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**NANYANG
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UNIVERSITY**

SINGAPORE

**ADVANCED GAS SEPARATION VIA COMBINED USE OF
CARBON NANOMATERIALS AND MICROPOROUS
MATERIALS**

LI WEN

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

STATEMENT OF ORIGINALITY

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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SUPERVISOR DECLARATION STATEMENT

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Bae Tae-Hyun

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains material from 4 paper(s) published in the following peer-reviewed journal(s) where I was the first author.

Chapter 3 is published as **Li, W.**, Chuah, C. Y., Yang, Y., & Bae, T. H. (2018). Nanocomposites formed by in situ growth of NiDOBDC nanoparticles on graphene oxide sheets for enhanced CO₂ and H₂ storage. **Micropor. Mesopor. Mat.**, 265, 35-42.

The contributions of the co-authors are as follows:

- Asst/Prof Bae Tae-Hyun provided the initial project direction and revised the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Chuah Chong Yang.
- I co-designed the study with Asst/Prof Bae Tae-Hyun and I performed all the laboratory work at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- All characterizations, including sample preparation, were conducted by me.
- Dr Yang Yanqin assisted in the collection of the thermal stability and N₂ physisorption data.
- Dr Chuah Chong Yang assisted in the collection and provided guidance in the interpretation of the CO₂ and H₂ adsorption data.

Chapter 4 is published as **Li, W.**, Chuah, C. Y., Nie, L., Bae, T. H. (2019), Enhanced CO₂/CH₄ selectivity and mechanical strength of mixed-matrix

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The contributions of the co-authors are as follows:

- Asst/Prof Bae Tae-Hyun revised the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Chuah Chong Yang.
- I performed all the laboratory work at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- All X-ray diffraction patterns and field emission-scanning electron microscope, thermal stability, mechanical strength, N₂ physisorption, CO₂ & CH₄ uptake and CO₂/CH₄ separation, were conducted by me.
- Dr Nie Lina assisted in the collection of the differential scanning calorimetry data.
- Dr Chuah Chong Yang assisted in the interpretation of CO₂ and CH₄ uptake data.

Chapter 5 is published as **Li, W.**, Samarasinghe, S. A. S. C., & Bae, T. H. (2018). Enhancing CO₂/CH₄ separation performance and mechanical strength of mixed-matrix membrane via combined use of graphene oxide and ZIF-8. **J. Ind. Eng. Chem.**, 67, 156-163.

The contributions of the co-authors are as follows:

- Asst/Prof Bae Tae-Hyun suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript.
- I performed all the materials synthesis, collected X-ray diffraction patterns and field emission-scanning electron microscope, thermal stability, N₂ physisorption, CO₂ & CH₄ uptake and CO₂/CH₄ separation, and conducted data evaluation.

- Dr Samarasinghe, S. A. S. C. assisted the preparation of house-made polymer.

Chapter 6 is published as **Li, W.¹**, Goh, K.¹, Chuah, C. Y., Bae. T. H. (2019). Mixed-Matrix Carbon Molecular Sieve Membranes using Hierarchical Zeolite: A Simple Approach Towards High CO₂ Permeability Enhancement, **J. Membr. Sci.**, 588, 117220.

The contributions of the co-authors are as follows:

- Asst/Prof Bae Tae-Hyun provided the initial project direction and revised the manuscript drafts.
- I and Dr Goh Kunli prepared the manuscript drafts. The manuscript was revised by Dr Goh Kunli and Dr Chuah Chong Yang.
- I co-designed the study with Asst/Prof Bae Tae-Hyun and I performed all the laboratory work at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- All X-ray diffraction patterns and field emission-scanning electron microscope, thermal stability, N₂ physisorption, CO₂ & CH₄ uptake and CO₂/CH₄ separation, was conducted by me.
- Dr Chuah Chong Yang assisted in the synthesis of the carbon membranes.

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LI WEN

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1. **Li, W.**¹, Chuah, C. Y.¹, & Bae, T. H.*¹, Zeolite 5A/porous carbon mixed-matrix membranes for O₂/N₂ separation: effect of particle size and mesoporosity of 5A, (2019) *submitted*.
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3. **Li, W.**, Chuah, C. Y., Nie, L., & Bae, T. H.*¹, Enhanced CO₂/CH₄ selectivity and mechanical strength of mixed-matrix membrane incorporated with NiDOBDC/GO composite. **J. Ind. Eng. Chem.**, (2019) 74, 118-125.
4. **Li, W.**, Samarasinghe, S. A. S. C., & Bae, T. H.*¹, Enhancing CO₂/CH₄ separation performance and mechanical strength of mixed-matrix membrane via combined use of graphene oxide and ZIF-8. **J. Ind. Eng. Chem.**, (2018) 67, 156-163.
5. **Li, W.**, Chuah, C. Y., Yang, Y., & Bae, T. H.*¹, Nanocomposites formed by in situ growth of NiDOBDC nanoparticles on graphene oxide sheets for enhanced CO₂ and H₂ storage. **Micropor. Mesopor. Mat.**, (2018) 265, 35-42.
6. Chuah, C. Y., Goh, K., Yang, Y., Gong, H., **Li, W.**, Karahan, H. E., Guiver, M. D., Wang, R., & Bae, T. H.*¹, Harnessing filler materials for enhancing biogas separation membranes. **Chem. Rev.**, (2018) 118, 8655-8769.

7. Chuah, C. Y., **Li, W.**, Samarasinghe, S. A. S. C., Sethunga, G. S. M. D. P., Bae, T. H.*, Enhancing the CO₂ separation performance of polymer membranes via the incorporation of amine-functionalized HKUST-1 nanocrystals, **Micropor. Mesopor. Mat.**, (2019) 290, 109680.
8. Samarasinghe, S. A. S. C., Chuah, C. Y., **Li, W.**, Sethunga, G. S. M. D. P., & Bae, T. H.*, Incorporation of Co^{III} Complex and SNW-1 Nanoparticles to Tailor O₂/N₂ Separation Performance of Mixed-Matrix Membrane, **Sep. Purif. Technol.**, (2019) 23, 133-141.

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LIST OF SYMBOLS

H ₂ O	Water
CO ₂	Carbon dioxide
CH ₄	Methane
O ₃	Ozone
H ₂	Hydrogen
H ₂ S	Hydrogen sulfide
NH ₃	Ammonia
O ₂	Oxygen
N ₂	Nitrogen
He	Helium
Ar	Argon
CFC	Chlorofluorocarbon
GWP	Global warming potential
PSA	Pressure swing adsorption
VPSA	Vacuum pressure swing adsorption
0-D	Zero-dimensional
1-D	One-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
GO	Graphene Oxide
rGO	Reduced graphene oxide

CNT	Carbon nanotube
SWNT	Single-walled carbon nanotube
MWNT	Multi-walled carbon nanotube
MOFs	Metal-organic frameworks
PCPs	Porous coordination polymers
BDC	Benzene-1,4-dicarboxylic
NiDOBDC	Ni-MOF-74/Ni ₂ (dobdc)
ZIFs	Zeolitic imidazolate frameworks
ZIF-8	Zeolitic imidazolate framework -8
HKUST-1/CuBTC	Hong Kong University of Science and Technology-1
UiO-66	Universitetet i Oslo-66
MMMs	Mixed-Matrix Membranes
ODPA-TMPDA	4,4'-oxydiphthalic anhydride-2,4,6-Trimethyl-mphenylenediamine
6FDA	4,4'-(hexafluoroisopropylidene) diphthalic anhydride
CA	Cellulose acetate
PEI	Polyetherimide
PFR	Phenol – formaldehyde resin
PSF	Polysulfone
PVC	Polyvinylchloride
PP	Polypropylene
PET	Polyethylene terephthalate
PEO	Poly(ethylene oxide)
PBT	Polybutylene terephthalate

PI	Polyimides
PIM-1	Polymers of intrinsic microporosity-1
PEG-PEI	Polyethylene glycol- and polyethylenimine
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PES	Polyethersulfone
PTMSP	Poly(1-methylsilyl-1-propyne)
ZSM-5	Zeolite Socony Mobil-5
LTA	Linde type A
FAU	Faujasite
MFI	Zeolite Socony Mobil-five (ZSM-5) (five)
MOR	Mordenite
FER	Ferrierite
BEA	Zeolite beta
H-zeolite 5A	Hierarchical zeolite 5A
CMSMs	Carbon molecular sieve membranes
AAO	Anodic aluminum oxide
KClO ₃	Potassium chlorate
HNO ₃	Nitric acid
KMnO ₄	Potassium permanganate
H ₂ SO ₄	Sulfuric acid
H ₂ CrO ₄	Chromic acid
Mg(OH) ₂	Magnesium hydroxide

Ni(NO ₃) ₂ ·6H ₂ O	Nickel(II) nitrate hexahydrate
DMF	N,N'-dimethylformamide
DMAc	N,N-dimethylacetamide
TEA	Triethylamine
Ac ₂ O	Acetic anhydride
H ₄ DOBDC	2,5-Dihydroxy-1,4-benzenedicarboxylic acid
Zn(NO ₃) ₂ ·6H ₂ O	Zinc nitrate hexahydrate
Hmim	2-methylimidazole
TPOAC	Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride solution
DI	Deionized
PXRD	Powder X-ray diffraction
XRD	X-ray diffraction
FE-SEM	Field emission-scanning electron microscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
DFT	Density functional theory
IAST	Ideal Adsorbed Solution Theory
J	Flux
L	Membrane thickness
T _g	Transition temperature
Q _{st}	Isosteric heat of adsorption

q	Gas adsorption (mmol/g)
$q_{\text{sat, 1 or 2}}$	Saturation loadings for site 1 or 2
b_1 or b_2	Langmuir parameters for site 1 or 2
f_1 or f_2	Freundlich parameters for site 1 or site 2
p	Pressure (bar)
Δp	Pressure drop (bar)
x	Gas molar fractions in the adsorbed phases
y	Gas molar fractions in the bulk phases
T	Temperature (K)
2θ	Two theta angle
P	Gas permeability
S	Solubility
D	Diffusivity
α	Selectivity of gas pairs
α_S	Solution selectivity
α_D	Diffusion selectivity
ρ	Membrane density
F_{index}	Filler enhancement index
P_{filled}	CO ₂ permeability of mixed-matrix CMSMs
P_{unfilled}	CO ₂ permeability of unfilled CMSMs
α_{filled}	CO ₂ /CH ₄ selectivity of mixed-matrix CMSMs
α_{unfilled}	CO ₂ /CH ₄ selectivity of unfilled CMSMs
η	Enhancement coefficient

ABSTRACT

Extensive research on gas adsorption and separation has been widely developed in view of the requirement of effective CO₂ and H₂ capture as well as biogas upgrading (CO₂/CH₄ separation) so as to ensure a sustainable environment for future generation. Thus, with regards to this behavior, microporous materials and carbon nanomaterials are potential candidates to be developed and utilized as adsorbents and membranes, due to their excellent capabilities for effective gas separation, lower capital cost and energy penalty, together with feasibility of scale-up into industrial operations. Herein, the objectives of this thesis are: (1) Tailoring gas uptake capacities for a three-dimensional nanocomposite that leads to an increase of overall gas adsorption sites; (2) Optimizing mixed-matrix membranes (MMMs) with the combined use of carbon nanomaterials and microporous materials to achieve improved gas separation performance; (3) Developing carbon molecular sieve membranes (CMSMs) with functionalized microporous materials to fulfill excellent gas permeation.

The investigation began with the adjustment of surface area and porosity in NiDOBDC/GO nanocomposites with well-designed 3-D architecture. NiDOBDC (MOF) which possessed unsaturated open metal sites exhibited outstanding CO₂ adsorption capability which was attributed to its high accessible surface area. In this case, the incorporation of GO can be served as a structural agent that can be assisted in the formation of MOF/GO 3-D hybrid. Such configuration was feasible in reducing the aggregation effects that were present in MOF nanocrystals as well as creating additional

adsorption sites for gas molecules, thus resulting in significant improvement in gas uptake capacity. Interestingly, the nanocomposites exhibited remarkable CO₂ and H₂ uptake, especially for the case of nanocomposite with 10 wt% of GO, which showed an increase in adsorption amount of 24% (at 25 °C and 1 bar) and 50% (at 25 °C and 20 bar) for CO₂ and H₂, respectively. Results proved that the novel methodology for improving gas adsorption via incorporating GO was highly effective, which indicated promising applications in gas storage.

Then, the utilization of NiDOBDC/GO nanocomposite in Matrimid[®] polymer has been conducted to fabricate MMMs. Attributing to the excellent CO₂ adsorption performance of nanocomposite with 10 wt% loading of GO, NiDOBDC/GO-10% composite was chosen as the filler in Matrimid[®] so as to realize desirable CO₂/CH₄ separation ability without the trade-off effect. It was reported that CO₂/CH₄ selectivity in Matrimid[®]/Composite-20% membrane has been enhanced up to 60% as compared to nascent Matrimid[®] membrane (at 25 °C and 1 bar), without any noticeable loss in CO₂ permeability. Furthermore, the NiDOBDC/GO nanocomposite did not weaken the mechanical strength of MMMs in this work, as compared to the incorporation of pristine NiDOBDC in Matrimid[®] membrane where substantial decrease in mechanical strength has been observed.

On the other hand, apart from the utilization of MOF/GO nanocomposite, the effectiveness of MOF or GO that was separately incorporated into polymer matrix has also been investigated for CO₂/CH₄ separation. It is reported that ZIF-8 is feasible to

improve CO₂ permeability due to its high surface area together with good thermal, mechanical and chemical stabilities, which could be prepared via an easy synthesis procedure. Besides, ODPA-TMPDA polyimide, which has greater permeability than commercial polymers and is also readily synthesized in large quantities, was used as the polymer matrix. Results exhibited that both CO₂ permeability and CO₂/CH₄ selectivity were improved by 60% and 28% (at 25 °C and 1 bar), respectively, when ZIF-8 and GO were introduced together. Importantly, the mechanical strength of mixed-matrix membrane with the incorporation of both ZIF-8 and GO was improved as compared to the nascent membrane, whereas the incorporation of ZIF-8 alone decreased the mechanical strength.

Subsequently, CO₂/CH₄ separation performance has been further improved via the carbonization process, where high temperature and inert atmosphere were applied. Carbonization process is considered to be a promising approach to optimize the structure of the polymer chain or disrupt polymer's rigidity, which is effective to alleviate the inherent limitations in polymeric membranes. It is well-known that zeolite 5A is facile to tune the pore structure, leading to a hierarchical structure with both mesopores and micropores. Also, Matrimid[®] has been applied as the matrix by taking its cheap cost, strong chemical resistance as well as high solubility towards organic solvents into consideration. As a whole, the mixed-matrix CMSM (Matrimid[®]/H-zeolite 5A–30%) was feasible in surpassing the 2008 Robeson upper bound limit, which was attributed to its huge enhancement of CO₂ permeability.

In a nutshell, the utilization of microporous materials (NiDOBDC, ZIF-8 and zeolite 5A) as well as carbon materials (GO, CMSMs) has proven to be promising candidates in advanced CO₂ separation, which can be conducted in an energy-effective manner. Particularly, in each work, CO₂ adsorption or separation (CO₂ permeability and/or CO₂/CH₄ selectivity) has been significantly improved via the combined use of microporous materials and carbon materials, namely NiDOBDC/GO nanocomposite, ZIF/GO binary fillers and zeolite 5A/carbon membranes. Considering the potential of microporous and carbon materials in other gas pairs as well as particle size effect, future work is mainly focused on the application of such strategies (combination of microporous and carbon materials) in O₂/N₂ separation in view of tunable particle size and pore structure.

CHAPTER 1

Introduction

1.1. Background

Gases are typically present everywhere on the surface of earth. The presence of numerous gases in the atmosphere has drawn tremendous attention among researchers, thus leading to continuous investigation on the gases in the surrounding atmosphere throughout the years. Nevertheless, over the past centuries, air pollution has become a serious global issue that requires substantial efforts among communities worldwide to address this problem. In particular, an increase in environmental events that relates to the climate change (i.e. global warming) has been a well-known phenomenon across the world [1]. This has been further proven by an enhancement in the global surface temperature, where the average temperature in 2009 was around 0.8 °C warmer than that of the early 20th century (1880-1920), as shown in Figure 1-1 [2]. Besides, it has been projected that the mitigation of climate change (i.e. global warming) behavior would lead to severe snowballing effects such as extreme weather events and a rise in sea level, as well as a decrease in habitable space for the ecosystem because of glacier retreat and declines in sea ice.

Figure 1-1. Global surface temperatures relative to 1951-1980 mean for (a) annual and 5-year running as well as (b) 12-month running [3].

In general, there are several factors which could lead to the effect of global warming, including the presence of greenhouse gases [4], increase in solar activity [5], emission of aerosols and soot [6], as well as variations in earth's orbit [7]. Among them, greenhouse gases are regarded as the major contributors to global warming attributing to their massive emission, which is responsible for absorbing and emitting infrared radiation to the earth [8]. As a whole, the major contribution in greenhouse gases that is present in earth's atmosphere includes carbon dioxide (CO_2), methane (CH_4), water vapor (H_2O) and ozone (O_3) [9]. Specially, CO_2 emission to atmosphere is considered to be one of the crucial factors that leads to greenhouse effects, as listed in Table 1-1 (GWP: global warming potential; CFC: chlorofluorocarbon). The increase of CO_2 emission basically comes from human activities with the industrial development as burning of fossil fuel has contributed to the majority of the increase in greenhouse gas emission for the past 20 years [10]. Therefore, the increment of CO_2 concentration in earth's atmosphere has become a serious crisis needed to be solved.

Table 1-1. Potential of individual greenhouse gases in relation to global warming [11].

Gas	Residence time (yr)	Instantaneous forcing (W m ⁻² p.p.m. ⁻¹)	(Molar basis)		(Weight basis)	
			Cumulative forcing (W m ⁻² yr Pmol ⁻¹)	Global warming potential	Cumulative forcing (W m ⁻² yr Pg ⁻¹)	Global warming potential
CO ₂	230	0.015	19	1.0	0.42	1.0
CO	(2.1)	(0.65)	26	1.4	0.94	2.2
CH ₄	(14.4)	(0.65)	71	3.7	4.4	10
N ₂ O	160	3.8	3,400	180	77	180
HCFC-22	15	190	15,000	810	180	410
CFC-11	60	220	74,000	4,000	540	1,300
CFC-12	120	280	190,000	10,000	1,600	3,700

Residence times are derived as follows: CO₂ (ref. 14), CH₄ and N₂O (ref. 20) and CFCs (ref. 6). The residence times of CO₂ and CH₄ are adjusted as discussed in the text. CO is ascribed a residence time equivalent to 0.22 times that of methane (see text). The cumulative forcing and GWPs for CO and CH₄ are based on net carbon and therefore include the warming potential of CO₂. Instantaneous radiative forcings are based on the parameterized model given in ref. 3, except for HCFC-22 which is calculated from tables in ref. 4. Values that depend on concentration are based on increasing CO₂ from 350 to 450 p.p.m., increasing CH₄ from 1.7 to 2.7 p.p.m. with a 70% amplification (see text), and increasing N₂O from 0.31 to 0.41 p.p.m. Climate sensitivity is estimated to be 0.5–1.3 °C W⁻¹ m², corresponding to a warming of 2–5 °C for a doubling of CO₂ (ref. 12).

On the other hand, rapid blooming of industrial development [12] together with rapid increase in world population [13] generally attribute to an increase in demand for more energy resources. Clean energy resources have attracted substantial research interest in view of the traditional conventional resources that have been utilized in recent years, namely coal and fossil fuels which are non-renewable. Clean energy is generally defined in such a way that the energy generated through these sources does not generate any waste that could potentially harm the environment. Till date, a wide variety of clean energy sources have been applied in industry and daily life, including wind power [14], hydropower [15], solar energy [16] and bioenergy [17]. As a renewable energy source, hydrogen (H₂) gas which could be produced via water-splitting [18] (Figure 1-2) has showcased its usefulness as it is categorized as zero-emission fuel, with only water as the by-product. As a result, methodology for effective H₂ storage has been the main focus of attention by researchers so as to meet a strong rise in energy demand in recent years.

Figure 1-2. The solutions for solar hydrogen via water splitting [19].

In the meantime, biogas that contains methane (CH_4) in large quantities is also feasible to serve as an important renewable energy source as it can be readily generated from fermentation or anaerobic digestion of organic waste [20, 21]. Furthermore, as reiterated above, CH_4 is also categorized as a greenhouse gas which also possesses a high potential to cause global warming. Thus, rather than emitting CH_4 to the atmosphere, the recycling of CH_4 can be regarded as an effective strategy to provide useful energy source and reduce greenhouse gas effect. Nevertheless, the presence of large amounts of carbon dioxide (CO_2) (Table 1-2) in biogas can be served as the major hurdle in effective energy generation for the usage in industrial processes as the feed tends to present in a lower calorific value, together with potential corrosion of gas transportation pipelines. Therefore, biogas upgrading is required to increase the CH_4 purity and to remove harmful impurities, such as hydrogen sulfide (H_2S) and ammonia (NH_3) [22, 23]. Similarly, such pre-treatment process has been developed in natural gas purification process in order to obtain high-purity CH_4 .

Table 1-2. The composition of biogas and natural gas [24].

content	unit	composition		
		biogas from organic wastes	landfill biogas	natural gas ^a
methane, CH ₄	vol %	60–70	35–65	75–90
carbon dioxide, CO ₂	vol %	30–40	15–50	1–10
nitrogen, N ₂	vol %	~0.2	5–40	>4
oxygen, O ₂	vol %	0	0–5	0
water vapor, H ₂ O	vol %	~6 ^b	~6 ^b	— ^c
hydrogen sulfide, H ₂ S	ppm	0–5000	0–100	4–10000
ammonia, NH ₃	ppm	~100	~5	0
siloxane, [—SiRR'O—] _x	—	traces	traces	0
calorific value	kJ g ⁻¹	20.2	12.3	48.0

^aThe range of natural gas composition is specific to U.S. wells. ^bThe amount of water vapor content reported is based on a feed condition at 40 °C. ^cWater vapor is present in natural gas due to the use of hydraulic pressure for natural gas extraction, which causes the gas to rise above the water surface before collection. Typical range of water vapor in natural gas coming from U.S. wells is 800–1200 ppm.

1.2. Capture of gases

Based on the discussion above, prior to the emission of gases to the atmosphere, effective capture of gases is indeed crucial to store desirable gases and minimize any plausible air pollution, besides ensuring that the feed is sufficiently clean with minimal impurities so as to be utilized effectively as a source of energy. Through the years, various approaches had been developed for effective gas capture, including storage in typical high-pressure vessels or under cryogenic temperatures, as well as storage via chemical hydrides, similarly as described in Figure 1-3. Nevertheless, these approaches suffer from several limitations, as illustrated in Table 1-3. For instance, compressed gas tank which is commercial available requires a careful selection of storage materials to overcome the potential stress which could be exerted by the compressed gas together with high thermal conductivity so as to manage the strong release of exothermic heat during the

compression process. What's more, higher cost (16-19 \$/kWh) for compressed gas technique is required compared to other approaches. On the other hand, storage under cryogenic condition shows high volumetric capacity together with relative lower cost (12 \$/kWh), but generally requires large energy penalty, together with the potential safety risk with reference to the usage of these gases at low temperatures. Despite chemical hydrides offer good volumetric capacity, large footprint and periodic regeneration is required once the samples has been fully occupied by the adsorbed gases, as shown in Figure 1-3. [25]

In total, these approaches generally share the following limitations in common: high energy consumption (high pressure or low temperature), high cost and large plant footprint. Therefore, more safe and effective approaches are required for better utilization of gas capture and storage, like solid adsorption (sorbents), as demonstrated in Figure 1-3.

Figure 1-3. Classification of hydrogen storage methods [25].

Table 1-3. Comparison of hydrogen storage technologies.

Technologies	Pros.	Cons.	Costs (\$/kWh)
Compressed gas	<ul style="list-style-type: none"> • Commercial available 	<ul style="list-style-type: none"> • High compression energy • Strict requirement for storage materials • Low volumetric capacity 	16-19
Cryogenic gas	<ul style="list-style-type: none"> • High volumetric capacity • Reversible on-board 	<ul style="list-style-type: none"> • High compression energy • Heat management during charging Required • High operating temperature for gas release 	12
Chemical hydrides	<ul style="list-style-type: none"> • Good volumetric capacity • Proper operating temperature 	<ul style="list-style-type: none"> • Thermal management required • Large footprint • Off-board regeneration 	TBD
Sorbents	<ul style="list-style-type: none"> • High storage density • Safe • Reversible on-board • Scalable 	<ul style="list-style-type: none"> • Low operating temperature 	TBD

1.3. Microporous materials as a solution

For gas capture, solid adsorption using adsorbents (microporous materials) has demonstrated its usefulness in gas storage technology for industrial applications. Several advantages of storing gases using microporous materials have been highlighted as shown in Table 1-3. First, the incorporation of microporous materials into a typical gas storage cylinder is feasible in increasing the gas storage density as compared to storage in a typical gas cylinder. Second, storage of gases using microporous materials is generally safer as a reasonable quantity of gases can be captured by the microporous materials without compressing the gases under extraordinarily high pressure. Third, the required

gas storage capacity can be easily predicted and estimated as the gas storage using microporous materials is generally constant at fixed temperature and pressure. [26] Therefore, such an approach would be relatively cost-effective and energy-saving. Till date, different types of adsorbent have been widely applied in gas capture, not limited to zeolites, porous organic polymers (POPs), mesoporous silica, metal-organic frameworks (MOFs), carbon materials, to name a few.

1.4. Biogas upgrading

On the other hand, improving the purity of CH_4 in biogas can be conducted via biogas upgrading or natural gas purification (i.e. CO_2/CH_4 separation), where it is generally necessary and critical before utilizing these gases as the source of energy generation. Figure 1-4 displays the pathway of biogas which is produced from organic waste and used to supply electricity and heat. Conventional technologies that has been developed for biogas upgrading are pressure swing adsorption (PSA), water scrubbing, physical scrubbing, and chemical scrubbing [27], as summarized in Table 1-4. It is observed that chemical (amine) scrubbing shows the best upgrading efficiency with more than 99% of CH_4 which is present in the upgraded gas together with lowest electricity consumption as compared to other technologies. However, it is generally a huge challenge for chemical scrubbing to perform in an environmental friendly manner as it involves the usage of chemicals which are not reusable after each scrubbing process. Furthermore, all these technologies generally require high costs to successfully achieve biogas upgrading. For instance, the typical investment cost for ammine scrubbing ($100 \text{ m}^3 \text{ h}^{-1}$ biomethane) reaches as high as $9500 \text{ €}/(\text{m}^3 \text{ h}^{-1})$. Thus, to improve the economic feasibility of biogas,

more efficient upgrading technology should be developed and implemented, which will be discussed in the following chapter.

Figure 1-4. The pathway of biogas production and usage [23].

Table 1-4. Comparison between selected parameters for conventional upgrading processes [23].

Parameter	Water scrubbing	Organic physical scrubbing	Amine scrubbing	PSA
Typical methane content in biomethane (vol%)	95.0-99.0	95.0-99.0	>99.0	95.0-99.0
Methane recovery (%)	98.0	96.0	99.96	98.0
Typical delivery pressure bar(g)	4-8	4-8	0	4-7
Electric energy demand (kWhel m ⁻³ biomethane)	0.46	0.49-0.67	0.27	0.46
Heating demand & temperature level	N.A.	70-80°C	120-160°C	N.A.
Desulphurization requirements	Process dependent	Yes	Yes	Yes
Consumables demand	Antifouling agent drying agent	Organic solvent (non-hazardous)	Amine solution (hazardous, corrosive)	Activated carbon (non-hazardous)
Partial load range (%)	50-100	50-100	50-100	85-115
Number of reference plants	High	Low	Medium	High
Typical investment costs €/ (m ³ h ⁻¹)				
100 m ³ h ⁻¹ biomethane	10100	9500	9500	10400
250 m ³ h ⁻¹ biomethane	5500	5000	5000	5400
500 m ³ h ⁻¹ biomethane	3500	3500	3500	3700
Typical operational costs ct m ³ h ⁻¹				
100 m ³ h ⁻¹ biomethane	14.0	13.8	14.4	12.8
250 m ³ h ⁻¹ biomethane	10.3	10.2	12.0	10.1
500 m ³ h ⁻¹ biomethane	9.1	9.0	11.2	9.2
Pros.	• Minor pre-treatment	• Non-hazardous	• Excellent upgrading efficiency • No delivery pressure	• No heating demand
Cons.	• Energy consuming • Requirement of antifouling	• Low market share • Heating demand	• High consumable/temperature demand	• Energy consuming • High cost

1.5. Biogas upgrading using membrane

Several new technologies have been investigated so as to complement the conventional approaches that have been utilized thus far. In general, membrane-based technology has demonstrated its promising application in separating CH_4 and CO_2 , as depicted in Figure 1-5, owing to several competitive advantages. First, membranes for biogas separation require low capital cost, simplified operating condition together with the feasibility in scaling up. Second, membrane technology could offer high energy efficiency as compared to conventional approaches. Third, membranes are generally chemical stable, even at high pressure. Fourth, comparable CH_4 recovery can be achieved in membrane technology as compared to conventional gas separation process. [28] All in all, because of these preponderant merits, membrane technology used for CO_2/CH_4 separation has widely drawn researchers' attention and a great deal of investigation has been done so far.

Figure 1-5. Membrane for CO_2/CH_4 separation [29].

1.6. Research objectives

In the thesis, the overarching objective is to develop the combined use of carbon nanomaterials and microporous materials for advanced CO_2 and H_2 capture as well as CO_2/CH_4 separation. In detail, these studies aim to achieve the primary objectives and address the challenges of nanomaterials and porous materials for gas capture and

membrane-based technology for gas separation, which is listed as follow:

- Tailoring and enhancing gas uptake capacities for the three-dimensional nanocomposites with an increase in overall gas adsorption sites.
- Optimizing mixed-matrix membranes (MMMs) with the combined use of carbon nanomaterials and microporous materials to achieve improved gas separation performance, thus reducing the trade-off effect of gas permeability and selectivity.
- Developing carbon molecular sieve membrane with functionalized microporous materials to fulfill excellent gas permeation.

CHAPTER 2

Literature review

2.1. Introduction

Throughout the past few decades, microporous materials and carbon-based materials for gas applications have been intensively investigated due to their extraordinary properties. Carbon-based material that was used in this study, graphene oxide (GO), is a two-dimensional (2-D) honeycomb lattice of dense packed hybridized carbon atoms. GO is feasible to act as a structural agent for the formation of a 3-dimensional (3-D) architecture together with microporous functional materials (e.g. metal-organic frameworks (MOFs)), thus serving as a potentiator to provide synergic effect with MOFs for advanced gas separation process. Besides, the binary fillers of both GO and MOFs in mixed-matrix membranes (MMMs) have proven to be effective for optimizing overall gas separation performance. In addition, the microporous carbon molecular sieve membrane was fabricated via carbonization process, which was developed via mixed-matrix membrane that contained porous zeolite, subjected under high temperature together with inert feed gas. Hence, as discussed in following sections, the key properties of microporous materials and carbon materials which are believed to possess promising applications in gas capture and separation processes will be summarized. Moreover, the theoretical mechanism and current study status of solid adsorption and membrane-based technology will be reviewed.

2.2. Microporous materials for gas adsorption

As introduced above, a vast amount of solid adsorbent materials have been developed and applied in gas adsorption, like zeolites, mesoporous silica, porous organic polymers, metal-organic frameworks and carbon materials, as shown in Figure 2-1 and Table 2-1.

Among all these gas adsorbents, zeolites are the most conventional materials which have been widely studied and utilized in gas adsorption, particularly in the field of CO₂ capture.

On the other hand, as the compounds of metal ions/clusters and organic ligands, metal-organic frameworks (MOFs) have become the most popular porous adsorbents in recent years owing to the synergic advantages of both inorganic and organic counterparts, as illustrated in Table 2-1.

Figure 2-1. Adsorbent materials for gas adsorption. (zeolites [30], mesoporous silica [31], porous organic polymers [32], metal-organic framework [33], carbon materials [34])

Table 2-1. Comparison between adsorbent materials.

Materials	Pros.	Cons.	Usage as adsorbents
Zeolites	<ul style="list-style-type: none"> • Easy synthesis • Low cost • Moisture stable • Thermal stable • Tunable pore size 	<ul style="list-style-type: none"> • Limited surface area 	High
Mesoporous silica	<ul style="list-style-type: none"> • Uniform pore size • Good mechanical property 	<ul style="list-style-type: none"> • Difficulty in synthesis 	Low
Carbon materials (graphene oxide)	<ul style="list-style-type: none"> • Chemical stable • Good mechanical/thermal property • Tunable interlayer space 	<ul style="list-style-type: none"> • No appropriate pores 	Low
Porous organic polymers	<ul style="list-style-type: none"> • Tunable pore size 	<ul style="list-style-type: none"> • Relative harsh synthesis conditions 	Low
Metal-organic frameworks	<ul style="list-style-type: none"> • Ultrahigh surface area • High porosity • Tunable functionality 	<ul style="list-style-type: none"> • Moisture sensitive • Particle aggregation 	High

2.2.1. Zeolites

Zeolites are defined as microporous crystalline aluminosilicates which are composed of SiO_4 and AlO_4 tetrahedra, where positive cations were incorporated into the framework in order to ensure that overall framework remains neutral. The composition of zeolites can be described as below, with Y^{x+} can be described as the positive cations:

Based on the structural formula, it can be indicated that positive cations are exchangeable, resulting in the formation of zeolite framework with various topologies, as demonstrated in Figure 2-2. Depending on the type of zeolite frameworks, pore size that ranges from 0.3-1 nm can be formed [35]. In addition, zeolites are also well-known as unique pore properties which are highly accessible with the surface area value ranging from 300 to 700 m^2/g [36]. Besides, water molecules would easily occupy the voids of zeolites during synthesis procedures. After thermal treatment, the water phase and organic cations that are

present in the zeolite framework will be removed, thus ensuring that zeolite pores are available for effective adsorption of gas molecules. It should be well-noted that the structural integrity and crystallinity of zeolites can be retained after the release of water molecules, indicating that the crystallinity of zeolite framework remains stable in the existence of moisture. [36]

Figure 2-2. Comparison of zeolites with different frameworks structures. (A: LTA; B: FAU; C: MFI; D: MOR; E: FER; F: BEA [37]).

Zeolites in general can be found naturally on the earth since 18th century, where more than 40 types of natural zeolites have been determined. Nevertheless, these zeolites tend to show low Si/Al ratios as there is an absence of structure-directing agents that allows an effective synthesis of zeolites with high crystallinity. Thus, the synthesis of zeolites has been developed and widely investigated to develop various types of zeolite framework with variation of zeolite topology. As low-silica zeolites, zeolite A and X have excellent ion-exchange capabilities and high cation contents. Subsequently, zeolite Y which shows similar topology with zeolite X, has been developed to obtain good thermal and chemical

stabilities via decreasing Al content leading to intermediate silica content. [36] Next, zeolites with high-silica content (e.g. Zeolite Socony Mobil-5 (ZSM-5)) [38, 39] that were developed in 1970s, demonstrate favorable thermal stabilities over a wide temperature range. For instance, the decomposition temperature of low-silica zeolites is typically observed to be 700 °C, and even much higher for zeolites with high-silica content. [36]

Linde type A (LTA) (3-5A), which has been studied intensively in gas adsorption [40], can be prepared in large-scale production with minimal cost. Furthermore, the pore size of zeolite LTA is feasible to be tuned via substitution of various cations which can be conducted via ion-exchange, thus resulting in its promising application for gas separation processes. [41] In particular, the pore opening of Ca-A is around 4.8 Å, which allows effective passing through of CO₂ molecules [42]. Nevertheless, due to its hydrophilic nature, extraordinary degassing condition is required for the removal of residual water that could be potentially present during the synthesis of zeolite 5A. Furthermore, the incorporation of various cations is also feasible to tune the overall structural polarity of the framework, which is crucial to achieve good separation capability. For example, high electrostatic field inside the cavity of zeolite LTA is generally favorable towards the adsorption of polar molecules (e.g. CO₂). [43] This can be verified in Figure 2-3, where good CO₂ affinity and high CO₂/CH₄ selectivity of zeolite LTA has been illustrated, indicating its promising capability in biogas separation. Moreover, based on optimized free space and void volume for effective CO₂ transport provided by molecular channels and rigid cavities in zeolites, researchers have made great efforts on the investigation of zeolite-based MMMs in gas separation process.

Figure 2-3. (a) CO₂ and CH₄ uptake capacities of (red) NaK-LTA, (blue) NaCs-LTA and (black) NaKCs-LTA [44]; (b) CO₂ separation from CH₄ [43].

2.2.2. Metal-organic frameworks

Metal-organic frameworks (MOFs), which are also classified as porous coordination polymers (PCPs) [45], are categorized as a new class of microporous materials consisting of metal ions/clusters and organic ligands to form one-, two-, or three-dimensional (1-, 2-, or 3-D) hybrid structures [46], as illustrated in Figure 2-4. In comparison to conventional materials (i. e. zeolites) for gas adsorption process, MOFs have been regarded as the most potential microporous materials attributing to the ultrahigh surface area (up to 6000 m²/g) and porosity (up to 90% of total pore volume) as well as tunable pore size [47]. Furthermore, as compared to other porous materials, MOFs exhibit a very high designability in the structures. For instance, MOFs can be produced readily via mild synthesis condition, where organic ligands can be designed and adjusted to tune the gas

adsorption capability. Besides, it is feasible to develop post-synthetic functionalization in both inorganic and organic compositions. In total, dynamic/flexible frameworks in MOFs prove to be very unique and promising among other porous solids, especially for gas adsorption applications. [48]

Figure 2-4. Schematic representations of the general classification of porous solids (top) and a typical construction procedure of a MOF (bottom) [48].

In the year of 1965, the design of MOFs with high thermal stabilities was reported by Tomic et al [49]. Until 1999, MOF-5, which was one of the representative MOFs [50], was published and subsequently a fast growing research works on MOFs have been addressed in recent years. In general, MOFs can be synthesized readily via one-step reaction where metal salts and organic ligands can be self-assembled in the organic solvent under a wide range of temperatures. At room temperature, single large crystals could be prepared due to the low reaction rate resulting from slow ion diffusion and solvent evaporation. On the other hand, the purity of final products will be affected if the reaction is conducted within a shorter reaction time at higher temperature. Therefore, the

synthesis temperature (which relates to the reaction rate) as well as pH value can be regarded as important factors which can influence the quality of final products. Besides, it has been reported that the synthesis of MOFs will be challenging in terms of the final product purity as well as undesirable contaminants that will be present during synthesis procedures. For example, it is difficult to isolate the desired product from varying by-products. Hence additional purification technologies or advanced synthesis methods have also been carried out in recent research works. [48]

Figure 2-5. The summary of microporous MOFs synthesized with various structures [51, 52].

Table 2-2. Comparison of representative MOFs.

MOFs	Synthesis	Formula	Structure	BET surface area (m ² /g)	Pore size (Å)	Pros.	Cons.	Ref.
MOF-5	Room temperature	Zn ₄ O(BDC) ₃ ^a	Cubic	3800	8.4	Scalable	Safety concern	[53-56]
MOF-74	Room temperature	X ₂ (DOBDC) (X=Mg, Ni, Fe) ^b	Hexagon	400-1000	11-98	Ultrahigh CO ₂ adsorption	Moisture & air sensitive	[57-59]
HKUST-1	Heat requirement	Cu ₃ (BTC) ₂ ^c	Cubic	1000-1300	5.13	Size controllable Commercially available	Inactive pore space	[60-62]
ZIF-8	Room temperature	Zn(mIm) ₂ ^d	Cubic	1000-1200	11.6	Easy synthesis Low cost Stable	Low CO ₂ adsorption	[63-65]
UiO-66	Heat requirement	Zr(1,4-dicarboxybenzene)	Cubic	1500-1700	6.0	Stable Scalable	Low productivity	[66, 67]
MIL-101	Heat requirement	Cr ₃ O(OH)(H ₂ O) ₂ (BDC) ₃	Octahedra	2600	18-23	Ultrahigh CO ₂ adsorption Stable	High cost	[68-70]

Note: ^a BDC: 1,4-benzodicarboxylate;

^b DOBDC: 2,5-dihydroxyterephthalic acid;

^c BTC: 1,3,5 benzenetricarboxylate;

^d mIm: 2-methylimidazole;

Figure 2-5 generally displayed some well-known MOFs that have been designed and synthesized till date. And Table 2-2 summarized and made a comparison of several representative MOFs which have been widely applied. For instance, MOF-5 with zinc salts and typical benzene-1,4-dicarboxylic (BDC) acid was prepared in the very early stage of MOF's development [50]. Besides, HKUST-1 (CuBTC) which is available under the tradename of BASOLITE[®] C300 also demonstrates reasonable gas adsorption behavior [52]. The structure of the MIL series is composed of MO₄(OH)₂ (M: metal ions)

which is interconnected by dicarboxylate groups, where the pore aperture is determined to be 0.85 nm [71]. As a popularly investigated MOF material, zeolitic imidazolate framework-8 (ZIF-8) is composed of tetrahedrally-coordinated transition metal (Zn) which requires simple one-step synthesis and offers favorable thermal and chemical stabilities [72]. Moreover, X-MOF-74 (X=Mg, Ni, Co, Fe, Mn, Zn) demonstrates extraordinary high gas adsorption ability, especially CO₂ due to their outstanding high surface areas resulting from the presence of coordinatively unsaturated open metal sites, as illustrated in Figure 2-6. In particular, CO₂ adsorption of Mg-MOF-74 could reach as much high as 7.5 mmol/g (25 °C, 1 bar) which is almost the highest value thus far [73].

Figure 2-6. (1) Particle morphologies of (a) Mg-, (b) Ni- and (c) Zn-MOF-74; (d) XRD patterns for the three samples; (2) Pure CO₂ (squares) and N₂ (circles) uptake of Mg- (blue), Ni- (red) and Zn-MOF-74 (green) tested at room temperature [59].

Therefore, owing to the extraordinary advantages in terms of their surface areas and porosity properties, MOFs have been readily applied in a variety range of applications, which are not limited to catalysis, gas purification, gas storage and gas separation [74]. For instance, Rosi et al [53] reported that MOF-5 was feasible to adsorb H₂ up to 4.5 wt%

(78 K, 20 bar) because of its favorable interaction with hydrogen [75]. Besides, Cu-BTC has been applied in the removal of SO₂ from natural gas, which was resulting from its dual type sorption to polar components provided by the special arrangement of open metal sites [76]. Moreover, in the work of Wu et al, MOF-74 was successfully synthesized and characterized with adsorption equilibrium and kinetics of hydrocarbon gases, where the resulting high selectivity of CO₂/CH₄, C₂H₄/C₂H₆ or C₃H₆/C₃H₈ has been reported [77]. What's more, the potential of MOFs in serving as functional porous fillers that can be possibly incorporated into polymer matrix is applied so as to optimize and improve the overall gas separation performance [78].

2.3. Graphene oxide

As emerging porous materials for gas separation, carbon materials with one- or two-dimension have stimulated researchers' interest which was eventually followed by a series of investigation works, including carbon nanotubes (CNT) and graphene-family materials, as depicted in Figure 2-7. Multi-walled carbon nanotube (MWNT) which was categorized as one-dimensional (1-D) carbon material has been applied in the adsorption of CO₂ from flue gas [79] as well as act as a filler in polymer matrix to offer great enhancement in CO₂ permeability [80]. This is attributed to its cylindrical nanostructure together with ultrahigh length-to-diameter ratio [81]. On the other hand, graphene can be described as a two-dimensional (2-D) nanomaterial that is made up of a single layer of carbon atoms, which could be exploited to form graphene oxide (GO) and reduced graphene oxide (rGO). This unique layered structure suggests the potential application of graphene-family nanomaterials in gas separation process.

Figure 2-7. Schematic structures of (a) graphene and graphene oxide (GO) and (b) single-walled carbon nanotube (SWNT) and multi-walled carbon nanotube (MWNT); Fluorescence spectra of (c) GO, (d) CNT and (e) SWNT [82].

2.3.1. Structural and physicochemical properties

Graphene-family is a 2-D layered nanomaterial that is made up of sp^2 -hybridized carbon atoms which are arrayed in a honeycomb (hexagonal) lattice. Interestingly, graphene performs highly flexible and processable into various structures, as well as remarkable mechanical strength. In this case, two popular derivatives (GO and rGO) of graphene-family have been successfully synthesized and attracted much attention, as illustrated in Figure 2-8. Among the derivatives, GO has shown its attractiveness in the past ten years owing to its extraordinary structural features together with physical and chemical properties.

Figure 2-8. Layered structures of (a) graphene, (b) GO and (c) rGO [24].

Similarly to graphene, GO is a 2-D lattice of carbon atoms that contains hydroxyl, epoxy, and carboxylic groups where its atoms are interconnected by strong covalent σ bond [83]. In this structure, the oxygen functional groups are sp^3 -hybridized, thus disrupting the extended sp^2 -hybridized network of graphene. The distribution of sp^3 -hybridized clusters is relatively uniform despite the oxygen atoms are randomly located above or below the graphene plane [84]. Microscopy characterization of GO has indicated that the height dimension is approximated to be 0.7-1 nm, with large variation of lateral dimension (due to variation of synthesis method), thus leading to a high aspect ratio [85]. In addition, theoretical studies have been taken into consideration for the exploration of GO structure as possible kinetics and thermodynamics can be conducted to further understand the structural properties of the functional groups. For instance, based on density functional theory (DFT) calculation, Lahaye et al. [86] reported that oxygen and carbon is preferred to form epoxides, and in the meantime the hydroxyl groups are formed on the opposite side.

To date, various synthesis methods for the preparation of GO were investigated. The first example was reported by Brodie [87] in 19th century where potassium chlorate ($KClO_3$)

was added into graphite solution containing nitric acid (HNO_3), resulting in the final C:H:O composition of 61:2:37. Decades later, Staudenmaier [88] improved Brodie's preparation with the addition of chlorate and sulfuric acid so as to obtain an extended oxidation of GO (C:O = 2:1). Subsequently, Hummers and Offeman [89] explored another synthesis approach to achieve the oxidation of graphite via a mixture of sulfuric acid (H_2SO_4) and potassium permanganate (KMnO_4) in 20th century. As such, the common source for this chemical oxidation is flake graphite which has been naturally produced and purified before use. Under such circumstance, the intrinsic defects of graphite could provide seed sites for the oxidation of GO. Based on Hummers method, some other oxidants have also been applied for GO formation, such as chromic acid (H_2CrO_4). [90] Therefore, the Hummers method of using both $\text{KMnO}_4/\text{H}_2\text{CrO}_4$ and H_2SO_4 has become a popular approach for the preparation of GO.

In view of the carbon nature and unique 2-D structure decorated with functional groups, GO exhibits excellent physical and chemical properties, namely electronic, optical, mechanical, thermal properties as well as chemical reactivity. For instance, the presence of disrupted sp^2 network has led to its electrically insulating properties. Besides, the reduction of GO is one of the most key reactions resulting in the formation of reduced GO (rGO). The reduction procedures can be conducted via thermal, chemical or electrochemical approaches. For instance, GO would be exfoliated by the extrusion of CO_2 during heating process ($\sim 1000^\circ\text{C}$). Under such operation, the gas which was subjected to high temperature and pressure ($\sim 130\text{ MPa}$) has assisted in conducting effective separation between GO layers. As a result, the total mass of GO is lost during

the reduction process, while giving rise to structural defects which will influence the overall electronic property. [90] On the other hand, the mechanical property of GO was conducted by evaluating the elastic modulus and fracture strength. It was observed that an individual paper-like GO (Figure 2-9) was reported to obtain an average modulus value of ~ 32 GPa together with extraordinary high fracture strength value of ~ 120 MPa [91]. Hence the strong mechanical stability of GO suggests its potential in various practical applications.

Figure 2-9. SEM morphologies of (a) GO paper and (b) cross-section of GO paper [91].

In summary, GO has been widely investigated and used in a variety range of applications due to its unique and outstanding electronic, optical, thermal and mechanical properties. Up to now, GO has been involved in the development of field effect transistor, sensors, conductive films, clean energy devices, graphene nanocomposites and so on [85]. For instance, attributing to the large specific surface area, GO is feasible to serve as bio-sensors or gas sensors that can be used to detect various molecules [92]. Furthermore, GO can be used in the fabrication of conductive films attributing to its good electrical conductivity and high carrier mobility [93]. Since GO has been regarded as a potential electrode material owing to the high aspect ratio together with high surface area, leading

to the utilization in lithium ion batteries [94].

As demonstrated in Table 2-3, zeolites with tunable pore size are easy to synthesize, meanwhile MOFs show ultrahigh surface area and tunable functionality. Therefore, zeolites and MOFs as microporous materials have been popularly applied in gas applications. In summary, MOFs show the highest surface area compared to other two materials, leading to excellent CO₂ adsorption capacities, as displayed in Table 2-3. As for zeolite, it performs more environmental stable than MOFs and GO. Owing to the unique mechanical and chemical properties, GO has also been regarded as a promising aid who could be feasible in improving gas adsorption.

Table 2-3. Comparison between microporous materials and graphene oxide.

Materials	Surface area (m ² g ⁻¹)	Stability	Compatibility with polymer	CO ₂ uptake (mmol/g, 1 bar)	CO ₂ /CH ₄ adsorption selectivity	Ref.
Zeolites	300-700	Moisture/thermal stable	Poor	Up to 3.72	Up to 70	[95, 96]
Metal-organic frameworks	Up to 6000	Moisture sensitive	Medium	Up to 7.50	Up to 350	[59, 97]
Graphene oxide	~300	Mechanical stable	Good	Less than 0.50	Less than 4	This work

2.3.2. Graphene oxide-based nanocomposite materials

It is well-known that GO has been utilized effectively in polymer matrix so as to fabricate composite membranes for various applications, especially in the area of gas separation process, which will be discussed in the following chapters. In addition, GO has acted as a structural agent to form a 3-D composites that was incorporated with other microporous

materials, especially MOFs with high surface area, porosity and adsorptive properties. The combination of 2-D materials and nanoparticles will give rise to exceptional properties compared to one material alone, as listed in Table 2-4. It is summarized that MOF/GO composites could be developed via the addition of GO into the mixture of MOF precursors. In this case, MOF crystals could grow and stabilize on GO surface with a tunable 3-D architecture. Owing to the unique structure, the porosity and surface area are feasible to be improved, which prove to be promising in various application fields, such as gas sensors, solvent adsorption, gas adsorption and separation.

Table 2-4. The summary of MOF/GO composites in the literature.

Samples	Synthesis	Crystal structure	Porosity ^a	Pros	Application	Ref.
MOF-5/GO	GO added during MOF formation	distortion lattice of MOF	+	flexible functionality	Gas adsorption	[98]
MOF-5/BFG ^b	BFG added during MOF formation	distortion lattice of MOF	+	adjustable metrics	Organocatalysis/sensors	[99]
MIL-100/GO	GO added during MOF formation	MOF	+	pore structure stable	NH ₃ adsorption	[100]
HKUST-1/GO	GO added during MOF formation	MOF	+	moisture stable	H ₂ adsorption	[101]
ZIF-8/GO	GO added during MOF formation	distortion lattice of MOF	-	tunable morphology	CO ₂ adsorption	[102]
HKUST-1/GO	MOF precursor added during formation of GO	MOF	+	pressure stable	CO ₂ , H ₂ adsorption	[103]
HKUST-1/GrO ^c	GO added during MOF formation	MOF	+	strong interaction to CO ₂	CO ₂ /CH ₄ separation	[104]
MIL-101/GO	GO added during MOF formation	MOF	+	excellent reversibility	n-Hexane adsorption	[105]
HKUST-1/GO	GO added during MOF formation	MOF	+	moisture stable	Toluene adsorption	[106]
MOF-505/GO	GO added during MOF formation	MOF	+	moisture stable	CO ₂ /(CH ₄ , N ₂) separation	[107]

^a + (increase), - (decrease) in porosity, which can be verified from surface area; ^b benzoic acid-functionalized graphene; ^c reduced graphene oxide.

The effect of the formation of 3-D composite on gas adsorption has been actively reported, as shown in Table 2-4. For instance, Kumar et al. [102] reported a ZIF/GO hybrid with tunable porosity and morphology which gave rise to a high CO₂ adsorption capacity. As a new class of zeolite-like MOF, ZIF-8 possesses high porosity, excellent chemical and thermal stabilities together with scalable synthesis protocol. In particular, with GO loading of 20 wt%, the ZIF/GO composite exhibited the best CO₂ uptake of 72 wt% (195 K, 1 bar), which is owing to the creation of the additional interaction sites of different polar groups on GO surface. Besides, HKUST-1 was famous for its reasonable stability towards water, high porosity and low cost. Herein, quite a few studies about HKUST-1/GO composites have been investigated, as shown in Table 2-4. For example, Liu et al. [103] claimed that the introduction of GO effectively enhanced surface area, resulting in improved CO₂ and H₂ storage capacities. Moreover, its feasibility on CO₂-based separation has been observed based on its high selectivities of CO₂/CH₄ and CO₂/N₂ in this composite. Therefore, it can be concluded that these advantages determine MOF/GO composites to be very promising candidates in terms of optimizing surface area and porosity for practical use, especially in the process of gas adsorption and separation.

2.4. Current status of membrane categories for gas separation

On the other hand, membrane-based technology used for gas separation has been intensively investigated in recent years on account of the advantages over conventional technologies, including feasibility to scale up, easy operation, low cost, high energy efficiency as well as good mechanical and chemical stabilities. Hence a huge amount of material types have been widely developed for the preparation of membranes, like

polymeric membranes, porous membranes (zeolite membranes or MOF membranes), mixed-matrix membranes (MMMs) and carbon-based membranes [108].

2.4.1. Polymeric membranes

In principle, a tremendous variety of materials could be applied for membrane fabrication, including glass, ceramics, metals, porous materials and polymers. Among them, polymeric membranes have become the most widely investigated materials used in gas separation thus far, due to the exceptional advantages over other membrane types. Firstly, owing to the polymer nature, polymeric membranes possess high processability to be fabricated into various configurations, including flat sheets, hollow fibers and spiral wounds. Secondly, polymeric membranes demonstrate good chemical and thermal stabilities. [28] Thirdly, as compared to other membrane materials, polymers are relatively cost-effective, which leading to the development of several types of polymers that have been commercially available, such as Matrimid[®], Kapton[®], Cellulose acetate (CA), Polysulfone (PSF), Polyvinylchloride (PVC), Polypropylene (PP) and Polyethylene terephthalate (PET). Therefore, a tremendous amount of research works on these materials have been widely conducted during the past few decades.

In 1980's, the first polymeric membrane used for industrial application was fabricated from cellulose acetate, owing to its stability in membrane performance. Subsequently, several studies about polymeric membranes were developed with the substantial efforts in increasing the capability to develop large-scale membrane modules with high gas permeance [109, 110]. These attempts have been successfully developed in 1990's, where

the first biogas upgrading membrane plant was founded, with the separation capacity of 25 N m³/h [23]. It has been projected that the capacity could be feasible in achieving as high as 10,000 N m³/h after several modifications in order to cater the increasing demand for energy production [111]. Apart from practical applications, membranes that were synthesized for the use in research have been conducted, as summarized in Table 2-5. In general, poly(ethylene oxide)-based (PEO) polymers, 6FDA-based and commercial polyimides (PI) have been commonly reported for the application in biogas upgrading, where 6FDA-based polymers present excellent CO₂ permeability compared to commercial polymers, such as Matrimid and P84. However, the requirement of monomer purification, harsh synthesis conditions and high cost limit the practical applications of 6FDA-based polymers, as described in our previous work [112].

Table 2-5. Comparison of CO₂ permeation performance reported in commonly used polymers [24].

polymer	T_g (°C)	testing condition ^a		plasticization pressure, P_{pl} (bar) ^b	$P(\text{CO}_2)$ at P_{pl} (barrer)
		ratio of CO ₂ /CH ₄	temp (°C)		
6FDA-6FpDA	295	1:1	35	14	61.0
6FDA-DAM	393	1:1	35	15	600.0
6FDA-DAM:DABA (3:2)	365	1:9	35	4	17.0
6FDA-DAT	319	1:1	35	>30	— ^c
6FDA-DAT:DAM (1:1)	372	1:1	35	15	160.0
6FDA-durene	422	1:1	35	10	850.0
BPA-PC	151	pure CO ₂	25	31	4.7
BPZ-PC	175	pure CO ₂	25	24	1.0
CA	187	pure CO ₂	27	11	6.0
CTA	185	pure CO ₂	24	10	7.3
Matrimid	313	pure CO ₂	22	12	4.8
PEIm	199	pure CO ₂	21	28	0.8
PES	222	pure CO ₂	21	27	2.6
PPO	210	pure CO ₂	25	14	82.0
PSf	182	pure CO ₂	23	34	3.6
P84	300	pure CO ₂	23	22	0.9
TMBPA-PC	193	pure CO ₂	25	13	13.0

^a The upstream feed pressure of CO₂; ^b estimated based on the minimum point of CO₂ permeability against the feed pressure of CO₂; ^c No minimum point was observed until 30 bar.

It is well-known that polymeric membranes can be classified into two types: porous membranes and dense membranes. For porous polymeric membranes, gas transports can be transported via the mechanisms of surface diffusion, Knudsen diffusion, capillary condensation and molecular sieving [113]. In dense membrane, the transport of gas molecules through the membrane is governed by the mechanism of solution-diffusion [114, 115]. This mechanism indicates that gas molecules are first absorbed at the upstream boundary, followed by the diffusion of gas molecules passing through the membrane and gas molecules are eventually desorbed at the permeation side via chemical potential gradient, which can be served as the driving force, as displayed in Figure 2-10. In 1950's, Fick reported the theoretical calculation of gas diffusion through the dense membrane of cellulose nitrate [116]. According to Fick's first law, the gas flux (J_i) is depending on membrane thickness (L), pressure drop Δp (the difference between input and output pressure) as well as permeation coefficient (P_i). In which, permeability coefficient (P_i) is defined as the equation as below (2-1):

$$P_i = D_i \cdot S_i \dots \dots (2 - 1)$$

where D_i and S_i are diffusion and solution coefficients, respectively. P_i is commonly described in the unit of barrer, where 1 barrer = 10^{-10} cm³(STP) cm/cm² s cm Hg. In addition, another crucial indicator for gas separation performance is the selectivity ($\alpha_{A/B}$) of gas component A over component B, as described as following (2-2):

$$\alpha_{A/B} = P_A/P_B \dots \dots (2 - 2)$$

where P_A and P_B are permeability coefficients for gas component A and component B, respectively. Based on equations 2-1 and 2-2, gas selectivity can also be expressed as:

$$\alpha_{A/B} = (D_A/D_B) / (S_A/S_B) = \alpha_{A/B}^D \alpha_{A/B}^S \dots \dots (2-3)$$

As for gas molecules with high solubilities (like CO₂), the calculation of ideal selectivity as above does not reflect the true behavior of gas separation process as the feed typically contains other gas components. For the case of binary mixture, gas selectivity can be determined as shown below (2-4):

$$\alpha_{A/B} = (y_A/y_B) / (x_A/x_B) \dots \dots (2-4)$$

Where y_A and y_B are mole fractions of gas component A and B at the permeate side, as well as x_A and x_B are mole fractions of gas component A and B at the feed side. [117]

Figure 2-10. The solution-diffusion mechanism in dense membranes [118].

Although polymeric membranes have attracted much interest and have been regarded as a promising technology for gas separation, they always suffer a permeability-selectivity trade-off effect attributing to solution-diffusion mechanism which is limited by the Robeson upper bound (Figure 2-11). Under such mechanism, membranes that show high gas permeability because of high gas diffusivity resulting from its higher fractional free

volume, nonetheless a decrease in gas selectivity can be expected [119]. Thus, this upper bound can be served as an indicator to outline the state-of-the-art of the dense polymeric membranes, which is also applicable to other gas pairs, namely O_2/N_2 , H_2/CO_2 , H_2/CH_4 , He/CO_2 and He/CH_4 . Besides, most of the membranes that have been reported for gas separation have been made up of glassy polymers [120], thus leading to a high tendency to undergo physical aging due to the phase inversion (during the membrane casting) that occurs below the glass transition temperature (T_g) [121]. In addition, it is well-known that plasticization is a big drawback in polymeric membranes where gas diffusivity would increase but its corresponding selectivity decreases resulting from the expansion of free volume, where such phenomenon is typically evident under the measurement at high pressure [122].

Figure 2-11. The Robeson upper bound limit in CO_2/CH_4 separation [123].

2.4.2. Mixed-matrix membranes

Herein, in order to address these disadvantages of polymeric membranes, some strategies were investigated, including modification (blending, chemical grafting and

copolymerization) and cross-linking of polymeric membranes [124-126]. Furthermore, a more effective and feasible strategy in tuning the performance of polymeric membranes has drawn tremendous attention, which is named composite membranes or mix-matrix membranes (MMMs). This type of membrane aims to utilize the functional fillers into polymer matrix which could tune the solution and (or) diffusion of gas molecules, with the eventual goal is to improve gas permeability and (or) selectivity [127]. Due to the incorporation of filler materials, the utilization of the advantages of both polymer and filler materials can be achieved.

Accordingly, a great deal of filler materials has been utilized in MMMs because of their tunable physicochemical properties. As a whole, the conventional fillers which have been widely investigated are zeolites, mesoporous silica, metal oxides and carbon molecular sieves. This has been further investigated by the development of new and emerging filler materials that are feasible in optimizing the overall gas separation performance, including layered silicate, metal-organic frameworks, carbon nanotubes and graphene, as concluded in Figure 2-12. In summary, the overall gas transport properties can be improved via a few ways in MMMs. Firstly, the neighboring polymer matrix (packing, density, conformation) surrounding filler particles could be modified in such a way that gas transport of desired gas molecules can be favored, particularly if the fillers are well-dispersed in MMM. Secondly, the gas transport can be escalated by reducing the length of the gas transport pathway through the membrane. In addition, the interfaces between the filler and polymer matrix could serve as a barrier to allow selective gas transport and block the movement of undesired gas components. [128] Hence,

tremendous amount of studies have been conducted in optimizing CO₂/CH₄ separation in the past few decades.

Figure 2-12. Conventional and emerging filler materials in MMMs [24].

2.4.2.1. Zeolites

As the traditional microporous materials used for gas adsorption, zeolites have been intensively applied in MMMs for gas separation owing to their tunable pore channels and cavities that allows favorable adsorption and diffusion of gas molecules. Besides, it has been reported that the transport properties in MMMs can be significantly influenced by the incorporation of various zeolite types which sits in between the pore size range of 4-10 Å [129]. As an example, zeolite 4A is favorable for air separation owing to its pore size of 3.4 Å which is feasible in showing molecular sieving effect between O₂ (3.46 Å) and N₂ (3.64 Å) molecules [130, 131]. Besides, the incorporation of zeolites in polymer matrix will provide an increase in CO₂ adsorption capacity by offering additional extra reactive sites, leading to enhanced CO₂ separation performance, as demonstrated in Figure 2-13. In this case, CO₂ solubility enhances and diffuses through optimized pore

size, while CH_4 which are of a larger kinetic diameter tends to show a lower solubility as it is expected to pass through a more tortuous pathway in MMMs.

Figure 2-13. The mechanism of CO_2 and CH_4 transport in MMMs with zeolites [24].

As an example, the first investigation of MMMs in the gas separation process was conducted with the introduction of zeolites which was claimed by Paul and Kemp, where zeolite 5A was introduced in PDMS membrane. Result has shown that substantial enhancement in CO_2 diffusion was reported [132]. Subsequently, a huge number of MMMs were incorporated with zeolite LTA. As reported by Bahtiyar and Firuze, LTA with various pore sizes has been applied for improving CO_2/CH_4 separation, such as zeolite 3A (3 Å), 4A (4 Å) and 5A (5 Å) [133]. In conclusion, CH_4 permeability can be enhanced with the increase of pore size, resulting in a decrease in the selectivity of CO_2/CH_4 . On the other hand, it was observed that both CO_2 permeability and CO_2/CH_4 selectivity could be achieved via the introduction of zeolite 5A into PI polymer. It was reported that the performance of MMM was generally close to the upper bound limit, as illustrated in Figure 2-14. Following this, other types of zeolites were also adopted in the fabrication of MMMs. For instance, the incorporation of Na-FAU zeolites into PI is capable of performing significant enhancement of both CO_2 permeability and selectivity for CO_2/CH_4 separation without defects, even the zeolite loading was increased up to 40%

[134]. In addition, zeolite SAPO-34/44 was added into PSF to prepare asymmetric membranes, where 10-fold improvement of CO₂ permeance was obtained [135, 136].

Figure 2-14. The biogas separation abilities of MMMs incorporated with zeolites in CO₂ permeability-CO₂/CH₄ selectivity plot [133].

2.4.2.2. Metal-organic frameworks

MOF materials show exceptional gas adsorption properties due to their ultrahigh surface area and porosity, making them to be promising filler materials in MMMs. Apart from zeolites, MOFs have become the most popular fillers which have attracted tremendous attention owing to the good interactions between MOFs with organic ligands and polymer matrix. The first MMM incorporated with MOF was prepared in 2004 where copper-based MOF was loaded into poly(3-acetoxyethylthiophene) polymer. It was observed that the enhancement in CH₄ permeability with the incorporation of this filler was obtained [137]. Subsequently, the development of MOF-based MMMs has been

rapidly developed, which includes MOF-5, MOF-74, MIL series, HKUST-1, UiO-66 and ZIF-8 [23, 138-140]. Besides, a variety of polymer types have also been intensively applied as the continuous matrix in MMMs introduced with MOFs, like Matrimid, PSF, PDMS, Pebax and 6FDA-based polyimides [24].

For example, a series of MIL materials was introduced into 6FDA-based PI, where it was found that CO_2/CH_4 selectivity enhanced even though a reduction of CO_2 permeability was accompanied as compared to pure polymer [141]. Particularly, the amine group in MIL-53- NH_2 contributed to a good adhesion between MOFs and polymer matrix. Another example for MOF-based MMMs reported by Tien-Binh et al. claimed that both CO_2 permeability and CO_2/CH_4 ideal selectivity were successfully increased up to 90% and 160%, when UiO-66 was introduced into polymers of intrinsic microporosity-1 (PIM-1) [142]. Besides, MOF-74 owns extraordinary CO_2 adsorption capability when comparing with other MOF types. Hence Bae et al. reported MMMs introduced with Mg-MOF-74 (particle size of 100 nm), where 6FDA-TMPDA (PI) was used as polymer matrix. As shown in Figure 2-15 (a), results revealed that both CO_2 permeability and its selectivity over N_2 could be improved, with the performance reported to be closer to the upper bound. In addition, zeolite imidazolate frameworks (ZIFs) possess the merit of both benefits of zeolite and MOF materials, thus it is feasible to provide exceptional physicochemical properties for their utilization in MMMs. Specially, ZIF-8 is one of the most popular ZIFs which has been widely utilized into polymers. As an example, 15 wt% of ZIF-8 that was loaded in commercial Matrimid[®] polymer was feasible to achieve significant CO_2 permeability with slight change of CO_2/CH_4 selectivity, as depicted in Figure 2-15 (b).

Figure 2-15. (a) CO₂ and N₂ permeation performance of MOF-74-based MMMs in CO₂ permeability-CO₂/N₂ selectivity plot [59]; (b) CO₂ and CH₄ permeation performance of ZIF-8-based MMMs [143].

2.4.2.3. Low-dimensional fillers

Apart from popular filler materials that were applied in MMMs for CO₂/CH₄ separation, several new and emerging nanomaterials were also investigated in recent years, which the fillers with various dimensions have been developed. In Figure 2-16, carbon-based materials that are made up of zero-dimensional (0-D), one-dimensional (1-D) and two-dimensional (2-D) materials are fullerene, carbon nanotube (CNT) and graphene, respectively. Nevertheless, due to the limited pore size of fullerene, CNT and graphene are feasible to be incorporated in membranes for the effective transport of gas molecules. For example, MWNT was incorporated into cellulose acetate polymer, which was reported by Ahmad et al., to obtain a huge enhancement of CO₂ permeance up to 83.4% with slight increase of CO₂/N₂ selectivity at 1 bar. This was attributed to an increase in the interlayer spacing as well as good compatibility between MWNT and polymers [144]. Besides, Deng et al. claimed significant improvement in CO₂ permeance without large

change of CO₂/CH₄ selectivity when MWNT was added in polyvinyl amine/polyvinyl alcohol blend polymer [145]. Furthermore, MMMs with the incorporation of CNT displayed good mechanical strength, thus making it more promising to act as filler materials [145].

Figure 2-16. Low-dimensional carbon materials [128].

In addition, as a 2-D lateral carbon nanomaterial, graphene is observed to be an alternative cost-effective filler material as it possesses novel properties for effective gas transport, including the ultrahigh aspect ratio, the presence of CO₂-philic functional groups as well as excellent chemical, thermal and mechanical properties [128]. According to Kim et al., CO₂ permeability and its selectivity over CH₄ could reach as high as 8500 barrer and 10 in GO membrane that was supported by the substrate of poly(1-methylsilyl-1-propyne) (PTMSP), where the stacking feature of GO has been finely tuned [146]. On the other hand, a GO membrane that was deposited on anodic aluminum oxide (AAO) via vacuum filtration surprisingly exhibited lower CO₂ permeance with a huge improvement in CO₂/CH₄ selectivity [147]. Furthermore,

GO-based MMMs become more competitive as compared to free-standing GO membranes because of their ease of incorporation into polymeric membranes with various configurations, less requirement of GO modification for its utilization in MMMs as well as relative low-cost [24]. With regards to these observations, continuous studies were conducted in terms of the design of GO-based MMMs for gas separation.

An interesting MMM incorporated with GO which was fabricated by Shen et al.'s group demonstrated improvement in gas separation performance [148]. In their work, GO was assembled and dispersed in Pebax MH 1657 to obtain well-designed GO laminates due to the molecular interactions between GO and polymer chains, as displayed in Figure 2-17 (a). In Figure 2-17 (b), it was concluded that an improvement in CO_2/N_2 separation performance of MMM with 0.1% of GO was successfully acquired, with the performance surpassed the Robeson upper bound limit. Besides, Li et al. proposed a novel GO filler modified with polyethylene glycol and polyethylenimine (PEG-PEI), as described in Figure 2-17 (c) [149]. Upon the 10% loading of PEG-PEI-GO, enhanced CO_2 permeability of 1330 barrer together with high CO_2/CH_4 selectivity of 45 drove the separation performance to surpass the Robeson upper bound of CO_2/CH_4 separation, which was clearly illustrated in Figure 2-17 (d). However, except for modified GO, the 2-D lateral structure of pristine GO is more favorable to improve CO_2/CH_4 selectivity rather than CO_2 permeability, which can be ascribed to the presence of CO_2 -philic functional groups together with the size exclusion of the GO interlayers [150, 151]. Herein, Li et al. proposed a novel strategy to combine CNT and GO together to utilize the synergistic effect for efficient CO_2 separation [152]. It was clearly seen that high CO_2

permeability of 38.07 barrer and CO_2/CH_4 selectivity of 84.6 were achieved with the optimum loading of 5% GO and 5% CNT. In comparison, the enhancements of both CO_2 permeability and its selectivity over CH_4 were surprisingly reached as high as 330.7% and 148.8%, respectively, contributing to exceptional separation performance than the incorporation of either filler.

Figure 2-17. (a) Scheme of GO laminates assembly incorporated into Pebax matrix; (b) CO_2/N_2 separation performance of MMMs with GO and other representative membranes in the literature; [148] (c) Gas transport inside MMM incorporated with modified GO; (d) CO_2/CH_4 separation performance of MMMs with GO. [149]

2.4.3. Carbon molecular sieve membranes

As discussed, MMMs have been popularly developed owing to the synergistic effect of both polymers and fillers. It was observed that significant improvement of CO_2/CH_4

separation was successfully achieved as compared to pure polymeric membranes. Nonetheless, as demonstrated by permeability-selectivity limit, the continuous phase (polymer matrix) still plays the predominant role in gas separation performance even though functional filler materials could effectively enhance gas permeability and/or selectivity. In other words, despite the choice of filler materials that is feasible in improving the overall gas performance, the intrinsic nature of polymer may not change dramatically, especially for the case of polymers with low gas permeability or selectivity. In addition, the plasticization of polymers has been considered as another issue which constricts the effective utilization for industrial applications, especially for the case where high CO₂ concentration was applied in the feed. Under such circumstance, trade-off effect between the enhancement of CO₂ permeability and decrease of its corresponding selectivity can be expected [153].

Therefore, further efforts have been paid to alleviate the inherent natures in polymer-based membranes, such as fabrication methods (asymmetric or hollow fiber membranes), thermal treatment, cross-linking and polymer blending [140]. In comparison, thermal treatment is generally considered to be a promising approach. Thermal treatment is the process where thermal decarboxylation of polymer precursor at high temperatures is feasible to tune the structure of the polymer chain or disrupt polymer's rigidity [154]. Thus, the fractional free volume and chain's flexibility can be well-adjusted during the carbonization process (Figure 2-18) in order to achieve a well-optimized cavities and constriction that can be feasible to display substantial discrimination of gas molecules in terms of kinetic diameter. This results in substantial improvement in gas permeability

without sacrificing membrane's selectivity, together with reduced plasticization effect [155]. Such type of membranes are often termed as carbon molecular sieve membranes (CMSMs) as highly graphitic domains are formed after the thermal treatment process [156] which have a wide range of gas pairs in separation applications, like CO₂ separation, air and hydrocarbon gas separation. Moreover, this type of membranes shows excellent chemical stability and it is facile to surpass the permeability-selectivity trade-off limitations [157].

Figure 2-18. Scheme of carbon molecular sieve membrane via carbonization process derived from polymer precursor [158].

The first CMSM was fabricated and reported in 1980 [159]. Nonetheless, more studies of carbon membranes were re-started until 1990s where continuous investigations were developed [157]. As discussed, there are mainly four mechanisms defined for gas molecules transport through membrane: Knudsen diffusion, surface diffusion, capillary condensation and molecular sieving. Among them, molecular sieving is the predominant mechanism in CMSMs, as displayed in Figure 2-19. Accordingly, gas separation could be achieved by allowing smaller gas molecules passing through and hampering larger ones with the aid of constrictions that is close to molecular dimensions in CMSMs. In terms of

separation capability and chemical stability, CMSM has become a potential candidate for gas separation. For instance, high separation factors could be reached in CMSMs with the pore size of 3-5 Å for the separation of H_2/O_2 , H_2/N_2 , O_2/SF_6 and so on. Besides, CMSMs have been successfully developed into various membrane configurations, namely flat sheet, hollow fiber and capillary. [160]

Figure 2-19. Transport mechanism of molecular sieving [160].

In terms of gas separation performance, precursor selection and pyrolysis process play crucial roles in CMSMs. Researchers have prepared CMSMs that are derived from a great range of polymer types, including phenolic resin, polyetherimide and polyimides (PIs). In which, PIs are considered to be the most widely utilized precursors for the construction of CMSMs due to their excellent properties, such as Matrimid[®] [161-164], Kapton[®] [165] and P84[®] [166] which are commercially available. The CMSM derived from Matrimid[®] at high temperature contains micropores that offer molecular sieving effect which is favorable for the separation of CO_2/CH_4 , O_2/N_2 and hydrocarbon gases. Furthermore, CMSM derived from Matrimid[®] is considerably more selective as compared to P84[®] and Kapton[®], where the selectivity value of CO_2/CH_4 and O_2/N_2 in Matrimid[®] was reported as

high as 33 and 6 (25 °C), respectively [165].

On the other hand, pyrolysis is regarded as the most important process of CMSMs that are derived from polymer precursors, where the gas separation performance is strongly influenced by atmosphere, thermal soak time, heating rate and pyrolysis temperature [157]. As an example, pyrolysis process can be operated under the atmosphere of He, N₂, Ar, vacuum or CO₂, which is generally necessary to avoid the formation of by-products during carbonization, as concluded In Table 2-6. As for the case of soak time, it is strongly dependent on pyrolysis temperature, which can be finely adjustable for effective gas transport properties. It was proved that the gas selectivity would be enhanced at a longer soak time [167, 168]. Besides, pyrolysis has been conducted in the ramping rate that ranging from 1-13 °C/min, thus providing CMSMs with various pore size and crystallinity [169]. The investigation on the influence of heating rate was carried out for the carbonization of phenolic resin at the temperature of 700 °C. It was reported that the permeance of CO₂, N₂ and CH₄ was approximate to be 7, 13 and 20 times lower at the heating rate of 5 °C/min compared to those obtained at 1 °C/min [170]. Importantly, the pyrolysis temperature is a key factor for the development of final pore structure, gas transport mechanism and resulting gas separation, where a reduction of gas permeability would result from the increase of pyrolysis temperature [163]. Generally, carbonization process is conducted in the temperature range of 500-1000 °C, which is higher than the decomposition temperature of polymer precursors. Therefore, the optimized pyrolysis process is required to fulfill the variation of pore structures, which leads to the tuning of overall gas separation performance.

Table 2-6. Various pyrolysis atmosphere applied in the literature [157].

Pyrolysis media	Results
He	<ul style="list-style-type: none">• Increase CO₂ permeance but resulted in a significant loss of CO₂/CH₄ selectivity• More productive but less selective• Form a more open porous matrix• High weight loss• High BET pore surface area, total pore volume, and micropore volume were obtained
N ₂	<ul style="list-style-type: none">• High gas permeability• Accelerate the carbonization with temperature increase for which a more open porous structure were created
Ar	<ul style="list-style-type: none">• Less weight loss• High selectivity
Vacuum	<ul style="list-style-type: none">• Low d-spacing• Smaller pore size• Denser carbon structure formed• Low gas permeability and high selectivity
Oxidative (CO ₂)	<ul style="list-style-type: none">• More permeable and high permselectivity• High microporosity, total volume of pores and BET specific surface area

Till date, the membranes which have been widely investigated for gas separation are mainly focused on polymeric, mixed-matrix and carbon molecular sieve membranes. As shown in Table 2-7, polymeric membranes are easy to be synthesized with high processability and low cost, but the trade-off effect limits their gas separation performance. With the aid of filler materials, significant improvement of gas separation performance could be obtained in MMMs. There are even some well-designed MMMs which could locate very close to the upper bound. However, it is still challenging to further change the polymer nature. Therefore, an alternative effective strategy is needed for the further improvement. Although more harsh synthesis conditions are required, CMSMs are highly possible to achieve extraordinary gas separation performance which

could surpass the separation upper bound as compared to polymeric and mixed-matrix membranes.

Table 2-7. Comparison between different membranes.

Membranes	Synthesis conditions	Mechanical stability	Pathway	CO ₂ /CH ₄ separation	Pros.	Cons.
Polymeric	Easy, processable	Stable	Dense membrane	Low CO ₂ permeability /selectivity	Low cost High processability	Trade-off effect
MMMs	Easy, processable	Stable	Filler facilitates gas transport	Good CO ₂ permeability /selectivity	Tunable performance	High cost
CMSMs	Hard, High temperature	Poor	Thermal-rearranged micropore structure	Surpass the upper bound	Thermal/chemical stable Excellent separation	High cost

2.4.4. Challenges in membrane-based separation

Based on the discussion above, gas transport in MMMs is strongly dependent on the interfacial properties between fillers and continuous matrix. As demonstrated in Figure 2-20 (case 1), an ideal interfacial morphology is generally desirable so as to offer a good separation capability. Nonetheless, due to different nature of fillers and polymers, defects can be possibly existed at the interfacial area, resulting in the creation of interface voids, polymer rigidification and plugged pores, as depicted in Figure 2-20. Case 2 represents the presence of the interface voids that is attributed to poor attachment between filler particles and polymers, resulting in an increase in gas permeability but a decrease in gas selectivity. Also, polymer rigidification is typically developed when polymer chains directly contact with the surface of fillers, as described for case 3. In addition, case 4 generally occurs when the pores that are present in the filler particles are blocked by

polymer chains. The existence of case 3 and 4 at the interfaces between fillers and polymers would give rise to lower gas permeability as compared to ideal interface. In particular, these defects are generally easier to form in polymer/zeolite MMMs, where poor compatibility between them has been reported. [171]

Figure 2-20. The scheme of various defects in MMMs [171].

Hence, in order to address these drawbacks, different strategies have been developed and conducted to improve the interfacial morphologies. In which, the method that has been widely utilized is the surface modification of filler particles to enhance the adhesion between fillers and polymers. For instance, Shu et al. created a nanowhisker on the surface of fillers with a two-step reaction [172-174]. Accordingly, in Figure 2-21 (a), magnesium hydroxide ($\text{Mg}(\text{OH})_2$) nanowhiskers were prepared to increase the roughness of filler particles, thus resulting in enhanced contact with polymer chains. This modification aimed to produce a good filler-polymer interface and reduce the voids, as evidenced in Figure 2-21 (b). Besides, silane coupling agents were also applied to modify the surface of filler particles, especially for zeolites or silica, which resulted in strong

interaction between filler and polymer. Apart from surface modification of fillers, ionic liquids with good thermal stability together with good CO₂ solubility, demonstrate good compatibility with both organic and inorganic materials, thus helping mitigate the “sieve-in-a-cage” morphologies. Nonetheless, in terms of practical applications, there is no ideal strategy to solve all types of defects at the interfaces. Herein, all the physicochemical properties of fillers and polymer matrix as well as synthesis and measurement conditions should be taken into consideration to fulfill MMMs with excellent gas separation performance. [24]

Figure 2-21. The preparation procedures of magnesium hydroxide whiskers on the surface of zeolite 4A [24].

On the other hand, for CMSMs, it is well-known that a major disadvantage that hinders the practical applications of carbon molecular sieve membranes is their poor mechanical stability. Also, it is generally very challenging to verify the mechanical strength of the

CMSMs due to their brittleness and weakness. To date, researchers have utilized a few ways to meliorate the mechanical strength of CMSMs. For instance, Yoshimune and Haraya et al. introduced sulfonic groups into polyimide polymer and obtained carbon hollow fibers with a small diameter which had a more flexible carbon structure [175]. In addition, Ismail et al. claimed that the utilization of polyacrylonitrile (PAN) as the precursor, which was widely applied in high strength carbon fiber, was feasible in overcoming the brittleness of CMSMs [160]. However, the mechanical stability is also influenced by other factors, namely pyrolysis temperature [157]. Further studies on carbon membranes with high mechanical properties would help in advancing this type of membranes toward the commercialization. In addition, CMSMs are not favorable to separate some gas mixtures, like gas/vapor, air/hydrocarbon, iso-butane/n-butane and so on. [160]

2.5. Conclusions

All in all, porous materials together with membrane materials have proven to be very suitable and favorable for gas adsorption and separation. As traditional inorganic microporous materials, zeolites are defined as crystalline aluminosilicates which possess molecular channels and rigid cavities that can provide optimized free space and void volume for effective gas transport, especially CO₂ molecules. Also, MOFs are widely studied owing to their excellent surface and porous properties, as well as tunable functionality. The introduction of MOFs in MMMs has demonstrated a significant improvement in CO₂ permeability as compared to that of pure polymeric membranes. As for the emerging carbon nanomaterial used in gas applications, GO is a 2-D lattice of

carbon with carbonyl and hydroxyl functional groups. It is feasible to act as structural agent in nanocomposite and provide high gas selectivity in MMMs with GO due to CO₂-philic functional groups and size exclusion of interlayers. Furthermore, the CO₂/CH₄ separation of microporous carbon molecular sieves could be further optimized via the pyrolysis process from mixed-matrix membranes under high temperature and inert atmosphere.

CHAPTER 3

Nanocomposites Formed by In Situ Growth of NiDOBDC Nanoparticles on Graphene Oxide Sheets for Enhanced CO₂ and H₂ Storage

3.1. Introduction

It is well-known that CO₂ is one of the major contributors to global warming, meanwhile the demand for clean energy source is rapidly growing in recent years. Hence gas capture and storage become very crucial to reduce CO₂ emission and store energy gases. To date, plentiful solid adsorbents have been investigated for the use of gas storage, including zeolites [176-179], mesoporous silica [180, 181], carbon materials [182-188], porous organic polymers [189, 190], and metal–organic frameworks (MOFs) [53, 191-198]. Among them, metal-organic frameworks grew to be competitive candidates recently owing to the ultrahigh surface area, high porosity, low density, good thermal and mechanical stabilities [199-201]. Until now, numerous MOF materials have been studied and their types are still expanding rapidly, such as MOF-2 [202], MOF-5 [53], MOF-177 [203], MOF-505 [198], Cu₃(BTC)₂ [76] (or HKUST-1 [61]), ZIF-8 [204], and XDOBDC (X = Mg, Ni, Co, Fe, Mn, Zn) [59, 191]. Comparing to other MOFs, XDOBDC shows extraordinarily high CO₂ uptake, particularly at low partial pressures, and reasonable H₂ storage capacities, and thus they have attracted interest by many researchers.

For XDOBDC with various metal sites, NiDOBDC (Ni-MOF-74 or Ni₂(dobdc)) exhibits

outstanding CO₂ storage capacity. What's more, it is less sensitive to air and moisture, whereas the adsorption performance of MgDOBDC [205] degrades much under the humid conditions even though its CO₂ uptake owns the highest value (under dry conditions) compared to other XDOBDC MOFs. Therefore, NiDOBDC is highly favorable for gas storage owing to its high surface area, high gas uptake capacity and reasonable humid stability. However, NiDOBDC shares the same drawback with other nanoporous materials, namely aggregation. In this case, a certain amount of surface area will be sacrificed leading to less gas adsorption sites. Also, numerous synthesis protocols of NiDOBDC with various forms have been developed, particularly in nanocrystalline form [59]. The nanocrystalline form of NiDOBDC could possibly be used as building blocks for novel nanocomposite material with a 3-D architecture.

Graphene oxide (GO) is a 2-D lattice of carbon atoms containing hydroxyl, epoxy and carboxylic groups [83]. In the past few years, GO was emerging and has become a popular material owing to its high aspect ratio, tunable surface functionalization, and good thermal and mechanical properties [90, 206, 207]. Hybrid nanocomposites based on MOFs and GO have drawn much attention attributing to the unique properties of both the two prominent materials rather than focusing on either component. These nanocomposites display improved gas adsorption performance compared to the pristine MOFs. Bandosz et al. [98, 100, 101] reported MOF/GO composites with enhanced adsorption performance for smaller gas molecules. Meanwhile, Kumar et al. [102] made hybrid composite of ZIF-8 and GO which showed significant CO₂ uptake. In addition, Xia et al. [104-107] has successfully designed some kinds of MOF/GO composites, such as Cu-BTC/GO,

MIL-101/GO and MOF-505/GO which exhibited improved uptake capacities compared to pristine MOF materials. However, based on previous studies conducted thus far, MOF particles were larger than 50 nm or non-uniform crystals with a wide size distribution, which can lead to the development of irregular structures in the resultant MOF/GO composites. Smaller MOF nanocrystals with uniform sizes and morphologies are highly desirable to design a well-defined 3-D architecture providing additional adsorption sites for storage of gases.

In this study, our strategy focused on the design of a 3-D hybrid nanocomposite material with NiDOBDC and GO. The incorporation of GO could reduce the aggregation effect and create additional adsorption sites for gas molecules, resulting in increased gas storage capacity [208, 209]. It was noteworthy that the preparation procedure was easy to handle and the obtained NiDOBDC/GO nanocomposites have tunable surface areas and micropore volumes by optimizing the proportion of GO. Interestingly, the nanocomposites exhibited remarkable CO₂ and H₂ uptake, especially the sample with 10 wt% of GO showed an uptake increase of 23.7% and 49.8% for CO₂ (298 K, 1 bar) and H₂ (298 K, 20 bar), respectively. Results proved that our novel methodology for improving gas storage via incorporating graphene oxide was highly effective, which indicated promising applications in gas storage.

3.2. Experimental

3.2.1. Materials

Nickel(II) nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ ($\geq 99.9\%$), GO powder ($\geq 99.0\%$), methanol ($\geq 99.8\%$), ethanol ($\geq 99.5\%$), N,N'-dimethylformamide (DMF, $\geq 99.9\%$), and triethylamine (TEA, $\geq 99.0\%$) were purchased from Sigma-Aldrich, Merck. 2,5-Dihydroxy-1,4-benzenedicarboxylic acid (H_4DOBDC , $\geq 98.0\%$) was purchased from Tee Hai Chem Pte. Ltd. Pure carbon dioxide (CO_2), pure hydrogen (H_2), helium (He) and nitrogen (N_2) gases ($\geq 99.9\%$) were purchased from Airliquide. Prior to use, these chemicals were received without further purification.

3.2.2. Synthesis of nanocrystalline NiDOBDC

Nanocrystalline NiDOBDC was prepared as described in a previous report [59, 210] with substantial modification. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.46 mmol, 1.5877 g) and H_4DOBDC (1.7 mmol, 0.3368 g) were first dissolved in 135 mL of DMF. A separate solution of water/ethanol/TEA (9/9/1 mL) was prepared, which was then poured rapidly into the first solution. The resulting solution was subjected to 2 h of vigorous agitation at room temperature. The resulting precipitate was collected by repetitive centrifugation and washing with DMF. To ensure that the resulting crystals were free of impurities, the MOF crystals were redispersed in DMF and heated at 100 °C for 2 h. This process was repeated further by replacing the solvent with methanol without heating. The whole process was repeated twice. Before the necessary analysis and characterization, the residual solvent was removed under vacuum at 60 °C for 24 h, from which red-brown nanoporous MOF crystals were collected.

3.2.3. Synthesis of NiDOBDC/GO nanocomposites

The synthesis of the NiDOBDC/GO composite was conducted in a manner similar to that described in Section 3.2.2, where graphene oxide (5, 8, and 10 wt%) was added to the mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_4DOBDC in 135 mL DMF, as exemplified in Figure 3-1. After completion of the synthesis, the precipitate was similarly redispersed first with DMF and then with methanol, with the exception that the process was conducted at 60 °C overnight because of the sensitivity of graphene oxide at elevated temperatures [211].

Figure 3-1. Synthesis schematic of the NiDOBDC/GO nanocomposites.

3.2.4. Characterizations

Powdered X-ray diffraction (PXRD) patterns were measured using a Bruker D2 phaser diffractometer equipped with Cu $K\alpha$ source in the 2θ range from 5 ° to 50 °. Raman spectra was determined using Renishaw InVia Reflex Raman Spectrometer with a 633-nm incident laser source. The morphologies of the samples were observed using field emission-scanning electron microscopy (FE-SEM, JSM6700, Jeol). The particle size distribution of the NiDOBDC crystals was determined using Nano Measure based on the FE-SEM image. The thermal stabilities of the adsorbents were determined using a

thermogravimetric/differential thermal analyzer (Diamond TG/DTA, PerkinElmer). The analysis was conducted under pure N₂ purging from 40 °C to 700 °C at a heating rate of 10 °C/min. Quantification of the adsorbent's porosity was conducted using a N₂ physisorption isotherm at 77 K, which was performed using an Autosorb-6B instrument from Quantachrome. The adsorbents were loaded into the adsorption cell and activated under a high vacuum at 250 °C for 8 h. CO₂ and H₂ uptake capacities were acquired using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome), in which activated adsorbents were used to analyze the single-component gas uptake capacities of CO₂ and H₂ at 298 K and 313 K. The measurement conditions were controlled using a water circulator and an isothermal jacket, respectively. In this study, the pressure range of CO₂ and H₂ was 0 to 20 bar and 0 to 40 bar, respectively, for analysis of the gas uptake performance.

3.2.5. Evaluation of gas adsorption performance

The CO₂ adsorption isotherms were mathematically fitted with Dual-site Langmuir adsorption model [60]:

$$q = \frac{q_{sat,1}b_1p}{1 + b_1p} + \frac{q_{sat,2}b_2p}{1 + b_2p} \dots (3 - 1)$$

where q is the CO₂ adsorption (in mmol/g), $q_{sat,1}$ and $q_{sat,2}$ are the saturation loadings for site 1 and 2; b_1 and b_2 are Langmuir parameters [189] for site 1 and 2; p is the pressure (in bar). Besides, Single-site Langmuir adsorption model was used to fit N₂ adsorption isotherms:

$$q = \frac{q_{sat}bp}{1 + bp} \dots (3 - 2)$$

The determination of saturation loading of N₂ (q_{sat}) under ambient temperature or above is often difficult due to weak interaction between N₂ and adsorbent. Thus, in this study, it was estimated that all the adsorption sites in MOFs and MOF/GO composites were equally accessible towards CO₂ and N₂. Such assumptions have been valid for most

zeolites and MOFs [95]. The summary of the fitting parameters was provided in Table 3-5. With this, the selectivity of binary mixture gas (CO₂/N₂) was estimated by applying the Ideal Adsorbed Solution Theory (IAST) [212, 213] under the similar conditions with post-combustion CO₂ capture, by using the expression below:

$$\alpha = \frac{x_1/y_1}{x_2/y_2} \dots (3-3)$$

where α is the selectivity of CO₂/N₂, x_1 and x_2 are the gas molar fractions in the adsorbed phases; y_1 and y_2 are the gas molar fractions in the bulk phases.

In addition, the isosteric heat of adsorption (Q_{st}) was calculated by using the following equation:

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \dots (3-4)$$

where p is the pressure (in bar), T is the temperature (K), q is a constant adsorbate loading. For CO₂, q could be computed using dual-site Langmuir model, as expressed in Equation (3-1). The Equation (3-1) could be rewritten as a quadratic polynomial of pressures:

$$(q_{sat,1} + q_{sat,2} - q)b_1b_2p^2 + ((q_{sat,1} - q)b_1 + (q_{sat,2} - q)b_2)p - q = 0 \dots (3-5)$$

In order to facilitate the following calculation, we defined two parameters as follow:

$$u = (q_{sat,1} + q_{sat,2} - q)b_1b_2 \dots (3-6)$$

$$v = (q_{sat,1} - q)b_1 + (q_{sat,2} - q)b_2 \dots (3-7)$$

Based on Equation (3-5), p could be obtained as:

$$p = \frac{-v \pm \sqrt{v^2 + 4uq}}{2u} \dots (3-8)$$

In which, only one solution above is physically realizable, as given by:

$$p = \frac{-v + \sqrt{v^2 + 4uq}}{2u} \dots (3-9)$$

Then, the logarithm of p is displayed below:

$$\ln p = \ln(\sqrt{v^2 + 4uq} - v) - \ln 2u \dots (3-10)$$

Keeping q as the constant loading, the derivative of $\ln p$ can be obtained from Equation (3-10) as follow:

$$\frac{\partial \ln p}{\partial T} = \frac{\partial \ln(\sqrt{v^2 + 4uq} - v)}{\partial T} - \frac{\partial \ln 2u}{\partial T} \dots (3-11)$$

After a sequence of optimization, Equation (3-11) is expressed as below:

$$\frac{\partial \ln p}{\partial T} = \frac{1}{(\sqrt{v^2 + 4uq} - v)} \left(\frac{1}{2\sqrt{v^2 + 4u}} \right) \left(2v \frac{\partial v}{\partial T} + 4q \frac{\partial u}{\partial T} \right) - \frac{\partial v}{\partial T} - \frac{1}{u} \frac{\partial u}{\partial T} \dots (3-12)$$

The two derivatives in Equation (3-12) could be calculated as follow:

$$\frac{\partial u}{\partial T} = (q_{sat,1} + q_{sat,2} - q) \frac{\partial(b_1 b_2)}{\partial T} \dots (3-13)$$

$$\frac{\partial v}{\partial T} = (q_{sat,1} - q) \frac{\partial(b_1)}{\partial T} + (q_{sat,2} - q) \frac{\partial(b_2)}{\partial T} \dots (3-14)$$

We assumed that the two Langmuir constants b_1 and b_2 can be described by:

$$b_1 = b_{10} e^{\left(\frac{E_1}{RT}\right)}; b_2 = b_{20} e^{\left(\frac{E_2}{RT}\right)} \dots (3-15)$$

We can derive the parameters above, as listed below:

$$\begin{aligned} \frac{\partial b_1}{\partial T} &= -b_{10} e^{\left(\frac{E_1}{RT}\right)} \frac{E_1}{RT^2}; \frac{\partial b_2}{\partial T} = -b_{20} e^{\left(\frac{E_2}{RT}\right)} \frac{E_2}{RT^2}; \frac{\partial b_1 b_2}{\partial T} \\ &= -b_{10} b_{20} e^{\left(\frac{E_1 + E_2}{RT}\right)} \frac{E_1 + E_2}{RT^2} \dots (3-16) \end{aligned}$$

Then, combining Equations (3-4), (3-12), (3-13), (3-14), and (3-16), we could calculate the value of Q_{st} .

For H_2 , q could be computed using single-site Langmuir model, as expressed in Equation (3-2). Then, the value of Q_{st} could be determined by applying the same method as demonstrated above [214].

3.3. Results and discussion

3.3.1. Characterizations of NiDOBDC crystals and NiDOBDC/GO nanocomposites

Figure 3-2. (a) PXRD patterns and (b) Raman spectra (c) thermogravimetric analysis (TGA) curves of GO, NiDOBDC and NiDOBDC/GO composites (5, 8, and 10 wt% GO).

Table 3-1. Average particle sizes calculated by Debye-Scherrer method.

Samples	Particle size (nm)
NiDOBDC	9.3
NiDOBDC/GO-5wt%	8.9
NiDOBDC/GO-8wt%	8.2
NiDOBDC/GO-10wt%	7.4

Note: The 2θ peak is selected at 11.8°

The crystallinity of NiDOBDC and the NiDOBDC/GO composites was verified using PXRD, as shown in Figure 3-2 (a). With reference to the XRD pattern of NiDOBDC reported in the literature [59], significant peak broadening was observed, indicating the formation of nanoscale crystallites [60, 215]. Such behavior led to the formation of smaller crystallites (Table 3-1). Also, the identical diffraction patterns of the

NiDOBDC/GO nanocomposites and NiDOBDC demonstrated that the coordination bonding between the metal and the ligand was not affected by the presence of GO. In other words, NiDOBDC still played a predominant role in the composites despite the incorporation of GO. Nonetheless, the intensity of the respective peaks relatively decreased with increasing GO content [103]. The presence of the GO peak ($2\theta = 26^\circ$) was not observed in all series of composites, which was attributed to the fact that the GO content was not high enough to influence the overall diffraction patterns of the composites, where the XRD pattern of GO was generally broad, with a low-intensity peak. Therefore, Raman spectra on GO, NiDOBDC and NiDOBDC/GO composites was further conducted to provide a strong qualitative evidence of the presence of GO in the composites (G, D and 2D band) [216], as shown in Figure 3-2 (b). Meanwhile, the thermal stabilities of NiDOBDC and the NiDOBDC/GO composites depicted similar trends, with all samples demonstrating sudden weight loss at approximately 320 °C, indicating comparable decomposition temperatures, as demonstrated in Figure 3-2 (c).

Figure 3-3. FE-SEM images of (a) NiDOBDC, (b) GO, (c) NiDOBDC/GO-5 wt%, and (d) NiDOBDC/GO-10 wt%. (e) Particle-size distribution of NiDOBDC nanocrystals.

Through the FE-SEM analysis, Figure 3-3 (b) provides the morphology of graphene oxide. Meanwhile, as shown in Figures 3-3 (a),(c) and (d), the morphology of NiDOBDC was determined to be approximately 20 to 30 nm (Figure 3-3 (e)), which was generally comparable to the results obtained from Bae et al. [59]. Thus, the peak broadening phenomena in Figure 3-2 (a) proved the formation of nanocrystals in the NiDOBDC/GO composites.

Figure 3-4. N₂ sorption isotherm measured at 77 K of NiDOBDC and the NiDOBDC/GO composites.

Table 3-2. Surface areas and pore volumes for NiDOBDC and the NiDOBDC/GO composites computed from N₂ physisorption isotherm at 77 K.

Samples	S _{BET} ^a	S _{LANG} ^b	V _{micro} ^c
	(m ² /g)	(m ² /g)	(cc/g)
NiDOBDC	940	1330	0.238
NiDOBDC/GO-5%	1010	1380	0.242
NiDOBDC/GO-8%	1040	1430	0.257
NiDOBDC/GO-10%	1190	1530	0.313
NiDOBDC/GO-15%	706	1069	0.135

^a Surface areas were computed using BET theory at $P/P^0 = 0.05-0.2$; ^b Surface areas were calculated from Langmuir equation at $P/P^0 = 0.05-0.2$; ^c Micropore volumes were computed by using t-plot

method at $P/P^0 = 0.4-0.6$.

Table 3-3. Comparison with literature data.

Samples	Particle size of	S_{BET}	% increase	Ref.
	MOF (nm)	(m^2/g)	in S_{BET} ^a	
MOF-5/10% GO	~50	806	1.6	[98]
MOF-5/5% BFG ^b	220-260	810	1.1	[99]
MIL-100/4% GO	-	1464	3.6	[100]
HKUST-1/9% GO	~50	1002	10.2	[101]
ZIF-8/1% GO	100–150	819	-26.9	[102]
HKUST-1/9% GO	10–40	1532	17.4	[103]
HKUST-1/1% GrO ^d	-	1677	21.3	[104]
MIL-101/5% GO	~250	3502	21.6	[105]
HKUST-1/5% GO	-	1362	14.7	[106]
MOF-505/5% GO	micron-sized	1279	16.2	[107]
NiDOBDC/10% GO	20–35	1190	26.6	This work

^a comparison with BET surface area of pristine MOF; ^b benzoic acid-functionalized graphene; ^c reduced graphene oxide

Next, a N_2 physisorption experiment at 77 K was conducted to calculate the surface area and micropore characteristics of NiDOBDC and the NiDOBDC/GO composites. As shown in Figure 3-4, all samples demonstrated the existence of large micropore volume owing to huge N_2 sorption at low partial pressures. The N_2 sorption at low partial

pressures enhanced with the increase of GO loading up till 10 wt%, but the N₂ sorption at low P/P₀ value decreased at a higher loading (i.e. 15 wt%). In addition, the existence of a hysteresis loop between the adsorption and desorption branches demonstrated the presence of mesopores, which were attributed to external pores generated from the aggregation between nanocrystals. Meanwhile, the surface areas and pore volumes of each adsorbent were calculated via the N₂ sorption isotherms and were summarized in Table 3-2. It was found that the Brunauer–Emmett–Teller (BET), Langmuir surface areas, and the micropore volumes displayed drastic increase with increasing GO loading up till 10 wt% owing to the enhancement of N₂ sorption at low partial pressures. Nonetheless, decrease in N₂ sorption was observed as the GO loading was increased further, where such behavior was verified by the CO₂ adsorption of NiDOBDC/GO-15wt% at 298 K as shown in Figure 3-5. It was worth noting that the NiDOBDC/GO composite with 10 wt% of GO loading demonstrated the best surface area and micropore volume (Table 3-2). The NiDOBDC/GO composite with 10 wt% GO loading showed 27% and 32% improvement in both the BET surface area and the micropore volume, respectively, as compared to the pristine NiDOBDC. In particular, the enhanced surface area realized in this work was far better than that reported in any previous work, as shown in Table 3-3. This significant improvement of N₂ physisorption properties could be attributed to the improved dispersion of NiDOBDC in the presence of GO. As reported in several studies [103, 217], the presence of oxygen atoms in the GO epoxy group allowed favorable interactions with MOFs. Therefore, in this study, the epoxy group could similarly serve as the seed for the crystallization of NiDOBDC. Also, the porosity generated between NiDOBDC and GO could introduce additional microporosity, as verified from the N₂ physisorption

experiment. More importantly, this study included smaller nanocrystals with a narrower size range than used in previous studies. These particles may form a nanocomposite with a more uniform structure, resulting in additional pore spaces.

3.3.2. CO₂ adsorption of NiDOBDC crystals and NiDOBDC/GO nanocomposites

Figure 3-5. CO₂ adsorption isotherm measured at 298 K of NiDOBDC and the NiDOBDC/GO composites.

As illustrated in Figure 3-5, the pure-component CO₂ uptake of NiDOBDC and its composites was measured at 298 K between 0 and 1 bar as a pre-screening process. Without the addition of GO, NiDOBDC nanocrystals exhibited a high CO₂ uptake of 4.05 mmol/g at 1 bar, which was comparable to the data reported elsewhere [59]. A favorable interaction between CO₂ molecules and the coordinatively unsaturated open metal sites (Ni²⁺) in NiDOBDC resulted in promising adsorption properties. With this, the adsorption

properties of the NiDOBDC/GO composites were further verified with increasing GO loading. Interestingly, the addition of GO into NiDOBDC demonstrated substantial improvement in CO₂ adsorption as compared to NiDOBDC. Therefore, to identify the most optimum CO₂ uptake performance, the effective composition of GO in the NiDOBDC/GO composites was conducted to select the best NiDOBDC/GO proportion (GO loadings of 5, 8, 10, and 15 wt%) for subsequent analysis. In general, the CO₂ storage capacity at 1 bar increased with increasing GO loading until 10 wt%. However, this effect was not observed as the GO loading increased further to 15 wt%, which could be because increasing the loading of GO beyond 10 wt% would lead to an undesirable structure. Similar analysis has shown that the determination of optimal loading of GO would be required because an excessive amount of GO could drastically decrease the micropore volume [103]. In essence, at 15 wt% loading of GO, the presence of GO in the NiDOBDC/GO composite could serve as a barrier between the adsorbates and the active sites of the NiDOBDC/GO composite. In this study, remarkably, the NiDOBDC/GO composite with 10 wt% of GO loading showed CO₂ storage of 5.01 mmol/g at 298 K and 1 bar, a 23.7% increase from the pristine NiDOBDC. Such an effect can be explained by this sample having the best surface area and micropore volume of all samples, as described in Table 3-2. Such an effect was also a proof of the relationship between the accessible surface area of microporous materials and the uptake capacity of the adsorbates [60]. Therefore, the NiDOBDC/GO composite with 10 wt% loading of GO was chosen to measure CO₂ and H₂ uptake under high pressures for exploring the potential applications in CO₂ and H₂ storage under high pressures as compared to pristine NiDOBDC. With this analysis, NiDOBDC and NiDOBDC/GO-10wt% were selected for high pressure CO₂ and

H₂ uptake measurement together with the potential capability of these adsorbents in post-combustion CO₂ capture.

3.3.3. High-pressure CO₂ and H₂ adsorption of GO, NiDOBDC and NiDOBDC/GO nanocomposites

Figure 3-6. (a) CO₂ adsorption isotherms and (b) H₂ adsorption isotherms of GO, NiDOBDC and its composite with 10 wt% loading of GO.

Table 3-4. CO₂ and H₂ storage capacities of NiDOBDC and NiDOBDC/GO composites at 298K, 313 K and 20 bar.

Samples		CO ₂		H ₂	
		Uptake (mmol/g)	% increase ^a in uptake	Uptake (mmol/g)	% increase in uptake
NiDOBDC	298 K	9.4	—	0.93	—
	313 K	8.7	—	0.81	—
NiDOBDC /GO-10%	298 K	10.5	12	1.40	50
	313 K	9.5	9	0.94	16

^a as compared to gas uptake of pristine MOF.

The pure-component CO₂ and H₂ uptake capacities of GO, NiDOBDC and the NiDOBDC/GO composite with 10 wt% GO were tested at 298 K and 313 K between 0 and 20 bar and 0 to 40 bar, respectively, as revealed in Figure 3-6. As observed in Figure 3-5, the CO₂ adsorption of NiDOBDC and its composites did not display saturation at 1 bar. This behavior suggested that NiDOBDC and its composites could provide promising gas (i.e. CO₂ and H₂) storage in the environmental field and in energy-related applications under high pressures [26]. In this work, not surprisingly, the CO₂ storage amount of the NiDOBDC/GO composite with 10 wt% GO was much higher than that of NiDOBDC at both 298 K and 313 K, where the adsorption behavior decreased with increasing temperature. This is true because gas adsorption is generally an exothermic process. As a comparison, the CO₂ storage of the NiDOBDC/GO composite with 10 wt% GO showed a storage value of 10.5 mmol/g at 298 K and 20 bar, which was a 12% improvement from pristine NiDOBDC (Table 3-4). Notably, the H₂ adsorption performance of the NiDOBDC/GO composite with 10 wt% of GO was remarkably higher (50%) than that of pristine NiDOBDC, with an H₂ uptake of 1.39 mmol/g at 298 K and 20 bar. Similar results were seen at elevated temperatures, where the CO₂ and H₂ adsorption of the NiDOBDC/GO composite with 10 wt% GO at 313 K was comparable to that of pristine NiDOBDC at 298 K. Overall, the incorporation of GO generally improved the gas storage performance effectively, an effect that was predominant in H₂ storage applications. As shown in Figure 3-6, low CO₂ and H₂ adsorption was observed in GO as the presence of epoxy and hydroxyl groups in the GO interlayer spacing could effectively shield gas molecules, as well as H₂ with small kinetic diameter (3 Å) [218]. Hence, if only physical mixing between GO and NiDOBDC occurred in this synthesis, the overall CO₂ and H₂

uptake will be inferior as compared to pristine NiDOBDC. Nonetheless, in this work, the overall CO₂ and H₂ uptake capacities increased significantly (12% and 50%) as compared to pristine NiDOBDC synthesized in this work. Therefore, the increase in gas storage of the NiDOBDC/GO composite was not merely the effect of GO alone but also the synergistic effect of the highly microporous NiDOBDC with a large surface area together with GO, which provides effective sites for systematic arrangement of NiDOBDC, leading to the improved gas storage performance of the NiDOBDC/GO composites.

Figure 3-7. Isosteric heat of adsorption as a function of (a) CO₂ and (b) H₂ loading for NiDOBDC and NiDOBDC/GO-10 wt% composite.

Table 3-5. Fitting parameters for CO₂ and N₂ adsorption of NiDOBDC and NiDOBDC/GO-10 wt% at 298K and 313K.

Sample	Gas	Temperature (K)	b_1 (bar ⁻¹)	$q_{sat,1}$ (mmol g ⁻¹)	b_2 (bar ⁻¹)	$q_{sat,2}$ (mmol g ⁻¹)	R^2
NiDOBDC	CO ₂	298	23.77	2.136	0.1146	18.94	0.9998
		313	0.09089	17.66	12.96	2.247	0.9999
	N ₂	298	0.01682	21.076			0.9986
		313	0.01782	19.907			0.9987
NiDOBDC/GO-10wt%	CO ₂	298	0.1455	18.14	50.98	2.274	0.9998
		313	16.33	2.407	0.115	16.67	0.9999
	N ₂	298	0.02472	20.414			0.9979
		313	0.01861	19.077			0.9987

In addition, the trend of increased CO₂ and H₂ adsorption for MOF/GO-10wt% can be evaluated by the analysis of the interaction between CO₂ (or H₂) on the available active sites in MOF/GO composites. Figure 3-7 displayed the isosteric heat of adsorption as a function of CO₂ and H₂ loadings for NiDOBDC and NiDOBDC/GO-10 wt% calculated by dual- and single-site Langmuir models. In general, it can be depicted that the Q_{st} for NiDOBDC/GO-10wt% composite was higher than that of pristine NiDOBDC. This possibly depicted that stronger interaction between CO₂ (or H₂) and the framework was formed in the composite. Besides, the isosteric heat of CO₂ adsorption underwent a decrease process and gradually tended to be stable, where the large amount of strong adsorption sites were saturated. However, the isosteric heat capacity of CO₂ adsorption was still lower than that of conventional zeolites such as zeolite 5A, which possessed a

much higher CO₂ heat of adsorption (-58 kJ/mol) at zero coverage [95]. As for H₂ adsorption, the isosteric heat capacities tended to be constant, indicating relatively weak H₂-adsorbent interaction observed from the H₂ uptake.

3.3.4. CO₂/N₂ selectivity

Figure 3-8. (a) CO₂ and N₂ uptake capacities (0-1 bar) of NiDOBDC and NiDOBDC/GO-10 wt% composite; (b) IAST CO₂/N₂ selectivity for 20:80 gas mixture at 298 and 313 K.

In order to further evaluate the potential utilization of NiDOBDC/GO composites for post-combustion CO₂ capture process, the analysis of CO₂/N₂ separation was conducted on NiDOBDC and NiDOBDC/GO-10wt%. Figure 3-8 (a) displayed CO₂ and N₂ uptake capacities (0-1 bar) of NiDOBDC and NiDOBDC/GO-10 wt% composite, where the presence of coordinatively unsaturated open metal sites allowed a much higher CO₂ uptake capacities than N₂. Therefore, CO₂/N₂ separation performance, was evaluated by the calculation of selectivities predicted by Ideal Adsorbed Solution Theory (IAST)

(Figure 3-8 (b)). In general, CO_2/N_2 selectivities of NiDOBDC/GO-10 wt% were much higher than those of NiDOBDC at both 298 and 313 K. Such results illustrated that high CO_2/N_2 selectivities under low pressures may ascribe to the additional adsorption sites on CO_2 which were generated with the introduction of GO, with negligible change of N_2 adsorption as compared to pristine NiDOBDC.

3.4. Conclusions

A facile method to prepare NiDOBDC/GO nanocomposite with a 3-D architecture was reported. Despite NiDOBDC playing a dominant role in the composites, the porosity and surface area properties of the composites were significantly improved as compared to pristine NiDOBDC. Such properties were also tunable with the variation of GO loading, and optimal loading was required to obtain the maximum CO₂ and H₂ storage capacities. In particular, the NiDOBDC/GO composite with 10 wt% GO loading possessed the highest CO₂ and H₂ storage value up to 10.5 mmol/g (298 K, 20 bar) and 1.39 mmol/g (298 K, 20 bar), respectively, which represented 12% and 50% improvement, respectively, over pristine NiDOBDC under the same conditions. Furthermore, CO₂/N₂ selectivity also enhanced with the incorporation of GO in NiDOBDC/GO composite. Thus, owing to the extraordinary improvement of gas storage with the incorporation of GO, the NiDOBDC/GO composite with 10 wt% loading of GO can be regarded as a potential candidate for CO₂ and H₂ storage applications.

3.5. Declaration

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CHAPTER 4

Enhanced CO₂/CH₄ Selectivity and Mechanical Strength of Mixed-Matrix Membrane Incorporated with NiDOBDC/GO Composite

4.1. Introduction

It is widely noted that polymeric membranes suffer from the trade-off effect between permeability and selectivity, as depicted by the Robeson plot for several well-reported gas pairs, particularly CO₂/CH₄ [28, 220, 221]. Meanwhile, microporous membranes provide uniform pore structures with effective molecular sieving effect which are made of microporous materials, including carbon molecular sieves [222], alumina [223], zeolites [224], and MOFs [225, 226], which have showcased promising high CO₂ permeability or high CO₂/CH₄ selectivity. Nonetheless, at present, the poor mechanical properties of microporous membranes act as the major constraints against their large-scale production, particularly in the fabrication of large-area membrane modules with minimal production cost [171].

In order to overcome the trade-off limitation of polymeric membranes and the disadvantages of microporous membranes, a new category of membrane named MMM was proposed where filler materials were introduced in a continuous polymer matrix [128, 138, 139, 171, 227-229]. The strategy is to apply physicochemical properties of the fillers to facilitate the diffusivity or solubility of a specific gas component through the

continuous matrix, leading to a better gas permeability or selectivity. However, inappropriate selection of fillers may cause poor compatibilities with polymer matrix, resulting in the formation of defects or voids in membranes, such as “*sieve-in-a-cage*”. Besides, gas separation ability may fade away when the loading of fillers exceed the tolerance of polymer matrix [119, 221, 230, 231]. Thus wise selection of filler types as well as optimum filler loading become highly significant to accomplish the desired gas separation performance.

Among a large amount of filler materials, MOFs have potentially used in mixed-matrix membranes because of their outstanding surface area, high micropore volume and tunable porosity for gas transport [232, 233]. What’s more, the organic ligands of MOFs are very favorable to interact with organic polymer matrix [234]. Despite the positive aid of MOFs, high loading has more chance to induce particle aggregation or non-idealities that provide non-desirable transport pathways as well as worse mechanical stabilities [140]. Meanwhile, GO has been investigated as an emerging filler material owing to its high aspect ratio, size discrimination of interlayers, good thermal and mechanical stabilities as well as good compatibility with polymer chains [149, 150]. Recently, research has been studied that GO is a feasible and effective filler used in polymer matrix which could improve CO₂/CH₄ selectivity because of the functional polar groups with a good affinity for CO₂ between the interlayers. However, the addition of GO often limits membrane’s enhancement for CO₂ permeation ability as a result of restricted interlayer space and tortuous gas transport pathways. For example, Li et al. demonstrated a sharp fall in CO₂ permeability (27%) despite the large increase in CO₂/CH₄ selectivity (107%) when 10 wt%

of GO was incorporated in Matrimid[®] membrane [151].

To address this issue, we proposed a strategy to design a composite material with a 3-D architecture combining two types of fillers together which could realize high CO₂/CH₄ separation performance with no trade-off limitations. Among various types of MOFs, a series of XDOBDC (X-MOF-74 or X₂(dobdc)) that incorporate several open metal sites (Mg, Ni, Co and Fe) has been investigated. In particular, NiDOBDC exhibits an outstanding high CO₂ adsorption capacity due to its high surface area and reasonable stability to air and moisture [205]. Furthermore, numerous synthesis protocols have been applied to prepare various particle sizes, especially nanoparticles [235] which could possibly be used as building blocks for novel composite. Recently, the use of GO as a component in MOF-based composites has attracted much attention to form a 3-D architecture. For instance, Kumar et al. [102] reported a hybrid of ZIF-8 and GO by in situ growth of MOF crystals on the GO surface for higher CO₂ uptake capacity. Also, Xia et al. [104-107] successfully synthesized a series of MOF/GO hybrids that displayed larger surface areas compared to pristine MOFs, such as Cu-BTC, MIL-101, and MOF-505. Furthermore, ZIF-8/GO composite designed by Dong et al. [236] was incorporated in Pebax-2533 matrix to obtain both improved CO₂ permeability and CO₂/N₂ selectivity. Nevertheless, with the increasing loading of ZIF-8/GO composite, much loss of tensile strength was exhibited.

In this study, NiDOBDC nanoparticles with the size of 30 nm were grown homogeneously and sandwiched between GO sheets to prepare a 3-D NiDOBDC/GO

nanocomposite, as reported in our previous work [219]. Based on previous study, surface area and CO₂ uptake capacity were optimized via introducing 10 wt% of GO in NiDOBDC/GO composite. Herein, NiDOBDC/GO-10% composite was chosen as the filler in Matrimid[®] 5218 for realizing desirable CO₂/CH₄ separation performance. What's more, the NiDOBDC/GO composite did not weaken the mechanical strength of MMMs which would enable the negative effects of pristine NiDOBDC on membrane's mechanical strength.

4.2. Experimental

4.2.1. Materials

Nickel(II) nitrate hexahydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] ($\geq 99.9\%$), graphene oxide (GO, $\geq 99.0\%$) powder, triethylamine (TEA, $\geq 99.0\%$), and chloroform ($\geq 99.5\%$) were purchased from Sigma-Aldrich. 2,5-Dihydroxy-1,4-benzenedicarboxylic acid (H_4DOBDC , $\geq 98.0\%$) was purchased from Tee Hai Chem Pte. Ltd. Matrimid[®] 5218 was purchased from Ciba Specialty Chemicals. *N,N'*-dimethylformamide (DMF, $\geq 99.8\%$), methanol ($\geq 99.8\%$), and absolute ethanol ($\geq 99.5\%$) were purchased from VWR. $\text{CO}_2\text{:CH}_4$ (50:50) mixture, He, N_2 , pure CO_2 and CH_4 gases ($\geq 99.9\%$) were purchased from Airliquide. Prior to use, all chemicals and solvents were received without further purification.

4.2.2. Synthesis of NiDOBDC and NiDOBDC/GO composite

NiDOBDC/GO composite was synthesized by repeating the procedures described in previous works [210, 235] with substantial modification. Similarly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.46 mmol) and H_4DOBDC (1.7 mmol) were first dissolved in DMF (135 mL), followed by the addition of GO (10 wt%). Next, water/ethanol/TEA mixture (volume ratio = 9:9:1 mL) was then added rapidly into the solution. Then the solution was agitated vigorously for 2 h at ambient temperature, where repetitive centrifugation-washing with DMF was conducted to collect the precipitates formed. To ensure that the final products were free of impurities, the precipitates were re-dispersed in DMF and heated at 60 °C overnight. Further purifications were performed by conducting solvent exchange with methanol, with this procedure being repeated at least two times. The residual solvent was eventually removed at 60 °C for 24 h in a vacuum before the subsequent characterizations. For

comparison, nanocrystalline NiDOBDC was prepared using nearly the same method as described above, without the addition of GO.

4.2.3. Fabrication of mixed-matrix membranes

The dense MMMs were prepared via solution-casting as reported elsewhere [234, 237]. The NiDOBDC/GO composite was first dispersed in chloroform, and the resulting suspension was sonicated with a sonication horn (Q125, Qsonica) to reduce the possibility of nanoparticle agglomeration. Matrimid[®] 5218 was then subsequently added into the suspension (controlled at the concentration of 10–15 wt%), followed by agitation at room temperature for 24 h. The doped solution was then cast onto a glass plate with the aid of a doctor blade, after which the glass plate was placed in a transparent plastic bag in an environment filled with chloroform vapor. The flat sheet membrane was kept in the plastic bag for 1 day to allow sufficient time for the evaporation of solvent evaporation. The obtained membrane was annealed at 180 °C overnight in a vacuum oven, and was used for the subsequent gas permeation test.

4.2.4. Characterizations

4.2.4.1. Characterizations of NiDOBDC, GO and composite

Powder X-ray diffraction (PXRD) patterns of the respective fillers were measured in ambient conditions using a Bruker D2 phaser diffractometer that was equipped with a Cu K α source, in which the samples were scanned in the 2θ range from 5 ° to 60 °. The particle morphologies were observed with a field emission-scanning electron microscope (FE-SEM, JSM6701, Jeol). The thermal stabilities of the respective samples were

determined via a thermogravimetric/differential thermal analyzer (TGA, SDT Q600). This analysis was conducted under pure N₂ purging at 100 mL/min in the temperature range of 40-900 °C, at the heating rate of 10 °C/min. CO₂ and CH₄ adsorption isotherms of the samples were determined using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome) at 25 °C, with the temperature controlled using a water recirculator. The isotherms were measured in the pressure range of 0-1 bar. Prior to the analysis, the fillers were activated under high vacuum at the specified temperature (100 °C for GO, 250 °C for NiDOBDC) for 8 h to ensure that any residual solvent in the samples was removed effectively. The porosity properties of Matrimid[®], GO, NiDOBDC and NiDOBDC/GO composite were measured using N₂ physisorption at 77 K (-196 °C). Similarly, prior to the measurement, all materials were activated using the same conditions as mentioned above.

4.2.4.2. Characterizations of mixed-matrix membranes

The cross-section morphologies of the MMMs were observed using an FE-SEM (JSM6701, Joel), where the membranes were first cryogenically fractured in liquid nitrogen (-196 °C) to maintain the overall morphologies. The glass transition temperatures (T_g) of the membranes were measured using differential scanning calorimetry (DSC) (Cryo DSC 822e, Mettler Toledo). This analysis was operated under pure N₂ purging with a flow rate of 50 mL/min in the temperature range from 25 to 400 °C (with a heating rate of 5 °C/min). The CO₂ and CH₄ uptake capacities of the membranes were determined using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome), and were measured at 25 °C, in which the temperature was closely controlled using a water recirculator. The uptake isotherms were tested in the pressure

range of 0-1 bar. The membranes were first activated under high vacuum at 180 °C for 8 h before the analysis. The mechanical properties of the membranes were tested at room temperature using an Instron 5543 tensile meter that was equipped with a 100 N load cell and grip. The flat sheet membranes were cut into rectangular strips with the approximate dimension of 30 mm (length) $\times$ 5 mm (width) $\times$ 30-50 μ m (thickness). To check the reproducibility of the results, five different samples per each membrane were tested and the error bar was determined by the standard deviation. The density of the membranes was measured via an analytical balance (ME204, Mettler Toledo), based on the Archimedes principle (ethanol was used as the auxiliary liquid).

4.2.4.3. CO₂/CH₄ permeation measurement

The gas permeation performance of the membranes was analyzed using a mixture-gas permeation system as explained in the previous work [238]. The membrane samples were first mounted into the permeation cell. Prior to the analysis, any residual gases present in the permeation chamber were cleared up using a vacuum pump. Then, the mixture gas (CO₂:CH₄ = 50:50) was supplied into the feed chamber of the permeation cell, which was set at 1 bar. The gases that passed through the samples were eventually swept with He gas. The permeabilities of CO₂ and CH₄ of the membrane samples were determined based on the concentration of the gases collected downstream (analyzed by gas chromatography). The temperature of the apparatus was kept at 25 °C during the whole experiments. The measurements were repeated at least three times to ensure the reproducibility of the performance.

4.2.4.4. Solubilities and diffusivities of CO₂ and CH₄

The solubilities (S , mol/m³ bar) of both CO₂ and CH₄ were calculated from the amount of gas adsorbed (q , mol/kg), membrane density (ρ , kg/m³), and pressure (p , bar), as described in Equation 4-1. The value of q for both CO₂ and CH₄ was determined by measuring the adsorbed amount of both gases at the partial pressure of 0.5 bar. The CO₂ and CH₄ isotherms were fitted using dual- and single-site Langmuir–Freundlich models, respectively, as illustrated in Equation 4-4 & 4-5 (Table 4-4: fitting parameters). The diffusivities (D , m²/s) of the gases, meanwhile, can be obtained from Equation 4-2, as the transport of gas molecules in polymeric membranes is described by the solution–diffusion mechanism. The value of the permeabilities, P (mol m/m² s bar), was determined under the conditions of 25 °C and 1 bar. The permselectivity, α (Equation 4-3), could be determined as the product of solution selectivity, α_S and diffusion selectivity, α_D .

$$S = \frac{q\rho}{p} \dots \dots (4 - 1)$$

$$D = \frac{P}{S} \dots \dots (4 - 2)$$

$$\alpha = \frac{P_{CO_2}}{P_{CH_4}} = \frac{S_{CO_2}}{S_{CH_4}} \times \frac{D_{CO_2}}{D_{CH_4}} = \alpha_S \times \alpha_D \dots \dots (4 - 3)$$

Single-site Langmuir-Freundlich equation:

$$q = \frac{q_{sat,1}b_1p^{1/f_1}}{b_1p^{1/f_1}} \dots \dots (4 - 4)$$

Dual-site Langmuir-Freundlich equation:

$$q = \frac{q_{sat,1}b_1p^{1/f_1}}{b_1p^{1/f_1}} + \frac{q_{sat,2}b_2p^{1/f_2}}{b_2p^{1/f_2}} \dots \dots (4 - 5)$$

4.3. Results and discussion

4.3.1. Properties of NiDOBDC, GO and composite

Figure 4-1. (a) PXRD patterns of graphene oxide, NiDOBDC, and composite; FE-SEM morphologies of (b) graphene oxide, (c) NiDOBDC, and (d) composite.

The successful synthesis of NiDOBDC and NiDOBDC/GO composite was first verified by the PXRD patterns, as shown in Figure 4-1 (a). Additionally, PXRD analysis of GO was also conducted as a reference for the synthesized samples. As shown in Figure 4-1 (a), the signature peak of GO was located at $2\theta = 26.7^\circ$. This was attributed to the low oxidation level of the GO used in this work (c.a. 4%). As a rule of thumb, the characteristic peak position of GO shifted toward higher 2θ angles with decreasing oxidation levels, as well illustrated by Krishnamoorthy et al. [239]. The PXRD pattern of NiDOBDC herein generally coincided with the data in the literature in terms of the peak

locations [235]. In the composite, the characteristic patterns of NiDOBDC were preserved, but the characteristic GO peak was not detected. Hence, it can be inferred that the GO content (10 wt%) in the composite was not sufficiently high to influence the overall crystallinity, so that the diffraction patterns of the composite were not influenced by the presence of GO. Interestingly, a peak broadening effect was observed for the composite (the intensity of the respective peaks have decreased compared with those in NiDOBDC), indicating that smaller crystal size have been developed in the composite [60]. This result possibly implied that the addition of GO in the reagent solution can restrict the formation of larger crystallites. Meanwhile, as displayed in Figure 4-1 (b), the morphology of GO was observed to consist of several GO platelet layers, with an approximate size of 1-3 μm . As a comparison, the NiDOBDC crystals were spherical in shape with a size of c.a. 30 nm (Figure 4-1 (c)). The FE-SEM image of the composite (Figure 4-1 (d)) revealed that the NiDOBDC particles were homogeneously deposited onto the surface of GO platelets, indicating the stable formation of a 3-D NiDOBDC/GO architecture, with good adhesion between them.

Figure 4-2. (a) N_2 physisorption isotherms measured at 77 K (-196 °C); (b) CO_2 and CH_4 adsorption at 25 °C in the pressure range from 0 to 1 bar for GO, NiDOBDC, and

composite.

Table 4-1. Surface areas and pore volumes for Matrimid[®], GO, NiDOBDC and NiDOBDC/GO-10% composite determined from N₂ physisorption isotherm at 77 K.

Samples	S _{BET} ^a	S _{LANG} ^b	V _{micro} ^c
	(m ² /g)	(m ² /g)	(cc/g)
Matrimid[®]	39.2	56.4	0.005
GO	319	454	0.048
NiDOBDC	940	1333	0.238
NiDOBDC/GO-10%	1190	1530	0.313

^a Surface areas were computed using BET theory at $P/P^0 = 0.05-0.2$; ^b Surface areas were calculated from Langmuir equation at $P/P^0 = 0.05-0.2$; ^c Micropore volumes were computed by using t-plot method at $P/P^0 = 0.4-0.6$.

Next, N₂ physisorption isotherms of Matrimid[®], GO, NiDOBDC and NiDOBDC/GO-10% composite were measured at 77 K (Figure 4-2 (a)). In general, Matrimid[®] and GO depicted low N₂ sorption behavior (Type III isotherm) that led to a low accessible surface area. On the other hand, both NiDOBDC and NiDOBDC/GO composite demonstrated the existence of large surface areas and micropore volumes (Type I isotherm) in view of its high N₂ sorption at low partial pressures. It should be noted that the N₂ sorption in NiDOBDC/GO-10% composite was observed to be higher than that in NiDOBDC owing to the additional pore spaces formed in MOF-inserted GO interlayers. The surface areas and pore volumes of each material were also determined from the N₂

sorption isotherms and the results were listed in Table 4-1. Furthermore, the CO₂ and CH₄ uptake capacities of GO, NiDOBDC, and the composite were measured at 25 °C, with the results shown in Figure 4-2 (b). As expected, the NiDOBDC framework demonstrated high CO₂ adsorption (c.a. 4.03 mmol/g) as compared to that of GO (c.a. 0.34 mmol/g) at ambient pressure, resulting from favorable interaction between CO₂ molecules and unsaturated open metal sites (Ni²⁺) of NiDOBDC. The composite, by comparison, demonstrated even further enhanced CO₂ adsorption performance (c.a. 4.58 mmol/g) under the same measurement conditions. This observation clearly indicated that the formation of the composite created additional gas adsorption sites that allowed more CO₂ gas to be adsorbed into, and stored in the microporous space as compared to NiDOBDC. Additionally, the addition of GO platelets allowed a more uniform growth of NiDOBDC nanoparticles with reduced aggregation. Interestingly, the CH₄ adsorption performance of NiDOBDC and the composite was relatively similar, indicating that the latter possessed higher CO₂/CH₄ selectivity. In contrast, for GO, both CO₂ and CH₄ adsorption can be described with linear isotherms, and the adsorption capacities were substantially lower as compared to NiDOBDC and the composite.

4.3.2. Properties of Matrimid[®] and mixed-matrix membranes

Figure 4-3. Cross-section FE-SEM morphologies for (a, b) Matrimid[®]; (c, d) Matrimid[®] with 10 wt% GO; (e, f) Matrimid[®] with 10 wt% NiDOBDC; and (g, h) Matrimid[®] with 10 wt% composite.

Having been successfully synthesized by the solution-casting method, the cross-section morphologies of pure Matrimid[®] and the MMMs were exhibited in Figure 4-3. As expected, the morphology of pure Matrimid[®] membrane was highly regular together with

an uniform cross-section morphology. Upon the introduction of fillers, the filler materials interacted strongly with the polymer chains and distributed homogeneously in polymer matrix. The “*sieve-in-a-cage*” morphology, which is commonly observed in zeolite-based MMMs, was not observed in this study as there were no visible defects or voids [240].

Table 4-2. Mechanical strength of Matrimid[®] and mixed-matrix membranes.

Membranes	Tensile strength (MPa)	% Change	Modulus (MPa)	% Change
Matrimid [®]	91.07 ±4.71	-	2294 ±33	-
Matrimid [®] /GO-5%	93.31 ±2.47	2.5	2352 ±16	2.5
Matrimid [®] /GO-10%	97.00 ±2.55	6.5	2565 ±55	11.8
Matrimid [®] /NiDOBDC-5%	63.95 ±8.67	-29.7	2005 ±68	-12.6
Matrimid [®] /NiDOBDC-10%	59.65 ±5.16	-34.5	2097 ±23	-8.6
Matrimid [®] /Composite-5%	97.73 ±3.05	7.3	2704 ±10	17.9
Matrimid [®] /Composite-10%	96.20 ±5.18	5.6	2653 ±43	15.6
Matrimid [®] /Composite-15%	80.05 ±0.98	-12.1	2691 ±23	17.3

Subsequently, the mechanical properties of the membranes were tested to evaluate the practicability of these membranes in industrial operations (Table 4-2). The incorporation of NiDOBDC nanoparticles weakened the overall membrane strength ascribing to the poor adhesion between NiDOBDC nanoparticles and polymer chains, which was exacerbated if the fillers agglomerated during the formation of the doped solution.

Promisingly, the Matrimid[®]/Composite was demonstrated to be favorable in improving or maintaining the mechanical strength of the MMMs, with a slight enhancement (5.6%) of tensile strength for the case of 10 wt% composite. This result was considerably preferable to the significant decrease in tensile strength (34.5%) for the case of 10 wt% NiDOBDC nanoparticles in Matrimid[®] membrane. As compared to the pristine MOF, the existence of GO in the 3-D composite exerted a clear positive effect on the overall mechanical strength, as the presence of the surface functional groups in GO led to a stronger interfacial interaction between GO and polymer [241]. However, no further enhancement in mechanical strength was obtained when the composite loading increased to 15 wt%, presumably due to the formation of a weak junction between the polymer chains and fillers caused by the increased filler/polymer interface area.

4.3.3. CO₂/CH₄ permeation performance

Figure 4-4. CO₂ and CH₄ permeation performance of Matrimid®, Matrimid®/GO, Matrimid®/NiDOBDC, and Matrimid®/Composite membranes.

MMMs containing the composite as the filler were tested for mixture-gas CO₂:CH₄ (50:50) separation performance at 25 °C and 1 bar, while the gas permeation performance of MMMs containing GO or NiDOBDC was also included as a comparison, as demonstrated in Figure 4-4. After introducing GO into Matrimid®, the selectivity of CO₂ over CH₄ was improved, with a minor reduction in CO₂ permeability. Such a trade-off effect has been widely reported in the literature [242, 243]. This phenomenon was ascribed to the presence of interlayer channels in GO, which could selectively transport CO₂ over CH₄, despite the fact that the pathways for all gases are generally convoluted in two-dimensional (2-D) materials [234]. In contrast, the addition of NiDOBDC nanocrystals into Matrimid® polymer reduced the overall CO₂ permeability without

improving its selectivity.

Figure 4-5. (a) Differential Scanning Calorimetry (DSC) and (b) thermogravimetric analysis (TGA) curves of Matrimid[®] and MMMs.

Hence, to investigate the cause of this undesirable phenomenon, the glass transition temperatures (T_g) of the membranes were tested using DSC with the scan range from 25 to 400 °C (Figure 4-5 (a)). The T_g of nascent Matrimid[®] membrane, which was used as a benchmark, was registered to be 302 °C. This result was acceptably comparable with the reported value (304 °C) [244]. The addition of NiDOBDC nanocrystals into the membrane resulted in a 26 °C increase in the T_g (328 °C) of the Matrimid[®]/NiDOBDC-10% membrane. This observation possibly indicated the increase in rigidity of the polymer chains caused by the NiDOBDC nanoparticles, as reported by Bachman et al. [245]. In general, the behavior of polymer rigidification in mixed-matrix membrane can be verified by measuring the T_g of the membrane [240, 246]. In the case of the Matrimid[®]/Composite-10% membrane, although its T_g value was substantially higher than pure Matrimid[®] membrane due to the dominant role of MOF in the MMMs, the T_g value was lower than that of the Matrimid[®]/NiDOBDC-10% membrane. This behavior

illustrated the possibility that the presence of GO in the composite effectively reduced the overall structural rigidity of the Matrimid[®]/Composite membrane as compared to the Matrimid[®]/NiDOBDC membrane. In addition, the thermal properties of Matrimid[®] and the MMMs were screened from 40 to 900 °C. As presented in Figure 4-5 (b), all the membranes exhibited similar thermal behavior and decomposition temperatures, as the properties of the MMMs were still predominantly contributed by the Matrimid[®] polymer. Also, the residual weight of the Matrimid[®]/GO-10% membrane after high-temperature treatment (700-900 °C) was higher than that of pure Matrimid[®] membrane owing to the high thermal stability of GO. As for the introduction of NiDOBDC and the composite into the Matrimid[®] 5218 polymer, the residual weight (after the decomposition of the polymer network) was smaller than that of the pure polymer due to the early decomposition of NiDOBDC.

Table 4-3. CO₂/CH₄ selectivity of MMMs incorporated with MOF/GO composites as well as MOFs and GO.

Fillers	Ratio	Matrix	Loading (wt%)	Testing conditions	CO ₂ /CH ₄ selectivity	Enhancement (%)	Ref.
ZIF-8+GO	^[a]	ODPA-TMPDA	10+5	25 °C, 1 bar, 50/50 mixture gas	41	28	[247]
ZIF-8/GO	50/50	Polysulfone	10	25 °C, 2.5 bar, single gas	6..3	60	[248]
UiO-66/GO	70/30	Polysulfone	24	35 °C, 3.4 bar, 50/50 mixture gas	~44	~47	[249]
		Matrimid [®] 5218		50/50 mixture gas	~49	~48	
NiDOBDC/GO	90/10	Matrimid [®] 5218	20	25 °C, 1 bar, 50/50 mixture gas	58.3	59	This work

Note: ^a ZIF-8 and GO were incorporated in a separate manner (not as composites).

Subsequently, CO₂/CH₄ separation performance of Matrimid[®] and the MMMs was evaluated, and the results were demonstrated in Figure 4-4. With the systematic increase in the loading of composite in the MMMs, a steady increment in CO₂/CH₄ selectivity was acquired. Specifically, the selectivity of CO₂ over CH₄ was reached to 58.3 for the case of Matrimid[®]/Composite-20% membrane, which corresponded to an enhancement of 59% compared to pure Matrimid[®] membrane. Hence, the incorporation of composite filler allowed an enhancement in CO₂/CH₄ selectivity due to the presence of GO, in contrast to the incorporation of NiDOBDC nanocrystals into the Matrimid[®] membrane. Such phenomenon was also reported in the studies as listed in Table 4-3. Moreover, and again in contrast to the Matrimid[®]/NiDOBDC membrane, the addition of composite allowed a modest enhancement in CO₂ permeability owing to the alleviated polymer chain rigidification as compared to the Matrimid[®]/NiDOBDC membrane. All in all, the introduction of the composite into Matrimid[®] was proven to be a feasible strategy to improve the overall CO₂/CH₄ permeation performance without suffering from any significant trade-off behavior.

Figure 4-6. CO₂ and CH₄ uptake capacities of Matrimid[®], Matrimid[®]/GO-10%, Matrimid[®]/NiDOBDC-10%, and Matrimid[®]/Composite-10% membranes.

Table 4-4. Fitting parameters for CO₂ and CH₄ adsorptions at 25 °C for Matrimid[®] and mixed-matrix membranes.

Membranes	Gas	b_1^a	$q_{sat,1}^b$	f_1	b_2	$q_{sat,2}$	f_2	R^2
Matrimid	CO ₂	31.16	0.1473	0.597	0.8334	0.9272	0.752	1.0000
	CH ₄	2.039	0.05582	0.3408				0.9999
Matrimid/GO-10%	CO ₂	0.02315	3.183	0.4966	1.768	0.7617	0.8992	0.9997
	CH ₄	1.733	0.06629	0.3357				0.9973
Matrimid/NiDOBDC-10%	CO ₂	51.19	0.1551	0.5543	0.9857	0.8489	0.7134	1.0000
	CH ₄	1.543	0.09429	0.3676				0.9994
Matrimid/Composite-10%	CO ₂	0.8462	-3.995	0.6756	0.7238	5.725	0.7709	0.9994
	CH ₄	1.902	0.07195	0.3251				0.9994

Note: a: Langmuir parameter, b : bar^{-1} ;

b: Saturation loading, q_{sat} : mmol g^{-1} .

c: Freundlich parameter, f : dimensionless

Table 4-5. The densities of Matrimid[®] and mixed-matrix membranes.

Membranes	Density (g cm^{-3})
Matrimid	1.210 ± 0.010
Matrimid/GO-10%	1.246 ± 0.002
Matrimid/NiDOBDC-10%	1.287 ± 0.016
Matrimid/Composite-10%	1.268 ± 0.006

Table 4-6. Solubilities and diffusivities of Matrimid[®] and mixed-matrix membranes.

Membranes	$P_{(\text{CO}_2)}$ ($\times 10^{-10}$) ^a	$S_{(\text{CO}_2)}$ ^b	$D_{(\text{CO}_2)}$ ($\times 10^{-13}$) ^c	$P_{(\text{CH}_4)}$ ($\times 10^{-12}$)	$S_{(\text{CH}_4)}$	$D_{(\text{CH}_4)}$ ($\times 10^{-13}$)	α_s^d	α_D^e
Matrimid [®]	3.36	882.03	3.81	9.15	28.45	3.22	31.01	1.18
Matrimid [®] /GO-10%	2.44	899.23	2.71	5.35	29.77	1.80	30.21	1.51
Matrimid [®] /NiDOBDC-10%	2.58	967.19	2.67	6.28	46.03	1.37	21.01	1.96
Matrimid [®] /Composite-10%	3.48	945.18	3.68	6.97	33.57	2.08	28.15	1.77

Note: ^a permeability, P : $\text{mol m/m}^2 \text{ s bar}$;

^b solubility, S : $\text{mol/m}^3 \text{ bar}$;

^c diffusivity, D : m^2/s ;

^d CO₂/CH₄ solution selectivity;

^e CO₂/CH₄ diffusion selectivity.

The enhanced gas permeation performance of Matrimid[®] and the MMMs was further studied via the solubility-diffusivity analysis. First, the CO₂ and CH₄ uptake capacities of Matrimid[®], Matrimid[®]/GO-10%, Matrimid[®]/NiDOBDC-10%, and Matrimid[®]/Composite-10% membranes were acquired at 25 °C under the pressure range from 0 to 1 bar, as depicted in Figure 4-6. In general, all of the membranes exhibited similar CO₂ and CH₄ uptake capacities, reflecting the fact that Matrimid[®] still played the dominant role in the MMMs. Therefore, the gas solubilities and diffusivities of the membranes were calculated based on the CO₂ and CH₄ uptake capacities, membrane density, and the pressure during the gas permeation test. The density of Matrimid[®] and the MMMs was given in Table 4-5. Lastly, the respective diffusivities of each gas in the membrane were estimated by taking the quotient between the permeabilities and solubilities. The solubilities, diffusivities, and the respective selectivities were listed in Table 4-6. The incorporation of GO into the Matrimid[®] 5218 membrane allowed a 28% enhancement in diffusion selectivity, without significantly changing the solution selectivity. This can be ascribed to the selective gas transport of CO₂ over CH₄ through the GO interlayers. For the NiDOBDC nanoparticles, in contrast, a 10% improvement in the CO₂ solubility was accomplished at the expense of a drastic decrease in CO₂ diffusivity (30%) as compared to pure Matrimid[®] membrane. This was generally consistent with our observation of increased polymer chain rigidity caused by the incorporation of NiDOBDC nanoparticles (Figure 4-5 (a)). However, the diffusion

selectivity of the Matrimid[®]/Composite-10% membrane increased significantly with only a slight decrease in solution selectivity, resulting in a huge enhancement of CO₂/CH₄ selectivity. Hence, it can be concluded that the incorporation of the 3-D architecture of NiDOBDC and GO allowed the overall performance of the MMM to be favorably tuned without any permeability-selectivity trade-off effect.

4.4. Conclusions

In conclusion, a noticeable enhancement in CO₂/CH₄ selectivity has been achieved in the Matrimid[®] membrane through the incorporation of a NiDOBDC/GO composite. The CO₂/CH₄ mixture-gas selectivity gradually increased, with a marginal increase in CO₂ permeability, as the filler (NiDOBDC/GO composite) loading increased. Specifically, a high CO₂/CH₄ selectivity (58.3) was reported for the Matrimid[®]/Composite-20% membrane, which was 59% higher than that of the nascent Matrimid[®] membrane, without any noticeable loss in CO₂ permeability. In addition, the overall mechanical stabilities of the Matrimid[®]/Composite membranes were unaffected, due to the presence of GO sheets, which possessed surface functional groups that preferentially interact with the polymer chains. Importantly, such enhancement could not be realized by membranes containing NiDOBDC or GO alone. Hence, the incorporation of NiDOBDC/GO composite with 3-D architecture was a facile and efficient approach to design high-performance CO₂/CH₄ separation membranes. Future efforts will be devoted to incorporating these fillers into the skin layer of asymmetric or thin film composite membranes which are typical industrial membrane platforms.

4.5. Declaration

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CHAPTER 5

Enhancing CO₂/CH₄ Separation Performance and Mechanical Strength of Mixed-Matrix Membrane via Combined Use of Graphene Oxide and ZIF-8

5.1. Introduction

Polymeric membranes that are readily produced with various configurations in a cost-effective manner, have been commonly used for industrial applications [251]. However, because the solution-diffusion mechanism is the dominant mechanism for gas transport in polymeric membranes, their separation performance is often limited, as depicted by the trade-off effect of permeability-selectivity in the Robeson plot [28, 220, 221]. In contrast, pure molecular sieve membranes made of microporous materials, namely carbon molecular sieves [222], alumina [223], zeolites [224], and MOFs [225, 226], possess a uniform pore structure that allows effective molecular discrimination by size effect. Nevertheless, these molecular sieve membranes suffer from poor scalability, insufficient mechanical stability, and high production cost [171]. Thus, MMMs have been made to develop membranes that can alleviate the drawbacks of both types of membranes (polymeric and microporous).

In recent years, the utilization of zeolitic imidazolate framework-8 (ZIF-8) in polymeric membranes has been widely investigated for gas separation attributing to its easy-synthesis, tunable pore size as well as good thermal, chemical and mechanical

stabilities [252-255]. Results demonstrated that both CO₂ and CH₄ permeabilities enhanced rapidly with an increasing loading of ZIF-8, without significant change of CO₂/CH₄ selectivity [256]. For instance, Bushell et al. reported that the incorporation of ZIF-8 into polymers of intrinsic microporosity-1 (PIM-1) matrix led to an enhancement in free volume for gas adsorption [257]. Dai et al. also claimed that ZIF-8/Ultem[®] hybrid hollow fiber membrane with 17 vol% of ZIF-8 presented 85.7% increase compared to pure Ultem[®] hollow fiber for CO₂ permeation performance [258]. Besides, Song et al. observed an improved CO₂ permeability with negligible loss in the selectivity of CO₂ over CH₄ for ZIF-8-based polymer composite membranes [259]. In addition, in Nafisi's work, CO₂ permeability enhanced with the increasing loading of ZIF-8 in PEBAX-2533 matrix in both dry and humid conditions [260].

Besides, the utilization of GO has become an emerging candidate as a nanofiller in composite membranes due to its high aspect ratio (> 1000), good compatibility with polymers, good thermal and mechanical properties [149]. Recent studies revealed that GO nanosheets could act as barriers in polymer matrix resulting in the hindered diffusion pathways which would hamper the diffusion of larger gas molecules but favor the diffusion of smaller gas molecules. Hence, these increased tortuous pathways contributed to the improvement of mixture-gas selectivities. For example, Koolivand and co-workers reported 59% enhancement and 112% enhancement in CO₂/CH₄ selectivity for PEI and PDMS due to the introduction of very low amount of GO [150]. Also, according to Li et al.'s study, a 106.7% increase of CO₂/CH₄ selectivity was fulfilled by the incorporation of 10 wt% GO in Matrimid[®] matrix [152].

Basically, one filler could only enhance gas permeability or selectivity alone, or even suffers the trade-off effect of gas permeability and selectivity. In order to further enhance both CO₂ permeability and CO₂/CH₄ selectivity capacities, one feasible approach is to incorporate two kinds of fillers where one contributes to enhanced CO₂ permeability and the other one is used for increasing CO₂/CH₄ selectivity. In this case, the synergic effect of two fillers would become an effective methodology to force the gas separation performance approach to the Robeson upper bound limit. As illustrated, ZIF-8 could effectively improve CO₂ permeability as well as GO nanosheets are good candidates for enhancing CO₂/CH₄ selectivity. Therefore, incorporating both ZIF-8 and GO in polymer matrix should be regarded as a promising approach.

To validate the preceding idea, we reported mixed-matrix membranes that contained both ZIF-8 and GO as fillers. ODPA-TMPDA polyimide, which has greater permeability than commercial polymers and is also readily synthesized in large quantities without rigorous monomer purifications [261, 262], was used as the polymer matrix. A systematic study of CO₂/CH₄ separation performance and mechanical properties were conducted after the fabrication of three different mixed-matrix membranes containing ZIF-8 alone, GO stacks alone, and both ZIF-8 and GO. Overall, the results illustrated that the use of both fillers together was an effective way to design high-performance membranes for applications in biogas upgrading and natural gas treatment.

5.2. Experimental

5.2.1. Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\geq 99.0\%$), 2-methylimidazole (Hmim; $\geq 99.0\%$), 4, 4'-oxydiphthalic anhydride (ODPA, $\geq 97\%$), 2, 4, 6-Trimethyl-mphenylenediamine (TMPDA; $\geq 96\%$), GO ($\geq 99.0\%$) powder, triethylamine (TEA; $\geq 99\%$), acetic anhydride (Ac_2O ; $\geq 99.0\%$), N,N-dimethylacetamide (DMAc; $\geq 99.8\%$), and chloroform ($\geq 99.5\%$) were purchased from Sigma-Aldrich, Merck. Methanol ($\geq 99.8\%$) and ethanol absolute ($\geq 99.5\%$) were purchased from VWR, Singapore. $\text{CO}_2:\text{CH}_4$ (50:50) mixture, He, N_2 , pure CO_2 and CH_4 gases ($\geq 99.9\%$) were purchased from Airliquide. Prior to use, these chemicals and solvents were received without further purification.

5.2.2. Synthesis of nanocrystalline ZIF-8

The ZIF-8 nanocrystals were synthesized using a one-step procedure reported in the literature [263]. A solution of zinc nitrate hexahydrate (2.933 g) in 200 ml of methanol was rapidly poured into a solution of Hmim (6.489 g) in 200 ml of methanol. After mixing for 1 h, the white nanocrystals were collected by centrifugation and washed with fresh methanol by repeating centrifugation-redispersion. The ZIF-8 crystals were then dried at 40 °C in a vacuum.

5.2.3. Synthesis of polyimide ODPA-TMPDA

ODPA-TMPDA polyimide was synthesized following the work of Duan et al. [261], as explained in Figure 5-1. TMPDA (3.263 g) was dissolved in 40 g of DMAc, followed by

stirring for 30 min to ensure complete dissolution. ODPA (6.737 g) was then added into the solution in batches and magnetically stirred for 1 day under a flow of N₂ to form the polyamic acid. Next, the mixture of Ac₂O (8.870 g) and TEA (8.791 g) was added slowly to the solution to chemically imidize the polyamic acid. The mixture solution was stirred for another 1 day under N₂ flow. The imidized polymer was then slowly poured into 300 ml of ethanol under slow agitation to precipitate polymer. The white polymer was collected by filtration and washed with large amount of fresh ethanol. Finally, the polyimide was dried at 150 °C in a vacuum.

Figure 5-1. Procedure of ODPA-TMPDA synthesis.

5.2.4. Fabrication of mixed-matrix membranes

The dense flat sheet membranes were fabricated with the solution-casting technique reported elsewhere [234, 237]. ZIF-8 (10 wt%) nanoparticles were dispersed in chloroform with the aid of a sonication horn (Qsonica, Q125). GO (5 wt%) stacks were added, followed by vigorous stirring. After dispersing the fillers, ODPA-TMPDA polyimide was then added to the suspension, and the whole solution was agitated at room temperature until the polymer was completely dissolved. Typically, the concentration of the polyimide in the solvent was controlled to be 10 to 15 wt%. The polymer solution was then poured onto a glass plate and casted with a doctor blade in a transparent plastic bag, which was filled with chloroform vapor. The nascent membrane was kept in the plastic bag for 1 day to ensure slow evaporation of chloroform. Finally, the obtained flat sheet

dense membrane was heated and annealed at 160 °C for 24 h in a vacuum.

5.2.5. Characterizations

5.2.5.1. Characterizations of ZIF-8 and GO

Powdered X-ray diffraction (PXRD) patterns were measured with a Bruker D2 phaser diffractometer equipped with a Cu K α source in the 2θ range from 5 ° to 40 °. The morphologies were observed with a field emission-scanning electron microscope (FE-SEM, JSM6701). The thermal stabilities of the adsorbents were determined using a thermogravimetric/differential thermal analyzer (Diamond TG/DTA, PerkinElmer). The analysis was conducted under pure N₂ purging from 50 to 800 °C at a heating rate of 10 °C/min. The pore characteristics were investigated by N₂ physisorption isotherms measured with an Autosorb-6B instrument from Quantachrome at -196 °C (77 K). The fillers were loaded into the adsorption cell and activated in a high vacuum (< 0.0001 bar) generated by a molecular turbo pump at elevated temperatures (100 °C for GO, 120 °C for ZIF-8) which were controlled by a heating mantle for 8 h. CO₂ and CH₄ uptake capacities were acquired using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome) at a pressure range from 0 to 1 bar at 25 °C. The temperature was precisely controlled using a water circulator equipped with a temperature controller.

5.2.5.2. Characterizations of mixed-matrix membranes

The successful preparation of ODPDA-TMPDA was verified by Fourier-transform infrared spectroscopy-attenuated total reflectance (Bruker MPA NearIR). The cross-section morphologies of the membranes were observed with a field emission-scanning electron

microscope (FE-SEM, JSM6701). In this case, membranes were cryogenically fractured in liquid nitrogen to maintain the original cross-section morphologies. The thermal stabilities of the membranes were also investigated using Diamond TG/DTA. The mechanical strength of the membranes was measured at room temperature using the Instron 5543 tensile meter equipped with 100 N grip. The tested flat sheet membranes were cut into a rectangle with dimension of 5 mm×30 mm (width×length) prior to the loading. The density of the membranes was determined with a Quantachrome Ultrapyc 1200e pycnometer for evaluation of the solubilities and diffusivities of CO₂ and CH₄ in membranes (Table 5-5).

5.2.5.3. CO₂/CH₄ permeation test

The gas permeation test was carried out using the mixture-gas permeation system described in our previous work [238]. The membrane samples were first mounted into the permeation cell. Prior to the analysis, any residual gases presented in the permeation chamber were cleared up using a vacuum pump. Then, the mixture gas (CO₂:CH₄ = 50:50) was supplied into the feed chamber of the permeation cell, which was set at 1 bar. The gases that passed through the sample were eventually swept with He gas. The permeabilities of CO₂ and CH₄ of the membrane samples were determined based on the concentration of the gases collected downstream (analyzed by gas chromatography). The temperature of the apparatus was kept at 25 °C during the whole experiments. The measurements were repeated at least three times to ensure the reproducibility of the performance.

5.2.5.4. Gas solubilities and diffusivities

The solubility (S , mol/m³ · bar) of gas in the membrane could be estimated from gas adsorption isotherms (q , mol/kg), membrane density (ρ , kg/m³), and pressure (p , bar) using the following equation:

$$S = \frac{q\rho}{p} \dots \dots (5 - 1)$$

where q is the gas uptake capacity of the membrane at a partial pressure of 0.5 bar estimated by the fitting of gas uptake isotherms with dual- or single-site Langmuir-Freundlich models. The diffusivity (D , m²/s) of gas through the membrane was determined by dividing gas permeability by gas solubility as follows:

$$D = \frac{P}{S} \dots \dots (5 - 2)$$

where P (mol · m/m² · s · bar) is the gas permeability obtained from permeation testing.

CO₂ adsorption isotherms were mathematically fitted with Dual-site Langmuir-Freundlich adsorption model [60], which is interpreted below:

$$q = \frac{q_{sat,1}b_1p^{1/f_1}}{1+b_1p^{1/f_1}} + \frac{q_{sat,2}b_2p^{1/f_2}}{1+b_2p^{1/f_2}} \dots \dots (5 - 3)$$

where q is the total CO₂ adsorption quantity, $q_{sat,1}$ and $q_{sat,2}$ are the saturation adsorption quantities for site 1 and site 2; b_1 and b_2 are binding energies [264] for site 1 and site 2, which are Langmuir parameters; f_1 and f_2 are Freundlich parameters for site 1 and site 2. Besides, Single-site Langmuir-Freundlich adsorption model was used to fit CH₄ adsorption isotherms:

$$q = \frac{q_{sat,1}b_1p^{1/f_1}}{1 + b_1p^{1/f_1}} \dots \dots (5 - 4)$$

The fitting parameters were listed in Table 5-3.

5.3. Results and discussion

5.3.1. Properties of ZIF-8 and GO

Figure 5-2. FE-SEM morphologies of (a) ZIF-8 nanocrystals and (b) graphene oxide; (c) PXRD patterns of ZIF-8 and GO; (d) thermogravimetric analysis curves of ZIF-8 and GO.

As reported elsewhere, ZIF-8 was successfully synthesized with a one-step reaction at room temperature [64, 263]. As shown in Figure 5-2 (a), uniform nanocrystals with an average particle size of around 50 nm were formed by the reaction. The small nanocrystals were typically well dispersed in organic solvent, resulting in uniform distribution of the fillers in a MMM. The morphology of GO was also shown in Figure 5-2 (b), in which platelets formed by a few GO layers were clearly visible. The sizes of GO platelets were observed to be in the range from 1 to 5 μm . Powdered X-ray diffraction

analysis further confirmed the crystal structures of ZIF-8 [263] and GO stacks (Figure 5-2 (c)). As for the pattern of GO, the characteristic peak was located at $2\theta = 26.6^\circ$ due to the low oxidation level (about 4%) , as compared to the reduced GO (rGO), which showed a signature peak at 25.8° [265]. It was reported that the peak position of GO was shifted to a higher 2-theta with the decrease in the level of oxidation [239]. The thermogravimetric analysis in Figure 5-2 (d) demonstrates decent thermal stability up to 600°C for ZIF-8, whereas the GO stacks were more stable in the temperature range tested (up to 800°C).

5.3.2. Gas adsorption of ZIF-8 and GO

Figure 5-3. (a) N_2 sorption isotherms measured at -196°C (77 K) in the pressure range from 0 to 1 bar; (b) CO_2 and CH_4 uptake capacities at 25°C in the pressure range from 0 to 1 bar.

Table 5-1. Surface areas and pore volumes of ZIF-8 and GO determined from N₂ physisorption isotherm at -196 °C.

Fillers	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	$S_{\text{LANG}}^{\text{b}}$ (m ² /g)	$S_{\text{micro}}^{\text{c}}$ (m ² /g)	$V_{\text{micro}}^{\text{d}}$ (cc/g)
ZIF-8	1160.0	1483.0	1017.0	0.4546
GO	318.8	454.0	94.6	0.0479

^a Surface areas were computed using BET theory at $P/P^0 = 0.05\text{--}0.2$; ^b Surface areas were calculated from Langmuir equation at $P/P^0 = 0.05\text{--}0.2$; ^{c,d} Micropore areas and volumes were computed by using t-plot method at $P/P^0 = 0.4\text{--}0.6$.

Figure 5-3 (a) showed the N₂ sorption isotherms of ZIF-8 and GO measured at -196 °C (77 K) from 0 to 1 bar. ZIF-8 exhibited high N₂ sorption in the low pressure range leading to high microporosity and BET surface area of 1160 m²/g (Table 5-1), which was comparable with the value (1079 m²/g) reported elsewhere [64]. Such a high surface area and micropore volume can effectively contribute to the improvement in CO₂ permeability when ZIF-8 is incorporated in polymer membranes. In contrast, GO showed much lower N₂ uptake than ZIF-8 in the low-pressure region and thus owned a far smaller BET surface area of 319 m²/g. Hence, the role of GO in improving gas permeability in a mixed-matrix membrane may be limited as compared to ZIF-8. Therefore, the CO₂ and CH₄ uptake capacities of both ZIF-8 and GO stacks were obtained at 25 °C from 0 to 1 bar to investigate the affinities for CO₂ and CH₄. As shown in Figure 5-3 (b), both ZIF-8 and GO possessed low CO₂ and CH₄ adsorption capacities with a linear isotherm. However, due to the large surface area and micropore volume, ZIF-8 could take up more CO₂ and CH₄ than the GO stacks.

5.3.3. Properties of mixed-matrix membranes

Figure 5-4. FTIR spectrum of ODPA-TMPDA polyimide.

In this study, ODPA-TMPDA polyimide was synthesized and used as a polymer matrix for the fabrication of composite membranes comprising ZIF-8 and GO. The successful synthesis of ODPA-TMPDA was verified by fourier-transform infrared spectroscopy (FTIR), as exhibited in Figure 5-4. The characteristic imide peaks were examined at 1720 cm⁻¹ (symmetric C=O), 1779 cm⁻¹ (asymmetric C=O), and 1361 cm⁻¹ (C-N).

Figure 5-5. Cross-section FE-SEM morphologies of membranes. (a) and (b) ODPA-TMPDA; (c) and (d) ODPA-TMPDA with 5 wt% GO; (e) and (f) ODPA-TMPDA with 10 wt% ZIF-8; and (g) and (h) ODPA-TMPDA with 5 wt% GO and 10 wt% ZIF-8.

Figure 5-5 displayed the morphologies of ODPA-TMPDA and those of composite membranes containing ZIF-8 and GO. As expected, pure ODAP-TMPDA polymer had a neat and tidy morphology. As fillers were incorporated, we observed changes in the

cross-sectional morphologies. In general, no defects were visible at the filler-polymer interfaces in any mixed-matrix membranes that contained ZIF-8 particles and/or GO stacks. Although portions of some fillers were aggregated, the fillers were generally well distributed in the continuous matrix. Overall, high-quality MMMs were successfully synthesized without any additional filler-polymer compatibilization. It is worth noting that when the filler and polymer are not compatible, such as a glassy polyimide-zeolite pair, interfacial voids and a non-uniform distribution of fillers will be typically observed [266, 267].

Table 5-2. Mechanical strength of the mixed-matrix membranes.

Membranes	Tensile strength (MPa)	Modulus (MPa)
ODPA-TMPDA	33.4 ± 0.3	599.8 ± 1.0
ODPA-TMPDA/5% GO	39.2 ± 2.4	620.1 ± 9.3
ODPA-TMPDA/10% ZIF-8	29.6 ± 2.4	553.5 ± 9.9
ODPA-TMPDA/5% GO+10% ZIF-8	36.4 ± 1.8	606.8 ± 10.8

The mechanical strength of MMMs was also measured, and the results were listed in Table 5-2. It was clear that the incorporation of GO can improve the mechanical strength of mixed-matrix membrane, whereas ZIF-8 made the membrane mechanically weaker than pure ODPA-TMPDA membrane. Such decrease in mechanical stability caused by the incorporation of ZIF-8 has been mentioned in previous works [268, 269] since the mechanical strength of ZIF-8 crystal was inherently poor as compared to those of polymeric materials. The mechanical stability can be further lowered when the ZIF-8/polymer adhesion was weak or ZIF-8 fillers were agglomerated within a polymer

matrix. It was worth noting that the mechanical strength of MMMs that contained both ZIF-8 and GO exceeded that of pure ODPA-TMPDA membrane, which indicated that the positive contribution of the GO stack was greater than the negative effect of ZIF-8 on mechanical strength. The positive effect of mechanical strength for GO was due to the surface functional groups which gave rise to a strong interfacial interaction between GO and polymers [241]. Enhanced mechanical properties are highly desirable for practical applications, in which a substantial pressure differential is often used to ensure a sufficient driving force.

5.3.4. CO₂/CH₄ permeation performance

Figure 5-6. Mixture gas (CO₂:CH₄, 50:50) permeation properties of mixed-matrix membranes measured at 25 °C and under 1 bar upstream pressure. (a) CO₂ permeabilities in barrer; (b) CO₂/CH₄ selectivities.

The synthesized membranes prepared using GO, ZIF-8, and both fillers were tested for CO₂/CH₄ separation at 25 °C under 1 bar upstream pressure, where the results were

shown in Figure 5-6. ZIF-8 was an effective filler for the enhancement of CO₂ permeability, given that 10 wt% loading in ODPDA-TMPDA enhanced CO₂ permeability from 91 barrers to 146 barrers, which translated into a 61% increase in the CO₂ permeability compared to pure polymer. However, no significant change was seen in the selectivity of CO₂ over CH₄ upon the incorporation of the filler. Such results were consistent with the studies in the literature [256, 259, 270], where the use of ZIF-8 was only able to increase CO₂ permeability but not CO₂/CH₄ selectivity because of its open structure yet limited affinity for CO₂. In contrast, as exhibited in Figure 5-6 (b), the incorporation of 5 wt% GO increased CO₂/CH₄ selectivity from 32 to 41 (c.a. 29% increase) with no significant effect on its corresponding CO₂ permeability. This result may imply that the interlayer channels in GO stacks can selectively transport CO₂ over CH₄. This effect of GO on the performance of MMMs has also been reported elsewhere [242, 243]. As a result, both CO₂ permeability and its selectivity increased to 145 barrers and 41, respectively, translating into 60% and 28% increase, respectively, by incorporating two fillers together. The foregoing results proved that the addition of both fillers allowed both gas permeability and selectivity to be enhanced significantly without any negative effects.

Figure 5-7. CO₂/CH₄ separation performance of MMMs. The Robeson upper bound limit for polymeric membranes was established in 2008.

By incorporating two fillers that possess different properties, the direction of performance enhancement can be tailored to the desirable direction on the permeability-selectivity map. Figure 5-7 showed that the performance was moving toward the upper bound line (as of 2008) [221]. In order to realize the performance moving across the upper bound, the optimization of polymer matrix may be necessary since the resulting performance of MMM is still predominantly governed by the continuous phase. To this end, it is recommended to use polymers possessing high fractional free volumes such as 6FDA-based polyimides and PIM (polymer of intrinsic microporosity). However, much more complex synthesis conditions and higher cost are required to obtain these polyimides successfully. In addition to the mechanical property study discussed previously, the permeation testing proved that the addition of GO stacks as a secondary filler was an efficient way to overcome the drawbacks of ZIF-8 filler.

Figure 5-8. CO₂ and CH₄ uptake capacities at 25 °C in the pressure range from 0 to 1 bar for ODPA-TMPDA, MMMs with 5 wt% GO and/or 10 wt% ZIF-8.

Table 5-3. Fitting parameters for CO₂ and CH₄ adsorption at 25 °C under 0-1 bar of composite membranes.

Membranes	Gas	b_1^a	$q_{sat,1}^b$	f_1	b_2	$q_{sat,2}$	f_2	R^2
ODPA-TMPDA	CO ₂	0.004485	47.21	0.3931	2.582	1.435	0.8888	0.9999
	CH ₄	0.1667	1.4082	0.4971				0.9935
ODPA-TMPDA/5% GO	CO ₂	0.008511	9.63	0.2866	1.183	1.821	1.032	0.9995
	CH ₄	0.08366	2.659	0.6065				0.9938
ODPA-TMPDA/10% ZIF-8	CO ₂	0.01059	10.34	0.35	1.196	1.739	1.009	0.9992
ZIF-8	CH ₄	0.2072	1.1257	0.5055				0.9919
ODPA-TMPDA/5% GO+10% ZIF-8	CO ₂	2.437	1.188	0.9095	0.02476	9.147	0.4261	0.9997
GO+10% ZIF-8	CH ₄	0.253	0.9948	0.4611				0.9871

Note: ^a b : bar⁻¹;

^b q_{sat} : mmol g⁻¹.

Table 5-4. Measured density of mixed-matrix membranes.

Membranes	Density (g cm ⁻³)
ODPA-TMPDA	1.355 ± 0.005
ODPA-TMPDA/5% GO	1.376 ± 0.003
ODPA-TMPDA/10% ZIF-8	1.327 ± 0.001
ODPA-TMPDA/5% GO+10% ZIF-8	1.345 ± 0.009

Table 5-5. CO₂ and CH₄ solubilities and diffusivities for composite membranes.

Membranes	CO ₂	CO ₂	CO ₂	CH ₄	CH ₄	CH ₄	α_S^d	α_D^e
	permeability ^a	solubility ^b	diffusivity ^c	permeability	solubility	diffusivity		
ODPA-TMPDA	3.07 × 10 ⁻⁹	2206	1.39 × 10 ⁻¹²	9.68 × 10 ⁻¹¹	151	6.39 × 10 ⁻¹³	14.56	2.18
ODPA-TMPDA/ GO	3.30 × 10 ⁻⁹	1908	1.73 × 10 ⁻¹²	8.03 × 10 ⁻¹¹	190	4.22 × 10 ⁻¹³	10.04	4.10
ODPA-TMPDA/ ZIF-8	4.95 × 10 ⁻⁹	1774	2.79 × 10 ⁻¹²	1.59 × 10 ⁻¹⁰	149	1.07 × 10 ⁻¹²	11.91	2.61
ODPA-TMPDA/ GO+ZIF-8	4.91 × 10 ⁻⁹	1820	2.70 × 10 ⁻¹²	1.20 × 10 ⁻¹⁰	143	8.45 × 10 ⁻¹³	12.73	3.20

Note: ^a permeability: mol m/m² s bar;

^b solubility: mol/m³ bar;

^c diffusivity: m²/s;

^d CO₂/CH₄ solution selectivity;

^e CO₂/CH₄ diffusion selectivity.

To further understand the reason for the improvement of CO₂ permeability and CO₂/CH₄ selectivity, the gas solubilities and diffusivities of CO₂ and CH₄ in mixed-matrix membranes were determined based on the gas permeabilities and gas uptake capacities. To do this, the CO₂ and CH₄ uptake capacities were measured at 25 °C from 0 to 1 bar for pure polymer and mixed-matrix membranes (Figure 5-8). Note that neither filler could improve the CO₂ solubility of ODPA-TMPDA, which had a decent CO₂ uptake property. As shown in Figure 5-3 (b), both fillers do not possess a strong affinity for CO₂. Table 5-5 summarized the calculated solubilities and diffusivities of CO₂ and CH₄. ZIF-8 dramatically increased both CO₂ and CH₄ diffusivities so that the overall CO₂ and CH₄ permeabilities could be enhanced despite the loss in solubilities. Such enhanced diffusivity was ascribed to a high porosity as well as a sufficiently large pore window allowing the access of both CO₂ and CH₄ [259, 271]. We were interested to find that the addition of GO decreased the solution selectivity of the MMMs compared to that of pure ODPA-TMPDA. However, the CO₂/CH₄ diffusion selectivity increased to a larger extent than the loss in solution selectivity, leading to an increase in the CO₂/CH₄ permselectivity of MMMs containing GO. Such enhanced diffusion selectivity suggested that the interlayer spacing in GO stacks was capable of molecular sieving of CO₂-CH₄ pair as reported previously [151]. In summary, ZIF-8 and GO can significantly improve the CO₂

diffusivity and CO_2/CH_4 diffusion selectivity, respectively, and therefore the mixed-matrix membrane that contained both fillers can enhance both CO_2 permeability and CO_2/CH_4 permselectivity.

5.4. Conclusions

In summary, the use of GO as the secondary filler in a mixed-matrix membrane proved feasible and effective in overcoming the drawbacks of ZIF-8 filler which could improve the permeability of gas due to its open structure. By incorporating GO and ZIF-8 together, the mechanical strength of the OPDA-TMPDA membrane increased, whereas the use of ZIF-8 filler alone decreased the mechanical strength. In addition, by using the two fillers together, both CO₂ permeability and its selectivity over CH₄ were improved by 60% and 28%, respectively, whereas ZIF-8 or GO alone could only increase the CO₂ permeability or CO₂/CH₄ selectivity, respectively. This implied that the performance enhancement can be tailored in the desirable direction on the permeability-selectivity map. Hence, the combined use of GO and ZIF-8 was a facile and effective approach to fabricate membranes for potential applications in biogas upgrading and natural gas sweetening.

5.5. Declaration

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CHAPTER 6

Mixed-Matrix Carbon Molecular Sieve Membranes using Hierarchical Zeolite: A Simple Approach Towards High CO₂ Permeability Enhancements

6.1. Introduction

It is generally challenging to improve both gas permeabilities and selectivities simultaneously by relying solely on polymeric membranes ascribing to the trade-off effect caused by solution-diffusion mechanism. Further efforts have been focused to alleviate the inherent limitations in polymer membranes, such as fabrication methods (asymmetric or hollow fiber membranes), thermal treatment, cross-linking and polymer blending [140]. In comparison, thermal treatment is generally considered to be a promising approach. Thermal treatment is the process where thermal decarboxylation of polymer precursor at high temperatures is feasible to change the structure of the polymer chain or disrupt polymer's rigidity [154]. Thus, the fractional free volume and chain's flexibility can be well-adjusted during the carbonization process in order to achieve a well-optimized cavities and constriction that can be feasible to display discrimination of gas molecules in terms of kinetic diameter. This results in substantial improvement in gas permeability without sacrificing membrane's selectivity, together with reduced plasticization effect [155]. Such type of membranes is often termed as carbon molecular sieve membranes (CMSMs) as highly graphitic domains are formed after the thermal treatment process [156], which have a wide range of gas pairs in separation applications, like CO₂

separation, air and hydrocarbon gas separation. Furthermore, this type of membranes shows excellent chemical stability and it is facile to surpass the permeability-selectivity limitations [157].

Researchers have paid much attention on improving high-performance CMSMs in the past decades. One strategy was to optimize the carbonization conditions, including atmosphere (He, Ar, N₂, CO₂, vacuum), heating rates (1-13 °C/min), thermal soak time and pyrolysis temperatures (500-1000 °C) [157, 273]. For instance, He is more favorable in increasing CO₂ permeance but leads to a huge loss of CO₂/CH₄ separation factor. In contrast, as for Ar, it is more beneficial for obtaining higher gas selectivity. Besides, mechanical strength of CMSMs somehow is feasible to be improved under pyrolysis at higher temperatures. On the other hand, another strategy for achieving good gas separation performance of CMSMs could be fulfilled by the selection of precursor polymers which own outstanding gas separation ability, such as highly permeable/selective polyimides (6FDA-based polymers) [157].

Even so, no matter how optimized carbonization conditions have been conducted, the resulting gas separation performance is still restricted by the intrinsic nature of polymer types, especially for less permeable/selective polymers, such as Matrimid[®] and Phenol formaldehyde resin (PFR) which are far below permeability-selectivity upper bound. Whereas, if highly permeable polymer precursors are chosen, more negative effects should be taken into consideration as most excellent separation polymers face difficulties in cost factors as well as synthesis procedures. In essence, the high cost for monomers

limit the scale-up of CMSMs preparation. Subsequently time-consuming pre-purification of monomers is necessary and crucial before the synthesis process starts. Sometimes, very harsh reaction conditions must be fulfilled to ensure the success of final products, like always keeping the reaction under inert atmosphere.

Therefore, continuous attempts have been made to enhance the overall gas separation performance via the combination of polymer and microporous filler, which can be described as mixed-matrix membranes (MMMs) or composite membranes [128]. In these hybrid membranes, microporous fillers serve as structural agents to create favorable transport pathways for particular gas components, or act as barriers to hinder undesired gas molecules, resulting in remarkable separation behavior which could be superior to the intrinsic properties of polymer matrix. Thereby, it was illustrated that more extraordinary gas separation performance could be achieved when MMMs served as the precursors for carbon molecular sieve membranes and similar research works have been conducted in the literature. Based on their results, significant improvement of either CO₂ permeability or CO₂/CH₄ selectivity were achieved in CMSMs derived from MMMs with the incorporation of porous materials, including mesoporous silicas (SBA-15 and MCM-48 [274]) and zeolites (zeolite T [275], zeolite KY [276] and zeolite L [277]). Basically, these porous fillers were introduced into the polymer matrix (continuous phase) without any treatment in the reported works and there were nearly no references reported about the influence of functional pores on the improvement of gas separation in carbon molecular sieve membranes.

In particular, zeolites which are classified as microporous crystalline aluminosilicates, possess molecular channels and rigid cavities that can provide optimized free space and void volume for effective gas transport, especially CO₂ molecules. These attractive properties has led to the investigation of zeolite-based MMMs in gas separation process, namely zeolite 5A into polydimethylsiloxane (PDMS) polymer in early 1970s for CO₂/CH₄ separation [132, 278] and zeolite 5A in polyethersulfone (PES) that reported improvement in both CO₂/CH₄ and O₂/N₂ separation performance with the systematic increase in the loading of zeolite 5A [129, 279]. In addition, appropriate fine tuning of pore aperture of zeolite framework via ion-exchange with various cations can portray substantial enhancement in overall gas permeability, as reported by Li et al. [129, 279]. Based on our previous work [280], it is facile and effective to tune the pore structure of zeolite 5A with the aid of pore expanding agent leading to a hierarchical structure with both mesopores and micropores. Comparing with bulk zeolite 5A with only micropores, the formation of mesopores in hierarchical zeolite 5A creates more open channels and highways for CO₂ transport and the remaining micropores still guarantee selective ability for hindering undesired gas components. Consequently, increased gas permeability without significant loss of selectivity would be successfully achieved in CMSMs derived from MMMs with the incorporation of hierarchical zeolite 5A.

Regarding of the polymer matrix, Matrimid[®] 5218 polyimide has been applied readily in CO₂/CH₄ separation process by taking its cheap cost, strong chemical resistance as well as high solubility towards common organic solvents into consideration. Nonetheless, Matrimid[®] polymer possesses very low CO₂ permeability (7.60 barrers) in spite of its

high CO₂/CH₄ selectivity (37.5) under the measurement condition of 35 °C and 2 bar feed pressure [281]. It has been illustrated that the improvement of CO₂/CH₄ separation performance by the incorporation of microporous materials solely is still far below the Robeson upper bound limit [78]. In addition, plasticization of polymers has been commonly occurred in gas separation process if high concentration of CO₂ is permeated through the membrane [153]. In order to overcome these drawbacks, the carbonization process was conducted for Matrimid® polyimide to fabricate carbon molecular sieve membranes as it has been reported that CO₂ permeability can be enhanced substantially after carbonization process due to the optimization of the microporous matrix [162, 165]. However, the overall separation performance is still challenging to surpass Robeson upper bound limit. Under such circumstances, the carbonization of Matrimid®-based MMMs is considered as a feasible and promising strategy for improving CO₂/CH₄ separation capacity with the assistance of functional zeolite 5A with both mesopores and micropores.

In this context, we proposed that using MMMs as the polymer precursors can be considered as the most probable candidate in improving the overall gas permeability and selectivity by utilizing the positive effect of functional porous filler. Hierarchical zeolite 5A (LTA topology), which was a mesoporous & microporous material with strong affinity towards CO₂, was developed as it was feasible to demonstrate significant enhancement towards CO₂ permeability in MMMs. Besides, the performance was compared between MMMs that containing bulk zeolite 5A with purely microporous domain and hierarchical zeolite 5A with both microporous and mesoporous domains. Based on the results reported in this work, CMSMs that were derived from Matrimid®/hierarchical zeolite 5A exhibited

extraordinary high CO₂ permeability and its overall CO₂/CH₄ separation behavior was able to surpass the Robeson upper bound limit (2008).

6.2. Experimental

6.2.1. Materials

Sodium metasilicate pentahydrate ($\geq 95.0\%$), sodium hydroxide ($\geq 98.5\%$), sodium aluminate (Al: 50-56%; Na: 37-45%) and dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride solution (TPOAC, 42 wt% in methanol) were purchased from Sigma-Aldrich, Merck. Chloroform ($\geq 99.8\%$) was purchased from VWR. Matrimid[®] 5218 was purchased from Ciba Specialty Chemicals. CO₂:CH₄ (50:50) mixture, He, Ar, N₂, pure CO₂ and CH₄ gases ($\geq 99.9\%$) were purchased from Airliquide. The reagents and solvent were used as-received.

6.2.2. Synthesis of bulk and hierarchical zeolite 5A

Bulk and hierarchical zeolite 5A (H-zeolite 5A) were synthesized as described in the literature [280]. For H-zeolite 4A (with both microporous and mesoporous domains), the precursor gel with a molar ratio of 10 Al₂O₃/40 Na₂O/15 SiO₂/2400 H₂O/1.25 TPOAC was prepared at room temperature. In separate polypropylene bottles, one solution containing sodium metasilicate pentahydrate, sodium hydroxide, TPOAC and deionized (DI) water was mixed, while another solution comprising sodium aluminate dissolved in DI water was separately prepared. After the solutions were strongly agitated for 2 h, both solutions were mixed and heated at 100 °C for 4 h. Once the reaction completed, the products were collected via vacuum filtration, which were then washed with copious amount of DI water to remove unreacted raw materials and impurities. The resulting products were dried at 100 °C overnight in a convection oven, followed by a calcination at 550 °C for 3 h in a furnace at a heating rate of 1 °C/min. This step helped to remove

TPOAC that was present in the mesopores, affording hierarchical zeolite 4A. In the following step, Na^+ cations in LTA zeolite domains (zeolite 4A) was replaced with Ca^{2+} cations using ion-exchange to yield zeolite 5A. Briefly, 1 g of zeolite 4A was first dispersed in 50 mL of 0.5 M $\text{Ca}(\text{NO}_3)_2$ solution before vigorous stirring at 60 °C for 12 h. This ion-exchange procedure was repeated once more time to ensure a higher degree of substitution to Ca^{2+} . The H-zeolite 5A was obtained by filtering the product solution and drying at 80 °C for 24 h. On the other hand, the synthesis of bulk zeolite 5A (with only microporous domains) was prepared using a similar procedure without the addition of TPOAC. The molar ratio of the precursor gel was 10 Al_2O_3 /40 Na_2O /15 SiO_2 /2400 H_2O .

6.2.3. Synthesis of mixed-matrix carbon molecular sieve membranes

The synthesis of CMSMs was summarized in Figure 6-1. Polymeric precursor membranes were fabricated using a solution-casting technique as reported elsewhere [237, 272]. For the synthesis of polymeric MMMs containing bulk and H-zeolite 5A (10, 20 and 30 wt%), the fillers were first ground and dispersed in chloroform with the aid of a sonication horn (Qsonica, Q125) to obtain a homogeneous dispersion. Next, Matrimid[®] powder was incorporated into the suspension, followed by vigorous stirring until the polymer was dissolved completely. The viscosity of the dope solution was controlled by fixing the concentration of Matrimid[®] in the range of 10-15 wt%. Flat sheet membranes were cast onto a glass plate with a doctor blade in a transparent plastic bag that was filled with chloroform vapor to slow down the solvent evaporation time. Upon phase inversion, the membranes were annealed at 180 °C overnight to remove the remaining solvents. The precursor membranes then underwent a carbonization process in a tube furnace (Carbolite

GERO, CTF 12/100/900). Ar gas was first purged into the quartz tube for approximately 1 h to create an inert environment and to remove any residual air and moisture that could be potentially trapped inside the tube. Following, the membrane precursors were treated via a two-step ramp-dwell profile comprising 380 °C heating for 30 min at a rate of 2 °C/min and 550 °C heating for 2 h at a rate of 0.5 °C/min. After completion, the carbonized membranes were cooled to room temperature before storing them for future performance evaluation and characterization.

Figure 6-1. Synthesis procedure of carbon molecular sieve membranes [282].

6.2.4. Materials and membranes characterizations

X-ray diffraction (XRD) patterns of zeolites, precursor membranes and CMSMs were measured with a Bruker D2 phaser diffractometer equipped with a Cu K α source in the 2θ range of 5 to 50°. Thermal stabilities of zeolites and precursor membranes were determined using a thermogravimetric/differential thermal analyzer (TGA, SDT Q600 TA Instrument). The experiments were operated under N₂ purging at 100 ml/min, with a heating rate of 10 °C/min and temperature ranging from 50 to 900 °C. The morphologies of zeolites, precursor membranes and CMSMs were observed using a field

emission-scanning electron microscope (FE-SEM, JSM6701 JOEL). To preserve the cross-sectional morphologies, the samples were first cryogenically fractured in liquid nitrogen prior to gold coating. N₂ physisorption at -196 °C (77 K) and a P/P₀ range of 0 to 1 bar (Autosorb 6B, Quantachrome) were used to evaluate the porosity properties of both bulk and H-zeolite 5A. The zeolites were first activated at 250 °C for 24 h under a high vacuum before the measurement and the mesopore size distribution was determined from a Barrett-Joyner-Halenda (BJH) algorithm. On the other hand, CO₂ and CH₄ uptake capacities were acquired via a volumetric gas sorption analyzer (iSorb HP1, Quantachrome) in a pressure range from 0 to 1 bar. The measurements were conducted at a controlled temperature of 35 °C using a water circulator.

6.2.5. Mixture gas permeation evaluation

Mixture gas permeation behavior was conducted via a constant pressure-variable volume system (GTR Tec Corporation). Membrane samples were first mounted onto a permeation cell before exposing to continuous flow of He and CO₂/CH₄ mixture gas on the down and upstream sides at a feed and permeate pressure of 1 bar, respectively. The testing temperature of the permeation cell was fixed at 35 °C. At a specific time interval, the downstream gas was swept by He until the concentration of the permeating gas remained unchanged. The CO₂ and CH₄ concentration of the permeate gas was calculated by the gas chromatogram. Each permeation measurement was repeated at least three times for both precursor membranes and CMSMs to ensure reproducibility in the results. Based on the separation performance obtained, a filler enhancement index, F_{index} , was calculated for each mixed-matrix CMSM using the following equation:

$$F_{index} = \ln\left(\frac{P_{filled}}{P_{unfilled}}\right) + \eta \ln\left(\frac{\alpha_{filled}}{\alpha_{unfilled}}\right) \dots \dots (6 - 1)$$

where P_{filled} and $P_{unfilled}$ refer to the CO₂ permeability while α_{filled} and $\alpha_{unfilled}$ are the CO₂/CH₄ selectivity of the mixed-matrix and unfilled CMSMs, respectively, and η is an enhancement coefficient of value 2.636, which stems from the slope of the 2008 Robeson upper bound. The F_{index} is empirically developed to evaluate the effectiveness of fillers in enhancing the separation abilities of MMMs [283], which we utilize here to help us understand the effects brought by the bulk and H-zeolite 5A fillers.

6.3. Results and discussion

6.3.1. Properties of bulk and hierarchical zeolite 5A

Figure 6-2. FE-SEM morphologies of (a) bulk and (b) H-zeolite 5A ; (c) PXRD patterns of bulk and H-zeolite 5A ; (d) Thermogravimetric analysis (TGA) curves of bulk and H-zeolite 5A from 50-900 °C.

Figure 6-2 (a) and (b) illustrated the overall morphologies of zeolite 5A, showing uniform structures for both bulk (cubic) and H-zeolite 5A (spherical). The particle size of bulk and H-zeolite 5A was estimated from the FE-SEM images to be around 2-3 μm and 6-7 μm respectively. Next, successful synthesis of bulk and H-zeolite 5A was verified by PXRD. As exhibited in Figure 6-2 (c), the characteristic peaks of both zeolites resembled the XRD patterns as those reported in the literature [280]. Noteworthy of mentioning was the

lower peak intensities of H-zeolite 5A as compared to the bulk zeolite 5A, suggesting a lower crystallinity of H-zeolite 5A probably because of the presence of mesoporosity, which led to a lower fraction of zeolitic domains. To determine the suitability of the zeolites for the subsequent carbonization process, the thermal stabilities were evaluated from 50-900 °C (Figure 6-2 (d)). Based on the TGA profile, a continuous weight loss (c.a. 15-20%) up to 220 °C was observed for both bulk and H-zeolite 5A, which we ascribed to the presence of moisture inside the pores. After heating beyond 220 °C, all moisture was removed and further weight loss was not observed for both zeolites even at a temperature as high as 900 °C. This suggested that both zeolites were capable of retaining their crystallinity and pore structures in the Matrimid[®] matrix after carbonization at 550 °C.

Figure 6-3. (a) N₂ physisorption isotherms of bulk and H-zeolite 5A measured at -196 °C (77 K) under the P/P₀ range of 0 to 1 bar; (b) pore size distribution of bulk zeolite 5A and H-zeolite 5A, which were determined via a BJH method.

Table 6-1. Surface areas and micropore volumes of bulk zeolite 5A and hierarchical zeolite 5A which were determined from N₂ physisorption isotherm at 77 K.

Fillers	S_{BET}^a	S_{Lang}^b	S_{Micro}^c	V_{Micro}^d
	(m ² /g)	(m ² /g)	(m ² /g)	(cc/g)
Bulk Zeolite 5A	501.8	678.5	482.6	0.2313
H-zeolite 5A	430.3	587.5	285.6	0.1343

Note: ^a Surface areas were computed using BET theory at $P/P^0 = 0.05-0.2$;

^b Surface areas were calculated from Langmuir equation at $P/P^0 = 0.05-0.2$;

^{c, d} Micropore areas and volumes were computed by using t-plot method at $P/P^0 = 0.4-0.6$.

Porosity properties of both bulk and H-zeolite 5A were quantified using N₂ physisorption isotherm at -196 °C (77 K) and P/P_0 range from 0 to 1 bar, as presented in Figure 6-3 (a). In general, both bulk and H-zeolite 5A demonstrated high N₂ sorption at low P/P_0 value, indicating the existence of large micropore volume. While the H-zeolite 5A exhibited relative lower N₂ sorption as compared to the bulk zeolite 5A at low P/P_0 value, the presence of the hysteresis loop between adsorption and desorption curves showed the existence of mesopores. The mesopore size determined by a BJH algorithm [284] was around 8 nm, as examined in Figure 6-3 (b). Based on the N₂ physisorption isotherms, surface area as well as the micropore surface area and micropore volume were computed using the BET theory, Langmuir equation and t-plot method, respectively. Our results illustrated that the surface area and micropore volume of H-zeolite 5A were found to be slightly lower than those of the bulk zeolite 5A, which was most likely due to the presence of mesoporosity (Table 6-1).

Figure 6-4. CO₂ and CH₄ adsorption capacities of bulk and H-zeolite 5A at 35 °C from 0 to 1 bar.

Next, pure component CO₂ and CH₄ adsorption of bulk and H-zeolite 5A was investigated to evaluate their affinities towards these gases. A close analysis of Figure 6-4 exhibited a rapid CO₂ adsorption at low CO₂ partial pressures for both zeolites. This suggested the presence of favorable interaction between CO₂ molecules and active sites in the zeolitic frameworks as facilitated by induced dipole-dipole interaction and driven by a stronger polarizability ($29.11 \times 10^{-25} \text{ cm}^3$ vs. $25.93 \times 10^{-25} \text{ cm}^3$) and quadrupole moment ($4.30 \times 10^{-26} \text{ esu cm}^2$ vs. 0 esu cm^2) of CO₂ as compared to CH₄ molecules. At increasing CO₂ partial pressure, both zeolites started to show a gradual saturation of the CO₂ adsorption with enhancing feed pressure. CH₄ adsorption, on the other hand, exhibited a linear CH₄ isotherm, indicating a weaker affinity of the CH₄ molecules towards both zeolites. A weaker CO₂ and CH₄ adsorption of the H-zeolite 5A as relative to the bulk zeolite 5A also implied a slight loss in the number of active sites as a result of the introduction of

mesoporous domains in the zeolitic framework of H-zeolite 5A.

6.3.2. Properties of precursor and carbon molecular sieve membranes

Figure 6-5. Thermogravimetric analysis curves of Matrimid[®]/zeolites mixed matrix membranes prior to the carbonization process.

Characterization of the as-prepared membranes was evaluated from three aspects, namely, thermal stability, structural intactness, and membrane morphology. Previously, the thermal stability of the zeolite 5A was demonstrated by heating up to 900 °C without showing signs of structural degradation (Figure 6-2 (d)). Similarly, the same phenomenon was observed when the zeolites were incorporated into the membrane matrix as evidenced by the TGA results represented in Figure 6-5. At a temperature of around 520 °C, the substantial weight loss observed by all membranes, including the unfilled Matrimid[®], suggested that the polymer started to undergo thermal rearrangement and carbonize at this temperature. In this regard, we have chosen a slightly higher carbonization temperature at

550 °C.

Figure 6-6. XRD patterns of pure Matrimid[®] membrane and mixed-matrix carbon molecular sieve membranes (a) before and (b) after carbonization.

The thermal stability of the zeolite 5A after incorporating into membrane matrix was also apparent from the XRD results. Particularly, membranes comprising bulk and H-zeolite 5A showed characteristic peaks of zeolite 5A, suggesting that the crystallinity of the zeolitic domains remained intact after carbonization, as illustrated in Figure 6-6. In fact, throughout the process of carbonization, the most significant change only happens to the Matrimid[®] matrix as corroborated by a shift in the broad XRD peak of the Matrimid[®] matrix from $2\theta = 16^\circ$ to a lower angle of $2\theta = 9^\circ$ (Figure 6-6). Structurally, this implied an enhancement in the d-spacing (fractional free volume) as the nature of the matrix changed from polymer to carbon [285, 286], which has important implications for the membrane performance.

Figure 6-7. Cross-section FE-SEM morphologies of Matrimid[®]/zeolites mixed-matrix membranes with (a) 10 wt% bulk zeolite 5A, (b) 20 wt% bulk zeolite 5A, (c) 30 wt% bulk zeolite 5A, (d) 10 wt% hierarchical zeolite 5A, (e) 20 wt% hierarchical zeolite 5A and (f) 30 wt% hierarchical zeolite 5A; carbon molecular sieve membranes with (A) 10 wt% bulk zeolite 5A, (B) 20 wt% bulk zeolite 5A, (C) 30 wt% bulk zeolite 5A, (D) 10 wt% hierarchical zeolite 5A, (E) 20 wt% hierarchical zeolite 5A and (F) 30 wt% hierarchical zeolite 5A.

The membrane morphologies after zeolite 5A incorporation were observed by probing the membrane cross-sectional images using FE-SEM. Critically, the mixed-matrix precursor

membranes displayed clear defects before carbonization. These defects appeared in the form of “*sieve-in-a-cage*” morphologies as exemplified by the existence of voids at the polymer/zeolite interfaces (Figure 6-7 (a-f)). *Sieve-in-a-cage* morphologies were reportedly attributing to the poor interfacial compatibility between the zeolite 5A and Matrimid[®] matrix, which was a common challenge arising from pairing an inorganic filler with an organic polymeric material [128, 240]. However, after carbonization, the interfacial voids between the zeolite 5A and carbon matrix were seemingly narrowed, as depicted in Figure 6-7 (A-F). We believed that the glassy Matrimid[®] polymer matrix became rubbery as it reached its glass transition temperature (T_g) of 319 °C during carbonization [287]. This rendered the polymer chains enough flexibility to close up the interfacial voids before matrix carbonization occurred at a higher temperature. Nevertheless, while no visible voids were observed under FE-SEM (Figure 6-7 (A-F)), we remain doubtful on the complete sealing of the interfacial voids. Realistically speaking, there was a possibility that microscopically invisible nanogaps may continue to linger at the carbon/zeolite interfaces, which we will provide evidence in the following section.

6.3.3. CO₂/CH₄ separation performance of precursor and carbon molecular sieve membranes

Table 6-2. Mixed gas permeation results measured at 35 °C and 1 bar feed pressure (CO₂:CH₄=50:50) and F_{index} values for Matrimid® precursor membrane as well as unfilled Matrimid® and mixed-matrix carbon molecular sieve membranes.

Carbonization	Membrane	CO ₂ permeability ^a (barrer)	CO ₂ /CH ₄ selectivity ^b	F_{index} ^c
Before	Matrimid®	11 ± 0	36.7 ± 1.3	—
After	Matrimid®	29 ± 1	49.2 ± 2.0	—
	Matrimid®/Zeolite 5A-10%	233 ± 2	26.3 ± 0.3	0.43
	Matrimid®/Zeolite 5A-20%	473 ± 19	20.5 ± 0.2	0.48
	Matrimid®/Zeolite 5A-30%	951 ± 3	23.0 ± 0.2	1.49
	Matrimid®/H-zeolite 5A-10%	704 ± 17	24.9 ± 0.5	1.39
	Matrimid®/H-zeolite 5A-20%	967 ± 24	19.7 ± 0.1	1.09
	Matrimid®/H-zeolite 5A-30%	2450 ± 40	19.3 ± 0.1	1.97

Note: ^a 1 barrer = $10^{-10} \frac{\text{cm}^3_{STP} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$

^b Ratio of CO₂ permeability over CH₄ permeability

^c Based on statistical analysis of 470 fillers in the literature, fillers having different F_{index} values are classified into 5 labels, namely, 1: ideal (> 8.00), 2: exemplary (8.00–4.00), 3: competent (4.00–1.50), 4: moderate (1.50–0.00) and 5: incompetent (<0.00) [283]

To substantiate our deductions in characterization and verify the success of our strategy used in membrane design, we next evaluated the separation performance of the CMSMs under mixture gas permeation conditions. The CO₂ permeability and its corresponding selectivity of unfilled Matrimid[®] precursor membrane were reported as 11.0 barrers and 36.7, respectively, as listed in Table 6-2. The value was comparable with data reported in the literature (10.2 barrers and 33.6 selectivity) which was measured under similar conditions of 40 °C and 1 bar pressure using CO₂:CH₄ (50:50) mixture gas [240]. Upon carbonization, the unfilled Matrimid[®] CMSM reported an enhanced CO₂ permeability of 29 barrers and CO₂/CH₄ selectivity of 49.2 (Table 6-2). As previously mentioned in our interpretation of the d-spacing in the Matrimid[®] matrix (Figure 6-6), this enhancement in separation performance can be owing to the increase in the fractional free volume brought by the thermal rearrangement of the matrix during carbonization. Without carbonization, enhancement in separation performances can also be achieved by incorporating bulk and H-zeolite 5A fillers into polymeric Matrimid[®] membranes. While the outcome of this standalone mixed-matrix approach was positive, the obtainable enhancement in performance was limited and insufficient for achieving our goal of surpassing the 2008 Robeson upper bound limit [123].

For this reason, we have adopted to combine a mixed-matrix approach with a membrane carbonization strategy. The incorporation of bulk and H-zeolite 5A into the carbon matrix has seen the CO₂ permeability of the mixed-matrix CMSMs demonstrating a different extent of increment with increasing filler loading. With bulk zeolite 5A, the CO₂

permeability was enhanced above 3000% as filler loading increased from 10 to 30 wt%. With H-zeolite 5A, we observed an exceptional two orders of magnitude enhancement, reaching an extraordinary high CO₂ permeability of 2450 barrers (Table 6-2). To determine the origin of the enhancement, we examined the CO₂/CH₄ selectivity of these membranes. Firstly, a decrease in the selectivity of about ~48% was observed with 10 wt% loading of each type of zeolite 5A. This was followed by another ~20% decrease in the selectivity as the loading increased to 20 wt% before stabilizing considerably at 30 wt% (Table 6-2). These results corroborated our deductions in FE-SEM characterization, which suggested that narrow nanogaps continued to remain at the carbon/zeolite interfaces after carbonization, leading to a decrease in the selectivity as loading increased. The impact caused by these nanogaps, however, has become weak as the loading entered the region of 20 to 30 wt%. At a loading of 30 wt%, the pore size effect arising from zeolite 5A became apparent. Matrimid[®]/H-zeolite 5A-30% was able to maintain an almost comparable selectivity as Matrimid[®]/Zeolite 5A-30% (Table 6-2), suggesting that the presence of mesopores in the filler exerted a nominal impact on the selectivity of the CMSMs. More importantly, the mesopores served with great capacity as transport pathways supplementary to the intrinsic micropores of zeolite 5A. This was evidenced by the 1.6-folds strong enhancement in the CO₂ permeability as we compared the performance of Matrimid[®]/Zeolite 5A-30% to Matrimid[®]/H-zeolite 5A-30% (Table 6-2).

According to the results above, the CO₂ permeability enhanced significantly with the increasing of hierarchical zeolite loading. However, we did not choose to make the membranes with higher loading because of the negative effects may occur. In general, 30%

loading of the filler materials is already much higher than the average loading of other mixed-matrix membranes where the loading is basically less than 10 wt%. If the loading is very high, the particle aggregation and “sieve-in-a-cage” effect would become more severe inside the membrane. Besides, the choice of much high loading is not a cost-effective strategy, especially in practical applications. On the other hand, although the CO₂ permeability dramatically enhanced with increasing zeolite loading, there was still a loss in its corresponding selectivity in this work. As expected, much significant loss of CO₂/CH₄ selectivity may be performed in mixed-matrix carbon molecular sieve membranes. Therefore, the loading higher than 30% was not evaluated in this work.

6.3.4. Benchmarking performance to Robeson upper bound and F_{index}

Figure 6-8. (a) Robeson plot comparing CO₂ permeabilities and CO₂/CH₄ selectivities of carbon molecular sieve membranes used in this work and those reported elsewhere. Matrimid[®]-1: 25 °C, 1 bar, CO₂/CH₄=10/90 [165]; Matrimid[®]-2: 35 °C, 10 bar, pure gas [288]; Matrimid[®]-3: 40 °C, pure gas [162]; Kapton[®]-1: 25 °C, 1 bar, CO₂/CH₄=10/90 [165]; PEI (polyetherimide): 25 °C, 2 bar, pure gas [289]; PFR (phenol-formaldehyde resin): 20 °C, pure gas [290]; Phenolic resin: 20 °C, pure gas [170]; 6FDA/BPDA-DAM:

22 °C [291]; BPDA-pPDA: 25 °C, pure gas [292]. (b) The separation performances reported in this study, showing clearly a gentler decrease in the slope (dotted line), which suggests a trade-off of less intensity. The F_{index} values of our mixed-matrix carbon molecular sieve membranes are included here. It is interesting to note that as the membrane performances approach or exceed the upper bound limit, the F_{index} values increase accordingly.

Up to now, our analysis appeared to demonstrate the success of our strategy in using filler design optimization alongside membrane carbonization to realize high CO₂/CH₄ separation performance. To attest this claim, we carried out benchmarking analysis to evaluate the positioning of our membrane performance, as illustrated in Figure 6-8 (a). As observed in the literature, it is generally challenging for current performance of CMSMs to surpass the 2008 upper bound limit except for one that was derived from an in-house made 6FDA/BPDA-DAM polymer, which is costly to synthesize and has little commercial value. On the other hand, in this work, the Achilles heel of our mixed-matrix CMSMs was in the permeability-selectivity trade-off as presence of interfacial nanogaps tended to reduce the membrane selectivity up to a filler loading of 20 wt%. This impact, however, diminished at 30 wt% filler loading. At this specific loading, the positive effect from the mesopores in H-zeolite 5A emerged and drove the performance of Matrimid[®]/H-zeolite 5A–30% to hit or slightly surpass the 2008 upper bound limit (Figure 6-8 (a)). In this regard, it was important to emphasize that, while our strategy was unable to completely reverse the trade-off phenomenon, the strong enhancement in CO₂ permeability by 30 wt% loading of H-zeolite 5A in the carbon matrix was able to alleviate

the intensity of the trade-off as exemplified by a gentler decrease in the performance of the CMSMs shown in the Robeson plot (dotted line in Figure 6-8 (b)). Such an assessment would more accurately reflect the impact resulting from our strategy.

We also contemplated with the F_{index} as a means to measure the effectiveness of our H-zeolite 5A when loaded at 30 wt% in the carbon matrix. The F_{index} is an empirical rating metric, which was recently developed by our group to evaluate the effectiveness of fillers [283]. By taking into consideration both gas permeability and selectivity enhancement, the F_{index} is aimed at providing a single rating that can accurately measure the effectiveness of the fillers irrespective of the matrix. The formula (Equation 6-1) has an extra weighting (designated as η) tagged on the selectivity enhancement term to emphasize the importance of upholding the selectivity of mixed-matrix membranes as well as to credit fillers that are capable of enhancing membrane selectivity with a higher F_{index} value. In view of this, we calculated the F_{index} value of all mixed-matrix CMSMs. Generally, the F_{index} value increased as membrane performance approach the Robeson upper bound limit. When the performance of Matrimid[®]/H-zeolite 5A-30% exceeded the upper bound, the F_{index} gave the highest value at 1.97 (Fig. 6-8 (b)). This suggested that, at 30 wt% loading, the H-zeolite 5A was effective in elevating the performance of the CMSM despite experiencing a significant drop in the CO₂/CH₄ selectivity (Table 6-2). Based on our statistical analysis of 470 fillers, a F_{index} value of 1.97 would make H-zeolite 5A at 30 wt% loading eligible for the “competent” filler label while the bulk zeolite 5A or H-zeolite 5A at lower loadings could only settle for an inferior “moderate” label (Table 6-2) [283]. Accordingly, the two orders of magnitude enhancement in the CO₂

permeability, enabled only by H-zeolite 5A at 30 wt% loading, overwhelmingly nullify the negative impact brought by the decrease in selectivity and compellingly pushed the F_{index} value into range of “competent” filler label.

6.4. Conclusions

In this study, we have successfully demonstrated the strategy of filler design optimization with membrane carbonization to realize mixed-matrix carbon molecular sieve membranes incorporating hierarchical zeolite 5A filler. The hierarchical filler not only possessed intrinsic micropores but also mesopores of around 8 nm to offer additional transport pathways to facilitate CO₂ diffusion through the carbon matrix of the membranes. For these reasons, a strong enhancement in the CO₂ permeability of two orders of magnitude was observed when 30 wt% loading of the hierarchical zeolite 5A filler was incorporated into the carbon molecular sieve membrane. Despite a decrease in the CO₂/CH₄ selectivity due to the presence of nanogaps at the filler/matrix interfaces, the mixed-matrix carbon molecular sieve membrane (Matrimid[®]/H-zeolite 5A–30%) was still able to surpass the 2008 Robeson upper bound limit. Using a different benchmark, the hierarchical zeolite 5A filler at 30 wt% loading was also deemed “competent” based upon our analysis of a recently developed filler enhancement index. Taken altogether, our strategy was both more cost-effective and less sophisticated in approach. In this regard, our mixed-matrix carbon molecular sieve membranes offered greater competitive advantages when compared to other CMSMs such as those derived from high-permeable polymers like 6FDA-based and PIM-1 polymers. Again, this demonstrates that our strategy holds promise in realizing high-performance membranes for CO₂/CH₄ separation.

6.5. Declaration

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CHAPTER 7

Future work

7.1. Introduction

In recent years, air separation processes have portrayed a pivotal role in numerous industrial applications, namely production of primary metals (non-ferrous metals or steel), fuel combustion process, gasification, petrochemical production, glass and concrete production. For instance, oxygen (O_2) with high purity is preferred in oxy-fuel combustion process as it is capable to provide a higher energy efficiency as compared to compressed air, as nitrogen (N_2) is typically acting as non-reactive gas which does not actively involved in the combustion process [293]. Besides, O_2 is heavily utilized in lowering the carbon content in an iron-steel alloy, leading to the formation of low-carbon steel [294]. On the other hand, N_2 which possesses highly inert properties ensures its capability to act as a shielding gas during the degassing of molten metals, thus preventing any plausible presence of oxidizing components (e.g. oxygen and moisture) which can lead to the oxidation of metals at elevated temperature [295]. N_2 is also feasible to be utilized in food preservation industries by replacing oxygen during the food packing process, leading to a drastic reduction of food waste [296].

In general, several methodologies have been developed for effective air separation process. Conventional cryogenic air separation process using distillation has been actively developed by major industrial gas companies, which showcased its capability to develop

large-scale O₂ production [297-299]. On the other hand, the utilization of pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA) is also feasible in generating O₂ with high purity via the selection of appropriate adsorbents that allow selective adsorption of O₂ [300-302]. Nevertheless, these technologies have suffered substantial limitations in terms of the high capital and operating cost as well as high energy consumption, which are required in maintaining its operating conditions for cryogenic distillation process as well as regeneration of adsorbents in PSA and VPSA process. Hence, membrane-based separation process has been considered as a promising alternative for gas separation process in view of its cost effectiveness, simplicity and small plant footprint.

However, the Robeson upper bound is constructed to demonstrate the limit of gas separation performance in polymeric membrane. Herein, researchers have investigated several approaches to thrive the performance towards the upper bound limit. However, it somehow remains challenging to surpass the Robeson upper bound as the performance of gas separation is still govern by the intrinsic nature of polymers. Interestingly, carbonization of polymer precursors has become one of the feasible methods to further develop high-performance membranes [154, 303, 304]. Apart from pyrolysis conditions, it has also been well-observed that the performance of CMSMs is strongly dependent on the choice of polymers. For example, membranes that are derived from highly permeable polymers tend to own extraordinary gas separation performance. However, the requirement of harsh synthesis conditions together with the high cost generally hampers these polymers towards industrial application [305-307].

Therefore, we have utilized an approach which involved carbonization of mixed-matrix membranes, where the polymer precursors with the incorporation of microporous fillers were prepared. The polymer precursor that was selected in this work was Matrimid[®] 5218, due to its commercial availability as compared to other glassy polymers (e.g. 6FDA-based polymer [112]) where sophisticated synthesis procedures were required. Besides, it has been observed that some materials such as zeolites, mesoporous carbon, SBA-15 and MCM-48 have been incorporated as the fillers for the fabrication of CMSMs [274, 308-311]. Thus, in this work, zeolite 5A which possesses the pore size of 4.8 Å [312] is an attractive candidate for effective transport of O₂ (3.46 Å) over N₂ (3.64 Å) [130] molecules, considering the application of zeolite 5A in chromatographic column for O₂/N₂ separation [313]. It has been observed that the gas separation performance of MMMs containing zeolite 5A can be tuned accordingly with the variation of particle sizes [314]. Besides, it was suggested that the creation of hierarchical microporous-mesoporous domains has become an attractive alternative considering the possibility of limited accessibility of gas molecules to small micropore channels, leading to a poor adsorption kinetics [315, 316].

In this study, we have developed CMSMs that were derived from Matrimid[®] 5218 precursors, where zeolite 5A fillers with different physical properties (300 nm, 3 µm and 6 µm (mesoporous)) were incorporated into the polymer matrix. Based on the gas permeation results, it can be observed that the introduction of particles with smaller size was feasible in improving the overall O₂ permeability as compared to larger particle size,

in view of its large accessible surface area. Furthermore, the addition of hierarchical zeolite 5A was feasible in achieving an extraordinary enhancement in O₂ permeability, with a marginal loss of O₂/N₂ selectivity, indicating that the creation of mesoporosity was effective to provide additional gas transport pathways for the diffusion transport of gas molecules. By applying this approach, the performance of CMSMs was reported to be closer to the Robeson upper bound limit (2008).

7.2. Experimental

7.2.1. Synthesis

Zeolite LTA (3 μm and hierarchical) was synthesized using the same methods as described in Chapter 6. Zeolite LTA (300 nm) was synthesized using the technique described in the literature [317]. The precursor solution was prepared with a molar ratio of $1 \text{ Al}_2\text{O}_3/6.12 \text{ SiO}_2/x \text{ TMAOH}/y \text{ NaOH}/3450 \text{ H}_2\text{O}$, and the $(x+y)$ and (x/y) value was fixed at 14.66 and 45, respectively. In this standard synthesis procedure, a precursor solution was prepared in a polypropylene (PP) bottle by dissolving NaOH and TMAOH in DI water. Next, the solution was divided into two different bottles with equal volumes. Subsequently, aluminium isopropoxide was dissolved in bottle 1, and colloidal silica was added to bottle 2. When the two solutions were fully homogeneous (transparent), Solution 2 was immediately poured into Solution 1, and the mixture was vigorously stirred for 72 h at room temperature. Once the reaction completed, the mixture solution was transferred into a Teflon-lined autoclave and thermally treated at 100 $^\circ\text{C}$ for 24 h in a tumbling oven. Finally, the final product was collected using repetitive centrifugation with copious amount of DI water and dried at 100 $^\circ\text{C}$ overnight in a convection oven. Subsequently, ion exchange was conducted to convert the zeolite 4A (Na^+) to zeolite 5A (Ca^{2+}) for all zeolite types (300 nm, 3 μm and hierarchical), as described in Chapter 6.

For the synthesis of polymeric membrane, a dope solution was made by dissolving dry Matrimid[®] powder in chloroform, where the concentration of the polymer solution was set at around 15 wt%. On the other hand, the dope solution of MMMs was prepared according to the following approach. The zeolites were first grounded before dispersing in

chloroform solution. To reduce the aggregation and improve the overall homogeneity of zeolites in the dope solution, a sonication horn (Qsonica, Q125) was utilized. Subsequently, dry Matrimid[®] powder was added into previous solution, followed by vigorous stirring until it was completely dissolved. Next, the dope solution was casted onto a glass plate by using the doctor blade, where the casting process was conducted in a transparent plastic bag which was full with chloroform vapor for slowing down the solvent evaporation. The flat sheet precursor membranes were annealed at 180 °C in a vacuum overnight to remove the solvent remaining in the membranes. Subsequently, membrane carbonization process was conducted to develop carbon molecular sieve membranes in a tube furnace (Carbolite GERO, CTF 12/100/900). Prior to the carbonization process, Ar gas was purged into the quartz tube (> 1 h) to remove residual air and moisture that can be potentially presented inside the tube. Then, the membrane precursors were carbonized via a two-step ramping procedure (380 °C for 30 min with a heating rate of 2 °C/min and 550 °C for 2 h with a heating rate of 0.5 °C/min). The carbonized membranes were allowed to be naturally cooled down until room temperature after the pyrolysis process completed.

7.2.2. Characterizations

The characterization methods were operated by following the similar procedures as discussed in Chapter 6. The morphologies of the zeolites and the cross-section morphologies of the carbon molecular sieve membranes were observed using field emission-scanning electron microscopy (FE-SEM, JSM6701 JOEL). X-ray diffraction (XRD) patterns of the zeolites and carbon molecular sieve membranes were measured

using a Bruker D2 phaser diffractometer with a Cu-K α source (1.5418 Å) in the 2θ range of 5-50 °. The thermal stabilities of the zeolites and membrane precursors were determined via a thermogravimetric/differential thermal analyzer (TGA, SDT Q600) within a temperature range of 40 to 900 °C. The measurements were conducted under pure N₂ purging at 100 ml/min, with a heating rate of 10 °C/min. N₂ physisorption measurement (Autosorb 6B, Quantachrome) of zeolites was conducted at -196 °C (77 K) under the relative pressure (P/P_0) range of 0-1 bar to investigate the porosity properties of the zeolites. The zeolites were activated at 250 °C for 24 h under a high vacuum prior to the measurement. The O₂ and N₂ adsorption isotherms of the zeolites were measured using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome) at 35 °C in the pressure range of 0-1 bar after the activation conducted under the same activation conditions mentioned above.

Mixture gas permeation measurement was operated via a constant pressure-variable volume permeation system (GTR Tec Corporation). The membrane samples were mounted inside the permeation cell, where the temperature was maintained at 35 °C. Throughout the measurement, continuous flow of He and O₂/N₂ mixture gases on the upstream side were supplied under the pressure of 1 bar. At a periodic time-interval, the gases that were permeated through the membrane (O₂ and N₂) were swept by He, where the respective concentration was tested and calculated using gas chromatography. To make sure the reproducibility of the permeation results, the measurement was repeated for at least three times

7.3. Preliminary results

Figure 7-1. FE-SEM morphologies of (a) zeolite 5A (300 nm), (b) zeolite 5A (3 μm), and (c) hierarchical zeolite 5A; (d) X-ray diffraction (XRD) patterns of three zeolites.

The overall morphologies of all of the zeolites synthesized in this study were demonstrated in Figures 7-1 (a), (b), and (c). In general, zeolite 5A has a uniform structural topology; the typical cubic LTA crystals were illustrated in Figures 7-1 (a) and (b) where TPOAC was not added to the precursor gel during the synthesis. In contrast, the overall shape of the particle was converted to a spherical shape (from a cubical shape) when TPOAC was incorporated into the reagent mixture, as shown in Figures 7-1 (c). According to the FE-SEM images, the particle sizes of the zeolites were estimated to be around 300 nm, 3 μm, and 6 μm respectively. In addition, the successful formation of all

the zeolites was verified using XRD, as exhibited in Figure 7-1 (d). The characteristic peaks and patterns of zeolite 5A were well-matched to those of the typical zeolite LTA framework reported in the literature [280]. In particular, the formation of hierarchical structure (containing both mesoporous and microporous domains) generally resulted in a clear decrease in the peak intensity, as smaller fractions of zeolite domains can be expected.

Table 7-1. O₂ and N₂ gas permeation results tested at 35 °C and 1 bar feed pressure (O₂/N₂=21/79) for CMSMs derived from pure Matrimid® 5218 and mixed-matrix membranes.

Membrane	O ₂ permeability ^a (barrer)	O ₂ /N ₂ selectivity ^b
Matrimid® 5218	4.8 ± 0.2	5.64 ± 0.13
Matrimid® 5218/Zeolite 5A-300 nm-10%	148 ± 8	4.11 ± 0.16
Matrimid® 5218/Zeolite 5A-300 nm-20%	160 ± 6	4.07 ± 0.10
Matrimid® 5218/Zeolite 5A-3 µm-10%	84 ± 4	4.38 ± 0.16
Matrimid® 5218/Zeolite 5A-3 µm -20%	142 ± 3	4.22 ± 0.08
Matrimid® 5218/H-zeolite 5A-10%	151 ± 9	4.36 ± 0.16
Matrimid® 5218/H-zeolite 5A-20%	185 ± 6	3.96 ± 0.04

^a1 barrer = 10⁻¹⁰ cm³_{STP} · cm/cm² · s · cmHg

^bRatio of O₂ permeability over N₂ permeability

After CMSMs were derived from zeolite-based mixed-matrix membranes, O₂/N₂ gas separation of CMSMs was evaluated at 35 °C and 1 bar under mixture gas permeation process, as summarized in Table 7-1. It can be observed that pure Matrimid[®] CMSM demonstrated an enhancement in O₂ permeability (4.8 barrers) with marginal dip in O₂/N₂ selectivity (5.64), by comparing the results of the pure Matrimid[®] precursor membrane [318]. Besides, the O₂/N₂ separation results of pure Matrimid[®] CMSM were comparable with the value reported, where O₂ permeability was 5.0 barrers and its selectivity over N₂ was 6.00 [165]. With this, the gas permeation analysis of CMSMs with the incorporation of zeolite 5A (300 nm, 3 μm) and H-zeolite 5A (6 μm) was conducted. According to the gas permeation results, it can be observed that the incorporation of both zeolites 5A (300 nm, 3 μm) and H-zeolite 5A into the carbon molecular sieve membranes were very effective in improving the O₂ permeability. Based on the comparison in terms of the particle size, smaller particles (300 nm) demonstrated a clearer enhancement as compared to larger particle size (3 μm), based on the same particle loadings. This was attributed to an increase in the interfacial area for particles with smaller particle size. Nonetheless, with the incorporation of H-zeolite 5A, it was observed that an exceptional enhancement in O₂ permeability was achieved, reaching a high O₂ permeability of 185 barrers with only slight decrease in O₂/N₂ selectivity. It should be well noted that the overall accessible surface area for H-zeolite 5A was the lowest among the three zeolites. In view of such behavior, the creation of mesopores has possibly served as the most probable transport pathways for rapid O₂ diffusion, supplementary to the presence of intrinsic micropores in zeolite 5A. This can be clearly evidenced by the exceptional enhancement in O₂

permeability (37.5-folds) for Matrimid[®]/H-zeolite 5A-20% as compared to its nascent membrane. Such performance was attractive as compared to the utilization of other zeolites (zeolite 5A-300 nm and zeolite 5A-3 μm) under the same particle loading (20%), with the enhancement of 32.3-folds and 28.6-folds, respectively. Although O_2/N_2 selectivity was slightly decreased for Matrimid[®]/H-zeolite 5A, the overall O_2/N_2 selectivity was still maintained comparable across zeolites with different particle size.

Figure 7-2. Robeson plot comparing O_2 permeabilities and O_2/N_2 selectivities of carbon molecular sieve membranes used in this work.

To investigate the success of our strategy in utilizing the optimal design of the filler properties (particle size and pore size) in carbon molecular sieve membranes for the realization of significantly improved O_2/N_2 separation performance, the gas permeation results were compared and plotted against upper bound limit for O_2/N_2 separation. Based on the comparison, it was undeniable that it was generally challenging for current performance of CMSMs to surpass the 2008 upper bound limit [319], as demonstrated in Figure 7-2. Still, it can be foreseen that this approach was feasible and effective in

improving the overall O_2/N_2 separation performance drastically as compared to the CMSM of pure Matrimid[®] membrane. The plausible reason was that the overall performance was generally difficult to overcome the upper bound limit as the presence of interfacial nanogaps would give rise to the reduction of the O_2/N_2 selectivity. Besides, the nature of zeolites which tended to absorb N_2 more preferentially as compared to O_2 was also possibly attributed to such behavior of decreased selectivity. In this regard, it was important to emphasize that, while our strategy was unable to completely reverse the trade-off phenomenon, the extraordinary enhancement in O_2 permeability by the incorporation of H-zeolite 5A in CMSMs has been capable to alleviate the shortcoming of the trade-off relationship as exemplified by a gentler decrease in the selectivity. Clearly, this approach drastically improved the overall O_2/N_2 separation performance relative to the pure CMSM. This implied that a performance beyond the upper bound can potentially be realized by using a different polymer precursor that gave higher O_2/N_2 selectivity instead of the inexpensive commercial polymer used in this study. However, using such precursor would inevitably increase the cost of membrane production.

7.4. Conclusions

In this work, the incorporation of zeolite 5A with the variation of particle and pore size (300 nm, 3 μm and hierarchical zeolite 5A) in pure Matrimid[®] membrane has been successfully constructed. It has been observed that smaller particle size was more feasible in improving the O_2 permeability as it resulted from the increase in the overall accessible surface area. Besides, H-zeolite 5A, which was built up based on hierarchical micropore and mesopores, generally offered additional gas transport pathways for effective O_2 diffusion through the CMSMs, leading to an extraordinary enhancement in O_2 permeability. Nevertheless, despite slight dip in O_2/N_2 selectivity which was generated due to the presence of interfacial nanogaps together with the nature of zeolite materials that preferentially adsorbed N_2 in view of its higher polarizability, the overall O_2/N_2 separation ability of MMMs-based CMSMs demonstrated exceptional improvement as compared to nascent pure Matrimid[®] CMSM. As a whole, such strategy was generally feasible and effective in developing high-performance membranes for O_2/N_2 separation.

CHAPTER 8

Conclusions

8.1. Overview

As a whole, microporous materials, which possess tunable surface and pore properties, have generated intensive interests in the field of gas adsorption and separation process. In this work, MOFs and zeolites have been applied to improve CO₂ separation. In general, Ni-MOF-74 demonstrates high accessible surface area due to unsaturated open metal sites, and extraordinarily high CO₂ uptake, particularly at low partial pressures. What's more, downsizing Ni-MOF-74 to nanocrystal formation has made it possible to create polymer-based composite materials for various applications, including mixed-matrix membranes for molecular separation. Also, the nanocrystalline form of Ni-MOF-74 could possibly be used as building blocks for the development of novel nanocomposite materials with a 3-D architecture. In addition, the use of ZIF-8 in polymeric membrane has been widely investigated for gas separation because of its easy synthesis, tunable pore size, together with high thermal, mechanical, and chemical stabilities. Besides, substantial studies have been reported that both CO₂ and CH₄ permeabilities could be increased significantly without marginal change in CO₂/CH₄ selectivity upon introduction of ZIF-8 in a mixed-matrix membrane. Besides, it is facile and effective to tune the pore structure of zeolite 5A with the aid of pore expanding agent, leading to the formation of hierarchical structure with both mesopores and micropores domains. In comparison with bulk zeolite 5A with only micropore domain, the formation of mesopores in hierarchical

zeolite 5A creates additional open channels or highways that allow effective CO₂ transport, where the remaining micropores still guarantee selective ability for CO₂/CH₄ separation.

On the other hand, carbon nanomaterials, appear to be alternative and promising candidates for gas separation process. As the most popular carbon nanomaterial, GO is a 2-D lattice of carbon atoms that contains hydroxyl, epoxy, and carboxylic groups, and its atoms are linked by strong covalent bonds. In recent years, GO has been used in several applications, particularly in gas separation, owing to its ultrahigh aspect ratio, tunable surface functionality, as well as good thermal and mechanical properties. The use of GO as a component in MOF composites has drawn significant attention as effective creation of 3-D architecture can be conducted. In this work, results reported that MOF/GO composite using Ni-MOF-74 showed larger surface area than that of pristine MOF. Furthermore, studies have shown that GO nanostacks are feasible in improving mixture gas selectivity (e.g. CO₂/CH₄) as a result of molecular sieving effect through the interlayer channels, which are decorated with various polar groups with favorable affinity towards CO₂. In addition, microporous CMSMs could be fabricated from MMMs via carbonization process at high temperature and inert atmosphere. The fractional free volume and chain's flexibility can be well-adjusted during the carbonization process in order to achieve a well-optimized cavities and constriction that can be feasible to display discrimination of gas molecules in terms of kinetic diameter.

As expected, advanced CO₂ adsorption and separation were successfully fulfilled in this

study. Firstly, owing to the improved surface area and porosity, the NiDOBDC/GO composite with 10 wt% GO loading possessed the highest CO₂ and H₂ storage value up to 10.5 mmol/g and 1.39 mmol/g (at 25 °C and 1 bar), respectively, which represented 12% and 50% improvement, respectively. Besides, NiDOBDC/GO composite was utilized into Matrimid[®] matrix to evaluate the improvement of CO₂/CH₄ separation performance. Interestingly, a high CO₂/CH₄ selectivity (58.3) was reported for the Matrimid[®]/Composite-20% membrane, which was 59% higher than that of the nascent Matrimid[®] membrane, where noticeable loss in CO₂ permeability was not observed. In addition, the overall mechanical stabilities of the Matrimid[®]/Composite membranes were unaffected, due to the presence of GO sheets, which possessed surface functional groups that can perform preferential interaction with the polymer chains.

Apart from the effectiveness of nanocomposite, we also would like to understand the roles of MOF and GO which were separately incorporated in polymer matrix on gas separation. It was observed that the use of GO as the secondary filler in a mixed-matrix membrane proved to be feasible and effective in overcoming the drawbacks of ZIF-8 filler which could improve the permeability of all gases due to its open structure. The combination of two fillers together in the polymer matrix allowed an improvement in both CO₂ permeability as well as CO₂/CH₄ selectivity by 60% and 28%, respectively. In comparison, the incorporation of ZIF-8 or GO alone could increase only the CO₂ permeability or CO₂/CH₄ selectivity, respectively. Furthermore, by incorporating GO and ZIF-8 together in polymer matrix, the mechanical strength of the OPDA-TMPDA membrane increased, whereas the use of ZIF-8 filler alone decreased the mechanical

strength. However, it was generally challenging to further improve both gas permeability and selectivity in simultaneous manner, by relying solely on polymeric membranes ascribing to the trade-off effect caused by solution-diffusion mechanism. Hence, membrane carbonization process is considered to be a promising approach to fabricate CMSMs with optimized pore sizes and cavities, which improve the gas separation performance, with the possibility of surpassing the upper bound limit. In this case, a strong enhancement in the CO₂ permeability by two orders of magnitude was observed when 30 wt% loading of the hierarchical zeolite 5A filler was incorporated into the carbon molecular sieve membrane. Despite a decrease in the CO₂/CH₄ selectivity due to the presence of nanogaps at the filler/matrix interface, the mixed-matrix carbon molecular sieve membrane (Matrimid[®]/H-zeolite 5A–30%) was still able to surpass the 2008 Robeson upper bound limit.

In summary, the CO₂ adsorption and separation performance were compared and evaluated for all products in this work. As illustrated in Table 8-1, the CO₂ adsorption capacity of NiDOBDC/GO-10% composite showed a significant increment compared to NiDOBDC, where the increase was much better than those of membranes. Besides, it was clear that the MMM with NiDOBDC/GO composite was effective to improve CO₂/CH₄ selectivity without the loss of CO₂ permeability, whereas MMM with ZIF-8 and GO could significantly enhance both CO₂ permeability and CO₂/CH₄ selectivity. It is noteworthy that an excellent membrane for gas separation should have both high permeability and selectivity without trade-off effect. In a word, the strategy of incorporating both ZIF-8 and GO was more favourable to optimize CO₂/CH₄ separation

than the introduction of NiDOBDC/GO composite in MMM. Besides, considering the synthesis procedures, MMM with binary fillers seems more stable and easy as there is no preparation of the composite is needed. Nonetheless, its resulting separation performance still can not beat the upper limit of CO₂/CH₄ separation. On the other hand, although the CO₂/CH₄ selectivity declined with the incorporation of hierarchical zeolite 5A, it was surprisingly observed that its CO₂ permeability underwent a huge increase in the mixed-matrix carbon molecular sieve membrane. As a result, the performance of CO₂/CH₄ separation in mixed-matrix CMSM was successfully surpassed the Robeson upper bound. Unfortunately, comparing with other two membranes, the synthesis of CMSM was more difficult because of the thermal treatment under high temperature as well as the weak mechanical strength.

Table 8-1. Comparison of the adsorbents and all membrane types.

Membranes	Synthesis	Test conditions	CO ₂ uptake (mmol/g)	Enh. (%)	P _(CO₂) (barrer)	Enh. (%)	α (CO ₂ /CH ₄)	Enh. (%)	Upper bound
NiDOBDC/GO-10% composite	Easy & moisture sensitive	25°C, 1 bar	5.01	23.7	N.A.	N.A.	N.A.	N.A.	N.A.
Matrimid/Composite -20%	Moisture sensitive	25°C, 1 bar	0.56	1.4	9.9	0	58.3	59	No
ODPA-TMPDA/10% ZIF+5% GO	Easy & stable	25°C, 1 bar	1.13	-13.1	145.0	60	41.0	28	No
Matrimid/H-zeolite 5A-30%	High temperature required & brittle	35°C, 1 bar	1.32	3.1	2450.0	22172	19.3	-47	Yes

Note: Enh.: Enhancement.

8.2. Challenges

In conclusion, microporous materials have shown excellent adsorption capability towards CO_2 and H_2 , owing to their ultrahigh surface areas and porosities. However, some drawbacks, which make it difficult to achieve the optimized performance, still exist in porous materials, namely nanoparticle aggregation and material stability. It is widely known that aggregation is commonly occurred in porous nanoparticles due to their small size effect. In general, substantial amount of positive or negative charge was accumulated on the surface once the particles were downsized into nanoscale, thus making nanoparticles to be extremely unstable. Besides, the van der Waals force between particles is much stronger than the particle gravity. As a result, nanoparticles tend to aggregate so as to remain in stable form. On the other hand, in the typical CO_2 adsorption process, such as post-combustion CO_2 capture, water vapor is existed in flue gas, thus the effect of water vapor on the overall CO_2 adsorption cannot be avoided. Therefore, the stability of porous materials in humid condition is an important criteria that needs to be considered for the utilization of porous materials in practical gas adsorption process [320]. For instance, MOF-74 shows extraordinarily high CO_2 and H_2 adsorption capabilities due to the presence of unsaturated open metal sites. However, the presence of water vapor would significantly decrease the gas adsorption capacity and even destroy the crystal structures of the MOF-74 family, which limits their practical use [321].

For the case of MMMs which have been intensively investigated, impressive improvement in terms of advancing membrane separation performance has been successfully achieved with the aid of functional fillers. Nonetheless, the polymer matrix

still plays the predominant role in gas separation performance. In other words, despite it is feasible for the filler materials to perform extraordinarily well, the intrinsic nature of polymer may not be changed so dramatically, especially for the polymers with low gas permeability or gas selectivity. Besides, polymers with intrinsic high gas separation abilities are mostly synthesized in-house by using more complex chemistries under harsher conditions (e.g. monomer purification, inert environment), thus leading to an escalated production cost. For example, the successful preparation of 6FDA-TMPDA polyimide polymer, requires additional precautionary steps during the synthesis, as described in our previous work [112]. Firstly, the purification processes at high temperatures in a high vacuum are crucial for both 6FDA and TMPDA monomers before the reaction. Secondly, all the synthesis procedures of 6FDA-TMPDA must be conducted under inert gas atmosphere to prevent degradation in quality due to the existence of air and moisture. Thirdly, complete removal of residual solvent must be carried out to get high-quality final product.

As a promising solution to further improve gas separation of polymer-based membranes, carbonization process is proven to be a feasible and effective approach which could significantly tune the structure of the polymer chain or disrupt polymer's rigidity. Unfortunately, it is well-known that a major disadvantage that hinders the practical applications of CMSMs is their poor mechanical stability. Moreover, it remains challenging to test the mechanical properties of the CMSMs due to their brittleness and weakness. Therefore, the scalability for fabricating CMSMs in a large quantity seems to be of uphill struggle at current stage. In addition, pyrolysis is the most important process

of CMSMs derived from polymer precursors which is strongly influenced by atmosphere (Ar, He, N₂, vacuum, CO₂), thermal soak time, heating rate (1-13 °C/min) and pyrolysis temperature (500-1000 °C) [157]. Thus, it is generally difficult to optimize the final membrane performance as there are too many factors which can affect the overall pyrolysis condition. As an example, in order to find the optimized preparation conditions for CMSMs, the pyrolysis temperature should be chosen at different carbonization temperatures by maintaining the same thermal soak time, heating rate and inert gas. Once pyrolysis temperature has been settled, other variations also need to be determined. As a whole, it is important to take extra control on the overall synthesis procedures so as to achieve extraordinary gas separation performance.

8.3. Perspectives

Apart from CO₂/CH₄ separation, MMMs and CMSMs are also feasible and effective to be utilized for air separation (O₂/N₂), hydrogen separation (H₂/CO₂, H₂/CH₄) and olefin/paraffin separation (C₂H₄/C₂H₆, C₃H₆/C₃H₈) [322, 323]. For example, carbon molecular sieve membranes exhibit exceptional O₂/N₂ separation performance which could successfully surpass the Robeson upper bound, as depicted in Figure 8-1 (a). Similarly in Figure 8-1 (b), the separation of C₂H₄/C₂H₆ in the membranes that have been reported thus far has been feasible in surpassing the upper bound limit, especially for CMSMs with optimized microporous structures. Moreover, the applications of membrane-based technology have been further expanded to vapor/gas and vapor/vapor separation. As listed in Table 8-2, extraordinary high permeability of water vapor together with H₂O/N₂ selectivity was feasible to be acquired with the utilization of high permeable

polymers. As an example, H₂O permeability and H₂O/N₂ selectivity of 1000_{PEO}56_{PBT}44 (PEO: Poly(ethylene oxide), PBT: Polybutylene terephthalate) block copolymers could be feasible in reaching as high as 85500 barrers and 40500, respectively. Also, the water vapor permeability proved to be strongly dependent on the feed pressure, where an increase of the pressure would lead to the reduction of total water vapor flux. [324] In addition, a PIM-1/PDMS blend membrane, which was fabricated by Zhang et al. was proven to own excellent flux of 1425 g m⁻² h⁻¹ as well as n-butanol/water selectivity of 30.7, respectively [325].

Figure 8-1. (a) O₂/N₂ separation performance of current membranes [326]; C₂H₄/C₂H₆ separation performance of polymeric membranes, ZIF-8 membranes and CMSMs [327].

Table 8-2. Water vapor and N₂ permeabilities as well as H₂O/N₂ selectivity of polymeric membranes reported in the literature [324].

Polymer	Abbreviation	H ₂ O Permeability (Barrer)	Selectivity (H ₂ O/N ₂)
Ethyl cellulose	EC	20000	6061
Cellulose acetate	CA	6000	24000
Natural rubber	NR	2600	299
1000 _{PEO} 56 _{PBT} 44	PEO-PBT	85500	40500
Polyacrylonitrile	PAN	300	1875000
Polyamide 6 (Nylon 6)	PA-6	275	11000
Polycarbonate	PC	1400	4667
Polydimethylsiloxane	PDMS	40000	143
Polyethersulfone	PES	2620	10480
Polyethylene	PE	12	6
Polyimide (Kapton)	PI	640	5333333
Polyphenyleneoxide	PPO	4060	1068
Polypropylene	PP	68	227
Polystyrene	PS	970	388
Polysulfone	PSF	2000	8000
Polyvinylalcohol	PVA	19	33333
Polyvinylchloride	PVC	275	12500
Sulfonated polyetheretherketon	SPEEK	61000	10166667
Sulfonated polyethersulofon	SPES	15000	214286

In general, membrane-based technology that has been developed till date tends to be more applicable under mild conditions, such as ambient temperature and pressure, as well as water/chemical-free environment. However, in real applications, more harsh operation conditions can be expected in gas separation process, thus calling membranes for good environment-resistance. In Table 8-3 reported by Mashallah et al., it was worth noting that these membranes exhibited the abilities to potentially tolerate high temperature operation. For instance, the fluorinated polymeric membranes have been applied for proton exchange fuel cells at a high temperature up to 200 °C. [328] Also, a thermal stable cross-linked P84 exhibited superior H₂ permeability and H₂/CO₂ permselectivity of 47 barrers and 14 at a high temperature of 100 °C, as illustrated by Omidvar et al. [329]. What's more, Richter et al. fabricated a resin-derived CMSM supported on porous ceramic tube, where pyrolysis was conducted at 800 °C under purging of Ar/N₂ mixture gas. In this work, the permeated concentration of CO₂ proved to be very stable towards different contents of H₂S existed in feed biogas, as demonstrated in Table 8-4 [330].

Table 8-3. The highest gas separation (GS) measuring temperature of thermal stable membranes in the literature [328].

Heat-resistant polymeric membranes	Maximum GS test temperature (°C)	Membrane material	Maximum reported T _g (°C)
Fluorinated polymeric membranes	75	FBP-6FPT	253
Inorganic polymeric membranes	100	POPs	91
Carbocyclic polymeric membranes	260	PEEK	230
Heterocyclic polymeric membranes	400	PBI	436
Ladder polymeric membranes	90	BTFDA-DAB	> 400
Polymer blends membranes	35	BMI/PEI	> 400
Mixed matrix membranes	400	PBI/ZIF-90	> 400

Table 8-4. Influence of H₂S content in biogas on permeated concentration of CO₂ [330].

H ₂ S-content (mg/m ³)	CO ₂ permeate
< 1	0.62
180	0.59
< 1	0.60

REFERENCES

- [1] J. Houghton, *Global warming: the complete briefing*: Cambridge university press, 2009.
- [2] J. Hansen, M. Sato, R. Ruedy, G. A. Schmidt, and K. Lob, "Global Temperature in 2018 and Beyond," 2019.
- [3] J. Hansen, R. Ruedy, M. Sato, and K. Lo, "Global Surface Temperature Change," *Reviews of Geophysics*, vol. 48, 2010.
- [4] D. C. Uprety, V. Reddy, and J. D. Mura, "Greenhouse Gases: A Historical Perspective," in *Climate Change and Agriculture*, ed: Springer, 2019, pp. 31-41.
- [5] J. C. Fyfe, G. A. Meehl, M. H. England, M. E. Mann, B. D. Santer, G. M. Flato, *et al.*, "Making sense of the early-2000s warming slowdown," *Nature Climate Change*, vol. 6, p. 224, 2016.
- [6] V. Ramanathan and G. Carmichael, "Global and regional climate changes due to black carbon," *Nature geoscience*, vol. 1, p. 221, 2008.
- [7] D. S. Kaufman, D. P. Schneider, N. P. McKay, C. M. Ammann, R. S. Bradley, K. R. Briffa, *et al.*, "Recent warming reverses long-term Arctic cooling," *Science*, vol. 325, pp. 1236-1239, 2009.
- [8] J. T. Kiehl and K. E. Trenberth, "Earth's annual global mean energy budget," *Bulletin of the American Meteorological Society*, vol. 78, pp. 197-208, 1997.
- [9] R. T. Watson, H. Rodhe, H. Oeschger, and U. Siegenthaler, "Greenhouse gases and aerosols," *Climate change: the IPCC scientific assessment*, vol. 1, p. 17, 1990.
- [10] C. Le Quéré, R. Andres, T. Boden, T. Conway, R. Houghton, J. House, *et al.*, "The global carbon budget 1959–2011. Earth System Science Data 5, 165–185," ed, 2013.
- [11] D. A. Lashof and D. R. Ahuja, "Relative contributions of greenhouse gas emissions to global warming," *Nature*, vol. 344, p. 529, 1990.
- [12] B. Ang, "Decomposition methodology in industrial energy demand analysis," *Energy*, vol. 20, pp. 1081-1095, 1995.
- [13] B. Gilland, "Population, economic growth, and energy demand, 1985-2020," *Population and Development Review*, pp. 233-244, 1988.
- [14] T. Ackermann, *Wind power in power systems*: John Wiley & Sons, 2005.
- [15] R. Sipahutar, S. M. Bernas, and M. S. Imanuddin, "Renewable energy and hydropower utilization tendency worldwide," *Renewable and Sustainable Energy Reviews*, vol. 17, pp. 213-215, 2013.
- [16] N. S. Lewis, "Toward cost-effective solar energy use," *science*, vol. 315, pp. 798-801, 2007.
- [17] E. M. Smeets, A. P. Faaij, I. M. Lewandowski, and W. C. Turkenburg, "A bottom-up assessment and review of global bio-energy potentials to 2050," *Progress in Energy and combustion science*, vol. 33, pp. 56-106, 2007.
- [18] M. Ni, M. K. Leung, D. Y. Leung, and K. Sumathy, "A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production," *Renewable and Sustainable Energy Reviews*, vol. 11, pp. 401-425, 2007.
- [19] R. Li, "Latest progress in hydrogen production from solar water splitting via photocatalysis, photoelectrochemical, and photovoltaic-photoelectrochemical solutions," *Chinese Journal of Catalysis*, vol. 38, pp. 5-12, 2017.
- [20] A. D. Cuéllar and M. E. Webber, "Cow power: the energy and emissions benefits of converting manure to biogas," *Environmental Research Letters*, vol. 3, p. 034002, 2008.
- [21] F. Tasnim, S. A. Iqbal, and A. R. Chowdhury, "Biogas production from anaerobic co-digestion of cow manure with kitchen waste and Water Hyacinth," *Renewable Energy*, vol. 109, pp. 434-439, 2017.
- [22] S. Cavenati, C. A. Grande, A. E. Rodrigues, C. Kiener, and U. Müller, "Metal organic framework

- adsorbent for biogas upgrading," *Industrial & Engineering Chemistry Research*, vol. 47, pp. 6333-6335, 2008.
- [23] X. Y. Chen, H. Vinh-Thang, A. A. Ramirez, D. Rodrigue, and S. Kaliaguine, "Membrane gas separation technologies for biogas upgrading," *Rsc Advances*, vol. 5, pp. 24399-24448, 2015.
- [24] C. Y. Chuah, K. Goh, Y. Yang, H. Gong, W. Li, H. E. Karahan, *et al.*, "Harnessing Filler Materials for Enhancing Biogas Separation Membranes," *Chem Rev*, vol. 118, pp. 8655-8769, Sep 26 2018.
- [25] H. T. Hwang and A. Varma, "Hydrogen storage for fuel cell vehicles," *Current Opinion in Chemical Engineering*, vol. 5, pp. 42-48, 2014.
- [26] R. E. Morris and P. S. Wheatley, "Gas storage in nanoporous materials," *Angew Chem Int Ed Engl*, vol. 47, pp. 4966-81, 2008.
- [27] A. Petersson and A. WeLLInGer, "Biogas upgrading technologies—developments and innovations," *IEA Bioenergy*, vol. 20, pp. 1-19, 2009.
- [28] S. Basu, A. L. Khan, A. Cano-Odena, C. Liu, and I. F. Vankelecom, "Membrane-based technologies for biogas separations," *Chemical Society Reviews*, vol. 39, pp. 750-768, 2010.
- [29] A. Hussain, S. Farrukh, A. Hussain, and M. Ayoub, "Carbon capture from natural gas using multi-walled CNTs based mixed matrix membranes," *Environ Technol*, vol. 40, pp. 843-854, Mar 2019.
- [30] A. Schüring, S. M. Auerbach, S. Fritzsche, and R. Haberlandt, "On entropic barriers for diffusion in zeolites: A molecular dynamics study," *The Journal of chemical physics*, vol. 116, pp. 10890-10894, 2002.
- [31] L. Gibson, "Mesosilica materials and organic pollutant adsorption: part A removal from air," *Chemical Society Reviews*, vol. 43, pp. 5163-5172, 2014.
- [32] P. Bhanja, A. Modak, and A. Bhaumik, "Porous Organic Polymers for CO₂ Storage and Conversion Reactions," *ChemCatChem*, vol. 11, pp. 244-257, 2019.
- [33] S. S. Kaye, A. Dailly, O. M. Yaghi, and J. R. Long, "Impact of preparation and handling on the hydrogen storage properties of Zn₄O (1, 4-benzenedicarboxylate)₃ (MOF-5)," *Journal of the American Chemical Society*, vol. 129, pp. 14176-14177, 2007.
- [34] S. Radic, N. K. Geitner, R. Podila, A. Kakinen, P. Chen, P. C. Ke, *et al.*, "Competitive binding of natural amphiphiles with graphene derivatives," *Sci Rep*, vol. 3, p. 2273, 2013.
- [35] R. Szostak, *Molecular sieves*: Springer, 1989.
- [36] S. M. Auerbach, K. A. Carrado, and P. K. Dutta, *Handbook of zeolite science and technology*: CRC press, 2003.
- [37] P. J. Smeets, J. S. Woertink, B. F. Sels, E. I. Solomon, and R. A. Schoonheydt, "Transition-metal ions in zeolites: coordination and activation of oxygen," *Inorganic chemistry*, vol. 49, pp. 3573-3583, 2010.
- [38] G. Kokotailo, S. Lawton, D. Olson, and W. Meier, "Structure of synthetic zeolite ZSM-5," *Nature*, vol. 272, p. 437, 1978.
- [39] R. J. Argauer and G. R. Landolt, "Crystalline zeolite ZSM-5 and method of preparing the same," ed: Google Patents, 1972.
- [40] G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu, *et al.*, "Synthesis and characterization of high-quality zeolite LTA and FAU single nanocrystals," *Chemistry of materials*, vol. 10, pp. 1483-1486, 1998.
- [41] S. Shirazian and S. N. Ashrafizadeh, "LTA and ion-exchanged LTA zeolite membranes for dehydration of natural gas," *Journal of Industrial and Engineering Chemistry*, vol. 22, pp. 132-137, 2015.
- [42] T. Montanari and G. Busca, "On the mechanism of adsorption and separation of CO₂ on LTA

- zeolites: An IR investigation," *Vibrational Spectroscopy*, vol. 46, pp. 45-51, 2008.
- [43] M. Palomino, A. Corma, F. Rey, and S. Valencia, "New insights on CO₂-methane separation using LTA zeolites with different Si/Al ratios and a first comparison with MOFs," *Langmuir*, vol. 26, pp. 1910-7, Feb 2 2010.
- [44] O. Cheung, D. Wardecki, Z. Bacsik, P. Vasiliev, L. B. McCusker, and N. Hedin, "Highly selective uptake of carbon dioxide on the zeolite [Na_{10.2}KCs_{0.8}]-LTA- a possible sorbent for biogas upgrading," *Phys Chem Chem Phys*, vol. 18, pp. 16080-3, Jun 28 2016.
- [45] J. R. Li, R. J. Kuppler, and H. C. Zhou, "Selective gas adsorption and separation in metal-organic frameworks," *Chem Soc Rev*, vol. 38, pp. 1477-504, May 2009.
- [46] Q. L. Zhu and Q. Xu, "Metal-organic framework composites," *Chem Soc Rev*, vol. 43, pp. 5468-512, Aug 21 2014.
- [47] H. C. Zhou, J. R. Long, and O. M. Yaghi, "Introduction to metal-organic frameworks," *Chem Rev*, vol. 112, pp. 673-4, Feb 8 2012.
- [48] J. R. Li, J. Sculley, and H. C. Zhou, "Metal-organic frameworks for separations," *Chem Rev*, vol. 112, pp. 869-932, Feb 8 2012.
- [49] E. Tomic, "Thermal stability of coordination polymers," *Journal of Applied Polymer Science*, vol. 9, pp. 3745-3752, 1965.
- [50] H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, "Design and synthesis of an exceptionally stable and highly porous metal-organic framework," *nature*, vol. 402, p. 276, 1999.
- [51] M. H. Yap, K. L. Fow, and G. Z. Chen, "Synthesis and applications of MOF-derived porous nanostructures," *Green Energy & Environment*, vol. 2, pp. 218-245, 2017.
- [52] P. Silva, S. M. Vilela, J. P. Tomé and F. A. A. Paz, "Multifunctional metal-organic frameworks: from academia to industrial applications," *Chemical Society Reviews*, vol. 44, pp. 6774-6803, 2015.
- [53] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'keeffe, *et al.*, "Hydrogen storage in microporous metal-organic frameworks," *Science*, vol. 300, pp. 1127-1129, 2003.
- [54] D. J. Tranchemontagne, J. R. Hunt, and O. M. Yaghi, "Room temperature synthesis of metal-organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0," *Tetrahedron*, vol. 64, pp. 8553-8557, 2008.
- [55] T. T. T. Huong, P. N. Thanh, and D. N. Son, "Metal-organic frameworks: state-of-the-art material for gas capture and storage," *VNU Journal of Science: Mathematics-Physics*, vol. 32, 2016.
- [56] G. BLĂNIȚĂ, O. Ardelean, D. Lupu, G. Borodi, M. MIHEȚ, M. COROȘ, *et al.*, "Microwave assisted synthesis of MOF-5 at atmospheric pressure," *Rev. Roum. Chim*, vol. 56, pp. 583-588, 2011.
- [57] J. Zheng, R. S. Vemuri, L. Estevez, P. K. Koech, T. Varga, D. M. Camaioni, *et al.*, "Pore-engineered metal-organic frameworks with excellent adsorption of water and fluorocarbon refrigerant for cooling applications," *Journal of the American Chemical Society*, vol. 139, pp. 10601-10604, 2017.
- [58] M. Díaz-García, A. Mayoral, I. Diaz, and M. Sánchez-Sánchez, "Nanoscaled M-MOF-74 materials prepared at room temperature," *Crystal Growth & Design*, vol. 14, pp. 2479-2487, 2014.
- [59] T.-H. Bae and J. R. Long, "CO₂/N₂ separations with mixed-matrix membranes containing Mg₂(dobdc) nanocrystals," *Energy & Environmental Science*, vol. 6, p. 3565, 2013.
- [60] C. Y. Chuah, K. Goh, and T.-H. Bae, "Hierarchically structured HKUST-1 nanocrystals for enhanced SF₆ capture and recovery," *The Journal of Physical Chemistry C*, vol. 121, pp. 6748-6755, 2017.
- [61] K.-S. Lin, A. K. Adhikari, C.-N. Ku, C.-L. Chiang, and H. Kuo, "Synthesis and characterization of

- porous HKUST-1 metal organic frameworks for hydrogen storage," *international journal of hydrogen energy*, vol. 37, pp. 13865-13871, 2012.
- [62] C. H. Hendon and A. Walsh, "Chemical principles underpinning the performance of the metal–organic framework HKUST-1," *Chemical science*, vol. 6, pp. 3674-3683, 2015.
- [63] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, *et al.*, "Exceptional chemical and thermal stability of zeolitic imidazolate frameworks," *Proceedings of the National Academy of Sciences*, vol. 103, pp. 10186-10191, 2006.
- [64] Y. Pan, Y. Liu, G. Zeng, L. Zhao, and Z. Lai, "Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system," *Chem Commun (Camb)*, vol. 47, pp. 2071-3, Feb 21 2011.
- [65] W. Li, S. A. S. C. Samarasinghe, and T.-H. Bae, "Enhancing CO₂/CH₄ separation performance and mechanical strength of mixed-matrix membrane via combined use of graphene oxide and ZIF-8," *Journal of Industrial and Engineering Chemistry*, vol. 67, pp. 156-163, 2018.
- [66] S. E. Bambalaza, H. W. Langmi, R. Mokaya, N. M. Musyoka, J. Ren, and L. E. Khotseng, "Compaction of a zirconium metal–organic framework (UiO-66) for high density hydrogen storage applications," *Journal of Materials Chemistry A*, vol. 6, pp. 23569-23577, 2018.
- [67] M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, *et al.*, "A facile synthesis of UiO-66, UiO-67 and their derivatives," *Chem Commun (Camb)*, vol. 49, pp. 9449-51, Oct 21 2013.
- [68] J. Yang, Q. Zhao, J. Li, and J. Dong, "Synthesis of metal–organic framework MIL-101 in TMAOH-Cr (NO₃) 3-H₂BDC-H₂O and its hydrogen-storage behavior," *Microporous and Mesoporous Materials*, vol. 130, pp. 174-179, 2010.
- [69] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of carbon dioxide by MIL-101 (Cr): regeneration conditions and influence of flue gas contaminants," *Scientific reports*, vol. 3, p. 2916, 2013.
- [70] M. S. Alivand, M. Shafiei-Alavijeh, N. H. M. H. Tehrani, E. Ghasemy, A. Rashidi, and S. Fakhraie, "Facile and high-yield synthesis of improved MIL-101 (Cr) metal-organic framework with exceptional CO₂ and H₂S uptake; the impact of excess ligand-cluster," *Microporous and Mesoporous Materials*, vol. 279, pp. 153-164, 2019.
- [71] S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, and G. Férey, "Different adsorption behaviors of methane and carbon dioxide in the isotypic nanoporous metal terephthalates MIL-53 and MIL-47," *Journal of the American Chemical Society*, vol. 127, pp. 13519-13521, 2005.
- [72] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'keeffe, and O. M. Yaghi, "Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks," *Acc. Chem. Res*, vol. 43, pp. 58-67, 2010.
- [73] S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna, *et al.*, "Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions," *Nature communications*, vol. 3, p. 954, 2012.
- [74] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, and J. Pastré, "Metal–organic frameworks—prospective industrial applications," *J. Mater. Chem.*, vol. 16, pp. 626-636, 2006.
- [75] S. Bordiga, J. G. Vitillo, G. Ricchiardi, L. Regli, D. Cocina, A. Zecchina, *et al.*, "Interaction of hydrogen with MOF-5," *The Journal of Physical Chemistry B*, vol. 109, pp. 18237-18242, 2005.
- [76] S. S.-Y. Chui, S. M.-F. Lo, J. P. Charmant, A. G. Orpen, and I. D. Williams, "A chemically functionalizable nanoporous material [Cu₃ (TMA) ₂ (H₂O) ₃] n," *Science*, vol. 283, pp. 1148-1150, 1999.
- [77] X. Wu, Z. Bao, B. Yuan, J. Wang, Y. Sun, H. Luo, *et al.*, "Microwave synthesis and

- characterization of MOF-74 (M=Ni, Mg) for gas separation," *Microporous and Mesoporous Materials*, vol. 180, pp. 114-122, 2013.
- [78] S. Basu, A. Cano-Odena, and I. F. Vankelecom, "MOF-containing mixed-matrix membranes for CO₂/CH₄ and CO₂/N₂ binary gas mixture separations," *Separation and Purification Technology*, vol. 81, pp. 31-40, 2011.
- [79] F. Su, C. Lu, W. Cnen, H. Bai, and J. F. Hwang, "Capture of CO₂ from flue gas via multiwalled carbon nanotubes," *Science of the total environment*, vol. 407, pp. 3017-3023, 2009.
- [80] B. Yu, H. Cong, Z. Li, J. Tang, and X. S. Zhao, "Pebax-1657 nanocomposite membranes incorporated with nanoparticles/colloids/carbon nanotubes for CO₂/N₂ and CO₂/H₂ separation," *Journal of Applied Polymer Science*, vol. 130, pp. 2867-2876, 2013.
- [81] X. Wang, Q. Li, J. Xie, Z. Jin, J. Wang, Y. Li, *et al.*, "Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates," *Nano letters*, vol. 9, pp. 3137-3141, 2009.
- [82] N. Li, X. Su, and Y. Lu, "Nanomaterial-based biosensors using dual transducing elements for solution phase detection," *Analyst*, vol. 140, pp. 2916-43, May 7 2015.
- [83] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. Dommett, G. Evmenenko, *et al.*, "Preparation and characterization of graphene oxide paper," *Nature*, vol. 448, pp. 457-60, Jul 26 2007.
- [84] D. Chen, H. Feng, and J. Li, "Graphene oxide: preparation, functionalization, and electrochemical applications," *Chem Rev*, vol. 112, pp. 6027-53, Nov 14 2012.
- [85] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, *et al.*, "Graphene and graphene oxide: synthesis, properties, and applications," *Adv Mater*, vol. 22, pp. 3906-24, Sep 15 2010.
- [86] R. Lahaye, H. Jeong, C. Park, and Y. Lee, "Density functional theory study of graphite oxide for different oxidation levels," *Physical Review B*, vol. 79, p. 125435, 2009.
- [87] B. C. Brodie, "XIII. On the atomic weight of graphite," *Philosophical Transactions of the Royal Society of London*, pp. 249-259, 1859.
- [88] L. Staudenmaier, "Verfahren zur darstellung der graphits äure," *Berichte der deutschen chemischen Gesellschaft*, vol. 31, pp. 1481-1487, 1898.
- [89] W. S. Hummers Jr and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the american chemical society*, vol. 80, pp. 1339-1339, 1958.
- [90] D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, "The chemistry of graphene oxide," *Chem Soc Rev*, vol. 39, pp. 228-40, Jan 2010.
- [91] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. Dommett, G. Evmenenko, *et al.*, "Preparation and characterization of graphene oxide paper," *Nature*, vol. 448, p. 457, 2007.
- [92] F. Schedin, A. Geim, S. Morozov, E. Hill, P. Blake, M. Katsnelson, *et al.*, "Detection of individual gas molecules adsorbed on graphene," *Nature materials*, vol. 6, p. 652, 2007.
- [93] S. Park and R. S. Ruoff, "Chemical methods for the production of graphenes," *Nature nanotechnology*, vol. 4, p. 217, 2009.
- [94] M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novak, "Insertion electrode materials for rechargeable lithium batteries," *Advanced materials*, vol. 10, pp. 725-763, 1998.
- [95] T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, *et al.*, "Evaluation of cation-exchanged zeolite adsorbents for post-combustion carbon dioxide capture," *Energy & Environmental Science*, vol. 6, pp. 128-138, 2013.
- [96] M. Mofarahi and F. Gholipour, "Gas adsorption separation of CO₂/CH₄ system using zeolite 5A," *Microporous and Mesoporous Materials*, vol. 200, pp. 1-10, 2014.
- [97] J. M. Simmons, H. Wu, W. Zhou, and T. Yildirim, "Carbon capture in metal-organic

- frameworks—a comparative study," *Energy & Environmental Science*, vol. 4, pp. 2177-2185, 2011.
- [98] C. Petit and T. J. Bandoz, "MOF-Graphite Oxide Composites: Combining the Uniqueness of Graphene Layers and Metal-Organic Frameworks," *Advanced Materials*, vol. 21, pp. 4753-4757, 2009.
- [99] M. Jahan, Q. Bao, J.-X. Yang, and K. P. Loh, "Structure-directing role of graphene in the synthesis of metal-organic framework nanowire," *Journal of the American Chemical Society*, vol. 132, pp. 14487-14495, 2010.
- [100] C. Petit and T. J. Bandoz, "Synthesis, Characterization, and Ammonia Adsorption Properties of Mesoporous Metal-Organic Framework (MIL(Fe))-Graphite Oxide Composites: Exploring the Limits of Materials Fabrication," *Advanced Functional Materials*, vol. 21, pp. 2108-2117, 2011.
- [101] C. Petit, J. Burrell, and T. J. Bandoz, "The synthesis and characterization of copper-based metal-organic framework/graphite oxide composites," *Carbon*, vol. 49, pp. 563-572, 2011.
- [102] R. Kumar, K. Jayaramulu, T. K. Maji, and C. N. Rao, "Hybrid nanocomposites of ZIF-8 with graphene oxide exhibiting tunable morphology, significant CO₂ uptake and other novel properties," *Chem Commun (Camb)*, vol. 49, pp. 4947-9, May 28 2013.
- [103] S. Liu, L. Sun, F. Xu, J. Zhang, C. Jiao, F. Li, *et al.*, "Nanosized Cu-MOFs induced by graphene oxide and enhanced gas storage capacity," *Energy & Environmental Science*, vol. 6, pp. 818-823, 2013.
- [104] W. Huang, X. Zhou, Q. Xia, J. Peng, H. Wang, and Z. Li, "Preparation and Adsorption Performance of GrO@Cu-BTC for Separation of CO₂/CH₄," *Industrial & Engineering Chemistry Research*, vol. 53, pp. 11176-11184, 2014.
- [105] X. Sun, Q. Xia, Z. Zhao, Y. Li, and Z. Li, "Synthesis and adsorption performance of MIL-101(Cr)/graphite oxide composites with high capacities of n-hexane," *Chemical Engineering Journal*, vol. 239, pp. 226-232, 2014.
- [106] Y. Li, J. Miao, X. Sun, J. Xiao, Y. Li, H. Wang, *et al.*, "Mechanochemical synthesis of Cu-BTC@GO with enhanced water stability and toluene adsorption capacity," *Chemical Engineering Journal*, vol. 298, pp. 191-197, 2016.
- [107] Y. Chen, D. Lv, J. Wu, J. Xiao, H. Xi, Q. Xia, *et al.*, "A new MOF-505@GO composite with high selectivity for CO₂/CH₄ and CO₂/N₂ separation," *Chemical Engineering Journal*, vol. 308, pp. 1065-1072, 2017.
- [108] P. Bernardo, E. Drioli, and G. Golemme, "Membrane gas separation: a review/state of the art," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 4638-4663, 2009.
- [109] A. Baudot, "Gas/Vapor Permeation Applications in the Hydrocarbon-processing Industry," in *Membrane Engineering for the Treatment of Gases*, ed, 2011, pp. 150-195.
- [110] W. Schell and C. Houston, "Spiral-wound permeators for purifications and recovery," *Chem. Eng. Prog. (United States)*, vol. 78, 1982.
- [111] M. Scholz, T. Melin, and M. Wessling, "Transforming biogas into biomethane using membrane technology," *Renewable and Sustainable Energy Reviews*, vol. 17, pp. 199-212, 2013.
- [112] H. Gong, C. Y. Chuah, Y. Yang, and T.-H. Bae, "High performance composite membranes comprising Zn (pyrz)₂ (SiF₆) nanocrystals for CO₂/CH₄ separation," *Journal of industrial and engineering chemistry*, vol. 60, pp. 279-285, 2018.
- [113] J. D. Perry, K. Nagai, and W. J. Koros, "Polymer Membranes for Hydrogen Separations," *MRS Bulletin*, vol. 31, pp. 745-749, 2011.
- [114] E. Perez, C. Karunaweera, I. Musselman, K. Balkus, and J. Ferraris, "Origins and evolution of inorganic-based and MOF-based mixed-matrix membranes for gas separations," *Processes*, vol. 4,

- p. 32, 2016.
- [115] T. Graunke, K. Schmitt, and J. Wöhlenstein, "Organic membranes for selectivity enhancement of metal oxide gas sensors," *Journal of Sensors*, vol. 2016, 2016.
 - [116] A. Fick, "Ueber diffusion," *Annalen der Physik*, vol. 170, pp. 59-86, 1855.
 - [117] Y. Yampolskii, "Polymeric Gas Separation Membranes," *Macromolecules*, vol. 45, pp. 3298-3311, 2012.
 - [118] J. Yao and H. Wang, "Zeolitic imidazolate framework composite membranes and thin films: synthesis and applications," *Chem Soc Rev*, vol. 43, pp. 4470-93, Jul 7 2014.
 - [119] R. D. Noble, "Perspectives on mixed matrix membranes," *Journal of membrane science*, vol. 378, pp. 393-397, 2011.
 - [120] T. Visser, N. Masetto, and M. Wessling, "Materials dependence of mixed gas plasticization behavior in asymmetric membranes," *Journal of Membrane Science*, vol. 306, pp. 16-28, 2007.
 - [121] J. M. Hutchinson, "Physical aging of polymers," *Progress in polymer science*, vol. 20, pp. 703-760, 1995.
 - [122] X. Duthie, S. Kentish, C. Powell, K. Nagai, G. Qiao, and G. Stevens, "Operating temperature effects on the plasticization of polyimide gas separation membranes," *Journal of membrane science*, vol. 294, pp. 40-49, 2007.
 - [123] L. M. Robeson, "The upper bound revisited," *Journal of Membrane Science*, vol. 320, pp. 390-400, 2008.
 - [124] S. E. Kentish, C. A. Scholes, and G. W. Stevens, "Carbon dioxide separation through polymeric membrane systems for flue gas applications," *Recent Patents on Chemical Engineering*, vol. 1, pp. 52-66, 2008.
 - [125] S. Luo, K. A. Stevens, J. S. Park, J. D. Moon, Q. Liu, B. D. Freeman, *et al.*, "Highly CO₂-selective gas separation membranes based on segmented copolymers of poly (ethylene oxide) reinforced with pentyptcene-containing polyimide hard segments," *ACS applied materials & interfaces*, vol. 8, pp. 2306-2317, 2016.
 - [126] C. E. Powell and G. G. Qiao, "Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases," *Journal of Membrane Science*, vol. 279, pp. 1-49, 2006.
 - [127] M. A. Aroon, A. F. Ismail, T. Matsuura, and M. M. Montazer-Rahmati, "Performance studies of mixed matrix membranes for gas separation: A review," *Separation and Purification Technology*, vol. 75, pp. 229-242, 2010.
 - [128] P. S. Goh, A. F. Ismail, S. M. Sanip, B. C. Ng, and M. Aziz, "Recent advances of inorganic fillers in mixed matrix membrane for gas separation," *Separation and Purification Technology*, vol. 81, pp. 243-264, 2011.
 - [129] Y. Li, T.-S. Chung, C. Cao, and S. Kulprathipanja, "The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes," *Journal of Membrane Science*, vol. 260, pp. 45-55, 2005.
 - [130] J.-R. Li, R. J. Kuppler, and H.-C. Zhou, "Selective gas adsorption and separation in metal-organic frameworks," *Chem. Soc. Rev.*, vol. 38, pp. 1477-1504, 2009.
 - [131] C. M. Zimmerman, A. Singh, and W. J. Koros, "Tailoring mixed matrix composite membranes for gas separations," *Journal of membrane science*, vol. 137, pp. 145-154, 1997.
 - [132] D. Paul and D. Kemp, "The diffusion time lag in polymer membranes containing adsorptive fillers," in *Journal of Polymer Science: Polymer Symposia*, 1973, pp. 79-93.
 - [133] B. Ozturk and F. Demirciyeva, "Comparison of biogas upgrading performances of different mixed matrix membranes," *Chemical engineering journal*, vol. 222, pp. 209-217, 2013.

- [134] H. Karkhanechi, H. Kazemian, H. Nazockdast, M. R. Mozdianfard, and S. M. Bidoki, "Fabrication of Homogenous Polymer-Zeolite Nanocomposites as Mixed-Matrix Membranes for Gas Separation," *Chemical Engineering & Technology*, vol. 35, pp. 885-892, 2012.
- [135] M. Junaidi, C. Leo, S. Kamal, A. Ahmad, and T. Chew, "Carbon dioxide removal from methane by using polysulfone/SAPO-44 mixed matrix membranes," *Fuel processing technology*, vol. 112, pp. 1-6, 2013.
- [136] M. Junaidi, C. Leo, A. Ahmad, S. Kamal, and T. Chew, "Carbon dioxide separation using asymmetric polysulfone mixed matrix membranes incorporated with SAPO-34 zeolite," *Fuel processing technology*, vol. 118, pp. 125-132, 2014.
- [137] H. Yehia, T. Pisklak, J. Ferraris, K. Balkus, and I. Musselman, "Methane facilitated transport using copper (II) biphenyl dicarboxylate-triethylenediamine/poly (3-acetoxyethylthiophene) mixed matrix membranes," in *Abstracts of Papers of the American Chemical Society*, 2004, pp. U351-U351.
- [138] B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, *et al.*, "Metal-organic framework based mixed matrix membranes: a solution for highly efficient CO₂ capture?," *Chemical Society Reviews*, vol. 44, pp. 2421-2454, 2015.
- [139] M. Rezakazemi, A. E. Amooghin, M. M. Montazer-Rahmati, A. F. Ismail, and T. Matsuura, "State-of-the-art membrane based CO₂ separation using mixed matrix membranes (MMMs): an overview on current status and future directions," *Progress in Polymer Science*, vol. 39, pp. 817-861, 2014.
- [140] N. Jusoh, Y. F. Yeong, T. L. Chew, K. K. Lau, and A. M. Shariff, "Current development and challenges of mixed matrix membranes for CO₂/CH₄ separation," *Separation & Purification Reviews*, vol. 45, pp. 321-344, 2016.
- [141] N. Tien-Binh, H. Vinh-Thang, X. Y. Chen, D. Rodrigue, and S. Kaliaguine, "Polymer functionalization to enhance interface quality of mixed matrix membranes for high CO₂/CH₄ gas separation," *Journal of Materials Chemistry A*, vol. 3, pp. 15202-15213, 2015.
- [142] N. Tien-Binh, D. Rodrigue, and S. Kaliaguine, "In-situ cross interface linking of PIM-1 polymer and UiO-66-NH₂ for outstanding gas separation and physical aging control," *Journal of membrane science*, vol. 548, pp. 429-438, 2018.
- [143] J. A. Thompson, J. T. Vaughn, N. A. Brunelli, W. J. Koros, C. W. Jones, and S. Nair, "Mixed-linker zeolitic imidazolate framework mixed-matrix membranes for aggressive CO₂ separation from natural gas," *Microporous and Mesoporous Materials*, vol. 192, pp. 43-51, 2014.
- [144] A. L. Ahmad, Z. A. Jawad, S. C. Low, and S. H. S. Zein, "A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO₂/N₂ separation," *Journal of Membrane Science*, vol. 451, pp. 55-66, 2014.
- [145] L. Deng and M.-B. Hägg, "Carbon nanotube reinforced PVAm/PVA blend FSC nanocomposite membrane for CO₂/CH₄ separation," *International Journal of Greenhouse Gas Control*, vol. 26, pp. 127-134, 2014.
- [146] H. W. Kim, H. W. Yoon, S.-M. Yoon, B. M. Yoo, B. K. Ahn, Y. H. Cho, *et al.*, "Selective gas transport through few-layered graphene and graphene oxide membranes," *Science*, vol. 342, pp. 91-95, 2013.
- [147] H. Li, Z. Song, X. Zhang, Y. Huang, S. Li, Y. Mao, *et al.*, "Ultrathin, molecular-sieving graphene oxide membranes for selective hydrogen separation," *Science*, vol. 342, pp. 95-98, 2013.
- [148] J. Shen, G. Liu, K. Huang, W. Jin, K. R. Lee, and N. Xu, "Membranes with fast and selective gas-transport channels of laminar graphene oxide for efficient CO₂ capture," *Angew Chem Int Ed Engl*, vol. 54, pp. 578-82, Jan 7 2015.

- [149] X. Li, Y. Cheng, H. Zhang, S. Wang, Z. Jiang, R. Guo, *et al.*, "Efficient CO₂ capture by functionalized graphene oxide nanosheets as fillers to fabricate multi-permselective mixed matrix membranes," *ACS Appl Mater Interfaces*, vol. 7, pp. 5528-37, Mar 11 2015.
- [150] H. Koolivand, A. Sharifa, E. Chehrizi, M. R. Kashani, and S. M. R. Paran, "Mixed-matrix membranes comprising graphene-oxide nanosheets for CO₂/CH₄ separation: A comparison between glassy and rubbery polymer matrices," *Polymer Science Series A*, vol. 58, pp. 801-809, September 01 2016.
- [151] X. Li, L. Ma, H. Zhang, S. Wang, Z. Jiang, R. Guo, *et al.*, "Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO₂ separation," *Journal of Membrane Science*, vol. 479, pp. 1-10, 2015.
- [152] X. Li, L. Ma, H. Zhang, S. Wang, Z. Jiang, R. Guo, *et al.*, "Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO₂ separation," *Journal of Membrane Science*, vol. 479, pp. 1-10, 2015.
- [153] A. F. Ismail and W. Lorna, "Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane," *Separation and purification technology*, vol. 27, pp. 173-194, 2002.
- [154] H. B. Park, C. H. Jung, Y. M. Lee, A. J. Hill, S. J. Pas, S. T. Mudie, *et al.*, "Polymers with cavities tuned for fast selective transport of small molecules and ions," *Science*, vol. 318, pp. 254-258, 2007.
- [155] Y. Zhang, J. Sunarso, S. Liu, and R. Wang, "Current status and development of membranes for CO₂/CH₄ separation: A review," *International Journal of Greenhouse Gas Control*, vol. 12, pp. 84-107, 2013.
- [156] R. Swaidan, X. Ma, E. Litwiller, and I. Pinnau, "High pressure pure- and mixed-gas separation of CO₂/CH₄ by thermally-rearranged and carbon molecular sieve membranes derived from a polyimide of intrinsic microporosity," *Journal of Membrane Science*, vol. 447, pp. 387-394, 2013.
- [157] W. N. W. Salleh, A. F. Ismail, T. Matsuura, and M. S. Abdullah, "Precursor Selection and Process Conditions in the Preparation of Carbon Membrane for Gas Separation: A Review," *Separation & Purification Reviews*, vol. 40, pp. 261-311, 2011.
- [158] M. Rungta, G. B. Wenz, C. Zhang, L. Xu, W. Qiu, J. S. Adams, *et al.*, "Carbon molecular sieve structure development and membrane performance relationships," *Carbon*, vol. 115, pp. 237-248, 2017.
- [159] J. Koresch and A. Soffer, "Study of molecular sieve carbons. Part 1.—Pore structure, gradual pore opening and mechanism of molecular sieving," *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 76, pp. 2457-2471, 1980.
- [160] A. F. Ismail and L. David, "A review on the latest development of carbon membranes for gas separation," *Journal of membrane science*, vol. 193, pp. 1-18, 2001.
- [161] K. M. Steel and W. J. Koros, "Investigation of porosity of carbon materials and related effects on gas separation properties," *Carbon*, vol. 41, pp. 253-266, 2003.
- [162] E. Favvas, G. Kapantaidakis, J. Nolan, A. C. Mitropoulos, and N. Kanellopoulos, "Preparation, characterization and gas permeation properties of carbon hollow fiber membranes based on Matrimid® 5218 precursor," *Journal of materials processing technology*, vol. 186, pp. 102-110, 2007.
- [163] D. Q. Vu, W. J. Koros, and S. J. Miller, "High pressure CO₂/CH₄ separation using carbon molecular sieve hollow fiber membranes," *Industrial & engineering chemistry research*, vol. 41, pp. 367-380, 2002.
- [164] P. S. Tin, T.-S. Chung, and A. J. Hill, "Advanced fabrication of carbon molecular sieve membranes by nonsolvent pretreatment of precursor polymers," *Industrial & engineering chemistry research*,

vol. 43, pp. 6476-6483, 2004.

- [165] A. Fuertes, D. Nevskaya, and T. Centeno, "Carbon composite membranes from Matrimid® and Kapton® polyimides for gas separation," *Microporous and Mesoporous materials*, vol. 33, pp. 115-125, 1999.
- [166] E. P. Favvas, E. P. Kouvelos, G. E. Romanos, G. I. Pilatos, A. C. Mitropoulos, and N. K. Kanellopoulos, "Characterization of highly selective microporous carbon hollow fiber membranes prepared from a commercial co-polyimide precursor," *Journal of Porous Materials*, vol. 15, pp. 625-633, 2007.
- [167] A. Singh-Ghosal and W. J. Koros, "Air separation properties of flat sheet homogeneous pyrolytic carbon membranes," *Journal of Membrane Science*, vol. 174, pp. 177-188, 2000/07/31/ 2000.
- [168] L. I. B. David and A. F. Ismail, "Influence of the thermastabilization process and soak time during pyrolysis process on the polyacrylonitrile carbon membranes for O₂/N₂ separation," *Journal of Membrane Science*, vol. 213, pp. 285-291, 2003/03/01/ 2003.
- [169] H. Suda and K. Haraya, "Alkene/alkane permselectivities of a carbon molecular sieve membrane," *Chemical Communications*, pp. 93-94, 1997.
- [170] T. A. Centeno, J. L. Vilas, and A. B. Fuertes, "Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation," *Journal of Membrane Science*, vol. 228, pp. 45-54, 2004/01/01/ 2004.
- [171] T.-S. Chung, L. Y. Jiang, Y. Li, and S. Kulprathipanja, "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation," *Progress in Polymer Science*, vol. 32, pp. 483-507, 2007.
- [172] Shu, S. Husain, and W. J. Koros, "Formation of Nanostructured Zeolite Particle Surfaces via a Halide/Grignard Route," *Chemistry of Materials*, vol. 19, pp. 4000-4006, 2007/08/01 2007.
- [173] Shu, S. Husain, and W. J. Koros, "A General Strategy for Adhesion Enhancement in Polymeric Composites by Formation of Nanostructured Particle Surfaces," *The Journal of Physical Chemistry C*, vol. 111, pp. 652-657, 2007/01/01 2007.
- [174] Shu, S. Husain, and W. J. Koros, "Sonication-Assisted Dealumination of Zeolite A with Thionyl Chloride," *Industrial & Engineering Chemistry Research*, vol. 46, pp. 767-772, 2007/01/01 2007.
- [175] M. Yoshimune and K. Haraya, "Flexible carbon hollow fiber membranes derived from sulfonated poly(phenylene oxide)," *Separation and Purification Technology*, vol. 75, pp. 193-197, 2010.
- [176] J. Weitkamp, M. Fritz, and S. Ernst, "Zeolites as media for hydrogen storage," *International Journal of Hydrogen Energy*, vol. 20, pp. 967-970, 1995.
- [177] J. Dong, X. Wang, H. Xu, Q. Zhao, and J. Li, "Hydrogen storage in several microporous zeolites," *International Journal of Hydrogen Energy*, vol. 32, pp. 4998-5004, 2007.
- [178] H. Langmi, D. Book, A. Walton, S. Johnson, M. Al-Mamouri, J. Speight, *et al.*, "Hydrogen storage in ion-exchanged zeolites," *Journal of Alloys and Compounds*, vol. 404, pp. 637-642, 2005.
- [179] R. F. Cracknell, P. Gordon, and K. E. Gubbins, "Influence of pore geometry on the design of microporous materials for methane storage," *The Journal of Physical Chemistry*, vol. 97, pp. 494-499, 1993.
- [180] Y. Zhu, J. Shi, H. Chen, W. Shen, and X. Dong, "A facile method to synthesize novel hollow mesoporous silica spheres and advanced storage property," *Microporous and Mesoporous Materials*, vol. 84, pp. 218-222, 2005.
- [181] S. Zheng, F. Fang, G. Zhou, G. Chen, L. Ouyang, M. Zhu, *et al.*, "Hydrogen storage properties of space-confined NaAlH₄ nanoparticles in ordered mesoporous silica," *Chemistry of Materials*, vol. 20, pp. 3954-3958, 2008.
- [182] S. Sircar, T. Golden, and M. Rao, "Activated carbon for gas separation and storage," *Carbon*, vol.

34, pp. 1-12, 1996.

- [183] K. R. Matranga, A. L. Myers, and E. D. Glandt, "Storage of natural gas by adsorption on activated carbon," *Chemical engineering science*, vol. 47, pp. 1569-1579, 1992.
- [184] E. Frackowiak and F. Beguin, "Carbon materials for the electrochemical storage of energy in capacitors," *Carbon*, vol. 39, pp. 937-950, 2001.
- [185] D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano, and D. Quinn, "Influence of pore size distribution on methane storage at relatively low pressure: preparation of activated carbon with optimum pore size," *Carbon*, vol. 40, pp. 989-1002, 2002.
- [186] S. Biloe, V. Goetz, and A. Guillot, "Optimal design of an activated carbon for an adsorbed natural gas storage system," *Carbon*, vol. 40, pp. 1295-1308, 2002.
- [187] J. Noh, R. Agarwal, and J. Schwarz, "Hydrogen storage systems using activated carbon," *International Journal of Hydrogen Energy*, vol. 12, pp. 693-700, 1987.
- [188] J. B. Mota, A. Rodrigues, E. Saadjan, and D. Tondeur, "Dynamics of natural gas adsorption storage systems employing activated carbon," *Carbon*, vol. 35, pp. 1259-1270, 1997.
- [189] Y. Yang, C. Y. Chuah, H. Gong, and T.-H. Bae, "Robust microporous organic copolymers containing triphenylamine for high pressure CO₂ capture application," *Journal of CO₂ Utilization*, vol. 19, pp. 214-220, 2017.
- [190] Q. Zhang, Y. Yang, and S. Zhang, "Novel Functionalized Microporous Organic Networks Based on Triphenylphosphine," *Chemistry-A European Journal*, vol. 19, pp. 10024-10029, 2013.
- [191] A. R. Millward and O. M. Yaghi, "Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature," *Journal of the American Chemical Society*, vol. 127, pp. 17998-17999, 2005.
- [192] O. K. Farha, A. Ö. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, *et al.*, "De novo synthesis of a metal-organic framework material featuring ultrahigh surface area and gas storage capacities," *Nature chemistry*, vol. 2, pp. 944-948, 2010.
- [193] J. L. Rowsell and O. M. Yaghi, "Strategies for hydrogen storage in metal-organic frameworks," *Angewandte Chemie International Edition*, vol. 44, pp. 4670-4679, 2005.
- [194] B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, *et al.*, "High-capacity hydrogen and nitric oxide adsorption and storage in a metal-organic framework," *Journal of the American Chemical Society*, vol. 129, pp. 1203-1209, 2007.
- [195] Y. Li and R. T. Yang, "Gas adsorption and storage in metal-organic framework MOF-177," *Langmuir*, vol. 23, pp. 12937-12944, 2007.
- [196] Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, *et al.*, "A metal-organic framework with optimized open metal sites and pore spaces for high methane storage at room temperature," *Angewandte Chemie International Edition*, vol. 50, pp. 3178-3181, 2011.
- [197] L. J. Murray, M. Dincă, and J. R. Long, "Hydrogen storage in metal-organic frameworks," *Chemical Society Reviews*, vol. 38, pp. 1294-1314, 2009.
- [198] B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, and O. M. Yaghi, "High H₂ adsorption in a microporous metal-organic framework with open metal sites," *Angewandte Chemie*, vol. 117, pp. 4823-4827, 2005.
- [199] S. Keskin and D. S. Sholl, "Assessment of a metal-organic framework membrane for gas separations using atomically detailed calculations: CO₂, CH₄, N₂, H₂ mixtures in MOF-5," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 914-922, 2008.
- [200] M. Eddaoudi, H. Li, and O. Yaghi, "Highly porous and stable metal-organic frameworks: structure design and sorption properties," *Journal of the American Chemical Society*, vol. 122, pp. 1391-1397, 2000.

- [201] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, and J. Pastre, "Metal–organic frameworks—prospective industrial applications," *Journal of Materials Chemistry*, vol. 16, pp. 626-636, 2006.
- [202] H. Li, M. Eddaoudi, T. L. Groy, and O. Yaghi, "Establishing microporosity in open metal– organic frameworks: gas sorption isotherms for Zn (BDC)(BDC= 1, 4-benzenedicarboxylate)," *Journal of the American Chemical Society*, vol. 120, pp. 8571-8572, 1998.
- [203] H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, *et al.*, "A route to high surface area, porosity and inclusion of large molecules in crystals," *Nature*, vol. 427, pp. 523-527, 2004.
- [204] H. Wu, W. Zhou, and T. Yildirim, "Hydrogen storage in a prototypical zeolitic imidazolate framework-8," *Journal of the American Chemical Society*, vol. 129, pp. 5314-5315, 2007.
- [205] D.-J. Lee, Q. Li, H. Kim, and K. Lee, "Preparation of Ni-MOF-74 membrane for CO₂ separation by layer-by-layer seeding technique," *Microporous and Mesoporous Materials*, vol. 163, pp. 169-177, 2012.
- [206] O. C. Compton and S. T. Nguyen, "Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials," *Small*, vol. 6, pp. 711-23, Mar 22 2010.
- [207] D. Chen, H. Feng, and J. Li, "Graphene oxide: preparation, functionalization, and electrochemical applications," *Chemical reviews*, vol. 112, pp. 6027-6053, 2012.
- [208] J. Li, X. Zeng, T. Ren, and E. van der Heide, "The preparation of graphene oxide and its derivatives and their application in bio-tribological systems," *Lubricants*, vol. 2, pp. 137-161, 2014.
- [209] M. Hakimi and P. Alimard, "Graphene: synthesis and applications in biotechnology-a review," 2012.
- [210] S. R. Caskey, A. G. Wong-Foy, and A. J. Matzger, "Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores," *Journal of the American Chemical Society*, vol. 130, pp. 10870-10871, 2008.
- [211] D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, *et al.*, "Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy," *Carbon*, vol. 47, pp. 145-152, 2009.
- [212] T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, *et al.*, "Evaluation of cation-exchanged zeolite adsorbents for post-combustion carbon dioxide capture," *Energy Environ. Sci.*, vol. 6, pp. 128-138, 2013.
- [213] A. Myers and J. M. Prausnitz, "Thermodynamics of mixed-gas adsorption," *AIChE Journal*, vol. 11, pp. 121-127, 1965.
- [214] J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, and J. R. Long, "Evaluating metal–organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption," *Energy & Environmental Science*, vol. 4, pp. 3030-3040, 2011.
- [215] H. Gong, T. H. Nguyen, R. Wang, and T.-H. Bae, "Separations of binary mixtures of CO₂/CH₄ and CO₂/N₂ with mixed-matrix membranes containing Zn (pyrz)₂ (SiF₆) metal-organic framework," *Journal of Membrane Science*, vol. 495, pp. 169-175, 2015.
- [216] I. Childres, L. A. Jauregui, W. Park, H. Cao, and Y. P. Chen, "Raman spectroscopy of graphene and related materials," *New developments in photon and materials research*, vol. 1, 2013.
- [217] C. Petit and T. J. Bandosz, "MOF–graphite oxide composites: combining the uniqueness of graphene layers and metal–organic frameworks," *Advanced Materials*, vol. 21, pp. 4753-4757, 2009.
- [218] G. Dolgonos, "How many hydrogen molecules can be inserted into C₆₀? Comments on the paper

- 'AM1 treatment of endohedrally hydrogen doped fullerene, nH 2@ C 60' by L. Türker and Ş. Erkoç [J. Mol. Struct.(Theochem) 638 (2003) 37–40], *Journal of Molecular Structure: THEOCHEM*, vol. 732, pp. 239-241, 2005.
- [219] W. Li, C. Y. Chuah, Y. Yang, and T.-H. Bae, "Nanocomposites formed by in situ growth of NiDOBDC nanoparticles on graphene oxide sheets for enhanced CO₂ and H₂ storage," *Microporous and Mesoporous Materials*, vol. 265, pp. 35-42, 2018.
- [220] L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes," *Journal of membrane science*, vol. 62, pp. 165-185, 1991.
- [221] L. M. Robeson, "The upper bound revisited," *Journal of Membrane Science*, vol. 320, pp. 390-400, 2008.
- [222] M. B. HÄGG, J. A. Lie, and A. Lindbråthen, "Carbon molecular sieve membranes," *Annals of the New York Academy of Sciences*, vol. 984, pp. 329-345, 2003.
- [223] A. Leenaars, K. Keizer, and A. Burggraaf, "The preparation and characterization of alumina membranes with ultra-fine pores," *Journal of Materials Science*, vol. 19, pp. 1077-1088, 1984.
- [224] A. Tavolaro and E. Drioli, "Zeolite membranes," *Advanced materials*, vol. 11, pp. 975-996, 1999.
- [225] M. Shah, M. C. McCarthy, S. Sachdeva, A. K. Lee, and H.-K. Jeong, "Current status of metal–organic framework membranes for gas separations: promises and challenges," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 2179-2199, 2012.
- [226] Y. S. Li, F. Y. Liang, H. Bux, A. Feldhoff, W. S. Yang, and J. Caro, "Molecular sieve membrane: supported metal–organic framework with high hydrogen selectivity," *Angewandte Chemie*, vol. 122, pp. 558-561, 2010.
- [227] M. Aroon, A. Ismail, T. Matsuura, and M. Montazer-Rahmati, "Performance studies of mixed matrix membranes for gas separation: a review," *Separation and purification Technology*, vol. 75, pp. 229-242, 2010.
- [228] G. Dong, H. Li, and V. Chen, "Challenges and opportunities for mixed-matrix membranes for gas separation," *Journal of Materials Chemistry A*, vol. 1, pp. 4610-4630, 2013.
- [229] T. Mitra, R. S. Bhavsar, D. J. Adams, P. M. Budd, and A. I. Cooper, "PIM-1 mixed matrix membranes for gas separations using cost-effective hypercrosslinked nanoparticle fillers," *Chemical Communications*, vol. 52, pp. 5581-5584, 2016.
- [230] T. T. Moore and W. J. Koros, "Non-ideal effects in organic–inorganic materials for gas separation membranes," *Journal of Molecular Structure*, vol. 739, pp. 87-98, 2005.
- [231] H. Vinh-Thang and S. Kaliaguine, "Predictive models for mixed-matrix membrane performance: a review," *Chemical reviews*, vol. 113, pp. 4980-5028, 2013.
- [232] O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, *et al.*, "Metal–organic framework materials with ultrahigh surface areas: is the sky the limit?," *Journal of the American Chemical Society*, vol. 134, pp. 15016-15021, 2012.
- [233] K. C. Stylianou and W. L. Queen, "Recent Advances in Carbon Capture with Metal–Organic Frameworks," *CHIMIA International Journal for Chemistry*, vol. 69, pp. 274-283, 2015.
- [234] Y. Yang, K. Goh, R. Wang, and T.-H. Bae, "High-performance nanocomposite membranes realized by efficient molecular sieving with CuBDC nanosheets," *Chemical Communications*, vol. 53, pp. 4254-4257, 2017.
- [235] T.-H. Bae and J. R. Long, "CO₂/N₂ separations with mixed-matrix membranes containing Mg₂(dobdc) nanocrystals," *Energy & Environmental Science*, vol. 6, pp. 3565-3569, 2013.
- [236] L. Dong, M. Chen, J. Li, D. Shi, W. Dong, X. Li, *et al.*, "Metal-organic framework-graphene oxide composites: A facile method to highly improve the CO₂ separation performance of mixed matrix membranes," *Journal of Membrane Science*, vol. 520, pp. 801-811, 2016.

- [237] T. H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones, and S. Nair, "A High-Performance Gas-Separation Membrane Containing Submicrometer-Sized Metal–Organic Framework Crystals," *Angewandte Chemie International Edition*, vol. 49, pp. 9863-9866, 2010.
- [238] H. Gong, T. H. Nguyen, R. Wang, and T.-H. Bae, "Separations of binary mixtures of CO₂/CH₄ and CO₂/N₂ with mixed-matrix membranes containing Zn(pyrz)₂(SiF₆) metal-organic framework," *J. Membr. Sci.*, vol. 495, pp. 169-175, 2015.
- [239] K. Krishnamoorthy, M. Veerapandian, K. Yun, and S.-J. Kim, "The chemical and structural analysis of graphene oxide with different degrees of oxidation," *Carbon*, vol. 53, pp. 38-49, 2013.
- [240] H. Gong, S. S. Lee, and T.-H. Bae, "Mixed-matrix membranes containing inorganically surface-modified 5A zeolite for enhanced CO₂/CH₄ separation," *Microporous and Mesoporous Materials*, vol. 237, pp. 82-89, 2017.
- [241] M. Ionita, A. M. Pandele, L. Crica, and L. Pilan, "Improving the thermal and mechanical properties of polysulfone by incorporation of graphene oxide," *Composites Part B: Engineering*, vol. 59, pp. 133-139, 2014.
- [242] H. Huang, Y. Ying, and X. Peng, "Graphene oxide nanosheet: an emerging star material for novel separation membranes," *J. Mater. Chem. A*, vol. 2, pp. 13772-13782, 2014.
- [243] S. Wang, Y. Wu, N. Zhang, G. He, Q. Xin, X. Wu, *et al.*, "A highly permeable graphene oxide membrane with fast and selective transport nanochannels for efficient carbon capture," *Energy & Environmental Science*, vol. 9, pp. 3107-3112, 2016.
- [244] S. M. Davoodi, M. Sadeghi, M. Naghsh, and A. Moheb, "Olefin–paraffin separation performance of polyimide Matrimid®/silica nanocomposite membranes," *RSC Advances*, vol. 6, pp. 23746-23759, 2016.
- [245] J. E. Bachman and J. R. Long, "Plasticization-resistant Ni₂(dobdc)/polyimide composite membranes for the removal of CO₂ from natural gas," *Energy & Environmental Science*, vol. 9, pp. 2031-2036, 2016.
- [246] Y. Yang, C. Y. Chuah, L. Nie, and T.-H. Bae, "Enhancing the mechanical strength and CO₂/CH₄ separation performance of polymeric membranes by incorporating amine-appended porous polymers," *Journal of Membrane Science*, vol. 569, pp. 149-156, 2019.
- [247] W. Li, S. Samarasinghe, and T.-H. Bae, "Enhancing CO₂/CH₄ separation performance and mechanical strength of mixed-matrix membrane via combined use of graphene oxide and ZIF-8," *Journal of Industrial and Engineering Chemistry*, 2018.
- [248] S. Anastasiou, N. Bhorla, J. Pokhrel, K. S. Kumar Reddy, C. Srinivasakannan, K. Wang, *et al.*, "Metal-organic framework/graphene oxide composite fillers in mixed-matrix membranes for CO₂ separation," *Materials Chemistry and Physics*, vol. 212, pp. 513-522, 2018.
- [249] S. Castarlenas, C. Tlez, and J. Coronas, "Gas separation with mixed matrix membranes obtained from MOF UiO-66-graphite oxide hybrids," *Journal of Membrane Science*, vol. 526, pp. 205-211, 2017.
- [250] W. Li, C. Y. Chuah, L. Nie, and T.-H. Bae, "Enhanced CO₂/CH₄ selectivity and mechanical strength of mixed-matrix membrane incorporated with NiDOBDC/GO composite," *Journal of Industrial and Engineering Chemistry*, 2019.
- [251] D. R. Paul and Y. P. Yampol'skii, *Polymeric gas separation membranes*: CRC press, 1993.
- [252] Y. Dai, J. Johnson, O. Karvan, D. S. Sholl, and W. Koros, "Ultem®/ZIF-8 mixed matrix hollow fiber membranes for CO₂/N₂ separations," *Journal of Membrane Science*, vol. 401, pp. 76-82, 2012.
- [253] M. J. C. Ordonez, K. J. Balkus, J. P. Ferraris, and I. H. Musselman, "Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes," *Journal of Membrane Science*, vol. 361, pp.

28-37, 2010.

- [254] V. Nafisi and M.-B. Hägg, "Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO₂ capture," *Journal of Membrane Science*, vol. 459, pp. 244-255, 2014.
- [255] A. F. Bushell, M. P. Attfield, C. R. Mason, P. M. Budd, Y. Yampolskii, L. Starannikova, *et al.*, "Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8," *Journal of membrane science*, vol. 427, pp. 48-62, 2013.
- [256] M. Askari and T.-S. Chung, "Natural gas purification and olefin/paraffin separation using thermal cross-linkable co-polyimide/ZIF-8 mixed matrix membranes," *Journal of Membrane Science*, vol. 444, pp. 173-183, 2013.
- [257] A. F. Bushell, M. P. Attfield, C. R. Mason, P. M. Budd, Y. Yampolskii, L. Starannikova, *et al.*, "Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8," *Journal of Membrane Science*, vol. 427, pp. 48-62, 2013.
- [258] Y. Dai, J. R. Johnson, O. Karvan, D. S. Sholl, and W. J. Koros, "Ultem®/ZIF-8 mixed matrix hollow fiber membranes for CO₂/N₂ separations," *Journal of Membrane Science*, vol. 401-402, pp. 76-82, 2012.
- [259] Q. Song, S. K. Nataraj, M. V. Roussanova, J. C. Tan, D. J. Hughes, W. Li, *et al.*, "Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation," *Energy & Environmental Science*, vol. 5, p. 8359, 2012.
- [260] V. Nafisi and M.-B. Hägg, "Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO₂ capture," *Journal of Membrane Science*, vol. 459, pp. 244-255, 2014.
- [261] C. Duan, X. Jie, D. Liu, Y. Cao, and Q. Yuan, "Post-treatment effect on gas separation property of mixed matrix membranes containing metal organic frameworks," *Journal of Membrane Science*, vol. 466, pp. 92-102, 2014.
- [262] M. Harasimowicz, P. Orluk, G. Zakrzewska-Trznadel, and A. Chmielewski, "Application of polyimide membranes for biogas purification and enrichment," *Journal of Hazardous Materials*, vol. 144, pp. 698-702, 2007.
- [263] J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber, and M. Wiebcke, "Rapid room-temperature synthesis and characterization of nanocrystals of a prototypical zeolitic imidazolate framework," *Chemistry of Materials*, vol. 21, pp. 1410-1412, 2009.
- [264] Y. Yang, C. Y. Chuah, H. Gong, and T.-H. Bae, "Robust microporous organic copolymers containing triphenylamine for high pressure CO₂ capture application," *Journal of CO₂ Utilization*, vol. 19, pp. 214-220, 2017.
- [265] G. Liu, L. Wang, B. Wang, T. Gao, and D. Wang, "A reduced graphene oxide modified metallic cobalt composite with superior electrochemical performance for supercapacitors," *RSC Advances*, vol. 5, pp. 63553-63560, 2015.
- [266] T.-H. Bae, J. Liu, J. S. Lee, W. J. Koros, C. W. Jones, and S. Nair, "Facile high-yield solvothermal deposition of inorganic nanostructures on zeolite crystals for mixed matrix membrane fabrication," *Journal of the American Chemical Society*, vol. 131, pp. 14662-14663, 2009.
- [267] H. Gong, S. S. Lee, and T.-H. Bae, "Mixed-matrix membranes containing inorganically surface-modified 5A zeolite for enhanced CO₂/CH₄ separation," *Microporous and Mesoporous Materials*, vol. 237, pp. 82-89, 2017.
- [268] N. P. Patel, J. M. Zielinski, J. Samseth, and R. J. Spontak, "Effects of Pressure and Nanoparticle Functionality on CO₂-Selective Nanocomposites Derived from Crosslinked Poly (ethylene glycol)," *Macromolecular Chemistry and Physics*, vol. 205, pp. 2409-2419, 2004.

- [269] L. Nicolais and M. Narkis, "Stress-strain behavior of styrene-acrylonitrile/glass bead composites in the glassy region," *Polymer Engineering & Science*, vol. 11, pp. 194-199, 1971.
- [270] V. Nafisi and M.-B. Hägg, "Gas separation properties of ZIF-8/6FDA-durene diamine mixed matrix membrane," *Separation and Purification Technology*, vol. 128, pp. 31-38, 2014.
- [271] H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, and J. r. Caro, "Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis," *Journal of the American Chemical Society*, vol. 131, pp. 16000-16001, 2009.
- [272] W. Li, S. Samarasinghe, and T.-H. Bae, "Enhancing CO₂/CH₄ separation performance and mechanical strength of mixed-matrix membrane via combined use of graphene oxide and ZIF-8," *Journal of Industrial and Engineering Chemistry*, 2018.
- [273] W. N. W. Salleh and A. F. Ismail, "Effects of carbonization heating rate on CO₂ separation of derived carbon membranes," *Separation and Purification Technology*, vol. 88, pp. 174-183, 2012.
- [274] L. Li, T. Wang, Q. Liu, Y. Cao, and J. Qiu, "A high CO₂ permselective mesoporous silica/carbon composite membrane for CO₂ separation," *Carbon*, vol. 50, pp. 5186-5195, 2012.
- [275] X. Yin, N. Chu, J. Yang, J. Wang, and Z. Li, "Thin zeolite T/carbon composite membranes supported on the porous alumina tubes for CO₂ separation," *International Journal of Greenhouse Gas Control*, vol. 15, pp. 55-64, 2013.
- [276] P. S. Tin, T.-S. Chung, L. Jiang, and S. Kulprathipanja, "Carbon-zeolite composite membranes for gas separation," *Carbon*, vol. 43, pp. 2025-2027, 2005.
- [277] X. Yin, J. Wang, N. Chu, J. Yang, J. Lu, Y. Zhang, *et al.*, "Zeolite L/carbon nanocomposite membranes on the porous alumina tubes and their gas separation properties," *Journal of Membrane Science*, vol. 348, pp. 181-189, 2010.
- [278] D. Bastani, N. Esmaeili, and M. Asadollahi, "Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review," *Journal of Industrial and Engineering Chemistry*, vol. 19, pp. 375-393, 2013.
- [279] Y. Li, H.-M. Guan, T.-S. Chung, and S. Kulprathipanja, "Effects of novel silane modification of zeolite surface on polymer chain rigidification and partial pore blockage in polyethersulfone (PES)-zeolite A mixed matrix membranes," *Journal of Membrane Science*, vol. 275, pp. 17-28, 2006.
- [280] T. H. Nguyen, S. Kim, M. Yoon, and T. H. Bae, "Hierarchical Zeolites with Amine-Functionalized Mesoporous Domains for Carbon Dioxide Capture," *ChemSusChem*, vol. 9, pp. 455-61, Mar 8 2016.
- [281] C. Duan, X. Jie, H. Zhu, D. Liu, W. Peng, and Y. Cao, "Gas-permeation performance of metal organic framework/polyimide mixed-matrix membranes and additional explanation from the particle size angle," *Journal of Applied Polymer Science*, vol. 135, p. 45728, 2018.
- [282] N. Prasetya, A. A. Teck, and B. P. Ladewig, "Matrimid-JUC-62 and Matrimid-PCN-250 mixed matrix membranes displaying light-responsive gas separation and beneficial ageing characteristics for CO₂/N₂ separation," *Scientific reports*, vol. 8, p. 2944, 2018.
- [283] C. Y. Chuah, K. Goh, Y. Yang, H. Gong, W. Li, H. E. Karahan, *et al.*, "Harnessing Filler Materials for Enhancing Biogas Separation Membranes," *Chemical reviews*, vol. 118, pp. 8655-8769, 2018.
- [284] C. Y. Chuah, S. Yu, K. Na, and T.-H. Bae, "Enhanced SF₆ recovery by hierarchically structured MFI zeolite," *Journal of industrial and engineering chemistry*, vol. 62, pp. 64-71, 2018.
- [285] M. Calle and Y. M. Lee, "Thermally rearranged (TR) poly (ether- benzoxazole) membranes for gas separation," *Macromolecules*, vol. 44, pp. 1156-1165, 2011.
- [286] S. H. Han, N. Misdan, S. Kim, C. M. Doherty, A. J. Hill, and Y. M. Lee, "Thermally rearranged (TR) polybenzoxazole: effects of diverse imidization routes on physical properties and gas

- transport behaviors," *Macromolecules*, vol. 43, pp. 7657-7667, 2010.
- [287] F. Weigelt, P. Georgopoulos, S. Shishatskiy, V. Filiz, T. Brinkmann, and V. Abetz, "Development and Characterization of Defect-Free Matrimid® Mixed-Matrix Membranes Containing Activated Carbon Particles for Gas Separation.," *Polymers* vol. 10, p. 51, 2018.
- [288] Y. Xiao, Y. Dai, T.-S. Chung, and M. D. Guiver, "Effects of brominating Matrimid polyimide on the physical and gas transport properties of derived carbon membranes," *Macromolecules*, vol. 38, pp. 10042-10049, 2005.
- [289] A. K. Itta, H.-H. Tseng, and M.-Y. Wey, "Effect of dry/wet-phase inversion method on fabricating polyetherimide-derived CMS membrane for H₂/N₂ separation," *International Journal of Hydrogen Energy*, vol. 35, pp. 1650-1658, 2010.
- [290] W. Wei, G. Qin, H. Hu, L. You, and G. Chen, "Preparation of supported carbon molecular sieve membrane from novolac phenol-formaldehyde resin," *Journal of Membrane Science*, vol. 303, pp. 80-85, 2007.
- [291] M. Kiyono, P. J. Williams, and W. J. Koros, "Effect of pyrolysis atmosphere on separation performance of carbon molecular sieve membranes," *Journal of Membrane Science*, vol. 359, pp. 2-10, 2010.
- [292] A. Fuertes and T. Centeno, "Preparation of supported asymmetric carbon molecular sieve membranes," *Journal of Membrane Science*, vol. 144, pp. 105-111, 1998.
- [293] P. Baskar and A. Senthilkumar, "Effects of oxygen enriched combustion on pollution and performance characteristics of a diesel engine," *Eng. Sci. Technol. Int J.*, vol. 19, pp. 438-443, 2016.
- [294] D. Gielen, "CO₂ removal in the iron and steel industry," *Energy Convers. Manag.*, vol. 44, pp. 1027-1037, 2003.
- [295] R. Chen and W. Yeun, "Review of the high-temperature oxidation of iron and carbon steels in air or oxygen," *Oxid. Met.*, vol. 59, pp. 433-468, 2003.
- [296] M. S. Rahman and C. O. Perera, "Drying and food preservation," in *Handbook of food preservation*, ed: Marcel Dekker, New York, 1999, pp. 173-216.
- [297] R. Cornelissen and G. Hirs, "Exergy analysis of cryogenic air separation," *Energy Convers. Manag.*, vol. 39, pp. 1821-1826, 1998.
- [298] Y. Zhu, X. Liu, and Z. Zhou, "Optimization of cryogenic air separation distillation columns," in *2006 6th World Congress on Intelligent Control and Automation*, 2006, pp. 7702-7705.
- [299] A. Smith and J. Klosek, "A review of air separation technologies and their integration with energy conversion processes," *Fuel Process. Technol.*, vol. 70, pp. 115-134, 2001.
- [300] D. Ruthven and S. Farooq, "Air separation by pressure swing adsorption," *Gas Sep. Purif.*, vol. 4, pp. 141-148, 1990.
- [301] M. Hassan, D. Ruthven, and N. Raghavan, "Air separation by pressure swing adsorption on a carbon molecular sieve," *Chem. Eng. Sci.*, vol. 41, pp. 1333-1343, 1986.
- [302] L. Jiang, L. T. Biegler, and V. G. Fox, "Simulation and optimization of pressure-swing adsorption systems for air separation," *AIChE J.*, vol. 49, pp. 1140-1157, 2003.
- [303] R. Swaidan, X. Ma, E. Litwiller, and I. Pinnau, "High pressure pure-and mixed-gas separation of CO₂/CH₄ by thermally-rearranged and carbon molecular sieve membranes derived from a polyimide of intrinsic microporosity," *J. Membr. Sci.*, vol. 447, pp. 387-394, 2013.
- [304] R. Kumar and W. J. Koros, "High performance carbon molecular sieve membranes resistance to aggressive feed stream contaminants," *Ind. Eng. Chem. Res.*, 2019/04/01 2019.
- [305] W. Salleh and A. Ismail, "Effects of carbonization heating rate on CO₂ separation of derived carbon membranes," *Sep. Purif. Technol.*, vol. 88, pp. 174-183, 2012.

- [306] H. Gong, C. Y. Chuah, Y. Yang, and T.-H. Bae, "High performance composite membranes comprising Zn(pyrz)₂(SiF₆) nanocrystals for CO₂/CH₄ separation," *J. Ind. Eng. Chem.*, vol. 60, pp. 279-285, 2018.
- [307] C. Zhang, Y. Dai, J. R. Johnson, O. Karvan, and W. J. Koros, "High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations," *J. Membr. Sci.*, vol. 389, pp. 34-42, 2012.
- [308] B. Zhang, Y. Shi, Y. Wu, T. Wang, and J. Qiu, "Towards the preparation of ordered mesoporous carbon/carbon composite membranes for gas separation," *Sep. Sci. Technol.*, vol. 49, pp. 171-178, 2014.
- [309] X. Yin, N. Chu, J. Yang, J. Wang, and Z. Li, "Thin zeolite T/carbon composite membranes supported on the porous alumina tubes for CO₂ separation," *Int. J. Greenh. Gas Con.*, vol. 15, pp. 55-64, 2013.
- [310] P. S. Tin, T.-S. Chung, L. Jiang, and S. Kulprathipanja, "Carbon-zeolite composite membranes for gas separation," *Carbon*, vol. 43, pp. 2025-2027, 2005.
- [311] X. Yin, J. Wang, N. Chu, J. Yang, J. Lu, Y. Zhang, *et al.*, "Zeolite L/carbon nanocomposite membranes on the porous alumina tubes and their gas separation properties," *J. Membr. Sci.*, vol. 348, pp. 181-189, 2010.
- [312] C. Y. Chuah, K. Goh, Y. Yang, H. Gong, W. Li, H. E. Karahan, *et al.*, "Harnessing filler materials for enhancing biogas separation membranes," *Chem. Rev.*, vol. 118, pp. 8655-8769, 2018.
- [313] X. Zhang, C. Y. Chuah, P. Dong, Y.-H. Cha, T.-H. Bae, and M.-K. Song, "Hierarchically Porous Co-MOF-74 Hollow Nanorods for Enhanced Dynamic CO₂ Separation," *ACS Appl. Mater. Int.*, vol. 10, pp. 43316-43322, 2018.
- [314] Ş. B. Tantekin-Ersolmaz, Ç. Atalay-Oral, M. Tatlier, A. Erdem-Şenatalar, B. Schoeman, and J. Sterte, "Effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membranes," *J. Membr. Sci.*, vol. 175, pp. 285-288, 2000.
- [315] A. Corma, "From microporous to mesoporous molecular sieve materials and their use in catalysis," *Chem. Rev.*, vol. 97, pp. 2373-2420, 1997.
- [316] C. Y. Chuah, K. Goh, and T.-H. Bae, "Hierarchically structured HKUST-1 nanocrystals for enhanced SF₆ capture and recovery," *J. Phys. Chem. C*, vol. 121, pp. 6748-6755, 2017.
- [317] S. Yu, S. Kwon, and K. Na, "Synthesis of LTA zeolites with controlled crystal sizes by variation of synthetic parameters: Effect of Na⁺ concentration, aging time, and hydrothermal conditions," *Journal of Sol-Gel Science and Technology*, pp. 1-11.
- [318] C. Y. Chuah and T.-H. Bae, "Incorporation of Cu₃BTC₂ nanocrystals to increase the permeability of polymeric membranes in O₂/N₂ separation," *BMC Chem. Eng.*, vol. 1, p. 2, 2019.
- [319] L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes," *J. Membr. Sci.*, vol. 62, pp. 165-185, 1991.
- [320] N. C. Burtch, H. Jasuja, and K. S. Walton, "Water stability and adsorption in metal-organic frameworks," *Chemical reviews*, vol. 114, pp. 10575-10612, 2014.
- [321] S. Zuluaga, E. M. Fuentes-Fernandez, K. Tan, F. Xu, J. Li, Y. J. Chabal, *et al.*, "Understanding and controlling water stability of MOF-74," *Journal of Materials Chemistry A*, vol. 4, pp. 5176-5183, 2016.
- [322] R. W. Baker, "Future directions of membrane gas separation technology," *Industrial & engineering chemistry research*, vol. 41, pp. 1393-1411, 2002.
- [323] R. W. Baker and B. T. Low, "Gas separation membrane materials: a perspective," *Macromolecules*, vol. 47, pp. 6999-7013, 2014.
- [324] S. Metz, W. Vandeven, J. Potreck, M. Mulder, and M. Wessling, "Transport of water vapor and

- inert gas mixtures through highly selective and highly permeable polymer membranes," *Journal of Membrane Science*, vol. 251, pp. 29-41, 2005.
- [325] G. Zhang, H. Cheng, P. Su, X. Zhang, J. Zheng, Y. Lu, *et al.*, "PIM-1/PDMS hybrid pervaporation membrane for high-efficiency separation of n-butanol-water mixture under low concentration," *Separation and Purification Technology*, vol. 216, pp. 83-91, 2019.
- [326] S. Heydari and V. Pirouzfard, "The influence of synthesis parameters on the gas selectivity and permeability of carbon membranes: empirical modeling and process optimization using surface methodology," *RSC Advances*, vol. 6, pp. 14149-14163, 2016.
- [327] Y. Zheng, N. Hu, H. Wang, N. Bu, F. Zhang, and R. Zhou, "Preparation of steam-stable high-silica CHA (SSZ-13) membranes for CO₂/CH₄ and C₂H₄/C₂H₆ separation," *Journal of Membrane Science*, vol. 475, pp. 303-310, 2015.
- [328] M. Rezakazemi, M. Sadrzadeh, and T. Matsuura, "Thermally stable polymers for advanced high-performance gas separation membranes," *Progress in Energy and Combustion Science*, vol. 66, pp. 1-41, 2018.
- [329] M. Omidvar, C. M. Stafford, and H. Lin, "Thermally stable cross-linked P84 with superior membrane H₂/CO₂ separation properties at 100 °C," *Journal of Membrane Science*, vol. 575, pp. 118-125, 2019.
- [330] H. Richter, N. Reger-Wagner, S. Kämnitz, I. Voigt, U. Lubenau, and R. Mothes, "Carbon membranes for bio gas upgrading," *Energy Procedia*, vol. 158, pp. 861-866, 2019/02/01/ 2019.