Mg$_2$(dobdc) crystals adhere to Matrimid matrix membranes bridged by diethylenetriamine (DETA) as an adhesion agent for efficient CO$_2$ separation

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**ABSTRACT**

Diethylenetriamine (DETA)-bridged Mg$_2$(dobdc) crystals were first synthesized and DETA molecule was acted as adhesion agent to stick Matrimid matrix together, fabricating the mixed matrix membranes (MMMs) with superior CO$_2$ separation performance from the biomethane (CO$_2$/CH$_4$) and flue gas (CO$_2$/N$_2$). The detected CO$_2$ adsorption isotherms (at 298 K and 1 bar) of Mg$_2$(dobdc) crystals and DETA-bridged Mg$_2$(dobdc) crystals demonstrated excellent CO$_2$ uptake of 7.15 and 6.45 mmol/g, as well as superior separation selectivity. The XPS and FTIR spectra revealed that unsaturated Mg$^{2+}$ sites in Mg$_2$(dobdc) tightly grasped DETA molecule and alter the surrounding binding environment. Density functional theory (DFT) calculation implied that active amine group (–NH$_2$) on DETA was bonded to unsaturated Mg$^{2+}$ sites through Mg$^{2+}$–O$^-$ and H$^+$–O$^-$ interaction with the calculated Mg-O distance of 2.22 Å and binding energy of 160.8 kJ/mol. For Mg$_2$(dobdc) crystals, one CO$_2$ molecule was firmly attracted by unsaturated Mg$^{2+}$ site via Mg$^{2+}$–O$^-$ and H$^+$–O$^-$ interaction with the calculated Mg-O distance of 2.32 Å and binding energy of 46.9 kJ/mol. For DETA-bridged Mg$_2$(dobdc) crystals, one CO$_2$ molecule was simultaneously caught by unsaturated Mg$^{2+}$ site of Mg$_2$(dobdc) and active amine group of DETA through Mg$^{2+}$–O$^-$ (distance = 4.13 Å) and N$^+$–C$^+$ (distance = 3.19 Å) interactions. DETA molecule as adhesion agent stick Mg$_2$(dobdc) crystals and Matrimid matrix together to eliminate interface defects and voids in MMMs, could dramatically increase CO$_2$ permeability as well as the superior CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity. Therefore, the CO$_2$ permeability of Matrimid-based MMMs incorporated with DETA-bridged Mg$_2$(dobdc) crystals first increased to a peak of 41.1 Barrers and then decreased, when Mg$_2$(dobdc) crystals loading increased from 2.5 wt% to 10 wt% and further to 15 wt%. This CO$_2$ permeability was 3.03 times higher than that (8.19 Barrers) of pristine Matrimid membrane and 17.8% higher than that (34.9 Barrers) of Matrimid-based MMMs incorporated with Mg$_2$(dobdc) crystals (without DETA). Positron annihilation lifetime spectroscopy experiments revealed the different dispersion states of crystals in the MMMs with 15 wt% crystals, compared to the MMMs with 2.5 to 10 wt% crystals.

1. Introduction

The use of fossil fuels, such as coal, gasoline, and natural gas, has resulted in a large-scale emission of greenhouse gases and, particularly for carbon dioxide (CO$_2$), in the atmosphere, leading to severe environmental issues and global warming [1–3]. Therefore, it is of great concern for implementing strict policies and effective technologies for the goal of achieving carbon neutrality.

Nowadays, the most commonly used CO$_2$ separation methods are based on cryogenic distillation, pressure swing adsorption (PSA), and amine-based absorption [4–6]. However, their high energy requirements and low reliability in long-term use have significantly limited their further development [7–8]. Membrane separation technologies have emerged as a strong competitor to such traditional CO$_2$ separation methods due to their i) lower energy consumption, ii) long term reliability, iii) stability at high pressures, iv) small footprint, and v)
high flexibility during operation [6-9,11]. However, their permeability and selectivity “trade-off” effects limit their commercialization in industrial separation processes. The existence of these effects was demonstrated by Robeson in 2008 by investigating the upper bound of polymers, such as polyacetylene oxide/PEO, polyimides, thermally-rearranged polymers, and polymers with intrinsic microporosity (PIMs) [12].

Polymides are generally obtained from the reaction of a diamine with a dihydride in an aprotic solvent via the generation of polyamic acid and are widely used as polymeric materials for membrane fabrication [13,14]. Matrimid, 6FDA-based polyimide and PIM-1 combine excellent thermal and chemical resistance with superior CO$_2$ permeability. For this reason, they are currently used in the laboratory as gas separation membrane. However, they also have disadvantages, such as non-ideal separation performance, easy plasticization, and high production costs [1]. Particularly, the “trade-off” effect also limits their separation performance. In order to overcome this effect, gas adsorption inorganic nanofillers, such as zeolites, graphene oxide, carbon nanotube, metal organic frameworks, and covalent organic frameworks, can be incorporated into the polyimide matrix to obtain the so-called mixed matrix membranes (MMMs) [15-17]. Amooghin et al. embedded modified NaY zeolite into a Matrimid 5218 matrix. The results show that the CO$_2$ permeability increases from 8.34 to 9.70 Barrers with a 15 wt% load of fillers as well as the increased CO$_2$/CH$_4$ selectivity [18]. Li et al. reported that 5 wt% of carbon nanotubes (CNTs) and 5 wt% of graphene oxide (GO) could increase the CO$_2$ permeability of 38.07 Barrers, accompanied by the enhanced CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity in Matrimid-based MMMs [19]. Shan et al. added an azine-linked covalent organic framework (ACOF-1) into a Matrimid and increased the CO$_2$ permeability to 17.7 Barrer with a 16 wt% loading of A-ACOF-1 [20].

Although multifarious nanofillers have been incorporated into polyimide to obtain MMMs, they are not enough compatible with the polymer matrix and induce the formation of non-selective voids [21,22]. Furthermore, in the case of glassy polimide polymers, a high filler loading leads to agglomerations of such nanofillers, increasing further the number of unselective defects. Therefore, several approaches, including the immobilization of the ionic liquid [23], the introduction of cohesive linkages via amine [24], the coating of MOF cores with COF layers [25], cross-linking reactions [26] and other surface modification strategies [4,27,28], were investigated to overcome this problem.

Mg$_2$(dobdc) (dobdc = 2,5-dihydroxystyrenehyphatic acid), also known as Mg-MOF-74 or Mg-CPO-27, whose structure consists of hydroxyl and carboxyl groups. Compared with the other related MOFs for CO$_2$ adsorption such as ZIF-8 (3.4Å), ZIF-72 (7.2Å), HKUST (9Å) and UiO-66 (7.1Å), the Mg$_2$(dobdc) crystals have the relatively larger pore size ranging from 11 to 13Å. Its characteristics promise a high hydrogen storage capacity, as well as high CO$_2$ adsorption and separation for CO$_2$/H$_2$/CH$_4$ [29]. These unsaturated metal sites on the Mg$_2$(dobdc) crystals are the adsorption sites for the gas molecules, which contribute to its high CO$_2$ adsorption capacity [30]. This implies that it can be used as a nanofiller for the fabrication of mixed matrix membranes for CO$_2$ separation. There are researchers that prepared high-quality MMMs with Mg$_2$(dobdc) crystals in 6FDA-TMPDA polyimide. However, although the Mg$_2$(dobdc) crystal could enhance the CO$_2$ permeability and CO$_2$/N$_2$ selectivity of the MMM, the interface defects and non-selective voids were observed in the microscopic cross-section images, which would cause the gas molecule cannot be effectively identified and separated, further decreasing the separation performance of the membrane. Consequently, this is an urgent obstacle to be conquered and there is an incredible room for improving their CO$_2$ permeability and separation selectively for the Mg$_2$(dobdc)-based mixed matrix membranes [27].

Therefore, for the first time, the MMMs consisting of a glassy polyimide polymer (Matrimid 5218) and diethylenetriamine (DETA)-bridged Mg$_2$(dobdc) crystals were fabricated. DETA, with its high affinity towards CO$_2$, was adopted as the adhesion agent for the Mg$_2$(dobdc) crystals to eliminate interface defects and non-selective voids. The overall preparation schematic of the DETA-bridged Mg$_2$(dobdc) crystals and the corresponding Matrimid-based mixed matrix membranes (MMMs) is illustrated in Fig. 1. These MMMs exhibit a significant increase in their CO$_2$ permeability as well as the CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity. An in-depth characterization via N$_2$-adsorption desorption, FTIR, XPS, TG-DTG, and SEM was conducted to shed the light on the physical and chemical properties of the crystals. The pure gas adsorption isotherms of CO$_2$, CH$_4$, N$_2$, of the Mg$_2$(dobdc) crystals, and of the DETA-bridged Mg$_2$(dobdc) crystals were measured at 298 K. DFT calculations revealed the interaction mechanism between CO$_2$, CH$_4$, and N$_2$ molecules and the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals. The Matrimid-based MMMs with varying content of Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals were prepared. Pure-gas and mixed-gas permeability of these prepared MMMs were investigated via the constant-volume/variable pressure method.

2. Experimental section

2.1. Chemicals

The chemicals employed in this work were reagent grade and they were used without further purification. Mg(NO$_3$)$_2$·6H$_2$O (99%, CAS: 13446-18-9) and 2,5-dihydroxystyrenehyphatic acid (98%, H$_2$dobdc, CAS: 610-92-4), and diethylenetriamine (99%, DETA, CAS: 111-40-0) were purchased from Sigma-Aldrich, whereas N,N-dimethylformamide (98%, DMF), anhydrous methanol, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). These chemicals were used to synthesize the Mg$_2$(dobdc) nanoparticles. These membranes were prepared by using the commercially available polyimide (PI, Matrimid 5218), which was purchased form Huntsman Chemical Company and used after drying it overnight at 125°C. The chloroform was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), whereas the ultrahigh purity (99.999%) CO$_2$, CH$_4$, and N$_2$ gas cylinders were obtained from Hangzhou Jingong Special Gas Co., Hangzhou, Zhejiang, China.

2.2. Synthesis of the Mg$_2$(dobdc) and DETA-incorporated Mg$_2$(dobdc) crystals

The Mg$_2$(dobdc) crystals were synthesized by using a conventional hydrothermal method with only minor modifications [29,30]. The procedure previously reported in literature was followed: Mg(NO$_3$)$_2$·6H$_2$O (1.424 g, 5.56 mmol) and H$_2$dobdc (0.334 g, 1.68 mmol) were initially dissolved and sonicated in a mixture of DMF (135 ml), ethanol (9 ml), and deionized water (9 ml). Successively, the solution was transferred into a 125 ml Teflon lined stainless-steel autoclave and heated up to 125°C for 26 h in a drying oven. The samples were then cooled down to room temperature and the mother liquor was exchanged over 3 days by fresh methanol to eliminate the residual DMF. The light-yellow precipitates were finally segregated by centrifuging and washing the sample thoroughly with methanol. During the activation process, the light-yellow precipitates were inserted in a vacuum chamber kept at 250°C for 15 h to remove the guest molecules. Finally, the dark-yellow Mg$_2$(dobdc) crystals were obtained.

In order to incorporate DETA into the samples, the activated Mg$_2$(dobdc) crystals (20 mg) and DETA (5 mg) were dissolved in a three-necked glass reaction vessel with 25 ml of toluene. The sample was flushed in an argon flow for 24 h at room temperature. The resulting compound was then filtered off and washed with toluene and methanol to obtain the DETA-incorporated Mg$_2$(dobdc) crystals.

2.3. Membrane synthesis

2.3.1. Preparation of pure Matrimid dense membrane

Commercially available Matrimid 5218 powder was dried at 125°C for 24 h in a vacuum oven and dispersed into a chloroform solution with...
a 6% mass fraction of polymer. Successively, the solution was sonicated for 3 h and stirred at room temperature for 6 h to obtain a homogeneous mixture. The sample was poured into a 2 mm deep Teflon Petri dish in a nitrogen bag and covered with a funnel to prevent solvent evaporation and the dust to enter in contact with the solution. The membrane solidified overnight due to solvent evaporation, and the yellow Matrimid membrane was annealed in an oven: The temperature was slowly increased to 160 °C and maintained for 6 h. The membrane was then carefully removed from the substrate.

2.3.2. Preparation of Matrimid membrane Mg\textsubscript{2}(dobdc)-Matrimid based MMMs

Mg\textsubscript{2}(dobdc) crystals with different mass fractions were incorporated into a Matrimid polyimide to obtain the MMMs. Dried Matrimid powder was initially added into chloroform, and the sample was stirred for 120 min to obtain a 6% polymer solution. Separately, Mg\textsubscript{2}(dobdc) nanoparticles were suspended into a little quantity of chloroform for wetting. They were then sonicated for 90 min and added into the initial solution. The resulting Mg\textsubscript{2}(dobdc)/Matrimid sample in the chloroform suspension was stirred for 120 min, sonicated for 120 min, and stirred again for 120 min to guarantee the complete dispersion of Mg\textsubscript{2}(dobdc) in the Matrimid polymer. Finally, the MMMs films were formed by transferring the specimen into a 2 mm Teflon Petri dish, as described in Section. The MMMs were labeled Matrimid-X-Y, where X corresponds to the weight percentage of the nanoparticles and Y to the Mg\textsubscript{2}(dobdc) nanoparticle type.

2.3.3. Preparation of defect free DETA-bridged Mg\textsubscript{2}(dobdc)-Matrimid based MMMs

Diethylenetriamine (DETA) was used as the bridging agent to obtain Matrimid-based MMMs with different mass fractions of Mg\textsubscript{2}(dobdc) nanoparticles. A certain content of DETA was introduced in chloroform with an injector and stirred for 60 min before adding the Matrimid powder. The synthesis procedure is similar to the aforementioned method used for the fabrication of Mg\textsubscript{2}(dobdc)-Matrimid based MMMs. The MMMs samples were dispersed with identical weight of DETA to obtain comparative data. The MMMs were labeled as DETA-Matrimid-X-Y. This means, for instance that the DETA-Matrimid-5-Mg\textsubscript{2}(dobdc) sample consists of 5 mg of DETA, which were added into 5.58 g of chloroform and stirred for 60 min at room temperature. At this point, 0.42 g of Matrimid powder was added into the solution, which was then stirred for 120 min. Simultaneously, the Mg\textsubscript{2}(dobdc) nanoparticles were dispersed in a little quantity of chloroform and sonicated for 90 min. Finally, the dispersed Mg\textsubscript{2}(dobdc) particles were added into the Matrimid sample. The specimen was sonicated for 120 min, stirred for another 120 min, and dropped onto a Teflon Petri dish to obtain the defect-free DETA-bridged Mg\textsubscript{2}(dobdc)-Matrimid-based MMMs. The specific mass fraction of the nanoparticles was calculated by using the following equation:

$$\text{Mg}_2(\text{dobdc})\text{loading (wt%)} = \frac{\text{wtMg}_2(\text{dobdc})}{\text{wtMg}_2(\text{dobdc}) + \text{wtMatrimid}} \times 100\%$$

The average thickness of each MMM measured 100–250 µm. These measurements were obtained by using a digital thickness gauge and each sample was weighted at least 30 times.

2.4. Gas transport measurement throughout membrane

The single gas permeabilities were determined by using a constant volume variable pressure pure gas permeator at 35 °C and 4 bar. The membranes were fixed in a stainless-steel metal flange. Before installing the membranes into a permeation cell, they were pre-activated at 120 °C for at least 3 h. The temperature was then slowly increased to 180 °C in a vacuum oven for approximately 4 h. Successively, the measurement system was left in a vacuum atmosphere overnight to remove the residual gas. The feed gases (H\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}, and CO\textsubscript{2}) were then injected into the membrane system, and the pressure of the downstream volume was recorded as a function of time. The gas transport measurements were performed in the following order: H\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}, and CO\textsubscript{2}. The permeability (P) was calculated by using the following equation:

$$P = \frac{J}{C}$$

where J is the flux and C is the partial pressure difference across the membrane.
\[ P = \frac{V_d}{p_1 \cdot A \cdot R \cdot T} \left( \frac{dp}{dt} \right)_{\text{test}} - \left( \frac{dp}{dt} \right)_{\text{leak}} \]

Here, \( p_1 \) corresponds to the feed pressure (4 bar), \( V_d \) to the calibrated permeate side volume, \( A \) to the membrane thickness, \( A \) (cm\(^2\)) to the effective area of the membrane, T to the experimental absolute temperature, and R to the ideal gas constant. The expressions \( \frac{dp}{dt} \) and \( \frac{dp}{dt} \) refer to the rates of the pressure changes in the permeate side at steady state during and before the test, respectively.

The ideal selectivity, \( \alpha_{A/B} \), was calculated by using the ratio between two individual single gas permeability values as follows:

\[ \alpha_{A/B} = \frac{P_A}{P_B} \]

Here, \( P_A \) and \( P_B \) correspond to the permeability of gas A and gas B, respectively.

Mixed-gas permeability was determined using a constant-pressure and variable-volume apparatus via a sweep gas of Ar on the permeate side and can be calculated with the following equation:

\[ P = \frac{\alpha_{A/B} Q_s}{A \cdot k_{\text{leak}} (P_{2,2A} - P_{1,2A})} \]

where \( Q_s \) is the flow rate of the sweep gas (Ar). The \( x_{A,B} \) and \( x_{\text{moop}} \) are the mole fractions of gas component A and Ar (Ar) in sweep-out stream, respectively, which were measured using an Agilent 7820A. \( x_{2A} \) is the mole fraction of component A in the feed gas.

### 2.5. Characterizations of Mg\(_2\)(dobdc) crystals and membranes

The \( N_2 \) adsorption and desorption isotherms of the Mg\(_2\)(dobdc) crystals were measured at 77 K via an automatic volumetric adsorption system (Micromeritics ASAP 2020C). The Brunauer-Emmett-Teller (BET) method was used to obtain the surface area, whereas the pore size distributions were estimated from the desorption branch via the Barrett-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) methods.

The CH\(_4\), \( N_2 \), and CO\(_2\) single gas adsorption isotherms of the Mg\(_2\)(dobdc) crystals at 298 K were detected by using a Micromeritics ASAP 2020 system. The light-yellow Mg\(_2\)(dobdc) crystals were activated at 250 °C to remove the guest molecules and then, they were placed in a glass test tube to carry out further gas adsorption analyses. In order to investigate the effect of the activation time on the CO\(_2\) adsorption capacity of the Mg\(_2\)(dobdc) crystals, the samples were activated at 250 °C for 6 h, 15 h, and 26 h.

The Mg\(_2\)(dobdc) morphology and the cross section of the membranes were obtained via field emission scanning electron microscopy (FE-SEM) by using a Hitachi SU70 instrument from Japan. The membrane was cryogenically fractured in liquid nitrogen and sputtered on a thin gold layer.

The Fourier transform infrared (FTIR) spectra of the Mg\(_2\)(dobdc) crystals and membranes were collected by using a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA) in the 4000–400 cm\(^{-1}\) range.

The surface composition and the chemical valence of the elements in Mg\(_2\)(dobdc) crystals and DETA-bridged Mg\(_2\)(dobdc) crystals were determined by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB MKII spectrometer (VG Scientific, UK) operating under a constant pass energy of 20 eV using Al K\(^\alpha\) radiation. The operating pressure in the chamber was maintained at 4 × 10\(^{-9}\) mbar. All the binding energies were calibrated based on the C 1 s peaks at 284.8 eV.

A thermogravimetric analysis (TGA) was performed with a TA-Q500, USA, to characterize the thermal stability of both Mg\(_2\)(dobdc) and the membranes in a nitrogen atmosphere. The 50–800 °C temperature range investigated in these experiments was sampled at a 10 °C/min rate prior to heating up the compounds to 100 °C to remove the adsorbed water.

The wide angle X-ray diffraction (XRD) analysis of the membranes was carried out by using an X’Pert Pro diffractometer (Philips/PANalytical, The Netherlands), with a Cu K\(_\alpha\) radiation of 1.54 Å and a 5–50° scanning range at 40 kV and 40 mA, to measure the degree of crystallinity of the membranes. The average d-space was evaluated via the Bragg’s law:

\[ n\lambda = 2\sin\theta \]

Here, \( n \) corresponds to an integer (1, 2, 3, …), \( \lambda \) represents the X-ray wavelength, \( d \) the intersegmental spacing between two polymer chains, and \( \theta \) the X-ray diffraction angle.

Differential scanning calorimetry (DSC) was carried out on a TA-Q2000, USA, to measure the glass transition temperature (\( T_g \)) of the membranes: The samples were heated up to 100 °C at a rate of 10 °C/min in a nitrogen atmosphere and then, they were left equilibrating for 5 min. Finally, the membranes were heated up to 400 °C while the calorimetry data was recorded to determined \( T_g \).

Positron annihilation lifetime spectroscopy (PALS) experiments were employed at University of Science and Technology of China to evaluate the free volume of Matrimid-based mixed matrix membranes. The experiments were performed on a conventional fast–fast coincidence spectrometer with a time resolution of 210 ps at room temperature. The \( ^{23}Na \) radioactive source (30 mCi) was sealed by two 7.5-μm-thick Kapton foils. PALS data were recorded with a total count of 4 million and analyzed using PATFIT-88 software. The mean free-volume hole radius, \( R \), was semi-empirically estimated based on the ortho-positronium (o-Ps) lifetime, \( \tau_3 \).

\[ \tau_3 = \frac{1}{2} \left( 1 - \frac{R}{R + \Delta R} \right) \left( \frac{\pi}{2\tau_R} \right)^{1/2} \left( \frac{2\pi R}{R + \Delta R} \right)^{-1} \]

where \( \Delta R \) is the fitted empirical electron layer thickness of 0.1656 nm. The fractional free volume (FFV) was calculated with the empirically fitted equation

\[ FFV = C \cdot V_{i,0} = C \cdot \frac{4}{3} R^3 \cdot V_{i,0} \]

where the o-Ps intensity, \( V_{i,0} \), represents the amount of free-volume holes.

### 2.6. Dispersion-corrected density-functional theory (DFT-D) calculations

In order to further investigate the interactions between the gas molecules and the Mg\(_2\)(dobdc) and DETA-incorporated Mg\(_2\)(dobdc) crystals, first-principles density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP 5.4.1) code. These calculations were conducted under the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) expression was employed as the exchange–correlation function. Dispersive forces (PEB-D2) were added into the calculation to include the van der Waals interactions. The kinetic energy cutoff of the plane-wave expansion was set to 520 eV, and a \( 1 \times 1 \times 4 \) k-point mesh was used to accurately simulate the compounds. The convergence criteria for the energy and the forces were set to \( 1 \times 10^{-5} \) eV and 0.05 eV Å\(^{-1}\), respectively. The adsorption process of the CO\(_2\), CH\(_4\), and N\(_2\) gas molecules on the surface of the crystals was simulated by using a model consisting of a supercell of gas molecules, Mg\(_2\)(dobdc), and DETA-incorporated Mg\(_2\)(dobdc) crystals. The simulation cell had a rhombohedral structure (Fig. 4) with dimensions 25 × 25 × 7 Å. Moreover, it had 12 Mg\(_2\)\(^{-}\) sites and 12 (dobdc\(^{-}\)) linker sites per pore. Initially, the CO\(_2\), CH\(_4\), and N\(_2\) gas molecules together with the Mg\(_2\)(dobdc), DETA-incorporated Mg\(_2\)(dobdc) crystals were optimized. Then, the optimized structures of the gas molecules were incorporated into the pore channel of the crystals to perform a full structural relaxation. The static binding energy at \( T = 0 \) K was then calculated by using the following expression:

\[ \Delta E_{\text{BE}} = E_{\text{guest-MOF}} - E_{\text{MOF}} - E_{\text{guest}} \]

Here, \( E_{\text{guest-MOF}} \)
corresponds to the total energy of the framework structure and the guest molecule, $E_{MOF}$ to the total energy of the MOF, and $E_{guest}$ to the total energy of guest molecule.

3. Results and discussion

3.1. Dispersion corrected density functional theory (DFT-D) simulations of gas molecules (CO$_2$, CH$_4$, and N$_2$) on Mg$_2$(dobdc) and DETA-incorporated Mg$_2$(dobdc) crystals

The Mg$_2$(dobdc) crystals, also labelled Mg-CPO-27 and Mg-MOF-74, possess the same structure of the Ni-MOF-74 and Zn-MOF-74 compounds: They exhibit a 3D hexagonal helical O$_2$Mg chain, which is coordinated with 2,5-dihydroxyterephthalate organic linkers [22,31]. Fig. 2 shows the Mg$_2$(dobdc) framework with its 1D arrangement of parallel hexagonal channels with a nominal diameter of 11–13 Å [22,31,32]. Here, the Mg$^{2+}$ ions are located at the vertices of the hexagons formed by 2,5-dihydroxyterephthalate, and they coordinate with the oxygen atoms of the hydroxyl and carboxylate groups. These structures contain 12 Mg$^{2+}$ metal sites and 12 (dobdc$^-$) linker sites per pore [33,34]. Each Mg$^{2+}$ ion connects with five oxygen atoms in its coordination sphere, whereas the sixth coordination site is generally occupied by a water molecule [35]. During the activation process at high temperature, the coordinated water molecule can be removed, creating Mg$^{2+}$ ions with an unsaturated active site, which can strongly interact with other polar molecules [33].

Consequently, in order to shed some light on the interaction between the CO$_2$, CH$_4$, and N$_2$ gas molecules with the unsaturated metal site and gain understanding of the selective adsorption mechanism between the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals, periodic density functional theory (DFT) calculations with dispersion correction (PBE-D2) were carried out. Fig. 3 (a-c) reveals the CO$_2$, CH$_4$, and N$_2$ gas binding sites on the Mg$_2$(dobdc) crystals: The structures with one CO$_2$, CH$_4$, and N$_2$ molecule per unit cell correspond to a loading of 1 gas molecule : 6 Mg$^{2+}$ sites. The DFT-D2 calculations reveal that one CO$_2$ molecule bind to the unsaturated Mg$^{2+}$ site via the Mg$^{2+}$-O(CO$_2$) interaction with a Mg-O-C angle of 128$^\circ$, as shown in Fig. 3 (a). The calculated Mg-O distance measures 2.32 Å, and it is much shorter than the sum of the Mg and O van der Waals radii (3.25 Å), contributing to the rather high binding energy of 46.9 kJ/mol. Fig. 3 (b) and (c) show the adsorption sites of the CH$_4$ and N$_2$ molecules: Both CH$_4$ and N$_2$ form almost 180$^\circ$ angles in the Mg$^{2+}$-C-H and Mg$^{2+}$-N-N interactions. The Mg-C and Mg-N distances measure 2.91 and 2.40 Å, respectively. Therefore, CH$_4$ and N$_2$ interact with the unsaturated Mg$^{2+}$ site via Mg$^{2+}$-C$^\delta$ and Mg$^{2+}$-N$^\delta$ with a binding energy of 37.1 kJ/mol and 35.4 kJ/mol, respectively. Due to the quadrupole moment of the CO$_2$ molecule, the synergistic effect between the unsaturated Mg$^{2+}$ site, with a positive potential, and the carboxylate group in the (dobdc$^-$) linker, with a negative potential, results into the angular geometry of the Mg$^{2+}$-O-C-O complex [33]. Such gas adsorption mechanism is consistent with the ones previously reported in the literature [33,34,36].

The optimized structure of the DETA-bridged Mg$_2$(dobdc) crystals was simulated by DFT calculations. In this case, each unsaturated metal site in the Mg$_2$(dobdc) unit cell was allowed to bind with one DETA molecule. Fig. 2 (d) illustrated the unit cell structure of the DETA-bridged crystals: The active amine group (–NH$_2$) on DETA binds to an unsaturated Mg$^{2+}$ site through the Mg$^{2+}$–N–interaction. The calculated Mg-N distance measures 2.22 Å and its binding energy 160.8 kJ/mol. The significantly high binding energy between DETA and the Mg$_2$(dobdc) crystals indicate their strong chemical interaction. Subsequently, a single CO$_2$ molecule was introduced into the optimized DETA-bridged crystals and the structure was simulated via DFT. Fig. 2 (e) demonstrated that one CO$_2$ molecule is shared between an unsaturated Mg$^{2+}$ site of Mg$_2$(dobdc) and an active amine group of DETA via the Mg$^{2+}$-O$^\delta$ and N$^\delta$-C$^\delta$ interaction. The calculated Mg-O and N-C distances measure 4.13 and 3.19 Å, respectively. In addition, the binding energy of the CO$_2$ molecule on the DETA-bridged Mg$_2$(dobdc) crystals measures 42.7 kJ/mol, which is a slightly smaller value than that found for the pristine Mg$_2$(dobdc) crystals. Such smaller binding energy suggests that asymmetric interaction forces originating from the unsaturated Mg$^{2+}$ site and the active amine group weaken the adsorption capacity for CO$_2$. Fig. 2 (f) shows the optimized structure of the CO$_2$ molecule adsorbed on pristine DETA via the N$^\delta$-C$^\delta$ interaction: The calculated N-C distance measures 2.89 Å and the binding energy for CO$_2$ 14.2 kJ/mol. This value is significantly lower than that obtained for the pristine Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals.

3.2. Physicochemical properties of the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals

Two distinct porous materials, Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals were synthesized by hydrothermal reaction at 125 °C and post-modification method. As illustrated in Fig. 2, the overall framework of the pristine Mg$_2$(dobdc) crystals have a 1D arrangement of parallel hexagonal channels with a diameter of 11–13 Å and each Mg$^{2+}$ ion coordinate to five oxygen atoms in its coordination sphere, which further create unsaturated metal (Mg$^{2+}$) site with intense attractions towards CO$_2$ molecules. After the incorporation of DETA molecule, as simulated by DFT calculation, the active amine group (–NH$_2$) on DETA molecule could tightly coordinate to an unsaturated metal (Mg$^{2+}$) site via the Mg$^{2+}$-N$^\delta$ interaction with high binding energy. Therefore, the DETA-bridged Mg$_2$(dobdc) crystals both have the abundant metal (Mg$^{2+}$) sites and the active chemical adsorption amine groups (–NH$_2$), exhibiting the great potential as a nanofiller to fabricate the mixed matrix membrane for the efficient separation of CO$_2$ from CO$_2$/N$_2$ and CO$_2$/CH$_4$ gas mixtures.

As it known to all, the porosity properties including the specific surface area, pore shape, size and volume, unique pore chemistry, different chemical functional groups, high thermal stability as well as the gas adsorption capacity of these Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals are the dominated factors for the determination of feasibility of these crystals as the nanofiller, to prepare mixed matrix membrane for selective CO$_2$ separation from gas mixtures. Fig. 4 (a) shows the N$_2$ adsorption and desorption isotherms of the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals at 77 K. The N$_2$ adsorption isotherms of the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals exhibit a typical type I isotherm, indicating the microporous nature of the materials [29,30], Table 1 lists the values of the textural properties of both the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals. The calculated Langmuir specific surface area and the BET specific surface area of pristine Mg$_2$(dobdc) crystals are 901 and 742 m$^2$/g, respectively. These values are slightly smaller than those previously reported in the literature, which can be attributed to different hydrothermal reactions.
Separation and Purification Technology 278 (2022) 119635

Fig. 3. Results of the DFT calculation on the CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} adsorption sites in the Mg\textsubscript{2}(dobdc) crystals and DETA-bridged Mg\textsubscript{2}(dobdc) crystals.

and activation times [29,30]. In the case of the DETA-bridged Mg\textsubscript{2}(dobdc) crystals, the calculated Langmuir specific surface area and the BET specific surface measure 200 and 143 m\textsuperscript{2}/g, respectively. Their significant difference compared to the values obtained for the Mg\textsubscript{2}(dobdc) crystals may be due to the wrapping and plugging of DETA around the surface and the inner microporous channels of the Mg\textsubscript{2}(dobdc) crystals [37,38]. In addition, the total pore volume and the t-Plot micropore volume of the DETA-bridged Mg\textsubscript{2}(dobdc) crystals exhibit a significant decrease from 0.33 to 0.08 cm\textsuperscript{3}/g and from 0.24 to 0.05 cm\textsuperscript{3}/g, respectively, when compared to pristine Mg\textsubscript{2}(dobdc) crystals. Simultaneously, the average pore size decreases from 12.1 Å to 10.6 Å after the incorporation of DETA, further indicating the grafting of DETA molecule into the pore channel of the Mg\textsubscript{2}(dobdc) crystals.

Fig. 4 shows the FTIR spectra of both the Mg\textsubscript{2}(dobdc) and the DETA-bridged Mg\textsubscript{2}(dobdc) crystals. The spectrum of the pristine Mg\textsubscript{2}(dobdc) crystals shows two characteristic peaks, which are located at 1416 and 1589 cm\textsuperscript{-1}: these features can be attributed to the O-C\textsuperscript{=}O functional groups of the organic ligands, whereas the adsorption band at 3340 cm\textsuperscript{-1} results from the –OH stretching vibration of the organic ligands-2,5-dihydroxyterephthalic acid [39,40]. The sharp adsorption peak at 582 cm\textsuperscript{-1} represents the stretching vibration of Mg-O, which corresponds to the bond between the metal ion and the organic ligand, forming unsaturated Mg-O metal sites [41]. In the spectrum of the DETA-bridged Mg\textsubscript{2}(dobdc) crystals, two distinct characteristic peaks at 1033 and 2838 cm\textsuperscript{-1} can be observed. These correspond to the bending vibration of the C-N and –NH\textsubscript{2} groups, respectively [42,43]. The features observed in the FTIR spectra indicated that Mg\textsubscript{2}(dobdc) crystals are successfully formed and incorporated with DETA.

Fig. 4 (c) shows the TG-DTG curves of the Mg\textsubscript{2}(dobdc) crystals and the DETA-bridged Mg\textsubscript{2}(dobdc) crystals. The thermal decomposition of the pristine Mg\textsubscript{2}(dobdc) crystals can be divided into three stages: the 1) 110–150 °C, 2) 380–420 °C, and 3) 590–630 °C temperature ranges. The first mass loss of about 10% occurs in the 110–150 °C range and it can be attributed to the desorption of the DMF and H\textsubscript{2}O solvent trapped in the micropores of the Mg\textsubscript{2}(dobdc) crystals [43,44]. The second mass loss of about 20% can be attributed to the decomposition of the framework structure. This results in the production of carbon-containing gases, such as CO, CO\textsubscript{2}, C\textsubscript{x}H\textsubscript{y} hydrocarbon mixtures, and a small amount of H\textsubscript{2}, and in the formation of metal oxides [18]. The third mass loss of about 25% occurs due to the release of CO and CO\textsubscript{2} together with Mg via the
reduction reaction of MgO after the attachment of one carbon: MgO + C = Mg(l) + CO (g) [45,46]. The thermal stability, which occurs during the first mass loss stage of the DETA-bridged Mg$_2$(dobdc) crystals, is higher than that of Mg$_2$(dobdc) crystals. Moreover, the temperature range of the process shifts to 170–200 °C, where the gasification of DETA takes place [47]. This indicates that the wrapping of DETA weakens the decomposition process. Nevertheless, after the volatilization process, the structure of the crystals displays decomposition characteristics similar to those of the Mg$_2$(dobdc) crystals.

Fig. 4 (d) shows the adsorption equilibrium isotherms of CO$_2$, CH$_4$, and N$_2$ on the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals. Table 1 lists the adsorption capacity of CO$_2$, CH$_4$, and N$_2$ for a temperature of 298 K and a pressure of 1 bar for the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Langmuir surface area (m$^2$/g)</th>
<th>BET surface area (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
<th>t-Plot micropore volume (cm$^3$/g)</th>
<th>Average pore size (Å)</th>
<th>CO$_2$ uptake (mmol/g)</th>
<th>CH$_4$ uptake (mmol/g)</th>
<th>N$_2$ uptake (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$(dobdc)</td>
<td>901</td>
<td>742</td>
<td>0.33</td>
<td>0.24</td>
<td>12.1</td>
<td>7.15</td>
<td>0.48</td>
<td>0.34</td>
</tr>
<tr>
<td>DETA-bridged Mg$_2$(dobdc)</td>
<td>200</td>
<td>143</td>
<td>0.08</td>
<td>0.05</td>
<td>10.6</td>
<td>6.45</td>
<td>0.36</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Fig. 4 (d) shows the adsorption equilibrium isotherms of CO$_2$, CH$_4$, and N$_2$ on the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals. Table 1 lists the adsorption capacity of CO$_2$, CH$_4$, and N$_2$ for a temperature of 298 K and a pressure of 1 bar. The low-pressure region of the CO$_2$ adsorption isotherms of the pristine Mg$_2$(dobdc) crystals exhibits a steep slope, indicating a strong interaction between CO$_2$ and the Mg$_2$(dobdc) crystals due to the unsaturated Mg-O metal sites [29,30]. Therefore, at 298 K and 1 bar, the CO$_2$ uptake of the Mg$_2$(dobdc) crystals measures 7.15 mmol/g, which is in good agreement with the values reported in the literature [29,30]. In addition, the CH$_4$ and N$_2$ isotherms show a linear-like trend. The CH$_4$ and N$_2$ adsorption capacity at 298 K and 1 bar measure only 0.48 and 0.34 mmol/g, respectively, which is mainly attributed to the relatively weak interaction between CH$_4$ or N$_2$ molecule and the Mg$_2$(dobdc) crystals. In the case of the DETA-bridged Mg$_2$(dobdc) crystals, although their porosity properties including BET specific surface and pore volume exhibit a reduce, their CO$_2$ adsorption capacity still achieve a very high value of 6.45 mmol/g. Moreover, the corresponding CH$_4$ and N$_2$ adsorption capacity significantly decrease by 25 and 50% to 0.36 and 0.17 mmol/g. Compared with the CO$_2$ uptake of DETA-bridged Mg$_2$(dobdc) crystals, their corresponding CH$_4$ and N$_2$ adsorption capacity demonstrate more remarkable degradation, which could contribute to the superior separation selectivity than pristine Mg$_2$(dobdc) crystals. Despite the incorporation of DETA molecule could generate the dense layer wraps around the surface of the Mg$_2$(dobdc) crystals and reduces the porosity of the crystals, it could also bring about
the active amine groups that possess chemical adsorption sites for CO\textsubscript{2} molecule, which could significantly boost the overall CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} separation selectivity [48].

Fig. 5 shows the X-ray photoelectron spectroscopy (XPS) spectra of Mg\textsubscript{2}(dobdc) and DETA-bridged Mg\textsubscript{2}(dobdc) crystals. As presented in Fig. 5 (a), the determined carbon, oxygen, and magnesium atomic contents of the Mg\textsubscript{2}(dobdc) crystals attain 59.4, 35.8, and 4.7 at.\%, respectively. After the incorporation of DETA, the analysis on the atomic content implies the presence of nitrogen with a content of 4.1 at.\%, which proves the impregnation of DETA on the surface of the Mg\textsubscript{2}(dobdc) crystals. Fig. 5 (b) shows the high-resolution of Mg 2p scans: The DETA-bridged Mg\textsubscript{2}(dobdc) crystals exhibit lower binding energy (~50.40 eV) than that of the Mg\textsubscript{2}(dobdc) crystals (~50.75 eV). The reduced binding energy (0.35 eV) of the DETA-bridged Mg\textsubscript{2}(dobdc) crystal, suggesting possible interaction with the amine-Mg complex [48], where the Mg unsaturated metal sites receive an electron from the DETA primary amine donors and become more electronegative [48,52]. Fig. 5 (c) shows high-resolution XPS O 1s spectrum of the pristine Mg\textsubscript{2}(dobdc) crystals, which exhibits three peaks at 530.2, 531.2, and 532.7 eV, assigned to the Mg-O, C=O, and C-O functional groups, respectively [53,54]. The atomic contents in percent of these three functional groups measure 9.2, 67.6, and 23.2%, respectively. However, only two bonding forms for the C=O and C-O functional groups can be observed in the XPS O 1s spectrum of the DETA-bridged Mg\textsubscript{2}(dobdc) crystals in Fig. 5 (d). They account for the 54.1 and 45.9%, respectively. It is worth noting that the disappearance of the Mg-O functional groups in the XPS O 1s spectrum after the incorporation of the DETA into Mg\textsubscript{2}(dobdc) crystals supports the hypothesis that the unsaturated Mg metal sites attract the DETA molecule and modify its surrounding binding environment simultaneously.

Fig. 6 demonstrated the surface morphology of the Mg\textsubscript{2}(dobdc) and DETA-bridged Mg\textsubscript{2}(dobdc) crystals observed via SEM. The goal of these measurements is to further investigate the interaction between the Mg\textsubscript{2}(dobdc)-based crystals and the Matrimid matrix. The SEM image of the Mg\textsubscript{2}(dobdc) crystals is shown in Fig. 6 (a) and (c): they exhibit a shuttle-like structure and are very tightly packed as a chrysanthemum [29,30]. This particle size lies in the 3–30 μm range with an average size of 15 μm. The surface of such pristine Mg\textsubscript{2}(dobdc) crystals exhibits several irregular voids, which, however, are not conducive to the fabrication of defect-free MMMs for gas permeation. The surface features and the overall morphology of the DETA-bridged Mg\textsubscript{2}(dobdc) crystals are shown in Fig. 6 (b) and (d), respectively: they exhibit smooth and rounded surface, which is distinctively different from that of the Mg\textsubscript{2}(dobdc) crystals. Liquid-phase DETA filters homogeneously into the
irregular voids on the surface of the Mg$_2$(dobdc) crystals. DETA is an amine-based CO$_2$ adsorbent, possessing a high CO$_2$ affinity, which significantly facilitates the solubility of the CO$_2$ molecules. Further, it also acts as a bridging agent, which can be used to reduce the interface defects within the membranes [55].

### 3.3. Characterization of Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals incorporated into Matrimid-based MMMs

The results of the DFT simulations and gas adsorption analyses (CO$_2$, CH$_4$ and N$_2$) indicate that the DETA-bridged Mg$_2$(dobdc) crystals exhibit superior CO$_2$ selective separation for the fabrication of MMMs. Fig. 1 presents the schematic preparation process of the Matrimid-based mixed matrix membranes with DETA-bridged Mg$_2$(dobdc) crystals. Raw Mg$_2$(dobdc) crystals were also loaded into the Matrimid matrix to obtain a comparative sample. Since a loading level of nanoparticles different from the optimal one would result into agglomeration and formation of nonselective voids [25], Matrimid-based MMMs containing Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals in the 2.5–15 wt% range were prepared to determine their optimal concentration.

The FTIR spectra of a pristine Matrimid membrane and Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals are shown in Fig. 7 (a). Three characteristic peaks, which are located at 1367, 1778 and 1716 cm$^{-1}$ and correspond to the C-N stretch, the C=O asymmetric stretch, and the C=O symmetric stretch in the imide carbonyl group, respectively, appear in the Matrimid membrane. Furthermore, two characteristic features at 1671 and 1514 cm$^{-1}$, which can be attributed to the C=O asymmetric stretch and the C=N vibration mode of the amide groups, are visible [56,57]. The intensity of the characteristic peak at 1416 cm$^{-1}$ in the spectrum of the DETA-bridged Mg$_2$(dobdc) crystals incorporated into the Matrimid-based MMMs increases upon an increase in the DETA-bridged Mg$_2$(dobdc) crystal content in the 2.5–15 wt% range. This phenomenon is related to the increase in the O-C=O functional groups present in the organic ligands of the DETA-bridged Mg$_2$(dobdc) crystals. In the DETA spectrum, the three adsorption bands, which are located at 1033, 1120, and 1550 cm$^{-1}$, correspond to the C-N and NH$_2$ stretching vibrations of the amino groups [42,43]. Moreover, the adsorption band at 1033 cm$^{-1}$ can be attributed to the C-N functional group of DETA, which is also present in the Matrimid-based MMMs spectrum. The FTIR results obtained confirm the successful incorporation of the DETA-bridged Mg$_2$(dobdc) crystal into the Matrimid matrix.

XRD analysis was carried out to determine the structure of both the Mg$_2$(dobdc) crystals and Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals, as well as the change in the d-spacing of the MMMs during the crystal incorporation. Fig. 7 (b) shows the XRD patterns of the Mg$_2$(dobdc) crystals: They exhibit two dominant peaks at 6.8$^\circ$ and 11.7$^\circ$, which are in good agreement with the simulated spectra and with the experimental results on the Mg$_2$(dobdc) crystals [29,30,58,59]. The two broad peaks at 16$^\circ$ and 22$^\circ$ in the spectrum of the pristine Matrimid membrane can be attributed the amorphous phase of the polymer matrix [60]. After the incorporation of the DETA-bridged Mg$_2$(dobdc) crystals in the Matrimid-based MMMs, the characteristic peak of the MMMs combines with the intense feature belonging to the Mg$_2$(dobdc) crystals and the broad amorphous peaks of the Matrimid polymer matrix. The intensity of the Mg$_2$(dobdc) crystals peaks increases, whereas the intensity of the Matrimid peak gradually decreases upon an increase in the content of Mg$_2$(dobdc) crystals in the 5–15 wt% range. The d-spacing of the polymers was calculated via Bragg’s equation, which was applied to the position of the most intense XRD peak in the amorphous polymer spectrum, as listed in Table S1. The d-spacing of pristine Matrimid measures 5.523 Å and its value is consistent with that...
previously reported in the literature [9,57]. Upon an increase in the Mg$_2$(dobdc) crystal load from 2.5 to 15 wt%, the calculated d-spacing of the MMMs increases from 5.649 Å to 5.864 Å. The increase in the interchain distance of the polymer in the MMMs is mainly due to the insertion of the DETA-bridged Mg$_2$(dobdc) crystals into the polymer chains, which contributes to the increase of the fractional free volume (FFV), as shown by the further PALS analysis.

The thermal degradation behavior of the pristine Matrimid membranes and the Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals was demonstrated in Fig. 7 (c). The thermal decomposition of the pristine Matrimid membranes can be divided into two primary stages. The first mass loss occurs in the 100–250 °C temperature range attributed to the evaporation of the residual solvent from the membrane structure [61,62]. The second weight loss starts at 450 °C and ends at 650 °C. It directly reflects the total degradation process of the polyimides chains in the membrane. The thermal decomposition behavior of the Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals is similar to that of a pristine Matrimid membrane and it exhibits two decomposition stages, as well. The decomposition stage occurs in the 100–250 °C temperature range and exhibited a sharp characteristic peak in the DTG curves corresponds to the gasification of DETA and to the partial decomposition of the Mg$_2$(dobdc) crystals.

DSC analysis was carried out to investigate the effect of the DETA-bridged Mg$_2$(dobdc) crystals on the glass transition temperature ($T_g$) of the Matrimid-based MMMs. The results are presented in Fig. 7 (d):

The $T_g$ value of 326.3 °C for the pristine Matrimid membrane is consistent with that reported in literature [7,63,64]. For the Matrimid-based MMMs, a higher $T_g$ is observed. Moreover, this value increases 328.3 °C to 337.4 °C by loading the membranes with 2.5 to 15 wt% of crystals. Such high $T_g$ values show the high affinity between Matrimid and the DETA-bridged Mg$_2$(dobdc) crystals due to the high compatibility and the adhesion between their two phases, as previously observed [65,66]. Moreover, the presence of hydrogen bonds between the DETA-bridged Mg$_2$(dobdc) crystals and the Matrimid matrix further contributes to the formation of a rigid interphase and a strong interfacial interaction between the polymer and the crystals. Particularly, the $T_g$ value of the MMMs with 15 wt% of DETA-bridged Mg$_2$(dobdc) crystals is significantly higher than that of the other MMMs. This is due to the high loading of crystals, which induces the penetration of the Matrimid chains into the pore channels of the DETA-bridged Mg$_2$(dobdc) crystals and causes a slight rigidification of the polymer chains outside the crystals [63,67,68]. Such high compatibility between the Matrimid chain and the DETA-bridged Mg$_2$(dobdc) crystals was also confirmed by the results on the FFV obtained via the PALS analysis.

The polymer-filler interfacial cross section morphology of the fabricated MMMs were observed via SEM. Figure S1 (a) presents the cross-section of Matrimid membrane, a few fissures and polymer veins could be observed due to the plastic deformation process via freeze fracturing in liquid nitrogen. Figure S1 (b)–(e) shows the cross-section of Matrimid-based membranes with 2.5, 5, 10, and 15 wt% of DETA-
bridged Mg$_2$(dobdc) crystal content. For the MMMs with a crystal content lower than 10 wt%, no significant agglomeration or unselective voids can be observed. These crystals can be efficiently embedded into the matrix polymer, confirming their strong interfacial interaction with the matrix [4, 7, 56]. However, as the crystal content reaches 15 wt%, unselective voids and agglomeration appear, limiting the permeation of the gas molecule throughout the MMMs.

In order to further investigate the role of DETA in the MMMs, Fig. 8 shows a comparison in the cross-section morphology of Matrimid-based MMMs incorporated with 10 and 15 wt% Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals. The raw Mg$_2$(dobdc) crystals could not strongly interact with Matrimid, and, as shown in Fig. 8 (a) and (c), interface defects and unselective voids can be observed in the MMMs, reflecting the difficulty in compliance between Mg$_2$(dobdc) crystals and Matrimid matrix. Fig. 8 (b) and (d) shows that the DETA-bridged Mg$_2$(dobdc) crystals in the MMM processing a high concentration of primary and secondary amine groups could act as an adhesion agent, fostering the interaction with the Matrimid matrix: in this case, a strong interface forms and defects and voids are no more visible.

Positron annihilation lifetime spectroscopy (PALS) was carried out to determine the free volume characteristics of both a pristine Matrimid membrane and a set of Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals [69]. The two short lifetime components ($\tau_1$ and $\tau_2$) are attributed to the $\pi\pi$-positronium (p-Ps) annihilation and the material specific positron annihilation. They do not depend on the free volume in the membranes [70, 71]. The third component, $\tau_3$, is attributed to the pick-off annihilation of ortho-positronium (o-Ps) in the free volumes of the membrane that was prepared from the addition of the DETA-bridged Mg$_2$(dobdc) crystals into Matrimid polymer. Therefore, the o-Ps lifetime ($\tau_3$) and its intensity ($I_3$) provide information on the mean radius and on the numerical concentration of both the free volume holes in the amorphous polymer and pores in the Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals of the MMMs.

The average mean radius of the free volume ($R$) could be estimated from the o-Ps lifetime ($\tau_3$):

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta R} \right]^{-1}$$

where $\Delta R$ is the thickness of the electron layer on the surface of free volume holes, which is an empirical parameter of 0.1656 nm [72]. The average volume ($V_3$) of free-volume holes, which is usually called as free-volume hole size, could be estimated from $V_3 = 4\pi R^3/3$. The fractional free volume (in %) is defined as $\text{FFV} = CV_3$, where $C$ is a constant and it is sufficient to utilize a simpler definition of relative fractional free volume: $\text{FFV} = V_3/V_1$ [73].

The lifetime and intensity of the o-Ps annihilation, the calculated mean radius of the free volume ($R$), and the fractional free volume (FFV) of each membrane are presented in and Fig. 9 and listed in Table 2. Fig. 9 (a) and (b) show the evolution of the $\tau_3$ values and of the calculated mean radius of the free volume ($R$) upon an increase in the load of DETA-bridged Mg$_2$(dobdc) crystals in MMMs. Obviously, these values increase almost linearly as increase the concentration of crystals with a higher average hole radius (6.25 Å from PALS results) from 2.5 to 10 wt%, indicating that the dispersion state of DETA-Mg$_2$(dobdc) crystals in these MMMs are almost similar. However, as the concentration of the DETA-bridged Mg$_2$(dobdc) crystals inside the MMM reaches 15 wt%, $R$ exhibits a slight decrease unexpectedly. This implies that the dispersion state of DETA-Mg$_2$(dobdc) crystals in the MMMs have totally changed.

Two factors contribute to the reduction in mean radius of the free volume ($R$) of Matrimid-based MMMs incorporated with 15 wt%: 1) Due to

![Fig. 8. Cross section SEM images of (a) 10-Mg$_2$(dobdc)-MMM, (b) 10-DETA-Mg$_2$(dobdc)-MMM, (c) 15-Mg$_2$(dobdc)-MMM, and (d) 15-DETA-Mg$_2$(dobdc)-MMM. (Please, note that the abbreviation 5-Mg$_2$(dobdc)-MMM consists of Matrimid-based mixed matrix membrane with 5 wt% of Mg$_2$(dobdc) crystals, whereas 5-DETA-Mg$_2$(dobdc)-MMM refers to a Matrimid-based mixed matrix membrane with 5 wt% of DETA-bridged Mg$_2$(dobdc) crystals.)](image-url)
the excessive concentration of DETA-bridged Mg$_2$(dobdc) crystals, the Matrimid chains stretch into the pore channels of the crystals and reduce their cavity size; 2) The addition of the crystals results in the rigidification of the polymer chain segments and in a decrease in the polymer free volume size [70]. Considering the o-Ps intensity ($I_3$), as presented in Fig. 9 (c), the $I_3$ value of the pristine Matrimid membrane achieves 0.202 %, which is extremely low, due to the polyimide polymer strongly inhibits the positronium formation [7,72]. After the incorporation of crystals from 2.5 to 10 wt%, the $I_3$ values of the MMMs firstly increase to a certain extent and then maintain almost unchanged, because o-Ps formation probability in DETA-bridged Mg$_2$(dobdc) crystals is much higher than that in pristine Matrimid membrane. When the loading of crystals attains 15 %, the $I_3$ value dramatically increase to 2.341 %, also indicating the different dispersion states of crystals from the MMMs incorporated with 2.5 to 10 wt%. The fractional free volume (FFV) in the MMMs consists of the free volume holes of Matrimid polymer and pore cavities of DETA-bridged Mg$_2$(dobdc) crystals in the MMMs. As shown in Fig. 9 (d), due to the calculated formular: $FFV = \frac{4\pi R^3}{3} I_3$, therefore, as similar with the variation trend of the mean radius of the free volume (R), the determined FFV in the MMMs increase linearly from 0.097 to 0.692 % with the crystals loading increasing from 2.5 to 10 wt%. When the concentration of crystals reaches 15 wt%, the FFV value of the MMMs dramatically jumps up to 0.692 %, due to the significant enhancement of

### Table 2

Position annihilation lifetime spectroscopy (PALS) analysis of Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals. (Please, note that the 2.5-DETA-Mg-M label refers to Matrimid-based mixed matrix membranes with 2.5 wt% of DETA-bridged Mg$_2$(dobdc) crystals.)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$\tau_3$ (ns)</th>
<th>$I_3$ (%)</th>
<th>R (Å)</th>
<th>$V_f$ (nm$^3$)</th>
<th>FFV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>1.881 ± 0.366</td>
<td>0.202 ± 0.050</td>
<td>2.761 ± 0.088</td>
<td>0.018 ± 0.011</td>
<td></td>
</tr>
<tr>
<td>Matrimid</td>
<td>0.366</td>
<td>0.050</td>
<td>0.357</td>
<td>0.343</td>
<td>0.014</td>
</tr>
<tr>
<td>2.5-DETA-Mg-M</td>
<td>2.377 ± 0.127</td>
<td>0.701 ± 0.036</td>
<td>3.203 ± 0.138</td>
<td>0.097 ± 0.036</td>
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</tr>
<tr>
<td>Mg-M</td>
<td>0.127</td>
<td>0.036</td>
<td>0.104</td>
<td>0.133</td>
<td>0.014</td>
</tr>
<tr>
<td>5-DETA-Mg-M</td>
<td>3.173 ± 0.204</td>
<td>0.537 ± 0.027</td>
<td>3.789 ± 0.228</td>
<td>0.122 ± 0.009</td>
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</tr>
<tr>
<td>M</td>
<td>0.204</td>
<td>0.027</td>
<td>0.136</td>
<td>0.255</td>
<td>0.019</td>
</tr>
<tr>
<td>10-DETA-Mg-M</td>
<td>3.957 ± 0.226</td>
<td>0.659 ± 0.027</td>
<td>4.273 ± 0.327</td>
<td>0.215 ± 0.029</td>
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</tr>
<tr>
<td>M</td>
<td>0.226</td>
<td>0.029</td>
<td>0.129</td>
<td>0.030</td>
<td>0.029</td>
</tr>
<tr>
<td>15-DETA-Mg-M</td>
<td>3.717 ± 0.491</td>
<td>2.341 ± 0.031</td>
<td>4.133 ± 0.296</td>
<td>0.692 ± 0.026</td>
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</tr>
<tr>
<td>M</td>
<td>0.662</td>
<td>0.031</td>
<td>0.037</td>
<td>0.008</td>
<td>0.026</td>
</tr>
<tr>
<td>DETA</td>
<td>8.491 ± 0.242</td>
<td>5.813 ± 0.137</td>
<td>6.254 ± 0.085</td>
<td>5.956 ± 0.042</td>
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</tr>
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</table>

Fig. 9. PALS analysis: (a) o-Ps lifetime ($\tau_3$), (b) mean radius of the free volume (R), (c) o-Ps intensity ($I_3$) and (d) fractional free volume (FFV) of Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals.
3.4. Gas transport behaviors of Mg$_2$(dobdc) and DETA-bridged Mg$_2$(dobdc) crystals incorporated in Matrimid-based MMMs

Pure gas permeability (CO$_2$, CH$_4$, and N$_2$) and ideal selectivity are listed in Table S2 and shown in Fig. 10. The CO$_2$ permeability of the Matrimid membrane reaches 8.14 Barrers with a CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity of 34.9 and 43.9 respectively, which are in good agreement with previously reported literature [19,74]. Fig. 10 (a) shows that the CO$_2$ permeability of the Mg$_2$(dobdc) crystals incorporated MMMs increases from 8.14 to 34.9 Barrers upon an increase in the 2.5–10 wt% range of Mg$_2$(dobdc) crystals. However, as the loading reaches 15 wt%, the CO$_2$ permeability decreases due to the agglomeration of the crystals. Therefore, the incorporation of Mg$_2$(dobdc) crystals into the Matrimid membrane leads to the formation of these CO$_2$-selective transit channels, increasing the permeability of CO$_2$ molecule through MMMs. Fig. 10 (c) shows the CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity in Matrimid-based MMMs with raw Mg$_2$(dobdc) crystals. However, as Mg$_2$(dobdc) crystal content increases from 2.5 to 15 wt%, the CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity decreases from 20.3 and 33.2 to 13.9 and 20.1, respectively. This is because the relatively large aperture in Mg$_2$(dobdc) crystals (11–13 Å) also allows the CH$_4$ and N$_2$ molecules traversing through the framework, which is not favor of the increasing of selectivity in the MMMs.

The CO$_2$ permeability and ideal selectivity of Matrimid-based MMMs with DETA-bridged Mg$_2$(dobdc) crystals are rather high. Fig. 10 (b) and (d) exhibit that the CO$_2$ permeability and ideal electivity of the MMMs are strongly related to the content of DETA-bridged Mg$_2$(dobdc) crystals. The CO$_2$ permeability of the MMMs increases from 25.5 to 41.1 Barrers when the DETA-bridged Mg$_2$(dobdc) crystal content increases from 2.5 to 10 wt%. This phenomenon is accompanied by a gradual decrease in the CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity from 26.6 and 36.9 to 22.6 and 30.6, respectively. Obviously, the CO$_2$ permeability as well as CO$_2$/CH$_4$ and CO$_2$/N$_2$ separation selectivity of DETA-bridged Mg$_2$(dobdc) crystals incorporated with Matrimid-based MMMs exhibit the significant boost, particularly for the CO$_2$ permeability, the value of the 10 wt% DETA-bridged Mg$_2$(dobdc) crystals incorporated MMM (41.1 Barrer) is 17.8% higher than that of the 10 wt% Mg$_2$(dobdc) crystals incorporated MMM (34.9 Barrer). Similarly to the case of the Mg$_2$(dobdc) crystals incorporated with MMMs, when the DETA-bridged Mg$_2$(dobdc) crystal content reaches 15 wt%, the CO$_2$ permeability and the CO$_2$/CH$_4$ and
CO₂/N₂ selectivity exhibit a sharp decrease to 35.8 Barrers, 12.7 and 14.3, respectively. As revealed by PALS analysis in Fig. 9, in the Matrimid-based MMMs incorporated with 15 wt% of crystals, the agglomeration phenomenon occurs and the dispersion state of the DETA-bridged Mg₂(dobdc) crystals is different from the MMMs with lower crystals loading (2.5, 5, and 10 wt%). Moreover, the excessive loading of crystals also leads to the plugging of Matrimid chains into the pore channels of DETA-bridged Mg₂(dobdc) crystals, which hinder the passage of gas molecules through the MMMs and further result a decrease in the CO₂ separation performance [7,25].

In order to achieve an in-depth insight of the solution-diffusion mechanism within the Matrimid membrane as well as Matrimid-based MMMs incorporated with DETA-bridged Mg₂(dobdc) crystals, their corresponding CO₂ adsorption isotherms were detected at 35 °C and up to 12 atm and the solubility and diffusivity coefficient of the MMMs were also determined. As illustrated in Fig. 11 (a), the pristine Matrimid membrane attains the CO₂ adsorption capacity of 13.13 cm³(STP) cm⁻³ atm⁻¹, which are higher than these Matrimid-based MMMs with varying content of DETA-bridged Mg₂(dobdc) crystals. The solubility and diffusivity coefficients of MMMs are presented in Fig. 11 (b) and the calculated solubility coefficient of pristine Matrimid is 3.30 cm³(STP) cm⁻³ atm⁻¹. However, after the incorporation of DETA-bridged Mg₂(dobdc) crystals, the solubility coefficient of MMMs with varying content of crystals (2.5, 5, 10 and 15 wt%) slightly decrease to 2.61, 2.49, 2.30 and 2.16 cm³(STP) cm⁻³ atm⁻¹. This is in good consistent with the reported literatures, the Matrimid membrane possesses the higher CO₂ adsorption capacity and solubility, which is due to the stronger interaction of Matrimid polymer towards CO₂ molecules than DETA-bridged Mg₂(dobdc) crystals [14]. On the contrary, despite the decreased solubility coefficient of Matrimid-based MMMs, their calculated diffusivity coefficient of the MMMs with varying content of crystals (2.5, 5,10 and 15 wt%) demonstrate the significant increment to 0.74, 1.08, 1.36 and 1.26 cm² s⁻¹ compared with the pristine Matrimid membrane (0.19 cm² s⁻¹). The dramatically enhancement of diffusivity in the MMMs is not only attributed to the increase in fractional free volume of the polymer chains (revealed by the PALS analysis), but also due to the DETA molecule that act as an adhesion agent and stick the Matrimid matrix and Mg₂(dobdc) crystals together to eliminate the unselective defects and voids. Due to the overall CO₂ permeability is determined by both diffusivity and solubility coefficient, the slightly decrease in solubility with the increasing of the crystals content in MMMs is compensated by the significant enhancement in diffusivity, further resulting in an overall increase of CO₂ permeability.

The DETA-bridged Mg₂(dobdc) crystals incorporated Matrimid-based MMMs have achieved the superior CO₂ permeability and selectivity compared with pristine Matrimid membrane and the Mg₂(dobdc) crystals incorporated Matrimid-based MMMs under the pure gas permeation experiment, therefore, in order to further evaluate the practical separation performance of these Matrimid-based incorporated DETA-bridged Mg₂(dobdc) crystals under the mixed-gas mixture condition, the mixed-gas permeation under binary gas mixtures of CO₂/CH₄(40/60) and CO₂/N₂(15/85) were carried out at 35 °C. As presented in Figure S2, the variation tendency of both the gas permeability (CO₂, CH₄, and N₂) and the separation selectivity (CO₂/CH₄ and CO₂/N₂) are similar to the results of pure gas permeation. However, the measured mixed-gas CO₂ permeability is slightly lower than pure-gas CO₂ permeability, while the mixed-gas CH₄ and N₂ permeability are higher than pure-gas permeability. Due to the plasticization effect of CO₂ molecule, as the membrane is highly adsorbed of CO₂, it can plasticize the polymer chain and increase the chain flexibility and free fractional volume of the membrane, further contributing to the increase of CH₄ and N₂ permeability [2]. On the contrary, these non-plasticizing CH₄ and N₂ molecule can cause the competitive adsorption with CO₂ molecule and lead to the decline of membrane CO₂ permeability and selectivity undoubtedly [75]. In conclusion, the drop of gas separation performance for mixed-gas mixture compared with pure-gas mixture is mainly attributed to the plasticization effect and the competitive adsorptions of mixed-gas mixtures, which was also found and discussed in the related literature as well [76,77].

Pure-gas and mixed-gas permeation experiment result in Fig. 10 and Figure S2 indicate that the Matrimid-based MMMs incorporated with DETA-bridged Mg₂(dobdc) crystals achieve a higher CO₂ permeability and selectivity compared to the pristine Matrimid membrane and MMMs with the identical weight percentage of raw Mg₂(dobdc) crystals. In the next section, three main factors inducing such significant enhancement in the CO₂ permeability and gas selectivity of the DETA-bridged Mg₂(dobdc) crystals incorporated MMMs are investigated in detail.

(i) Remarkably increased fractional free volume (FFV) and diffusivity coefficient. As revealed by PALS analysis, the fractional free volume (FFV) in MMMs consists of the free volume holes of Matrimid polymer and pore cavities of crystals. With the content of DETA-bridged Mg₂(dobdc) crystals increasing from 2.5 to 10 wt%, the mean radius of the free volume (R) of the MMMs increase linearly, indicating that the similar dispersion state. Therefore, the calculated formula: FFV = (4πR³)/3, exhibits the similar trend as the mean radius of the free volume (R), also increasing linearly from 0.097 to 0.215 %. Undoubtedly, the significantly increased fractional free volume could effectively facilitate the diffusivity of CO₂ molecules within the MMMs, further
enhance the CO₂ permeability. However, as the content of crystals reaches 15 wt%, the FFV of the MMMs dramatically decrease, due to the significant enhancement of α-PS intensity (I₂). This indicates the agglomerations of excessive DETA-bridged Mg₆(dobdc) crystals in the MMMs, which is not favorable for the permeation of CO₂ molecules.

(ii) Enhanced compatibility between DETA-bridged Mg₆(dobdc) crystals and Matrimid matrix via hydrogen bonding. The schematic of the reaction between DETA and Mg₆(dobdc) crystals is presented in the Supplemental Information Figure S3. The DETA molecule with the active N atom is strongly attracted by the unsaturated Mg²⁺ site and bring about the Mg²⁺⋯N⁻ interactions. Furthermore, the interaction mechanisms between the Matrimid matrix with pristine Mg₆(dobdc) and DETA-bridged Mg₆(dobdc) crystals are illustrated in Fig. 12. The parallel hexagonal channels of 11–13 Å of the Mg₆(dobdc) crystals are surrounded by the Matrimid chains, as illustrated in Fig. 12 (a). The DETA molecules could strongly bind the unsaturated Mg²⁺ sites of the Mg₆(dobdc) crystals not only via hydrogen bonding between the O atoms of the Matrimid chains and the H atoms of DETA, but also via an interaction between the N atoms of DETA and the H atoms in the Matrimid chains. The SEM images in Fig. 8 (b) and (d) and the DFT calculations also verify these observations. The interface between the polymer chains and the nanoparticles of the Matrimid-based MMMs with the DETA-bridged Mg₆(dobdc) crystals significantly reduce the gas transport resistance and increase the CO₂ permeability of the MMMs.

(iii) Reduced pore diameter and CO₂-selective channels. Pristine Mg₆(dobdc) crystals incorporated into Matrimid-based MMMs exhibit a relatively poor CO₂/CH₄ and CO₂/CH₄ separation selectivity when compared to DETA-bridged Mg₆(dobdc) crystals incorporated into Matrimid-based MMMs. Although the unsaturated Mg²⁺ sites in the Mg₆(dobdc) crystals possess a higher affinity to CO₂ than to CH₄ and N₂ molecules, the large channel diameter (Fig. 12 (a)) allows for the passage of the CH₄ and N₂ molecules, decreasing the CO₂ separation performance. As illustrated in Fig. 12 (b), the induction of DETA molecules on the unsaturated Mg²⁺ sites of the inner channels in the Mg₆(dobdc) crystals not only could reduce the pore diameter and limit the passage of the CH₄ and N₂ molecules, but also create primary and secondary amine adsorption sites, which have a high affinity toward CO₂. Therefore, the incorporation of DETA-bridged Mg₆(dobdc) crystals reduces the pore diameter of the CO₂-selective channels, improving the overall separation performance of the MMMs.

3.5. Separation performance of the MMMs and comparison with previously reported studies

A comparative study on the gas separation performance of Matrimid-based MMMs containing Mg₆(dobdc) and DETA-bridged Mg₆(dobdc) crystals was performed: The permeability and CO₂/CH₄ and CO₂/N₂ selectivity against Robeson’s findings in 2008 are shown in Fig. 13 [78,79]. The results of relevant studies on Matrimid-based MMMs are also provided here for comparison. These as-synthesized DETA-bridged Mg₆(dobdc) crystals incorporated Matrimid-based MMMs demonstrates the significant higher CO₂ permeability as well as the superior CO₂/CH₄ and CO₂/N₂ selectivity. The CO₂ permeability of the MMM with 10 wt% of DETA-bridged Mg₆(dobdc) crystals increases by 4.03 times, reaching 41.1 Barrers, when compared to a pristine Matrimid membrane (8.17 Barrers). Nevertheless, an uncontrolled increase to 15 wt% in the content of both the Mg₆(dobdc) and DETA-bridged Mg₆(dobdc) crystals could result in agglomerations and interface defects, deteriorating the overall membrane separation performance.

The Matrimid-based MMMs with DETA-bridged Mg₆(dobdc) crystals obtained in this work outperform the ZIF-8 [80], PEG + ZIF-8 [56], MOF-5 [81], MIL-125 [5], NH₂-MIL-53 [82], CuBTC-nanosheet [83], CuBPY-HFS [84], UIO-66 [7], Azo-UIO-66 [85], UIO-66-NH₂ [27], BILP-4 [86], and CSM-18.4 [87] doped Matrimid-based MMMs in terms of CO₂ permeability. It is critical that the DETA molecules play an important role in filling the interface defect, acting as the intermediate agent: This dramatically increases the CO₂ permeability of the MMMs. The results on the CO₂/CH₄ and CO₂/N₂ separation selectivity in Fig. 13 (a) and (b) show that the DETA-bridged Mg₆(dobdc) crystals incorporated in the MMMs exhibit relatively high values compared to the previously reported Matrimid-based MMMs. This implies that the grafting and blending of DETA onto the Mg₆(dobdc) crystals and the matrix during the synthesis of the DETA-bridged Mg₆(dobdc) crystals highly increases the CO₂ separation performance of these compounds, broadening the field of their industrial application in CO₂ capture and separation.

![Fig. 12. Interaction mechanism of the Matrimid-based MMMs with the Mg₆(dobdc) and DETA-bridged Mg₆(dobdc) crystals.](image-url)
4. Conclusions

Mg_2(dobdc) and DETA-bridged Mg_2(dobdc) crystals were synthesized and firstly incorporated into Matrimid matrix to fabricate the mixed matrix membranes, boosting their CO_2 separation performance of biomethane (CO_2/CH_4) and flue gases (CO_2/N_2). The CO_2 adsorption isotherms at 298 K and 1 bar of the Mg_2(dobdc) crystals and of the DETA-bridged Mg_2(dobdc) crystals show an excellent CO_2 uptake as well as a superior separation selectivity. Spectroscopic characterization indicates that the unsaturated Mg^{2+} sites in the Mg_2(dobdc) nanoparticles tightly grasp the DETA molecules and alter their surrounding binding environment. The DFT-D2 calculations also confirm that the active amine group (–NH_2) on DETA binds the unsaturated Mg^{2+} site via the Mg^{2+}…N^+ interaction. The DETA molecule was used as the adhesion agent to bind the Mg_2(dobdc) crystal and Matrimid matrix together, while eliminating interface defects and voids. This dramatically increases the CO_2 separation performance of the MMMs. The CO_2 permeability of the Matrimid-based MMMs with DETA-bridged Mg_2(dobdc) crystals increases and then, decreases as a function of the Mg_2(dobdc) loading. An optimal CO_2 permeability of 41.1 Barrers as well as the superior CO_2/CH_4 and CO_2/N_2 selectivity are achieved with a DETA-bridged Mg_2(dobdc) content of 10 wt%.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2021.119635.

References


