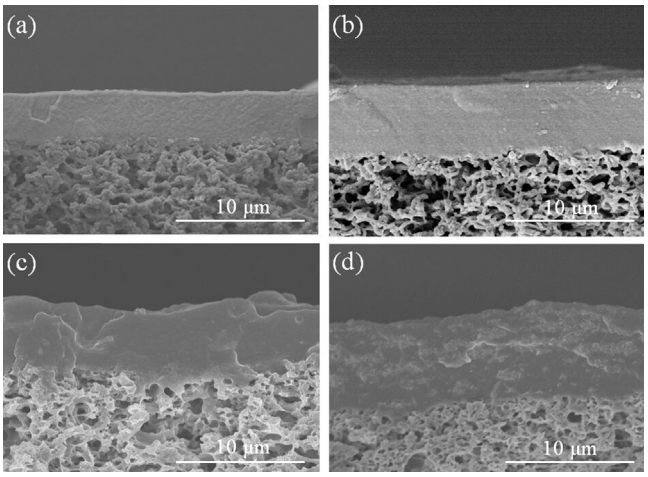


**Fig. 3.** Cross-sectional view of series MMMs with varied MIL-53-$NH_2$ loading: (a) 5%, (b) 10%, (c) 15%, (d) 20%.

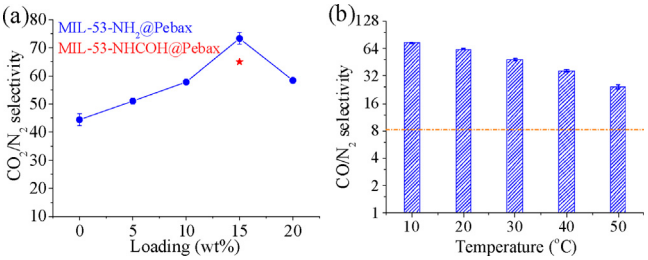


**Fig. 4.** (a) $CO_2$/$N_2$ selectivity of neat Pebax membrane and series of MIL-53-$NH_2$ based MMMs with varied filler loading; $CO_2$/$N_2$ selectivity of MIL-53-NHCOH@Pebax membrane (15 wt%) was highlighted by a red star; (b) Effect of operation temperature on $CO_2$/$N_2$ selectivity of MMM-15-$NH_2$.

means the nano-space between the fillers. Despite the uniform distribution of MOF fillers in polymer solution, such kind space cannot be fully filled by polymer chains.

In order to validate the positive effect of amide group and micro-channel, the formic acid modified MIL-53-$NH_2$ filler, named as MIL-53-NHCOH, was prepared. After modification, the relative intensity of IR absorption peak at 1670 $cm^{-1}$ that belongs to the bending vibration of N-H sharply decreased (Fig. S6 in Supporting information), reflecting successful condensation between carboxylate and amide group [31]. In addition, the X-Ray diffractions of (110) and (200) plane are same as that of MIL-53-$NH_2$, while the peak of (220) plane shifted to lower angle. This means a slight channel expansion was generated after introduction of additional HCO- group (Fig. S1). The particle size (150 nm) of MIL-53-NHCOH is same as that of MIL-53-$NH_2$ (Fig. S7 in Supporting information), while its micro-porosity was confirmed by gas adsorption experiments. As shown in Fig. S3, the $CO_2$ uptakes at 15 kPa of MIL-53-$NH_2$ (28 $cm^3$/g) is over nine times higher than that of MIL-53-NHCOH (3 $cm^3$/g). Based on this, a new MMM (MIL-53-NHCOH@Pebax) with 15 wt% fresh filler and same thickness was prepared (Fig. S8 in Supporting information). Binary gas permeation experiments showed that $CO_2$/$N_2$ separation selectivity of MIL-53-NHCOH@Pebax decreased to 65, demonstrating high importance of exposed amide group and micropore for preferred $CO_2$ permeation (Fig. 4a).

In addition, effect of operation temperature on $CO_2$/$N_2$ selectivity was studied on MMM-15-$NH_2$. As shown in Fig. 4b, the $CO_2$/$N_2$ selectivity decreases following elevated temperature from 10 °C to 50 °C, but all of them are far higher than 8 [32], a value indicates the possibility for practical separation. In addition, due to

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the none-porosity of Pebax polymer, $CO_2$ permeation of MMM-15-$NH_2$ is close to that of Pebax-based MMMs, but is lower than that of MMMs with porous polymer [33].

In summary, by incorporating amide functionalized MIL-53-$NH_2$ filler, Pebax-based MMMs showed significantly improved $CO_2/N_2$ selectivity. In addition, the decreased gas selectivity of the MMM with MIL-53-NHCOH filler demonstrates the importance of amide group and nanochannel in MIL-53-$NH_2$ filler for improved $CO_2$ permeation.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cclet.2017.11.008.

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