Microporous materials with tailored structural properties for enhanced gas separation

Chuah, Chong Yang

2019

Chuah, C. Y. (2019). Microporous materials with tailored structural properties for enhanced gas separation. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/90277>

<https://doi.org/10.32657/10220/48516>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**MICROPOROUS MATERIALS WITH
TAILORED STRUCTURAL PROPERTIES
FOR ENHANCED GAS SEPARATION**

CHUAH CHONG YANG

SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING

2019

CHUAH CHONG YANG

**MICROPOROUS MATERIALS WITH
TAILORED STRUCTURAL PROPERTIES
FOR ENHANCED GAS SEPARATION**

CHUAH CHONG YANG

SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING

A thesis submitted to Nanyang Technological
University in partial fulfilment 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.

28-Feb-2019

.....

Date

.....

CHUAH CHONG YANG

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.

28-Feb-2019

.....

Date

.....

BAE TAE-HYUN

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains materials from 6 papers submitted and (or) published in the following peer-reviewed journals where I was the first author.

Chapter 3 is published as **C. Y. Chuah**, S. Yu, K. Na and T-H. Bae. Enhanced SF₆ recovery by hierarchically structured MFI zeolite, *J. Ind. Eng. Chem.* **62**, 64-71 (2018).

The contributions of the co-authors are as follows:

- Prof Bae and Prof Na provided the initial project direction
- I prepared the manuscript draft, with the manuscript was revised by Dr Yu, Prof Na and Prof Bae
- Dr Yu provided the samples and provided the characterization data for the porous materials. Additional characterizations (gas adsorption analysis) were conducted by me at the School of Chemical and Biomedical Engineering.
- I analysed the data obtained from the characterization studies

Chapter 4 is published as **C. Y. Chuah**, K. Goh, and T-H. Bae. Hierarchically structured HKUST-1 nanocrystals for enhanced SF₆ capture and recovery, *J. Phys. Chem. C* **121** (12), 6748-6755 (2017).

The contributions of the co-authors are as follows:

- Prof Bae provided the initial project direction
- I prepared the manuscript draft, with the manuscript was revised by Dr. Goh and Prof Bae
- I conducted all the laboratory works (sample preparations, characterizations) at the School of Chemical and Biomedical Engineering.
- I analysed the data obtained from the characterization studies.

Chapter 5 is published as X. Zhang¹, **C. Y. Chuah¹**, P. Dong, T-H.. Bae, M-K. Song, Hierarchically porous Co-MOF-74 hollow nanorods for enhanced dynamic CO₂ separation, *ACS Appl. Mater. Interface*, *in press*

The contributions of the co-authors are as follows:

- Prof Bae and Prof Song provided the initial project direction
- Both Mr Zhang and I prepared the manuscript draft, with the manuscript was revised by Prof Bae and Prof Song
- Mr Zhang provided the samples and provided the characterization data for the porous materials. Additional characterizations (gas adsorption analysis) were conducted by me at the School of Chemical and Biomedical Engineering.
- I analysed the data obtained from the characterization studies.

Chapter 6 is published as **C. Y. Chuah¹**, Y. Yang¹ and T-H. Bae. Hierarchically porous polymers containing triphenylamine for enhanced SF₆ separation, *Microporous Mesoporous Mater.* **272**, 232-240 (2018).

The contributions of the co-authors are as follows:

- Prof Bae provided the initial project direction
- I prepared the manuscript draft, with the manuscript was revised by Prof Bae
- Dr Yang provided the samples. Additional characterizations (gas adsorption analysis) were conducted by me at the School of Chemical and Biomedical Engineering.
- I analysed the data obtained from the characterization studies.

Chapter 7 is published as **C. Y. Chuah**, T-H. Bae Incorporation of nanocrystal HKUST-1 nanocrystals to increase the permeability of polymeric membranes in O₂/N₂ separation, *BMC Chem. Eng.*, 1:2 (2019)

The contributions of the co-authors are as follows:

- Prof Bae provided the initial project direction
- I prepared the manuscript draft, with the manuscript was revised by Prof Bae
- I conducted all the laboratory works (sample preparations, characterizations) at the School of Chemical and Biomedical Engineering.
- I analysed the data obtained from the characterization studies.

Chapter 8 is published as **C. Y. Chuah**, W. Li, S.A.S.C. Samarasinghe, G. S. M. D. P. Sethunga and T-H. Bae. Enhancing the CO₂ separation performance of polymer membranes via the incorporation of amine-functionalized HKUST-1 nanocrystals, *manuscript under review*.

The contributions of the co-authors are as follows:

- Prof Bae provided the initial project direction
- I prepared the manuscript draft, with the manuscript was revised by Prof Bae
- W. Li, S.A.S.C Samarasinghe and G. S. M. D. P. Sethunga assisted in the characterization of the fillers and polymers. Additional characterizations (gas adsorption analysis) were conducted by me at the School of Chemical and Biomedical Engineering.
- I analysed the data obtained from the characterization studies.

28-Feb-2019

.....

Date

.....

CHUAH CHONG YANG

ACKNOWLEDGEMENTS

First and foremost, I would like to express my utmost sincere gratitude towards my main thesis advisor, Professor Bae Tae-Hyun who has encouraged me to involve in the research work during the last semester in my undergraduate study. With such exposure, it allows me to be confident enough to continue my research under his support, guidance and supervision. Throughout my Ph. D. study, I strongly appreciate his intention in forking out his valuable time to conduct weekly meeting as well as reviewing the manuscript drafts, thesis and presentation slides, thus ensuring that my research progress, writing and presentation skills can be monitored and improved effectively. Besides, I am fully appreciated by his effort in allowing me to involve in other research areas such as hydrocarbon separation and membrane contactors, which allows me to expand my current field of knowledge.

Next, I would like to thank Thesis Advisory Committee (TAC) members, Professor Wang Rong and Professor Chew Jia Wei for their valuable and constructive comments regarding my research topic. In addition, I would also like to thank TAC members and Professor Xu Rong who had provided useful suggestions during my qualifying examination, thus allowing me to finetune the current Ph. D. thesis further. I would also hope to use this opportunity to give special thanks to Professor Kim Kimoon from Pohang University of Science and Technology, Professor Lee Eunsung from Pohang University of Science and Technology, Professor Michael D. Guiver from Tianjin University, Professor Na Kyungsu from Chonnam National University and Professor Song Min-Kyu from Washington State University for their active involvement as a collaborator, thus allowing me to learn several useful insights on other research areas through meaningful discussions that will be useful for my future undertakings.

Undoubtedly, I am very thankful to my co-workers that have been actively assisting me through biweekly group meetings, literature reviews and research updates presentations so that I am able to acquire new knowledge, namely Dr. Goh Kunli, Dr. Gong Heqing, Dr. H. Enis Karahan, Dr. Lee Jaewoo, Dr. Lee Siew Siang, Dr. Low Jiun Hui, Dr. Nguyen Tien Hoa, Dr. Nie Lina, Dr. Piyarat Weeranchanchai, Dr. Sunee Wongchitphimon, Dr. Witchitpan Rongwong, Dr. Yang Euntae, Dr. Yang Yanqin, Dr. Yun Jeonghun, Ms. Dilhara, Ms Lee Junghyun, Ms. Li Wen, Ms. Margaret Heng and Ms. Sulashi. Moreover, I am fully appreciated on the efforts that has been done among the group members through informal get-together, lunches and dinners in order to foster unity in our research group. Apart from this, I would like to express my sincere appreciation to the administrative and professional staffs from the School of Chemical and Biomedical Engineering (SCBE), who includes Dr. Ong Teng Teng, Dr. Wang Xiujuan, Dr. Yu Shucong, Mr. Bobby Chow, Ms. Heng Kim Ying, Mr. Jason Quek, Ms. Jessica Gan, Mr. Ng Fu Song and Ms. Octavia Huang who have assisted me in the instrument training and other preparatory works for equipment set-ups, thus allowing me to conduct my research without much hurdles.

I would like to dedicate this thesis to my beloved parents who have demonstrated strong and active support towards me through endless support and patience, given the fact that I have been staying far from home for the past eight years to pursue my undergraduate and postgraduate studies in Nanyang Technological University (NTU). Without their unconditional help, I would not be able to complete this thesis by myself. Last but not least, I would like to thank NTU and Ministry of Education (MOE) Singapore for providing the required financial support throughout my Ph. D. study.

Chuah Chong Yang

TABLE OF CONTENTS

STATEMENT OF ORIGINALITY	I
SUPERVISOR DECLARATION STATEMENT	III
AUTHORSHIP ATTRIBUTION STATEMENT.....	V
ACKNOWLEDGEMENTS	XI
TABLE OF CONTENTS.....	XV
LIST OF PUBLICATIONS	XXII
LIST OF FIGURES	XXV
LIST OF TABLES	XXXII
LIST OF ABBREVIATIONS.....	XXXIV
ABSTRACT.....	XXXVIII
Chapter 1 INTRODUCTION.....	1
1.1 Background	1
1.2 Gas separation processes.....	2
1.2.1 Greenhouse gas (GHG) capture	2
1.2.2 Air separation.....	6
1.3 Challenges in gas separation process	7
1.3.1 Greenhouse gas (GHG) capture	7
1.3.2 Air separation.....	8
1.4 Nanoporous materials and membranes as a solution	10
1.5 Research objectives.....	12

1.6 Thesis outline	12
Chapter 2 LITERATURE REVIEW	14
2.1 Introduction.....	14
2.1.1 Zeolites and related materials	14
2.1.1.1 Si/Al ratio.....	16
2.1.1.2 Cation type and position	17
2.1.1.3 Zeolite structure	19
2.1.1.4 Zeotypes (zeolite-like materials).....	20
2.2 Metal-organic framework (MOF)	21
2.2.1 Molecular sieving.....	23
2.2.2 Flexible framework.....	24
2.2.3 Coordinatively unsaturated open metal sites	25
2.2.4 surface functionalization	27
2.2.5 Zeolitic imidazolate framework (ZIF)	29
2.3 Microporous organic polymer (MOP)	31
2.4 Mesoporous materials	35
2.5 Mixed-matrix membrane (MMM)	37
2.5.1 Mathematical model for gas permeation properties.....	38
2.5.2 Non-ideal interfacial morphologies	40
2.6 Conclusion	43
Chapter 3 Development of Hierarchically Structured MFI Zeolites	45

3.1 Introduction.....	45
3.2 Experimental methods	46
3.2.1 Materials	46
3.2.2 Synthesis of zeolite MFI	46
3.2.3 Characterization	47
3.2.4 Evaluation of SF ₆ and N ₂ uptake performance	48
3.2.5 Vacuum swing adsorption (VSA)	50
3.2.6 Breakthrough measurement	51
3.3 Results and discussion	52
3.3.1 Synthesis of hierarchical zeolite MFI	52
3.3.2 SF ₆ adsorption of zeolite MFI crystals.....	54
3.3.3 SF ₆ /N ₂ selectivity and isosteric heat of adsorption of zeolite MFI crystals.....	56
3.3.4 Potential applicability in idealized vacuum swing adsorption (VSA)	57
3.3.5 SF ₆ breakthrough analysis.....	58
3.4 Conclusion	59
3.5 Declaration	60
Chapter 4 Development of Hierarchically Structured HKUST-1	61
4.1 Introduction.....	61
4.2 Experimental Methods	62
4.2.1 Materials	62
4.2.2 Synthesis of HKUST-1	62

4.2.3 Characterization	63
4.2.4 Evaluation of SF ₆ and N ₂ uptake performance	63
4.3 Results and discussion	65
4.3.1 Synthesis and characterization of hierarchical HKUST-1 nanocrystals	65
4.3.2 SF ₆ adsorption and capacities of HKUST-1 crystals	67
4.3.3 SF ₆ /N ₂ selectivity and isosteric heat of adsorption	69
4.3.3 Potential utility in idealized vacuum swing adsorption	71
4.4 Conclusion	72
4.5 Declaration	73
Chapter 5 Development of Hierarchically Porous Co-MOF-74 Hollow Nanorods	74
5.1 Introduction	74
5.2 Experimental Methods	75
5.2.1 Materials	75
5.2.2 Synthesis of adsorbent	75
5.2.3 Characterization	77
5.2.4 Breakthrough and Chromatographic Separation	78
5.3 Results and discussion	79
5.3.1 Synthesis of Co-MOF-74	79
5.3.2 Gas adsorption behaviour of Co-MOF-74	85
5.4 Conclusion	88
5.5 Declaration	89

Chapter 6 Hierarchically Porous Polymers Containing Triphenylamine for Enhanced SF ₆ Separation.....	90
6.1 Introduction.....	90
6.2 Experimental Methods	91
6.2.1 Materials	91
6.2.2 Synthesis of adsorbents.....	91
6.2.3 Porosity and morphology characterization	92
6.2.4 SF ₆ /N ₂ adsorption behaviour of PPN _x copolymers	93
6.2.5 Breakthrough and chromatographic separation	93
6.3 Results and discussion	94
6.3.1 Synthesis of PPN _x adsorbents	94
6.3.2 SF ₆ and N ₂ adsorption of PPN _x	99
6.3.3 SF ₆ /N ₂ selectivity and isosteric heat of adsorption of porous polymers	101
6.3.4 Potential utilization of PPN _x in idealized VSA	103
6.3.5 Breakthrough and chromatographic measurements.....	104
6.4 Conclusion	106
6.5 Declaration	106
Chapter 7 Development of HKUST-1 nanocrystals in increasing the permeability of polymeric membrane in O ₂ /N ₂ and CO ₂ /CH ₄ separation.....	107
7.1 Introduction.....	107
7.2 Experimental Methods	108

7.2.1 Materials	108
7.2.2 Synthesis of HKUST-1 Nanocrystals	108
7.2.3 Membrane Fabrication	108
7.2.4 Characterization of HKUST-1 nanocrystals	109
7.2.5 Characterization of mixed-matrix membrane	109
7.2.6 Mixture gas permeation test.....	110
7.2.7 Gas adsorption analysis.....	110
7.3 Results and discussion	111
7.3.1 Synthesis of HKUST-1 nanocrystals	111
7.3.2 O ₂ , N ₂ , CO ₂ and CH ₄ adsorption of HKUST-1 nanocrystals.....	112
7.3.3 Fabrication of mixed-matrix membrane	113
7.3.4 Gas permeation properties	115
7.4 Conclusion	117
7.5 Declaration.....	118
Chapter 8 Effect of incorporating amine-functionalized HKUST-1 in polymeric membrane for CO ₂ /N ₂ separation	119
8.1 Introduction.....	119
8.2 Experimental Methods	120
8.2.1 Materials	120
8.2.2 Synthesis of HKUST-1 and amine-functionalized HKUST-1	120
8.2.3 Membrane fabrication.....	121

8.2.4 Characterization of HKUST-1 and amine-functionalized HKUST-1 nanocrystals.....	121
8.2.5 Characterization of mixed-matrix membranes containing HKUST-1 and amine-functionalized HKUST-1 nanocrystals.....	123
8.2.6 Mixture gas permeation test and gas adsorption analysis	123
8.3 Results and discussion	124
8.3.1 Synthesis of HKUST-1 and amine-functionalized HKUST-1 nanocrystals	124
8.3.2 CO ₂ and N ₂ adsorption of HKUST-1 and amine-functionalized HKUST-1 nanocrystals.....	128
8.3.3 Fabrication of mixed-matrix membrane	129
8.3.4 Gas permeation properties	131
8.4 Conclusion	134
8.5 Declaration.....	135
Chapter 9 Conclusions	136
9.1 Overview.....	136
9.2 Summary of empirical findings	136
9.3 Recommendations and future works.....	139
9.4 Outlook	143
Chapter 10 List of References.....	144

LIST OF PUBLICATIONS

1. **C. Y. Chuah**, W. Li, S.A.S.C Samarasinghe, G. S. M. D. P. Sethunga, T-H. Bae, Enhancing the CO₂ separation performance of polymer membranes via the incorporation of amine-functionalized HKUST-1 nanocrystals, *manuscript under review*.
2. Y. Yang¹, K. Goh¹, **C. Y. Chuah**¹, H. E. Karahan, Ö. Brier, T-H. Bae, Sub-Ångström-Level Engineering of Ultramicroporous Carbons for Enhanced Sulfur Hexafluoride Capture, *manuscript under review*
3. W. Li¹, **C. Y. Chuah**¹, S. Kwon, K. Na, T-H. Bae, Zeolite 5A/porous carbon mixed-matrix membranes for O₂/N₂ separation: Effects of the particle size and mesoporosity of 5A, *manuscript under review*.
4. S. A. S. C. Samarasinghe¹, **C. Y. Chuah**¹, W. Li, G. S. M. D. P. Sethunga, T-H. Bae, Incorporation of Co^{III} complex and SNW-1 nanoparticles to tailor O₂/N₂ separation performance in mixed-matrix membrane, *Sep. Purif. Technol.*, **2019**, 223, 133-141
5. **C. Y. Chuah**, T-H. Bae, Incorporation of HKUST-1 nanocrystals to increase the permeability of polymeric membranes in O₂/N₂ separation, *BMC Chem. Eng.*, 2019, 1:2
6. X. Zhang¹, **C. Y. Chuah**¹, P. Dong, Y. Cha, T-H. Bae, M. K. Song, Hierarchically Porous Co-MOF-74 Hollow Nanorods for Enhanced Dynamic CO₂ Separation, *ACS Appl. Mater. Interfaces*, **2018**, 10, 50, 43316-43322
7. **C. Y. Chuah**¹, K. Goh¹, Y. Yang, H. Gong, W. Li, H. E. Karahan, M. D. Guiver, R. Wang, T-H. Bae, Harnessing Filler Materials for Enhancing Biogas Separation Membranes, *Chem. Rev.*, **2018**, 118 (18), 8655-8769

8. **C. Y. Chuah**¹, Y. Yang¹, T-H. Bae, Hierarchically porous polymers containing triphenylamine for enhanced SF₆ separation, *Micropor. Mesopor. Mater.*, **2018**, 272, 232-240
9. **C. Y. Chuah**, S. Yu, K. Na, T-H. Bae, Enhanced SF₆ recovery by hierarchically structured MFI zeolite, *J. Ind. Eng. Chem.*, **2018**, 62, 64-71
10. **C. Y. Chuah**, K. Goh, T-H. Bae, Hierarchically structured HKUST-1 nanocrystals for enhanced SF₆ capture and recovery, *J. Phys. Chem. C*, **2017**, 121 (12), 6748-6755
11. Y. Yang, **C. Y. Chuah**, L. Nie, T-H. Bae, Enhancing the mechanical strength and CO₂/CH₄ performance of polymeric membranes by incorporating amine-appended polymers, *J. Membr. Sci.*, **2019**, 569, 149-156
12. Y. Yang, **C. Y. Chuah**, T-H. Bae, Polyamine-appended porous organic polymers for efficient post-combustion CO₂ capture, *J. Membr. Sci.*, **2019**, 358, 1227-1234.
13. W. Li, **C. Y. Chuah**, L. Nie, T-H. Bae, Enhanced CO₂/CH₄ selectivity and mechanical strength of mixed-matrix membrane incorporated with NiDOBDC/GO composite, *J. Ind. Eng. Chem.*, **2018**, 74, 118-125
14. S. A. S. C. Samarasinghe, **C. Y. Chuah**, Y. Yang, T-H. Bae, Tailoring CO₂/CH₄ separation properties of mixed-matrix membranes via combined use of two- and three-dimensional metal-organic frameworks, *J. Membr. Sci.*, **2018**, 557, 30-37
15. J. Lee, **C. Y. Chuah**, N. Ko, Y. Seo, K. Kim, T-H. Bae, E. Lee, Separation of Acetylene from Carbon Dioxide and Ethylene by a Water Stable Microporous Metal-organic Framework with Aligned Imidazolium Groups inside the Channels, *Angew. Chem. Int. Ed.*, **2018**, 130, 7955-7999

16. W. Li, **C. Y. Chuah**, Y. Yang, T-H. Bae, Nanocomposites formed by in situ growth of NiDOBDC nanoparticles on graphene oxide sheets for enhanced CO₂ and H₂ storage, *Microporous Mesoporous Mater.*, **2018**, 265, 35-42
17. H. Gong, **C. Y. Chuah**, Y. Yang, T-H. Bae, High performance composite membrane comprising Zn(pyrz)₂(SiF₆) nanocrystals for CO₂/CH₄ separation, *J. Ind. Eng. Chem*, **2018**, 60, 279-285
18. Y. Yang, **C. Y. Chuah**, H. Gong, T-H. Bae, Robust microporous organic copolymers containing triphenylamine for high pressure CO₂ capture application, *J. CO₂. Util.*, **2017**, 19, 214-220
19. W. Li¹, K. Goh¹, **C. Y. Chuah**, T-H. Bae, Mixed-matrix carbon molecular sieve membranes using hierarchical zeolite: a simple approach towards high CO₂ permeability enhancement, *manuscript under review*
20. S. Wongchitphimon, W. Rongwong, **C. Y. Chuah**, R. Wang, T-H. Bae, Polymer-fluorinated silica composite hollow fiber membranes for the recovery of biogas dissolved in anaerobic effluent, *J. Membr. Sci.*, **2017**, 540, 146-154

¹ These authors contributed equally to this work.

LIST OF FIGURES

Figure 1-1 Summary of carbon capture and sequestration (CCS) technology that could be possibly incorporated in the system. Reprinted with permission from [11], Copyright 2012 American Chemical Society and [12] Copyright 2013 John Wiley and Sons	4
Figure 2-1 Typical examples of common zeolite frameworks. Reprinted with permission from Reference [15], Copyright 2018 American Chemical Society	15
Figure 2-2 Comparison study ((a) CO ₂ uptake and (b,c) isosteric heat of adsorption) between LTA zeolites that are synthesised with numerous Si/Al ratio. The number indicated on the figure depicts Si/Al ratio of 1, 1.9, 3.5, 5.0 and ∞ respectively. Reprinted with permission from Reference [51], Copyright 2009 American Chemical Society.....	16
Figure 2-3 (a) Illustration of “molecular trapdoor” mechanism in Cs-CHA zeolite (b) Comparison between energy barrier between State 1 and 2 in (a). Reprinted with permission from Reference [55], Copyright 2012 American Chemical Society.	19
Figure 2-4 (a) Structure of TS-1 (Si and Ti were indicated as orange and green respectively) Reprinted with permission from Reference [65], Copyright 2016 Royal Society of Chemistry; (b) Structure of ETS-4 (Si, Ti and O were indicated as yellow, green and red respectively). Reprinted with permission from Reference [60], Copyright 2001 Nature Publishing Group; (c) Comparison of CO ₂ adsorption isotherm of divalent Ca ²⁺ , Sr ²⁺ and Ba ²⁺ ion-exchanged ETS-4 at 25 °C, with the degassing temperature of 100 °C and 200 °C respectively [63].....	21
Figure 2-5 Creation of isostructural MOF with the variation of ligand type. Reprinted with permission from Reference [77], Copyright 2002 American Association for the Advancement of Science.....	24

Figure 2-6 (a) Effect of CO ₂ adsorption of MIL-53 (Cr) at 31 °C. A clear stepwise growth of CO ₂ adsorption can be seen as the pressure increases. (b) X-ray diffraction profile of MIL-53 (Cr) with the alteration of CO ₂ partial pressure. Reprinted with permission from Reference [78], Copyright 2007 John Wiley and Sons.	25
Figure 2-7 (a) Structure of HKUST-1 and (b) M-MOF-74. Reprinted with permission from Reference [11], Copyright 2012 American Chemical Society.....	26
Figure 2-8 (a) Structure of NH ₂ -MIL-53 (Al). Reprinted with permission from Reference [85], Copyright 2009 Elsevier; (b) Comparison of CO ₂ and CH ₄ uptake of NH ₂ -MIL-53 (Al) at 30 °C. Reprinted with permission from Reference [84], Copyright 2009 American Chemical Society	28
Figure 2-9 (a) Comparison between Mg ₂ (dobdc) and Mg ₂ (dobpdc). Reprinted with permission from Reference [88], Copyright 2014 Royal Chemistry of Society; (b) Structure of mmen-Mg ₂ (dobpdc). Reprinted with permission from Reference [87], Copyright 2012 American Chemical Society	29
Figure 2-10 (a) Choice of different imidazolate group for the successful synthesis of ZIFs with LTA topology. Reprinted with permission from Reference [93], Copyright 2007 Nature Publishing Group; (b) Synthesis of ZIFs framework with CHA topology (ZIF-300, ZIF-301 and ZIF-302), with no significant change in CO ₂ adsorption in dry and humid condition. Reprinted with permission from Reference [94], Copyright 2014 John Wiley and Sons.....	31
Figure 2-11 (a) Co-condensation reaction if different strut length with the increase in the overall pore size of COF frameworks (COF-6, -8 and -10). Reprinted with permission from Reference [117], Copyright 2007 American Chemical Society (b) variation of CMP structures with change in strut length. The pore size distribution of	

CMPs that was derived from the NLDPT pore size distribution indicates a shifting to larger micropore size. Reprinted with permission from Reference [98], Copyright 2008 American Chemical Society; Reprinted with permission from Reference [119], Copyright 2009 John Wiley and Sons	33
Figure 2-12 (a) Impact of ideal (predict from Maxwell Equation) and non-ideal morphologies on the performance of MMM; (b) CO ₂ transport profiles of various interfacial morphologies of MMM. The normal profile refers to the diffusivity of CO ₂ molecules in the polymer phase [15].	40
Figure 3-1 Breakthrough system	51
Figure 3-2 PXRD pattern for zeolite MFI crystals	52
Figure 3-3 SEM images for zeolite MFI crystals (a) MFI-1; (b) MFI-2	53
Figure 3-4 (a) Ar and (b) N ₂ sorption isotherm (adsorption and desorption branches are indicated as closed and open symbols respectively) of MFI-1 and MFI-2; (c) Differential pore volume (dV/dW) and cumulative pore volume of MFI-1 and MFI-2 determined via HK method using Ar sorption isotherm (the value for MFI-2 were offset by 12 cm ³ g ⁻¹ nm ⁻¹ and 0.15 cm ³ g ⁻¹ respectively); (d) Mesopore size distribution of MFI-1 and MFI-2, which was determined using BJH method using Ar sorption isotherm (the value for MFI-2 was offset by 0.01 cm ³ g ⁻¹ nm ⁻¹).....	54
Figure 3-5 Pure component SF ₆ and N ₂ isotherm of (a) MFI-1 and (b) MFI-2 at 25 and 40 °C.....	55
Figure 3-6 SF ₆ adsorption kinetics at the dosing pressure of 1 bar at (a) 25 °C and (b) 40 °C.....	56
Figure 3-7 (a) IAST SF ₆ /N ₂ selectivities at 25 °C and 40 °C; (b) Isosteric heat of adsorption of MFI-1 and MFI-2 as a function of SF ₆ loading	57

Figure 3-8 SF₆/N₂ breakthrough curves of (a) MFI-1 and (b) MFI-2 at 1 bar 25 °C ..59

Figure 4-1 FESEM images and the scheme of HKUST-1 crystals (a) bulk crystal (HKUST-1a), (b) nanocrystal (HKUST-1b) and (c) nanocrystals with hierarchical structures (HKUST-1c).....65

Figure 4-2 (a) FTIR; (b) PXRD; (c) N₂ physisorption at 77 K and (d) pore size distribution of HKUST-1 crystals66

Figure 4-3 Pure component SF₆ adsorption of measured adsorbents at (a) 25 °C and (b) 40 °C; SF₆ adsorption kinetics of (c) HKUST-1 crystals and (d) zeolite 13X and activated carbon (with HKUST-1c as the reference), under the temperature of 25 °C with 1 bar as the dosing pressure.68

Figure 4-4 (a) SF₆/N₂ selectivities calculated by IAST at 25 °C and 40 °C (Partial pressure of SF₆ and N₂ were 0.1 and 0.9 bar respectively) (b) Isosteric heat of adsorption as a function of loading for all adsorbents70

Figure 5-1 Schematic of formation and unique architecture of Co-MOF-74 hollow nanorods; FT-IR curves of PVP and Co precursor nanorods (NR) after washing with ethanol.....79

Figure 5-2 (a) PXRD pattern of Co precursor nanorods and Co-MOF-74 hollow nanorods; (b) FT-IR curves of PVP and Co precursor nanorods (NR) after ethanol washing80

Figure 5-3 FE-SEM images of (a) Co precursor nanorods and (b, c) Co-MOF-74 hollow nanorods; TEM images of (d) Co precursor nanorods and (e, f) Co-MOF-74 hollow nanorods.....81

Figure 5-4 TEM images that shows the evolution of Co precursor nanorods to Co-MOF-74 hollow nanorods at (a-f) 0 minutes, 2 minutes, 5 minutes, 30 minutes, 60 minutes

and 120 minutes respectively. **(g)** PXRD pattern of the product after 30 minutes of conversion; **(h)** FESEM of Co-MOF-74 nanoparticles; **(i)** TEM images of Co-MOF-74 nanorods after 5 minutes transformation reaction, that was washed with methanol; **(j)** FE-SEM image of Co-MOF-74 bulk rods83

Figure 5-5 (a, b) PXRD patterns of Co-MOF-74 bulk rods and hollow nanorods treated at 30 °C and 180 °C overnight under vacuum; **(c, d)** TGA curves of bulk Co-MOF-74 bulk rods and hollow nanorods84

Figure 5-6 (a) N₂ adsorption and desorption curve of Co-MOF-74; **(b)** Pore size distribution of Co-MOF-74 bulk and Co-MOF-74 hollow nanorods85

Figure 5-7 CO₂ and N₂ **(a)** adsorption isotherm and **(b)** dynamic breakthrough measurement of Co-MOF-74 bulk and hollow nanorods at 25 °C; **(c, d)** Multiple adsorption-desorption cycling of Co-MOF-74 bulk and hollow nanorods at 25 °C. The feed gas for the breakthrough measurement is composed of 20% CO₂ and 80% N₂ ...87

Figure 5-8 Chromatographic separation of CO₂ and N₂ for **(a)** Co-MOF-74 bulk nanorods; **(b)** Co-MOF-74 hollow nanorods and **(c)** zeolite 5A. The feed gas is composed of 20% CO₂ and 80% N₂. The signals for CO₂ were intensified by factor of 10 to improve the visibility.88

Figure 6-1 Reaction scheme of PPNx91

Figure 6-2 (a) FT-IR spectra of PPNx copolymers; FE-SEM; EDX analysis of **(b)** PPN0, **(c)** PPN1 and **(d)** PPN2.....96

Figure 6-3 (a) TGA curve of PPNx copolymers; FE-SEM images of **(b)** PPN0, **(c)** PPN1 and **(d)** PPN2.....97

Figure 6-4 (a) N₂ sorption isotherm (adsorption and desorption branches are indicated as closed and open symbols respectively); **(b)** Mesopore size distribution (using BJH

method) and (c) Micropore size distribution (using HK method) of PPN0, PPN1 and PPN2	99
Figure 6-5 SF ₆ and N ₂ uptake of (a) PPN0; (b) PPN1 and (c) PPN2; (d) SF ₆ adsorption kinetics of PPN0, PPN1, PPN2 and zeolite 13X at 25 °C.....	100
Figure 6-6 (a) IAST SF ₆ /N ₂ selectivities of PPNx copolymers as a function of pressure at 25 °C; (b) Isosteric heat of adsorption of PPNx copolymers as a function of SF ₆ loading.....	101
Figure 6-7 SF ₆ /N ₂ breakthrough curves for PPNx copolymers at (a) 25 °C and (b) 40 °C. The breakthrough curves for zeolite 13X was served as a reference.....	104
Figure 6-8 SF ₆ /N ₂ chromatographic separation of (a) PPN0, (b) PPN1, (c) PPN2 and (d) zeolite 13X at 60 °C. The intensity of SF ₆ for PPNx copolymers and zeolite 13X was intensified for 50 and 200 times respectively for clarity purpose.....	105
Figure 7-1 (a) PXRD pattern, (b) FT-IR, (c) TGA and FESEM image of nanocrystal HKUST-1	111
Figure 7-2 (a) O ₂ , N ₂ and (b) CO ₂ , CH ₄ adsorption isotherm of HKUST-1 nanocrystal that was measured at 35 °C	112
Figure 7-3 (a) FT-IR spectra of polysulfone polymer; (b) TGA analysis of 10 wt% and 20 wt% HKUST-1 nanocrystal in polysulfone polymer.....	113
Figure 7-4 FESEM images of mixed-matrix membranes (a, b) 10 wt% HKUST-1 in polysulfone; (c, d) 20 wt% HKUST-1 in polysulfone.....	115
Figure 7-5 Pure component (O ₂ , N ₂ , CO ₂ and CH ₄) adsorption isotherms of pure polymer and mixed-matrix membranes for (a, b) polysulfone, (c, d) polysulfone + 20 wt% HKUST-1.....	116

Figure 8-1 Structure of ODPA-TMPDA polymer	120
Figure 8-2 (a) PXRD; (b) N ₂ physisorption isotherm (adsorption and desorption branch are indicated as open and closed symbol respectively); (c) FTIR and (d) TGA of HKUST-1 and amine-functionalized HKUST-1	124
Figure 8-3 FESEM images of (a) HKUST-1-0NH ₂ ; (b) HKUST-1-25NH ₂ ; (c) HKUST-1-50NH ₂ ; (d) HKUST-1-75NH ₂ ; (e) HKUST-1-100NH ₂	127
Figure 8-4 (a) CO ₂ and (b) N ₂ adsorption of HKUST-1-xNH ₂ nanocrystals at 35 °C; (c) IAST CO ₂ /N ₂ selectivity at 35 °C under 1 bar CO ₂ /N ₂ feed pressure under the ratio of 20/80.	128
Figure 8-5 FESEM images of mixed-matrix membrane for (a, b) 10 wt% HKUST-1-0NH ₂ with Matrimid; (c, d) 20 wt% HKUST-1-0NH ₂ with Matrimid; (e, f) 10 wt% HKUST-1-25NH ₂ with Matrimid; (g, h) 20 wt% HKUST-1-25NH ₂ with Matrimid.	130
Figure 8-6 TGA analysis of 10 wt% and 20 wt% (a) HKUST-1-0NH ₂ and (b) HKUST-1-25NH ₂ , using Matrimid as the polymer matrix	131
Figure 8-7 CO ₂ and N ₂ adsorption isotherm of (a) Matrimid; (b) Matrimid + 20 wt% HKUST-1-0NH ₂ ; (c) Matrimid + 20 wt% HKUST-1-25NH ₂ at 35 °C	134
Figure 9-1 (a) Permeability-selectivity plot that highlights the performance of different types of membrane; (b) CO ₂ /CH ₄ Robeson plot demonstrates plausible strategies in realizing the membranes with industrially attractive performance. Conventional polymers are membranes that demonstrate potential in terms of effective commercialization for large-scale industrial use for gas separation process.	140

LIST OF TABLES

Table 1-1. Atmospheric Lifetime and Global Warming Potential (GWP) of common greenhouse gases [6-9].....	2
Table 1-2 Summary of numerous CCS technology [11, 13, 15, 16].....	4
Table 1-3 Summary of polarizability and quadrupole moment of selected gases [3, 10, 41]	10
Table 2-1 Effect of different number of membered ring onto typical and maximum pore aperture that is feasible in CO ₂ or SF ₆ adsorption [50].....	19
Table 2-2 Properties of selected nanoporous materials [15]	44
Table 3-1 Surface area and pore volume of zeolite MFI (based on Ar physisorption at 87 K)	53
Table 3-2 Evaluation of zeolite MFI adsorbents using idealized VSA model.....	58
Table 4-1 Surface area and pore volumes of HKUST-1 samples	67
Table 4-2 Evaluation of zeolite MFI adsorbents using idealized VSA model.....	72
Table 5-1 Surface area and pore volume of Co-MOF-74 bulk rods and hollow nanorods	85
Table 6-1 Elemental analysis of PPNx sample	96
Table 6-2 Summary of reacted and unreacted C-Cl moiety in PPNx sample	96
Table 6-3 Surface areas and pore volumes of PPNx copolymers based on N ₂ physisorption at 77 K.....	98
Table 6-4 Evaluation of PPNx adsorbents in an idealized VSA model.....	103
Table 7-1 Permeation results of pure polymer and mixed-matrix membrane under 1 bar of upstream pressure with air (O ₂ /N ₂ = 21/79) at 35 °C	115

Table 7-2 Permeation results of pure polymer and mixed-matrix membrane under 1 bar upstream pressure with CO ₂ /CH ₄ mixture (50/50) at 35 °C	115
Table 7-3 O ₂ and N ₂ solubility and diffusivity data for pure polymer and mixed-matrix membrane at 35 °C.....	117
Table 7-4 CO ₂ and CH ₄ solubility and diffusivity data for pure polymer and mixed-matrix membrane at 35 °C	117
Table 8-1 Surface areas and pore volumes of HKUST-1 and amine-functionalized HKUST-1 nanocrystals (HKUST-1-xNH ₂) computed based on N ₂ physisorption at 77 K.....	126
Table 8-2 Elemental analysis of HKUST-1 and amine-functionalized HKUST-1 nanocrystals.....	127
Table 8-3 Mechanical test of pure polymer and mixed-matrix membrane	131
Table 8-4 Permeation results of pure polymer and mixed-matrix membrane under 1 bar CO ₂ /N ₂ mixture (20/80) at 35 °C	131
Table 8-5 CO ₂ and N ₂ solubility and diffusivity data for pure polymer and mixed-matrix membranes at 35 °C under 1 bar of total feed pressure (0.2 bar for CO ₂ and 0.8 bar for N ₂).....	134
Table 9-1 Summary of the major properties of the microporous materials and membranes that is reported in this thesis	137
Table 9-2 Comparison of C ₂ H ₂ , CO ₂ and C ₂ H ₄ adsorption across commonly reported MOFs [80].....	141

LIST OF ABBREVIATIONS

2D	Two-dimensional
6FDA	4,4'-(hexafluoroisopropylidene)diphthalic anhydride
AEL	Aluminophosphate-eleven ($\text{AlPO}_4\text{-11}$)
AET	Aluminophosphate-eight ($\text{AlPO}_4\text{-8}$)
AFI	Aluminophosphate-five ($\text{AlPO}_4\text{-5}$)
AMP	2-amino-2-methyl-1-propanol
ASU	Air separation unit
bdc	1,4-benzenedicarboxylate
BET	Brunauer-Emmett-Teller
btc	1,3,5-benzenetricarboxylate
BEA	Zeolite Beta
BJH	Barrett-Joyner-Halenda
Ca	Calcium
CCS	Carbon capture and sequestration
CH_4	Methane
CHA	Chabazite
CLO	Cloverite
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide

Cu	Copper
Cs	Caesium
dobdc	2,5-dihydroxyterephthalate
DON	University of Texas at Dallas – one (UTD-1)
EDX	Energy Dispersive X-ray Spectroscopy
EOR	Enhanced oil recovery
ETS	Engelhardt Titanosilicate
FAU	Faujasite
Fe	Iron
FE-SEM	Field Emission-Scanning Electron Microscopy
FT-IR	Fourier Transform-Infrared Spectroscopy
GHG	Greenhouse gas
H ₂	Hydrogen
H ₂ O	Water
HK	Horvath-Kawazoe
IAST	Ideal Adsorbed Solution Theory
IRMOF	Isorecticular metal-organic framework
K	Potassium
Li	Lithium
LMWM	Low Molecular Weight Materials

LTA	Zeolite A (Linde Type A)
LTL	Linde Type L
MCM	Mobil Composition of Mater
MFI	Zeolite Socony Mobil – five (ZSM-5)
Mg	Magnesium
MMM	Mixed-matrix membrane
Mn	Manganese
MOFs	Metal-organic frameworks
MOPs	Microporous organic polymers
MOR	Mordenite
MTPA	Metric Tonne Per Annum
MWW	Mobil Composition of Matter -twenty two (MCM-22)
Na	Sodium
Ni	Nickel
NLDFT	Non-linear density functional theory
N ₂	Nitrogen
ODPA	4,4'-oxydipthalic anhydride
O ₂	Oxygen
PCN	Porous Coordination Network
PCP	Porous Coordination Polymer

PSA	Pressure Swing Adsorption
PXRD	Powdered X-ray Diffraction
Q_{st}	Isosteric Heat of Adsorption
SF ₆	Sulfur Hexafluoride
SDA	Structural Directing Agent
TEM	Transmission Electron Microscopy
TMPDA	2,4,6-trimethyl- <i>m</i> -phenylenediamine
TSA	Temperature Swing Adsorption
TGA	Thermogravimetric Analysis
VFI	Virgina Polytechnic Institute -five (VPI-5)
VSA	Vacuum Swing Adsorption
Zn	Zinc

ABSTRACT

Extensive research on the gas separation process has been conducted in view of the current industrial gas separation processes which uses cryogenic distillation and liquefaction are energy-intensive. In this regard, adsorbents and membranes which demonstrate favourable interaction with the desired gases were selected in view of their capability in performing effective separation at a lower energy penalty together with smaller plant footprint. Hence, the main objective of this thesis is to investigate and develop novel nanoporous materials and membranes that are capable in providing effective separation and capture of desired gas components.

The study begins with the development of hierarchical zeolite MFI for its feasibility in SF₆ adsorption. Clear enhancement in overall SF₆ adsorption kinetics was observed with the creation of hierarchical structure, thus indicating its usefulness in rapid SF₆ adsorption-desorption cycling. Under similar strategy, hierarchical HKUST-1 and PPN were developed for its potential in SF₆ capture and recovery. HKUST-1 possess open metal sites allows reversible interaction with SF₆. Therefore, hierarchical structures were created to allow an increased accessibility of SF₆ to the active sites, as the kinetic diameter of SF₆ is larger as compared to CO₂. Besides, PPN which demonstrates better resistance towards chemical degradation and humidity was created by the variation of porosity properties. The incorporation of an optimal amount of tertiary amine allows an improvement in SF₆/N₂ selectivity in both equilibrium and dynamic condition, together with sharp segregation between SF₆ and N₂ peaks in chromatographic separation. Nonetheless, enhancement in SF₆ adsorption kinetics is limited by its large micropore size. Besides, the facilitation the overall adsorption-desorption cycling of adsorbate was verified by the creation hollow-structured nanomaterial. Based on the study conducted, creation of hollow structure (Co-MOF-74

hollow nanorods) allows the sharper CO₂ breakthrough curve together with sharper chromatographic separation between CO₂ and N₂.

On the other hand, the investigation of nanoporous materials was further conducted with the utilization as filler in mixed-matrix membrane (MMM). Permeability-selectivity trade-off in polymeric membrane has been well reported as solution-diffusion mechanism is the main transport mechanism of gases in membranes. The incorporation of nanoporous materials into polymeric membrane has been the most technical viable option to improve the gas separation performance. In general, MOFs has attracted vast research interest as the fillers in MMM in view of its large surface area and pore volume, where the functionalities can be tuned via pre- or post-synthetic functionalization. In this work, HKUST-1 nanocrystals were incorporated into polymeric membrane for O₂/N₂, CO₂/CH₄ and CO₂/N₂ separation. It has been observed that the utilization of HKUST-1 nanocrystal as the filler materials has demonstrated an increase in gas (O₂, CO₂) permeability, without compromising the mixed-gas selectivity. Besides, amine-functionalized HKUST-1 nanocrystals is feasible in improving CO₂/N₂ selectivity without compromising CO₂ permeability.

In conclusion, this thesis presents the development of nanoporous materials and membranes in the field of gas separation. Considering that the potential of nanoporous materials and membranes in other gas separation processes is immense, future work will be generally focussed on the application of nanoporous materials and membranes in terms of the plausible potentials in other separation process (e.g. olefin/paraffin). Besides, other factors that hamper the practicability of nanoporous materials in industrial gas separation process such as the presence of water in the feed will be conducted. It has been observed that the presence of water molecules can compete with the desired test gases, which in general limits the overall gas separation performance.

Chapter 1 INTRODUCTION

1.1 Background

Separation is defined as a process that separates the mixture of several components or substance into two or more products, which are technically differ from each other in terms of composition [1]. In general, as opposed to mixing, separation processes are generally non-spontaneous and requires the application of external sources (i.e. energy) to allow a well-selective separation. This is generally attributed to the fact that separation process are generally not favoured, based on the second law of thermodynamics [2, 3]. Hence, the inherent limitation that is present in the typical separation process has stimulated substantial research interests across the world, with the concerted efforts in developing an effective methodology for effective separation across multi-component mixture, as it is projected that such processes account for approximately 50% of the total energy usage in industries [4]. For instance, an approximate of 1.2×10^{18} Joule/year is required to sustain the operation for olefin/paraffin separation, which the capital cost of building up a large-scale ethylene unit could foresee the cost of whopping US\$500 million. Particularly, gas separation is comparatively challenging as compared to other separation processes if the desired gas mixture possesses similar physical properties. In this regard, gas separation processes such as greenhouse gas capture and air separation will be the introduced in this thesis, with the details of each separation processes will be introduced and elaborated in the subsequent sections.

1.2 Gas separation processes

1.2.1 Greenhouse gas (GHG) capture

The Intergovernmental Panel on Climate Change (IPCC)'s fourth assessment report highlighted the increase in the carbon dioxide (CO₂) global atmospheric concentration (410 ppm in 2018) as compared to the fluctuations for the past 400,000 years (100 – 300 ppm) [5]. Similarly, concerns on other potent greenhouse gases namely sulphur hexafluoride (SF₆) had been observed, where such gases possess higher Global Warming Potential (GWP) as well as longer atmospheric lifetime as compared to CO₂, which can be summarized as shown in **Table 1-1**. As such, despite the atmospheric concentration of the SF₆ is generally low, even with the constant and stabilize emission, such gases do possess significant radiative forcing with reference to CO₂. Therefore, it is not surprising that with the same rate of increase in economic activities and global population, serious environmental impacts such as a rise in sea levels, increases in average global temperature as well as species extinction have been observed.

Table 1-1. Atmospheric Lifetime and Global Warming Potential (GWP) of common greenhouse gases [6-9]

Greenhouse Gas	Global Warming Potential (GWP) ^[a]	Atmospheric lifetime (years)
Carbon dioxide (CO ₂)	1	5 – 200 ^[b]
Methane (CH ₄)	25	12
Nitrous oxide (N ₂ O)	298	114
Sulphur hexafluoride (SF ₆)	23,900	3200

[a] GWP for each greenhouse gas was determined based on 100-year horizon.

[b] The atmospheric lifetime of CO₂ is unable to be defined clearly as a single lifetime.

As research progresses, numerous methods have been proposed to allow the feasibility for effective GHG capture. Nonetheless, there are two salient points [10, 11] that require strong consideration if a methodology was to be successfully

commercialized for industrial use, which can be summarized as follows: (a) Any materials that would be used to capture GHG will suffer a rapid exhaust in the global supplies if such materials exhibit poor regenerability; (b) Any GHG that would be utilized as a reactant for a particular commodity product will lead to rapid saturation to the global market. This behaviour can be observed significantly for the case of CO₂ owing to its high emission (~ 30 Gt per year) [10]. As such, it is generally much more promising for the captured GHG to be utilized in demanding applications namely renewable energy or transportation fuels.

Notes:

[a] The most probable installation for CCS to capture CO₂ selectively with reference to other flue gases are shaded.

[b] For the case of oxy-fuel combustion, as the concentration of CO₂ is generally high (85 – 90%), thus capturing CO₂ from oxy-fuel combustion is generally simpler as compared to other processes.

Figure 1-1 Summary of carbon capture and sequestration (CCS) technology that could be possibly incorporated in the system. Reprinted with permission from [11], Copyright 2012 American Chemical Society and [12] Copyright 2013 John Wiley and Sons

In general, research on carbon dioxide (CO₂) capture technologies have been widely studied as compared to other gases. The first industrial application of CO₂ was with enhanced oil recovery (EOR), which utilises gases such as CO₂ to expand the reservoir so as to increase the crude oil extraction and recovery. This process has been proven for its effective economic viability over the years. In most circumstances, this process is usually linked to carbon capture and sequestration (CCS) if the concentration of the emitted flue gas is insufficient to adopt EOR process. After the subsequent capture process, CO₂ that is selectively removed from the gas stream is permanently stored in the underground containment. Particularly, power plants that uses coal, fossil fuels or biomass as the energy source generation are generally considered as the large stationary source for CO₂ emission, thus allowing such technology to be actively incorporated. As an estimate, the cost of mitigating CO₂ emission that was generated from the power plant which uses coal as the energy source is ranged from US\$ 23 – 92 per tonne of CO₂ if the CCS technology is incorporated into the system [13]. It should be well noted that despite CCS technology is not entirely perfect, 85 – 95% of CO₂ is still feasible to be removed from the flue gas [14]. CCS technologies can be adopted into: post-combustion capture, pre-combustion capture, oxy-fuel combustion and biogas upgrading, as summarized in **Figure 1-1**. The advantages and disadvantages of each processes are summarized in **Table 1-2**.

Table 1-2 Summary of numerous CCS technology [11, 13, 15, 16]

Types Components	Post-combustion	Pre-combustion	Oxy-fuel combustion	Biogas upgrading
---------------------	-----------------	----------------	---------------------	------------------

Characteristics	Flue gas are burnt with excess air	Fuels are converted to syngas before burning	Fuels are burnt with purified oxygen (from air)	Wastes are burnt is air to generate biogas
Common gas pairs	CO ₂ /N ₂	CO ₂ /H ₂	CO ₂ /H ₂ O	CO ₂ /CH ₄
Composition (vol%)[a]	20/80	40/60	95/trace	50/50
Flue gas condition (temperature, pressure)	40 – 60 °C, 1 bar	21 – 40 °C, 5 – 40 bar	high temperature, low pressure	25 °C, 1 bar
Merits	<ul style="list-style-type: none"> Flue gas stream is at ambient pressure 	<ul style="list-style-type: none"> Higher concentration of CO₂ in the feed (allows better CO₂ adsorption) 	<ul style="list-style-type: none"> Feed contains mainly CO₂, thus can be applied directly to EOR process 	<ul style="list-style-type: none"> Product contains mainly CH₄ (feasible as fuel source) Renewable energy
Challenges	<ul style="list-style-type: none"> Low CO₂ concentration in the flue gas Presence of other trace impurities (N₂, H₂O) 	<ul style="list-style-type: none"> High capital investment for syngas formation 	<ul style="list-style-type: none"> Expensive O₂ purification Dilution of O₂ with CO₂ is required due to high heat of reaction 	<ul style="list-style-type: none"> Presence of other trace impurities (H₂S, NH₃, siloxane)
Market share (MTPA)[b]	46.00	7.00	2.00	—[c]

Notes:

[a] Only the composition of the main gas pairs that is typically studied in the literature are indicated.

[b] Based on the market share in North America in 2024 (Projected), estimated from the graph

[c] The information is not furnished.

Despite extensive research on greenhouse gas has been conducted for CO₂ via CCS process, SF₆ capture on the other hand has received relatively less attention compared to CO₂. SF₆, which is classified as one of the per-fluorinated compounds that are non-polar, non-toxic, non-flammable, colourless, tasteless and odourless gas [17], has been widely used in numerous industrial sectors. For instances, SF₆ has been used as a surface film protection during the casting of molten magnesium and its alloy which

tend to oxidise completely upon contact with ambient air [6]. Besides, electrical equipment including circuit breaker, switchgear and transformers uses SF₆ in view of its good insulating properties. SF₆ also has played an important role in industrial plasma etching process which is required in the fabrication of integrated circuit (IC), photovoltaic (PV), flat panel display (FPD) and Micro Electro Mechanical System (MEMS) [18]. Nonetheless, in most circumstances, SF₆ is used as a mixture with N₂ to allow for a cheaper operation [19, 20], where such effect is more prominent in the case where SF₆ feed can be easily converted into SF₆/N₂ mixture during the blowing process[21], when SF₆ are utilized in the equipment as mentioned. Hence, effective separation and recovery of SF₆ from SF₆/N₂ mixture is of paramount importance owing to the release of strong greenhouse gas to the atmosphere, not to mention that SF₆ is considerably much expensive. However, this recovery process can be hampered by its low concentration of SF₆ in the mixture. In typical operation, the ratio of SF₆ in SF₆/N₂ mixture is in the ratio of 1:9 [22].

1.2.2 Air separation

In general, world energy consumption has demonstrated a drastic increase since the industrial revolution, which is generally attributed to the rapid economic growth and increase in human population. It has been projected that for the subsequent years, despite diversification of energy production to renewable sources (solar, wind, tide and others) have been rapidly conducted, 30% of the global energy production will still be dominated by primary energy sources, which is fossil fuels [23]. Besides, the energy production cost has been strongly affected by the strong volatility and fluctuation of the price of the fossil fuels together with the limitation of the available oil reserves, which it is expected that it will only be sufficient for the global production for ca. 50 years [24], leading to an increase in the overall energy generation for the upcoming years. In typical

traditional fuel combustion, air (21% O₂ and 79% N₂ in terms of composition) is utilized as the source of the oxygen content as such approach is the simplest way of energy generation. However, the presence of N₂ in the feed tends to siphon out the energy generated during the combustion process in view of the function of N₂ that acts as only the carrier gas in the feed stream [25, 26]. Therefore, it can be expected that the overall energy efficiency can be drastically affected with the presence of inert gas.

On the other hand, the presence of N₂ in the feed may possess the tendency to produce a large quantity of nitrogen oxides (NO_x) under such condition. This leads to severe environmental consequences namely photochemical smog and acid rain. Hence, increasing O₂ content in the feed is generally more preferable in view of the feasibility in increase the overall energy efficiency with the reduction of energy consumption together with a more effective temperature control. Besides, with the increase in O₂ concentration in the combustion medium generally leads to a decrease in the emission of carbon monoxides, particulates, hydrocarbons and smokes due to the incomplete combustion [27, 28]. Thus, this strategy can be developed on the oxy-fuel combustion process (**Figure 1-1**) where only CO₂ will only be released as the by-product. Therefore, through such protocol it is not required to install additional separation step under the CCS operation as the feed typically contains pure CO₂ [10].

1.3 Challenges in gas separation process

1.3.1 Greenhouse gas (GHG) capture

In general, approximately 70% of the cost of CCS is derived from the capture step. Effective strategies of capturing CO₂ with the least possible cost is vital so as to mitigate the negative effect of GHG to the environment to the least possible cost. At current stage, aqueous alkanolamine solution via wet scrubbing have been employed

industrially over the span of more than 50 years [11, 21]. Depending on the type of amine (primary (1°), secondary (2°) or tertiary (3°)), the nucleophilic attack of amine functionalities to CO₂ to form C-N bond results in the formation of carbamate or bicarbonate species [29]. The formation of bicarbonate species in 3° amine was attributed to its steric hindrance as compared to 1° and 2° amine. The reaction between amine and CO₂ can be described based on the affinity absorption between them, with the enthalpy of adsorption is within the range of – 50 to – 100 kJ/mol at low CO₂ loading at 25 °C [30]. Therefore, substantially high energy penalty is required so as to regenerate the amine for subsequent reuse so as to release CO₂ for subsequent CCS. With regards to the heat of reaction of these two reaction, despite 3° amine incurs a much lower energy requirement for regeneration as compared to 1° and 2° amine due to bicarbonate species is relatively unstable than carbamate [11], nonetheless the exact energy supplied to conduct the reverse process is strongly dependent on the concentration of amine in the aqueous solution. SF₆ recovery on the other hand was dominated by the liquefaction process. As mentioned previously, the recovery process of SF₆ can be difficult especially when the concentration of SF₆ in a mixture is too low (i.e. typically in 10% SF₆ in SF₆/N₂ mixture). This is because the aforesaid process is generally intensive due to its low normal boiling point (- 64 °C), thus such process must be conducted at high pressure (ranging from 2 – 20 MPa) [31] and low temperature. Therefore, an urgent quest on replacing the costly liquefaction process is of paramount importance so as to allow an effective recovery of SF₆ with limited release of SF₆ to the atmosphere.

1.3.2 Air separation

In industrial operation, cryogenic distillation and pressure swing adsorption (PSA) are the main conventional methods for air separation process. In general, cryogenic distillation is highly favoured in air separation process particularly in the

production of steel as high demand in terms of oxygen purity (> 99.5 vol%) [32, 33]. It is expected that cryogenic distillation requires substantially large amount of energy as it is necessary to cool down the air near to -170 °C via liquefaction process before sending to the air separation unit (ASU) so that other impurities such as CO_2 , H_2O and possibly hydrocarbon can be removed and filtered out [34], despite such process feasible to obtain a desired purity by merely tie-in from ambient air. In recent years, self-heat recuperation technology [33] has demonstrated its feasibility in reducing overall energy consumption by ca. 36% as compared to conventional cryogenic air separation. despite such analysis is still limited to process modelling and simulation. Nevertheless, the main advantage of this system is its feasibility in producing a large quantity of O_2 , with the values ranging from 5,000 to 30,000 tonnes per day (the specific power consumption ranges from 200 – 245 kWh/tonne, with an approximate of 30 – 38% of the cost is taken up by the compression process) [35]. Therefore, such separation is generally preferred if the liquefied O_2 and N_2 is the desired product.

PSA system on the other hand is also utilized to produce high purity oxygen product. Such system was first developed in the laboratory studies [36, 37], where profound applications in hydrogen purification and air separation process have been observed. The first generation of air separation process that uses PSA was designed to recover oxygen by using adsorbents that are capable to adsorb nitrogen, where such system is generally feasible if the required scale of O_2 production is small (i.e. ranging from 100 – 300 tonnes/day). It should be well noted that the production cost is strongly dictated by the size of the fixed bed system, thus the O_2 production cost rises linearly with the increase in the bed size of the PSA system [38]. Nonetheless, in view of the increasing number of PSA cycles is not techno-economically feasible despite a comparable purity as compared to cryogenic distillation process, it is technically more

desirable to use oxygen-selective adsorbents (e.g. carbon molecular sieve or 4A zeolite) to conduct air separation process [32, 39, 40]. However, PSA operation generally requires additional regeneration step once the adsorbents are fully saturated with captured gas.

1.4 Nanoporous materials and membranes as a solution

Table 1-3 Summary of polarizability and quadrupole moment of selected gases [3, 10, 41]

Gas	Kinetic diameter (Å)	Polarizability, $\times 10^{-25}$ (cm ³)	Quadrupole moment (esu cm ²)
CH ₄	3.80	25.9	0
C ₂ H ₂	3.30	33.3	0
C ₂ H ₄	4.16	42.5	1.50
C ₂ H ₆	4.44	44.3	0.65
CO ₂	3.30	29.1	4.30
H ₂ O	2.65	14.8	0
N ₂	3.64	17.6	1.52
O ₂	3.46	15.8	0.39
SF ₆	5.13	65.4	0

Currently, there are numerous approaches that have been conducted so as to address the challenges mentioned above. For instance, the selection of suitable adsorbents that allow selective capture of GHG as compared to other gases allow its feasibility to scale-up for industrial application. Such adsorbents can be designed or tuned in such a way that they allow for effective interaction between CO₂ and SF₆ due to its higher polarizability as shown in **Table 1-3**. Besides, the pore size of the adsorbents can also be designed in such a way that effective pore size discrimination can be observed despite of its close kinetic diameter between numerous gases. As a general rule, adsorbents which show promising CO₂ capture capability should demonstrate similar observation as compared to SF₆ due to similar polarizing capability,

nonetheless the pore size of adsorbents must be sufficiently large to accommodate easy entrance of SF₆ into the adsorbents. Several categories of nanoporous materials namely zeolites, metal-organic frameworks and microporous organic polymers demonstrates its attractive advantages as compared to amine solution particularly on its low energy penalty for regeneration of CO₂ or SF₆.

On the other hand, nanoporous materials could be used as a platform to develop high performance membrane with the incorporation of these materials into the polymeric membrane. In general, polymeric membrane has been well-studied in view of the ease of fabrication together with the low cost of raw materials. Nonetheless, as the performance of the polymeric membrane is generally limited by the trade-off relation between permeability and selectivity, as the gas transport properties of the polymeric membrane is typically described as solution-diffusion mechanism [42, 43]. This phenomenon is generally valid for all gas pairs. On the other hand, fabrication of pure nanoporous membrane that uses zeolites or MOFs can be difficult particularly in the industrial application as the fabrication of large-scale membrane module with large packing density is generally desirable. Thus, the cost of the production can be expected to escalate significantly. Hence, fabrication of mixed-matrix membrane (MMM) with the possibility of incorporating the advantages of both categories can be fulfilled in this process, thus striking the balance between them. With the incorporation of nanoporous materials, the solubility and diffusivity of the overall membrane can be tuned to improve the overall gas separation performance.

1.5 Research objectives

In this research, the main objective is to develop approaches that ensures effective capture and separation of greenhouse gases, with the following primary objectives as shown below:

- (a) Develop novel adsorbents that can provide effective separation and capture of GHG, particularly CO₂ and SF₆.
- (b) Develop novel adsorbents that can improve adsorption kinetics of GHG (CO₂ and SF₆) particularly SF₆ which is comparatively large molecule as compared to CO₂.
- (c) Develop high-performance membranes for CO₂/CH₄, CO₂/N₂ and O₂/N₂ separation.

Involvement in this research throughout my Ph. D. study allow me to put in the effort by fulfilling the objectives as specified.

1.6 Thesis outline

The thesis consists of ten chapters, with a brief highlight of the key findings of each chapter are summarized as follows. Chapter 1 indicates the background study of gas separation processes together with the expected challenges. Besides, the reasoning and research objectives of utilizing nanoporous materials in gas separation processes will be introduced in this chapter. In Chapter 2, literature review on potential nanoporous materials which will be utilized in the subsequent chapters will be introduced. In this chapter, attractive properties of these materials that allow selective capture of GHG (CO₂ and SF₆) as compared to other gases (e.g. N₂) with similar kinetic diameters will be discussed. In the subsequent chapters (Chapter 3, 4, 5 and 6) the development of hierarchically structured materials in zeolites, MOFs and MOPs will be

discussed. In these studies, the development of hierarchical structures has demonstrated its feasibility in improving the adsorption kinetics of polarizable gases. Besides, Chapter 7 and 8 describes the effect of incorporating nanoporous materials into polymeric membrane (mixed-matrix membrane), where a clear enhancement in the overall gas separation performance has been observed. Last but not least, summary of the major findings that can be identified in each chapter will be provided, together with expanding the current research directions for other potential gas separation process (Chapter 9), followed by the list of references (Chapter 10).

Chapter 2 LITERATURE REVIEW

2.1 Introduction

In the past decades, nanoporous materials had showcased its potential capability in numerous applications, namely molecular separation, gas storage, heterogeneous catalysis, drug delivery and ion-exchange. In particular, the physio-chemical properties of nanoporous materials had demonstrated its practicability in molecular separation due to attractive interaction between selected gases. Therefore, nanoporous materials possess attractive properties that could stamp out the limitations in current industrial molecular separation processes as described in Chapter 1. As such, a brief introduction of aforesaid nanoporous material will be introduced, together with a brief introduction of mixed-matrix membrane (MMM), as nanoporous materials have been utilized heavily as the filler in the polymeric membrane, thus tuning the overall separation performance.

2.1.1 Zeolites and related materials

Zeolites are crystalline hydrated aluminosilicates that comprises interconnected SiO_4^- and AlO_4^- tetrahedral as the primary building unit, which can be extended infinitely via effective sharing of oxygen atom to form three-dimensional porous structure. The incorporation of AlO_4^- tetrahedral results in an overall negative charge on the framework due to smaller valency of Al as compared to Si. Therefore, the resulting structure requires the accommodation of mainly Group IA and Group IIA cations such as Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , to name a few so as to preserve the overall structural neutrality of the framework. These incorporations can be conducted readily with the aid of ion-exchange despite effective 100% conversion was not feasible [44]. As a whole, the chemical formula of zeolites can be described as $M_{x/m}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, with M is described as cation with valence m , z is the number of water molecules that

could be present in each zeolite unit cell, x and y are integers where y/x can be ranged from 1 to infinity [45]. This range is set in the range between pure silica (uncharged solids with $y/x \rightarrow \infty$) and the state where the presence of electrostatic repulsion that does not favour effective bonding between AlO_4^- tetrahedral, with $y/x \rightarrow 1$.

Figure 2-1 Typical examples of common zeolite frameworks. Reprinted with permission from Reference [15], Copyright 2018 American Chemical Society

In general, zeolites can be formed naturally from the chemical reaction between the aluminosilicate ash from the volcanic eruption with salt water. Nonetheless, the synthesis of natural zeolites via such approach typically does not display high Si/Al ratio due to the absence of appropriate organic-structural directing agent. Therefore, scaling-up process via numerous synthesis route such as hydrothermal, solvothermal, ionothermal and solvent-free synthesis [46-49] are utilized to generate zeolite samples of high crystallinity [50]. Furthermore, these synthesis route allows the production of synthetic zeolites (LTA or FAU) that are unavailable in nature (**Figure 2-1**). As a whole, zeolites had been adopted readily in gas separation processes in view of its well-defined pores, not to mention its high chemical and thermal stability. Besides, CO_2 and SF_6 adsorption behaviour of zeolites can be tailored by properties namely Si/Al ratio, cation type and its position in the framework as well as zeolite structure.

2.1.1.1 Si/Al ratio

Figure 2-2 Comparison study ((a) CO₂ uptake and (b,c) isosteric heat of adsorption) between LTA zeolites that are synthesised with numerous Si/Al ratio. The number indicated on the figure depicts Si/Al ratio of 1, 1.9, 3.5, 5.0 and ∞ respectively. Reprinted with permission from Reference [51], Copyright 2009 American Chemical Society.

Numerous observations had displaced an increase in CO₂ (similarly SF₆) uptake capacity as Si/Al ratio decreases. Incorporation of additional Al³⁺ required additional cations to accommodate the charge composition due to the overall framework becomes more negative. Hence, lower ratio generally improves the electric field strength of the framework, thus fostering stronger coulombic interaction in the form of dipole-induced-dipole force between CO₂ or SF₆, particularly due to its higher polarizability (**Table 1-3**). In essence, such preferential adsorption via chemisorption process can be seen evidently at low feed pressure, which is attributed to its extraordinarily high isosteric heat of adsorption at zero coverage. For instance, Palomino et al. [51] compared the adsorption capacity of CO₂ and isosteric heat of adsorption using zeolite LTA with various Si/Al ratio. In general, high CO₂ adsorption in LTA-1 and LTA-2 zeolite can be attributed to its extraordinarily high isosteric heat of adsorption as compared to other LTA series, as shown in **Figure 2-2**. Nonetheless, such observation does not hold as feed pressure increases, thus expressing that dipole-induced-dipole interaction is only dominated at low pressure regime, which can be depicted from a large dip in isosteric heat of

adsorption beyond 2.5 mmol g⁻¹. Such analysis is also valid for other zeolite frameworks, namely CHA [52], MWW [53] and MFI [54]. Despite alteration of Si/Al ratio generally helps in improving overall adsorption, it is always critical to consider the effect of high isosteric heat of adsorption with the poor regenerability of the adsorbents due to increase difficult to perform the desorption process. Therefore, an optimal Si/Al ratio is always critical so that the adsorbent could display high adsorption capacity yet with minimal energy for effective adsorbent regeneration.

2.1.1.2 Cation type and position

As mentioned in section 2.1.1.1, the addition of cations which was used to compensate the overall negative charge of the framework instil significant implication on the electric field and the available pore volume of zeolite. Such incorporation can be done readily with ion-exchange, allowing significant modification in terms of CO₂ or SF₆ affinity to the zeolite framework as well as the modification of zeolite pores. For instance, a series of Ca, Na and Mg based ion-exchange LTA and FAU zeolites had been conducted by Bae et al. [44] so as to investigate the overall feasibility in CO₂ adsorption. From this study, at low partial pressure of CO₂ (0.15 bar) at 40 – 50 °C, Ca-exchanged LTA portray itself as the most promising candidate due to its high isosteric heat of adsorption (- 58 kJ mol⁻¹) at low adsorbate loading. Other than the verification studies conducted through neutron powder diffraction, an effective ion exchange of Ca²⁺ from Na⁺ sample in LTA zeolite can be observed (72 %) as compared to other cations such as Mg²⁺ (52 %). However, it is speculated that effective CO₂ adsorption can be typically seen for cations that possess high charge density with low atomic weight. This hypothesis can be observed for the case of Li⁺ exchanged Na⁺ in FAU zeolite, which Li⁺ displayed high CO₂ uptake (5.62 mmol g⁻¹) as compared to Na⁺ (4.98 mmol g⁻¹) at 1 atm and 25 °C.

As research progresses, large electropositive monovalent or multivalent cations are also adopted so as to enhance the adsorption of CO₂. Though a clear generalization is yet to be observed, such favourable behaviour can be identified across several zeolite frameworks. Such separation as opposed to conventional molecular sieving effect, “molecular trapdoor effect” are created by these cations that allows effective control of desired gas molecules (CO₂) as compared to N₂ and CH₄ with the proper selection of critical admission temperature (**Figure 2-3**). The presence of CO₂ allows a strong reduction of energy barrier that allows the cation to deviate itself from the original position, thus opening the pathway for CO₂ entrance. Besides, Jin et al. had synthesised a series of CHA zeolites with different Group IA and Group IIA (Li, Na, K, Rb and Cs), which a clear dip in the energy barrier, ΔE through *ab initio* Density Functional Theory (DFT) calculation was observed. Similarly, Cs-RHO zeolite displayed a clear molecular trapdoor mechanism with CH₄ uptake was merely 0.3 mmol g⁻¹ at 9 bar and 25 °C. Nonetheless, there are cases where the incorporation of large electropositive cations does not demonstrate its workability, such as Cr³⁺ ion-exchanged FAU zeolites, Cs⁺ ion-exchanged RHO zeolites and Sr²⁺ ion-exchanged KFI zeolites, thus detailed investigation on other zeolite categories are yet to be verified.

Figure 2-3 (a) Illustration of “molecular trapdoor” mechanism in Cs-CHA zeolite **(b)** Comparison between energy barrier between State 1 and 2 in **(a)**. Reprinted with permission from Reference [55], Copyright 2012 American Chemical Society.

2.1.1.3 Zeolite structure

The selection of an appropriate zeolite structure is critical particularly for effective CO₂ or SF₆ adsorption. In general, pore formation based on 6-membered ring and below (pore aperture < 0.28 nm) is inappropriate for effective CO₂/CH₄ or CO₂/N₂ separation in view of its small pore with reference to the kinetic diameter, therefore 8-membered ring zeolite namely LTA and CHA are the most probable candidate for effective separation due to their pore sizes are generally falls between the kinetic diameter of CO₂ and SF₆ [50]. On the other hand, due to substantial large kinetic diameter of SF₆, typically 10- and 12-membered ring is only feasible for effective SF₆/N₂ separation. A general comparison of pore aperture with different number of membered ring is provided in **Table 2-1**. Nonetheless, the effect of zeolite structure can be contributed significantly to the adsorption kinetics of adsorbents, particularly SF₆ which is much bulkier adsorbents as compared to CO₂ and N₂.

Table 2-1 Effect of different number of membered ring onto typical and maximum pore aperture that is feasible in CO₂ or SF₆ adsorption [50]

Number of membered ring	Maximum pore aperture (nm)	Typical pore aperture (nm)	Typical zeolite framework
8	0.43	0.30-0.45	LTA, CHA, DDR
10	0.63	0.45-0.60	MFI, MWW
12	0.80	0.60-0.80	FAU, BEA, MOR, LTL

2.1.1.4 Zeotypes (zeolite-like materials)

Zeotypes are defined as crystalline materials that portray similar topologies as zeolites, where such materials were first discovered with the successful incorporation of titanium (Ti) into pure silicon dioxide (SiO_2) instead of Aluminium (Al) (typically used in the synthesis of zeolites) which this framework was termed as TS-1 (Titanosilicate-1, which is the first derivative of ZSM-5) [56]. In this synthesis, it was observed that a similar effect (to typical aluminosilicate zeolites) was identified with the decrease in Si/Ti ratio, despite both Si^{4+} and Ti^{4+} are considered as isovalent species. This is generally attributed to a smaller electronegativity of Ti (1.32) as compared to Si (1.74) which affects the overall polarity of the linkages [57]. Thus, as the amount of titanium content increases, the number of available sites for effective adsorption increases. It has been reported that the available active sites can be well adsorbed by water molecules, which possess strong polarizability and dipole moment. However, the incorporation of Ti into the framework should not be added in excess as it creates amorphous TiO_2 that can reduce the available pore volume in the crystal.

With this, the successful incorporation of Ti-based molecular sieves had attributed to the subsequent studies of titanosilicates (termed Engelhardt Titanosilicates), namely ETS-4 and ETS-10 [58, 59]. ETS-4 is made up with a combination of both octahedral and tetrahedral framework (8-membered ring) which is similar to the structure of zorite mineral, with the pore size ranging from 0.3 – 0.4 nm [60, 61]. In comparison with ETS-10, the former demonstrates a much weaker thermal stability (< 200 °C) due to the destruction of the structural water chain at high temperature. However, with the assistance of ion exchange with suitable divalent ions namely Ca^{2+} , Mg^{2+} , Sr^{2+} and Ba^{2+} , the overall thermal stability can be enhanced [60]. The analysis of the effect

of divalent cation in ETS-4 have further confirmed that Ca-ETS-4 displayed a much higher CO₂ adsorption as compared to Sr²⁺ and Ba²⁺ ion-exchanged framework with the careful selection of pre-treatment temperature [62, 63]. On the other hand, ETS-10 which was developed through corner-sharing of TiO₆ octahedra and SiO₄ tetrahedra through bridging oxygen atom demonstrates favourable CO₂ adsorption due to its basicity that allows effective adsorption at low temperature [64].

Figure 2-4 (a) Structure of TS-1 (Si and Ti were indicated as orange and green respectively) Reprinted with permission from Reference [65], Copyright 2016 Royal Society of Chemistry; (b) Structure of ETS-4 (Si, Ti and O were indicated as yellow, green and red respectively). Reprinted with permission from Reference [60], Copyright 2001 Nature Publishing Group; (c) Comparison of CO₂ adsorption isotherm of divalent Ca²⁺, Sr²⁺ and Ba²⁺ ion-exchanged ETS-4 at 25 °C, with the degassing temperature of 100 °C and 200 °C respectively [63].

2.2 Metal-organic framework (MOF)

Metal-organic framework (MOF) which is also termed porous coordination polymer (PCP) or porous coordination network (PCN) have drawn significant attention

to researchers due to its unique structural properties. MOFs are crystalline materials that are linked together based on the linkage between metal or metal cluster with organic linkages via coordination bonding. In general, MOFs demonstrate strong competitive advantages in CO₂ or SF₆ adsorption due to its unique properties namely large accessible internal surface area, high pore volume, low density, well-defined pores together with more flexibility to perform pre- and post-synthetic functionalization as compared to zeolites [15, 66, 67]. Besides, numerous approaches are feasible to create high-crystallinity framework, thus allowing the morphology or chemical functionalities that are present in the framework can be adjusted readily to favour effective adsorption.

Conventional approach in MOF synthesis was originally dominated by hydrothermal [68] or solvothermal [69] approaches, which requires the usage of metal source, ligand with appropriate solvents and (or) water. Despite solvents and (or) water are utilized in MOF synthesis, there is no clear understanding on the role of the solvent to dictate the formation of MOF as compared to zeolites. However, solvents or water are typically present as space-filling molecules after successful formation of MOF, which these molecules can be removed effectively through heating. As research progresses, other reported synthesis route namely electrosynthetic deposition [70], microwave assisted synthesis [71], sonochemical [72] and mechanochemical (ball milling) [73] had been conducted so as to allow effective synthesis of MOF. The selection of appropriate synthesis approach generally affected by the requirement of the resultant product to be synthesised, particularly the synthesis of appropriate particle size or morphology that showcased its importance such as the fabrication of composite membrane.

Effective capture of CO₂ or SF₆ in MOF as a whole can be altered readily with the parameters such as variation of pore size via molecular sieving, framework

flexibility, presence of coordinatively unsaturated open metal sites together with appropriate surface functionalization, with the details will be elaborate further in the subsequent section. In general, versatility of MOFs in altering its physiochemical properties to favour CO₂ or SF₆ adsorption due to its higher affinity between adsorbates and adsorption sites in MOFs are more pronounced due to the surface chemistry can be modified much more easily, as compared to zeolites.

2.2.1 Molecular sieving

The creation of MOFs through reticular synthesis had showcased the possibility of MOF to be produced in the same framework topology with variation of pore size and functionalities. For instances, the creation of isorecticular (IR) MOF-5 [74], Zn₄O(bdc)₃ with numerous ligand functionalization, with the structure as shown in **Figure 2-5**. Such pore alteration from 3.8 to 28.8 Å can be done with the addition of bulky organic groups such as -Br, -NH₂, -C₃H₇, -OC₅H₁₁, -C₂H₄ and C₄H₄ onto the ligand. Besides, effective adjustment of pore size via the formation of interpenetrated framework [75] allows the pore size to be reduced from 5 – 6 Å from a comparatively large non-interpenetrated MOF-5 (8.6 Å) can be done so as to allow more effective selective capture of CO₂ as compared to other gases. Besides, a similar study was also conducted on the isorecticular SIFSIX series [76] that possess primitive cubic net structure. In this study, the alteration of ligand strut length allows substantial decrease in the overall pore size as the ligand length decreases. SIFSIX-Cu which was built up based on 4,4'-dipyridylacetylene and hexafluorosilicate ions (SiF₆²⁻) which possess large 13.1 Å pore was decreased eventually to 5.2 Å due to the formation of interpenetrated structure, thus allowing strong CO₂ adsorption capability (5.14 mmol g⁻¹ at 1 bar and 25 °C) than the former (1.84 mmol g⁻¹ at the same condition). Besides, SIFSIX-3-Zn (IRMOF of SIFSIX-2-Cu) which utilises even shorter organic ligand pyrazine that allows effective CO₂/CH₄

selectivity due to its smaller pore size, other than its favourable interaction between CO₂ and SiF₆²⁻ ions. Nonetheless, for effective SF₆/N₂ separation, care must always be taken on the selection of appropriate IRMOF due to the effective pore size generated may not be applicable to SF₆-based separation due to SF₆ possess large kinetic diameter, despite favourable CO₂-based separation can be achieved.

Figure 2-5 Creation of isostructural MOF with the variation of ligand type. Reprinted with permission from Reference [77], Copyright 2002 American Association for the Advancement of Science.

2.2.2 Flexible framework

Reversible changes in the overall structure of the framework in accordance to the effect of pressure, temperature together with the presence of guest molecules allow MOF to respond accordingly to the external stimuli, as compared to rigid framework that possess well-defined stable pores. In essence, clear “gate-opening” (breathing) mechanism at a particular pressure as well as hysteresis in the adsorption-desorption isotherm can be seen clearly in a particular isotherm. For instance, MIL-53 series framework that was building up based on 1,4-benzenedicarboxylate ligand with aluminium or chromium as the metal node have been the most commonly reported framework [78]. As a whole, two stepwise growth mechanisms can be observed as this framework was utilized for CO₂ adsorption: sharp increment of CO₂ uptake at low pressure with a plateau up till 4 bar, followed with another sharp adsorption, as shown

in **Figure 2-6 (a)**. This observation indicates that strong interaction between CO₂ molecules and the framework that results in significant pore opening at the pressure beyond 4 bar, which can be verified from the shift of powdered X-ray diffraction (PXRD) with the increase in partial pressure (**Figure 2-6 (b)**) [78]. Nonetheless, despite such materials does not suffer any loss of crystallinity despite of pore expansion behaviour, the feasibility of such category of adsorbents to ensure effective separation is typically questionable as the selectivity of different gases should not be computed based on typical Ideal Adsorbed Solution Theory (IAST) [79, 80], which is determined from pure component isotherm. This is because during the “breathing” process, the pores are generally accessible to all gases, leading to a drastic decrease in overall selectivity.

Figure 2-6 (a) Effect of CO₂ adsorption of MIL-53 (Cr) at 31 °C. A clear stepwise growth of CO₂ adsorption can be seen as the pressure increases. **(b)** X-ray diffraction profile of MIL-53 (Cr) with the alteration of CO₂ partial pressure. Reprinted with permission from Reference [78], Copyright 2007 John Wiley and Sons.

2.2.3 Coordinatively unsaturated open metal sites

The presence of unsaturated metal site in several MOFs depicts its feasibility in improving the overall affinity towards CO₂ and SF₆ which possess higher polarizability. Such sites are generated after effective solvent removal that was trapped during the synthesis process. Hence, the exposed sites allow strong interaction with CO₂ or SF₆ via

the formation of end-on adducts between oxygen atom in CO₂ or fluoride atom in SF₆ together with the metal sites [81]. Besides, such sites offer additional platform to conduct post-synthetic functionalization via amine grafting process by allowing enhanced interaction with the adsorbates. However, due to its reactive metal sites, its properties will be hampered strongly with the presence of water vapor due to competitive adsorption between water and CO₂ (or SF₆) molecules.

Figure 2-7 (a) Structure of HKUST-1 and (b) M-MOF-74. Reprinted with permission from Reference [11], Copyright 2012 American Chemical Society

HKUST-1 (or Cu₃(btc)₂, **Figure 2-7 (a)**) which was one of the commonly reported MOFs to date, possess Cu²⁺ metal centre that allows preferential adsorption of CO₂ (12.7 mmol g⁻¹ at 25 °C and 15 bar) as compared to CH₄ (4.6 mmol g⁻¹ at the same condition) [82]. It is built up based on the paddlewheel Cu₂(COO)₄ unit with the btc linkers. Besides, its large square-shaped pores (9 x 9 Å) allows effective SF₆ adsorption due to the accessible pore size. Besides, the isosteric heat of adsorption (for CO₂) is comparatively lower than other adsorbents namely zeolite 13X (30 kJ mol⁻¹ vs. 49 kJ mol⁻¹), allowing substantially lower energy penalty for possible reutilization for subsequent adsorption process. On the other hand, M₂(dobdc) or M-MOF-74 (M = Mg, Mn, Fe, Co, Ni, Cu or Zn, **Figure 2-7 (b)**) are adsorbents that had been reported by its extraordinarily high CO₂ and SF₆ adsorption. M₂(dobdc) framework is developed via

the formation of 11 – 12 Å honeycomb network topology with the exposure of M^{2+} sites [83]. As a comparison, $Mg_2(dobdc)$ reported the highest uptake of 23.6 wt% as compared to $Ni_2(dobdc)$ and $Co_2(dobdc)$ (11.6 wt% and 11.7 wt%) at 23 °C and 0.1 bar, which was due to the former possesses higher isosteric heat of adsorption (-47 kJ mol^{-1}) as compared to $Ni_2(dobdc)$ and $Co_2(dobdc)$, which was reported to be -41 kJ mol^{-1} and -37 kJ mol^{-1} . Such preferential adsorption of CO_2 or SF_6 onto $Mg_2(dobdc)$ was attributed to its strong ionic bonding character of Mg-O. Nonetheless, M-MOF-74 suffers significant difficulties in regeneration particularly in the presence of water vapor, as such the preparation of these samples must be conducted in an inert environment without destroying the overall crystallinity.

2.2.4 surface functionalization

In general, there are two main possibilities to perform surface functionalization on MOFs, which are pre-synthetic and post-synthetic functionalization. Pre-synthetic functionalization involves the utilization of functionalized ligand, which results in the formation of MOF with the desired pendant groups namely -Br, -CH₂, -CH₃ or other simpler substituents. For instance, $NH_2\text{-MIL-53 (Al)}$ was formed with the incorporation of 2-aminoterephthalic acid ($NH_2\text{-bdc}$) instead of the common terephthalic acid as the ligand [84]. A strong improvement of CO_2/CH_4 separation factor at zero surface coverage from 5 to 60 with an increased in isosteric heat of adsorption (of CO_2) from 20.1 to 38.4 kJ mol^{-1} was clearly observed. Besides, the addition of this substituent reduces the overall pore size of the framework, thus reducing the diffusivity of CH_4 . However, it is always imperative to ensure that the modified functional group is still comparable or stable during the synthesis process so as to assure that the CO_2 or SF_6 adsorption can be enhanced further with the role of the substituents.

Figure 2-8 (a) Structure of NH₂-MIL-53 (Al). Reprinted with permission from Reference [85], Copyright 2009 Elsevier; **(b)** Comparison of CO₂ and CH₄ uptake of NH₂-MIL-53 (Al) at 30 °C. Reprinted with permission from Reference [84], Copyright 2009 American Chemical Society

Post-synthetic functionalization is also another approach in enhancing the adsorption of CO₂ via increased affinity in MOFs. Such functionalization is generally feasible for MOFs that possess unsaturated metal sites as after solvent removal, the exposed sites can be used to attach additional functional groups (typically amines) which can improve CO₂ adsorption particularly at low pressure. For instance, amine functionalized Mg₂(dobpdc) was conducted to enhance CO₂ adsorption further despite promising adsorption of Mg₂(dobpdc) and Mg₂(dobdc) was reported. However, trials on the incorporation of amine functionalities was not feasible due to the one-dimensional pore of 11 Å was deemed insufficient to allow an effective incorporation of diamine into the framework [86]. Hence, ligand expansion via the usage of H₄dobpdc instead of H₄dobdc was feasible due to the effective pore size is increased to 21 Å, thus allowing an improved CO₂ adsorption from 2.52 mmol g⁻¹ to 3.26 mmol g⁻¹ for Mg₂(dobpdc) and *mmen*-Mg₂(dobpdc) at 0.18 bar and 25 °C respectively [87]. Besides, the stability of *mmen*-Mg₂(dobpdc) was enhanced further with the addition of amine, as no significant alteration of crystallinity was identified after *mmen*-Mg₂(dobpdc) was exposed to air for one week. As a comparison, exposure of Mg₂(dobpdc) in the same aforementioned condition suffers significant change in the colour from white to blue with a loss of crystallinity. Nonetheless, despite functionalization of MOFs via either post- or pre-

synthetic method is feasible in improving the overall affinity towards CO₂, addition of amines reduces the accessible pores to the framework. Therefore, the reduced pore size can be a major hurdle in improving overall SF₆ adsorption as well as SF₆ adsorption kinetics in the overall framework.

Figure 2-9 (a) Comparison between $\text{Mg}_2(\text{dobdc})$ and $\text{Mg}_2(\text{dobpdc})$. Reprinted with permission from Reference [88], Copyright 2014 Royal Chemistry of Society; **(b)** Structure of $\text{mmen-Mg}_2(\text{dobpdc})$. Reprinted with permission from Reference [87], Copyright 2012 American Chemical Society

2.2.5 Zeolitic imidazolate framework (ZIF)

Zeolitic imidazolate framework (ZIF) is categorized as a subclass of MOF that connects organic imidazolate (Im) linkers with several transition metals (T) such as cobalt, zinc, copper and iron. The structure of ZIF is comparable with the structure of zeolites, with the formation of T-Im-T configuration at a bond angle of 145° [89]. Thus, it is worth noting that the ZIFs typically share similar characteristics and advantages that are present in both zeolite and MOFs namely high surface area, high crystallinity, abundant sites of functionalities as well as high chemical and thermal stability. In general, it is well-known that the chemical and thermal stability of MOFs tends to be limited by the organic linkers, which is the weakest link in the overall framework's stability [90]. Hence, the study on the first series of ZIFs (ZIF-1 to -12) through variation of ligand composition had revealed that imidazolate linkers were comparatively stronger than common conventional carboxylate or phosphonate-based ligands. In particular, ZIF-

8 which possess SOD zeolite topology has been widely incorporated in various application due to the loss of crystallinity was not observed under harsh condition (e.g. boiling water, boiling methanol, elevated temperature (200 °C for 24 hours)) [89, 91]. Besides, ZIF-8 can be synthesised readily in aqueous solution without substantial loss in overall crystallinity.

Nonetheless, it has been reported that only several limited structures that can resemble the topology that could be found resembling the structure of conventional zeolites despite there are more than 100 types of reported ZIF structures [92]. Thus, the synthesis of ZIF framework that mimics the structure of zeolite are typically conducted with two common strategies. First and foremost, the formation of ZIF-20 which mimic the zeolite LTA topology were synthesised via the link-link interaction between linkers to develop the framework. In this study, the investigation of plausible ligands that allows the formation of framework similar to zeolite LTA was verified by selecting several ligands (**Figure 2-10 (a)**) [93]. In general, it was observed that the formation of ZIFs with LTA topology is feasible if the nitrogen atom is located at the position 5 of the ligand because the formation of dipole-dipole and electrostatic interaction can be formed at position 5 and 6 of the ligand, as compared to benzimidazole and 4-azabenzimidazole. However, as the choice of using single-linker is typically difficult to obtain ZIFs that are similar to the topology of common zeolite frameworks, studies have been focussed on the synthesis of mixed-linker to allow a proper development of ZIFs that resembles the structure of zeolite. Hence, in recent work, the formation of ZIFs that resembles zeolite CHA topology was synthesised using the aforementioned approach (**Figure 2-10 (b)**), which was determined as ZIF-300, ZIF-301 and ZIF-302 [94]. The water stability of these series of ZIF have been observed through dynamic CO₂/N₂ breakthrough

measurement under humid condition, which the presence of hydrophobic functionalities allows the overall crystallinity to be remained stable in the presence of water.

Figure 2-10 (a) Choice of different imidazolate group for the successful synthesis of ZIFs with LTA topology. Reprinted with permission from Reference [93], Copyright 2007 Nature Publishing Group; **(b)** Synthesis of ZIFs framework with CHA topology (ZIF-300, ZIF-301 and ZIF-302), with no significant change in CO₂ adsorption in dry and humid condition. Reprinted with permission from Reference [94], Copyright 2014 John Wiley and Sons.

2.3 Microporous organic polymer (MOP)

Microporous organic polymers (MOPs) are classified as porous materials that are built up based on strong covalent bonding with light elements namely H, B, C, N and O. In general, MOPs can be classified into different sub-categories, depending on the synthesis condition and the resulting structure, namely porous aromatic frameworks (PAFs) [95, 96], conjugated microporous polymers (CMPs) [97, 98], covalent organic frameworks (COFs) [99, 100], hyper-crosslinked polymers (HCPs) [101-103] and

polymers of intrinsic microporosity (PIMs) [104, 105]. The synthesis of MOPs can be ranged from a wide variety of plausible chemical reactions such as condensation polymerization [106-108], trimerization [109], oxidative polymerization [110-112], click reaction [113] and metal-catalyzed coupling [98, 114, 115]. As an overview, COFs are the only subclass of MOPs that demonstrate high crystallinity with clear well-defined two or three-dimensional porous structure. However, for other categories of materials that does not possess any crystallinity, the presence of linking points in between each building block is vital to prevent any possible collapsing of the porous materials into dense non-porous behaviour, which can be verified through N₂ sorption isotherm at 77 K [116]. As a comparison to other porous materials such as zeolites and MOFs, MOPs demonstrates several advantages namely strong physicochemical stability, resistance to attack of acidic environment and high permanent porosities, which showcase itself as a suitable candidate for effective CO₂ and SF₆ adsorption.

As a whole, as compared MOFs, the pore dimension and structure of COFs can be modified by altering the strut length of the monomer, which is similar to the formation of a series of IRMOF. Thus, systematic change in the length of the strut allows similar behaviour to the change in pore volume, pore size and surface area. For instance, increase in pore diameter from 6.4, 18.7 and 34.1 Å respectively for COF-6, COF-8 and COF-10 was observed with the increase in strut [117]. In comparison to other MOPs categories, direct relation between the overall strut length or structural design to the overall porosity was not demonstrated. For instance, it has been observed that while the micropore size distribution of CMPs series (CMP-0 to CMP-5) was deviated to a larger pore diameter with the increase in the strut length of the monomer, the total pore volume of the resulting CMP series decreases substantially from 0.38 to 0.16 cm³/g, with the pores synthesised in this series are mainly in the microporous range [98, 118]. Hence,

such observation implies that the porosity behaviour of CMP is not clearly defined from the structure of the monomer, despite in some circumstances, statistical copolymerization using monomer with various strut lengths are feasible in fine-tune the overall framework's porosity.

Figure 2-11 (a) Co-condensation reaction of different strut length with the increase in the overall pore size of COF frameworks (COF-6, -8 and -10). Reprinted with permission from Reference [117], Copyright 2007 American Chemical Society **(b)** variation of CMP structures with change in strut length. The pore size distribution of CMPs that was derived from the NLDPT pore size distribution indicates a shifting to larger micropore size. Reprinted with permission from Reference [98], Copyright 2008 American Chemical Society; Reprinted with permission from Reference [119], Copyright 2009 John Wiley and Sons

Reports have shown that other categories of MOPs have demonstrated its feasibility in utilizing two or more monomer struts to develop substantial difference in terms of its structural and chemical properties via copolymerization process. For instance, HCP materials namely PP-N-*x* copolymers which were developed with the copolymerization between triphenylamine and dichloro-*p*-xylene were successfully developed with the variation of the molar ratio between the two monomers. In general, it was observed that the overall accessible surface area showcased an increasing value from 318 to 1530 m² g⁻¹ with an increasing ratio of dichloro-*p*-xylene to triphenylamine [111, 120]. In terms of CO₂ adsorption, PP-N-25 depicts the highest CO₂ adsorption as compared to other counterparts in view of its highest microporous surface area and micropore volume. Moreover, nitrogen atoms that are present in the copolymers is feasible to act as Lewis base to provide a platform for strong affinity towards CO₂ molecule. Besides, the presence of large micropore also allows the active sites to be favourable to SF₆ adsorption [121] as both CO₂ and SF₆ possess strong polarizability.

CO₂ adsorption MOPs can be enhanced further by utilizing the similar strategies as MOFs via the utilization of pre- or post-synthetic functionalization. For instance, the ligands present in MOPs can be incorporated with several functional groups such as carboxylic acid, methyl group, hydroxyl group and amine, which was incorporated in CMP-1 using 1,3,5-triethynylbenzene as the monomer [122]. An increase in CO₂ adsorption can be identified with a substantial increase in isosteric heat of adsorption of CO₂ with the incorporation of polar groups as compared to bulky non-polar groups. On the other hand, post-synthetic functionalization on MOPs can be conducted to enhance CO₂ adsorption, which the grafting reaction between PPN-6-CH₂Cl with various CO₂-philic alkylamine groups [123]. In general, despite drastic decrease in surface area was reported as the accessibility of the gas molecules were limited due to the presence of

dangling amine functionalities, significant enhancement of CO₂ adsorption at low partial pressure together with increase in the isosteric heat of adsorption of CO₂ was observed.

2.4 Mesoporous materials

Mesoporous materials are defined as any porous substances that possess the diameter that ranged from 2 to 50 nm, in accordance to IUPAC nomenclature. As a whole, research on mesoporous materials had been dominated by the choice of mesoporous silica, namely MCM-41, MCM-41, COK-12 and SBA-15, together with substantial notable hierarchical microporous-mesoporous materials that was developed in nanoporous materials such as zeolites, metal-organic frameworks and microporous organic polymers. The development of hierarchical nanoporous materials typically demonstrates promising gas adsorption properties as compared to mesoporous silica as its domain wall does not contribute to gas adsorption as its thick pore walls will only increase the effective mass and volume of the overall adsorbents [124]. Besides, it can be expected that a clear improvement in overall adsorption kinetics particularly for bulkier adsorbates such as SF₆ can be observed, together with a potential room for post-synthetic functionalization such as the addition of amine groups that allows overall affinity towards polarizable adsorbates (e.g. CO₂) can be determined.

In a typical synthesis, the overall size of mesopore can be tuned via liquid crystal templating process by selecting suitable surfactant molecules created in a basic environment, together with the incorporation of covalent organic molecules (e.g. 1,3,5-trimethylbenzene) to increase the overall size of mesopore [125]. The first series of mesoporous molecular sieve (M41S) was first synthesised and explored by the research group in Mobil. As reported in numerous journals, MCM-41 and MCM-48 had been actively reported owing to attractive physical and chemical properties that favours CO₂

adsorption. For instance, MCM-41 possesses two-dimensional hexagonal system $p6mm$ space symmetry that contains one-directional mesopore 15 to 100 Å. On the other hand, MCM-48 was conducted based on cubic system with $Ia3d$ space symmetry that contains mesopore in the range of 15 to 30 Å. In general, the ratio of silicon source and surfactant will affect the final structure, which MCM-41 will be formed if the ratio between them is less than unity [126]. Besides, the size of mesopore can be readily altered with the choice of surfactant, particularly with the alteration of different alkyl chain length in quaternary directing agent. However, the mesopore can only be utilized by the removal of the excess surfactant that could be potentially clogged the pores, which can be processed via calcination or ion exchange process. As a whole, the former method is more preferable due to the simpler process handling [127].

In general, MCM-41 demonstrates strong flexibility in terms of variation of particle morphology and elemental composition. For example, Si/Al ratio can be used to tune the overall hydrophilicity of MCM-41 [128, 129]. Besides, synthesis of MCM-41 can be effectively synthesised with the utilization of aluminophosphates or transition metal oxides as the material source. Nonetheless, MCM-41 is more susceptible to pore blockage due to its one-dimensional straight pore channels, thus reducing the effective interaction between adsorbent and adsorbate. In comparison to MCM-48, its three-dimensional cubic pore structure is feasible in reducing the plausible clogging resistance [126]. With the successful incorporation of mesoporosity into the framework, incorporation of amines via post-synthetic functionalization with the available basic sites so as to improve the overall CO₂ adsorption via affinity-based adsorption. For instance, an increase in CO₂ adsorption from 0.12 mmol g⁻¹ to 0.7 mmol g⁻¹ at 0.1 bar and 30 °C was observed by comparing amine-grafted MCM-41 and non-grafted MCM-41, with similar results were also identified for MCM-48 [130, 131]. Nonetheless, the

trade-off between the incorporation of mesoporosity with the decrease in crystallinity is the major hurdle in improving the overall adsorption of these materials even further.

On the other hand, SBA-15 is also widely adopted in the application of CO₂ adsorption process. In contrast to the synthesis of MCM-41 and MCM-48, amphiphilic triblock copolymers were used as the structural directing agent (SDA) in acidic medium in the synthesis of SBA-15, which the excess SDA was removed by calcination process. SBA-15 is developed based on two-dimensional hexagonal system in the configuration of *p6mm* space symmetry where the cylindrical pores are tunable up till 300 Å [125]. Nonetheless, the presence of broad pore size distribution in SBA-15 is attributed to its strong connectivity between the inter-cylindrical pores within the primary mesopores [132, 133]. Similarly, the porous surface in SBA-15 can be post-grafted with the amine functional groups so as to allow additional reactive sites for effective CO₂ adsorption [134-139]. Besides, COK-12 which was built up based on highly ordered two-dimensional *p6mm* hexagonal structure with straight pores [140] (similar to MCM-41 and SBA-15) has been widely reported due to its ease of synthesis, as the materials can be obtained via quasi-neutral pH at room temperature [141]. The potential of COK-12 in CO₂ adsorption is yet to be verified, nonetheless the creation of mesoporosity allows an improvement in overall adsorption kinetics together with the propensity to conduct post-synthetic functionalization for favourable greenhouse gas capture process [142].

2.5 Mixed-matrix membrane (MMM)

MMMs are described as the case where the filler material (typically in solid phase) is integrated into the polymer matrix. In general, the design of effective MMM is related to several critical factors. For instance, the filler materials are expected to be uniformly distributed to the polymer matrix where the aggregation of fillers should be

kept minimal. Besides, interfacial gap between filler and polymer is critical as poor compatibility between them can lead to poor performance. Therefore, to provide a better understanding on these behaviour, a brief description of the mathematical models of gas transport in MMM together with the plausible presence of non-idealities in between polymer-filler interface will be elaborated in the subsequent section.

2.5.1 Mathematical model for gas permeation properties

The performance of gas separation membrane is generally evaluated using permeability, P . The permeability of the composite membrane is related to the properties of the permeating gas (polarizability, shape and size) as well as the chemical properties of the filler and polymer matrix. As the permeability of gas can be described as solution-diffusion mechanism, the permeability of a particular gas species can be defined based on the expression $P = S \times D$, where P is the permeability with the unit of barrer ($1 \text{ barrer} = 1 \times 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$), with S and D are defined as solubility and diffusion coefficients respectively [143]. Experimentally, the permeability of the membrane can be described using the expression (1) [144]:

$$\frac{P}{l} = \frac{Q}{A\Delta P} \dots (1)$$

In this expression, Q is the volumetric flow rate of a gas that was permeate through the membrane, A is the membrane's surface area, l is the effective thickness of the membrane, and ΔP is the pressure difference across the membrane.

In certain circumstances, the effectiveness of the filler can be quantified using mathematical model in order to provide a better understanding on the effect of the incorporation of nanoporous materials to the permeability of gases in MMM. Besides, such analysis may assist in providing some insights on the optimal loading and

morphology of the fillers on the membrane performance. In general, Maxwell model has been the most classical model that was used to describe the permeability of mixed-matrix membrane [145, 146]. This equation is defined based on the theory of electrical transport of composite materials with the presence of dielectric medium, as shown in equation (2):

$$P_{cm} = P_p \frac{1 + 2\phi_f(\alpha - 1)/(\alpha + 2)}{1 - \phi_f(\alpha - 1)/(\alpha + 2)} \dots (2)$$

In this expression, P_{cm} is the permeability of gas in MMM, P_p is the permeability of the polymer matrix, ϕ_f is the volume fraction of filler and α is the ratio of the permeability of filler to the polymer matrix.

Maxwell equation can be used to predict the gas permeability in the MMM, provided that the permeability of the filler and polymer as well as the volume fraction of filler is known. This equation is generally simple and effective in predicting the performance of MMM with ideal morphology, which in other words the transport profile of gas around a filler is not affected by the presence of other fillers. With this basis, this model is only relevant for the volume fraction of filler that is less than 0.2 [147, 148], which this parameter is often described as percolation threshold [149]. After this limit, it is expected that the interconnected channels between fillers will lead to a huge deviation of the Maxwell Model to the experimental result. Thus, as the fillers used in MMM has been developed in a wide variety of particle dimension and morphologies, Maxwell model tends to oversimplify the plausible non-ideal effects that could be present when fillers were incorporated in MMM. Thus, additional modifications on the Maxwell model have been conducted and reported in the review conducted by Hoang et al. [148] so as to account for a better prediction of gas permeability particularly at a wider range of filler loading.

2.5.2 Non-ideal interfacial morphologies

Figure 2-12 (a) Impact of ideal (predict from Maxwell Equation) and non-ideal morphologies on the performance of MMM; **(b)** CO₂ transport profiles of various interfacial morphologies of MMM. The normal profile refers to the diffusivity of CO₂ molecules in the polymer phase [15].

In any MMM, membranes that generally demonstrates improvement in both permeability and selectivity is the most favourable as it is the most probably method to surpass the upper bound limit. However, in practical basis, the presence of non-idealities

in MMM is unavoidable and it is required to mitigate such behaviour. Thus, three common types of non-idealities that could be potentially present in MMM will be elaborated, which are *sieve-in-a-cage*, rigidified interface and plugged sieves. The morphologies and the expected gas transport profile were depicted as shown in **Figure 2-12**.

Sieve-in-a-cage morphology is generally attributed to the unequal stress distribution in the MMM during the solvent evaporation process. In general, the polymer-filler interaction is typically weaker as compared to polymer-polymer interaction. Thus, if the choice of filler (particularly hydrophilic, inorganic filler) is inappropriate, the stress that is generated at the interface can lead to the poor adhesion on the polymer surface, which in turn leads to the formation of voids [150]. Such behaviour is typically present when zeolite particles are dispersed in polyimide membrane. Nevertheless, MOF which possess organic moieties tends to demonstrate a favourable compatibility with the polymer matrix, thus such non-ideal interfacial morphologies can be minimized [151, 152]. Besides, *sieve-in-a-cage* morphology could also be generated in view of the filler agglomeration in the MMM. Thus, it is generally recommended to disperse the filler homogeneously by utilizing a suitable solvent prior to the addition of polymer in the solution. Such action can be conducted by using sonication bath or horn to break apart the aggregation of particles. This is because as this interfacial void can serve as the supplementary gas transport channel that causes poor membrane performance, despite this defect may be feasible to heal these defects by annealing the temperature above the T_g of the polymer. Nonetheless, the difference in the thermal expansion in the filler and the polymer matrix may not guarantee its success [146].

On the other hand, it is also possible that during the solvent evaporation process, the polymer chain could face substantial difficulty in contracting isotopically in view of the filler's rigidity [153]. Thus, compressive stress around the filler-polymer interface will cause the polymer chains to be potentially pile up surrounding the filler surface, leading to the formation of condensed interface [146]. This phenomenon can be described as rigidified interface, where such behaviour can also be observed when silane coupling agent is used, as such coupling agent that was attached on the filler has been associated with the formation of such interface. Under such circumstance, the gas transport profile is comparatively different as compared to *sieve-in-a-cage* morphology because under such interface, the gas transport mechanism is still dominated by solution-diffusion. Nonetheless, due to the fractional free volume (FFV) was decreased substantially under such interface, the gas permeability decreases for about three to four times as compared to the reference membrane. Nevertheless, under such condition, the selectivity was expected to be enhanced due to the condensed interface [154].

Besides, the possibility that the pores that are present in the fillers could be blocked by the presence of other components. For instance, the pore of the fillers can be potentially plugged by solvents, water, contaminants, minor impurities that are present in the feed gas as well as the polymer chains that are flexible enough to block the pore during the membrane fabrication [146, 154, 155]. Thus, with the partial blockage of pores, the gas is eventually unable to pass through the fillers effectively, leading to a decrease in the gas permeability as compared to unplugged pores. At times, it may affect the overall membrane selectivity if the effect is substantial. Thus, it is generally more straightforward to verify such effect by the measurement of the gas adsorption of pure polymeric membrane and MMM to observe such behaviour [156]. Nonetheless, it is important to recognize that sufficient equilibration time for the gas adsorption for the

respective membrane is necessary so as to prevent any misinterpretation on the pore plugging phenomena.

Strategies on mitigating non-ideal morphologies have been widely proposed to promote interfacial adhesion between the filler and polymer matrix. In general, it can be conducted through various protocols, with the aim of release the interfacial stress and create the interface which are defect free. In general, thermal annealing, addition of low molecular weight materials (LMWMs) and plasticizers into the dope solution as well as surface modification of the filler [157-160] can help to assist *sieve-in-a-cage* and rigidified interface non-idealities. For the case of plugged sieve, it is generally recommended that the polymer and fillers are first pre-treated (heating under vacuum) to remove any unnecessary water and solvents that are present in the pores, as these components are feasible in blocking the pores.

2.6 Conclusion

In conclusion, there have been a wide variety of nanoporous materials and membranes that are feasible to show favourable interaction and separation with selected gas pairs. As research progresses, the choice of nanoporous materials are not exhaustive to zeolites, MOFs, MOPs and mesoporous materials that can be utilized to tune the overall porosity of the framework and the resulting affinity towards polarizable gases. Nonetheless, the evaluation of the overall practicability of such materials in industrial greenhouse gas capture process is required in order to ensure that the presence of undesirable impurities in the gas stream that did not limit the practical application of these materials. As a quick recap, the summary of the properties of aforementioned materials are summarized as follows (**Table 2-2**).

Table 2-2 Properties of selected nanoporous materials [15]

Category	Definition	Physio-chemical properties	Values	Limitations	Notable Examples
Zeolites and related materials	<ul style="list-style-type: none"> Aluminosilicate or titanosilicate materials 	<ul style="list-style-type: none"> Typical BET surface area < 1000 m²/g Hydrophilic or hydrophobic Crystalline 	<ul style="list-style-type: none"> Active sites allows selective capture of polarizable gases Well-defined pores Ion-exchange with various cations is feasible Strong chemical and thermal stability Common zeolites are commercially available in comparatively affordable price^[a] 	<ul style="list-style-type: none"> Active sites are also favourable to water adsorption. Creation of mesoporosity is necessary for post-synthetic functionalization using amines 	<ul style="list-style-type: none"> Na-A Na-X ZSM-5 ETS-10
Metal-Organic Framework (MOFs)	<ul style="list-style-type: none"> Microporous materials with metal or metal clusters are linked with ligands via coordination bonding 	<ul style="list-style-type: none"> Typical BET surface area > 1000 m²/g Hydrophilic or hydrophobic Crystalline 	<ul style="list-style-type: none"> MOFs with open-metal sites are feasible to conduct post-synthetic modifications Ligand strut length can be used to control the effective pore size Particle morphology can be tuned readily 	<ul style="list-style-type: none"> Commercial MOFs are expensive at present^[b] Weak coordination bonding leads to susceptibility to water hydrolysis Poorer chemical and thermal stability as compared to zeolites 	<ul style="list-style-type: none"> HKUST-1 ZIF-8 MIL-53 Mg-MOF-74
Microporous Organic Polymers (MOPs)	<ul style="list-style-type: none"> Periodic arrangement of light elements (C, H, N, O) via covalent bonding 	<ul style="list-style-type: none"> Typical BET surface area > 1000 m²/g Hydrophobic Crystalline or amorphous 	<ul style="list-style-type: none"> Length of monomer can be used to tune the effective pore size of MOPs Post-synthetic functionalization is feasible to enhance the adsorption of polarizable gases 	<ul style="list-style-type: none"> Challenging synthesis condition Poor scalability Generally demonstrates low adsorption as compared to zeolites and MOFs Difficult to control the particle morphology 	<ul style="list-style-type: none"> COF-8 PP-N-25 CMP-1 PPN-6
Mesoporous Materials	<ul style="list-style-type: none"> Materials with pore size in the range of 2 – 50 nm 	<ul style="list-style-type: none"> Typical BET surface area > 1000 m²/g Hydrophilic or hydrophobic Crystalline or amorphous 	<ul style="list-style-type: none"> The mesopore size can be altered with the length of the substituents Creation of mesopores allows post-synthetic functionalization with amines 	<ul style="list-style-type: none"> Commercial mesoporous materials are expensive at present^[c] Trade-off between increase mesoporosity to the resultant crystallinity Diffusion selectivity decreases due to large pores 	<ul style="list-style-type: none"> MCM-41 MCM-48 SBA-15 COK-12

All the information can be obtained from the Sigma Aldrich website, which is accurate as of 18-May-2019: ^[a] zeolite 5A (S\$0.26/g), zeolite 13X (S\$0.18/g); ^[b] ZIF-8 (S\$81.6/g); MIL-53(Al) (S\$81.6/g); HKUST-1 (S\$81.6/g), FeBTC (S\$44.0/g); MOF-177 (S\$49.1/g); ^[c] MCM-41 (S\$76/g)

Chapter 3 Development of Hierarchically Structured MFI Zeolites

3.1 Introduction

As mentioned in Chapter 2, zeolites which generally possess strong CO₂ capture capability is feasible to adsorb SF₆ in view of its high polarizability. In comparison to other porous materials, zeolites are capable to be generated in large-scale with low production cost. Besides, its strong chemical and thermal stability in contrast to newly developed porous materials namely MOFs, COFs, porous organic cages, etc. has led to its high attractiveness in industrial gas separation process. Nonetheless, the available pore window in zeolite framework is critical to ensure that effective transport of SF₆ into the resultant active sites can be feasible in view of its larger kinetic diameter as compared to CO₂. Moreover, the feasibility of commercial zeolite adsorbent (zeolite 13X) in SF₆/N₂ separation is limited by its poor adsorption kinetics in order to conduct an effective adsorption-desorption cycling, despite decent SF₆ adsorption at ambient condition can be demonstrated. Hence, in this chapter, the development of hierarchically structured zeolite MFI that is feasible to perform effective SF₆/N₂ separation was conducted. Considering the micropore size of zeolite MFI is comparable to the kinetic diameter of SF₆, it can be hypothesised that the creation of mesoporosity allows a strong facilitated transport between SF₆ molecules to the active sites that were stationed on the microporous space can be achieved. This allows a strong enhancement in the overall adsorption kinetics together with the ease in regeneration under dynamic breakthrough measurement.

3.2 Experimental methods

3.2.1 Materials

[3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride (TPOAc, 42 wt% in methanol), aluminium sulphate hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), sodium hydroxide (NaOH), tetrapropylammonium bromide (TPABr, 98%) were purchased from Sigma Aldrich. Water glass (29% SiO_2 and 9% Na_2O in water) was purchased from Daejung Chemical. Pure SF_6 , pure N_2 and SF_6/N_2 (1:9) mixture were purchase from Air Liquide. All the reagents mentioned above were used as received.

3.2.2 Synthesis of zeolite MFI

The synthesis of MFI zeolite with hierarchical microporous-mesoporous structure (MFI-2) was conducted by referring to the procedure as reported [161]. The molar composition of MFI-2 was determined as $40\text{Na}_2\text{O}/2.5\text{Al}_2\text{O}_3/100\text{SiO}_2/10\text{TPABr}/5\text{TPOAc}/26\text{H}_2\text{SO}_4/9000\text{H}_2\text{O}$. In the preparation of the synthesis gel, NaOH and TPABr was dissolved in H_2O at room temperature for 30 minutes to ensure that a clear solution is obtained. Next, water glass was added to the aqueous solution, which the mixture is eventually heated at $60\text{ }^\circ\text{C}$ for 6 h. Then, an aqueous solution containing $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and H_2SO_4 was added dropwise under agitation. The homogeneity of the resulting gel was ensured by stirring the gel for an additional of 2 h at room temperature, which was eventually poured into the hydrothermal reactor and heated at $145\text{ }^\circ\text{C}$ under vigorous stirring for 6 days. The white precipitate that was formed in the resulting solution was washed thoroughly with the distilled water and dried in the convection oven at $100\text{ }^\circ\text{C}$. The solid product was calcined in the furnace at $550\text{ }^\circ\text{C}$ for 4 h under continuous air flow. Similarly, the synthesis of MFI zeolite with only microporous domain (MFI-1) was developed

similarly to the synthesis of hierarchical MFI zeolite as mentioned, without the addition of TPOAc.

3.2.3 Characterization

The adsorption behaviour of both SF₆ and N₂ in MFI-1 and MFI-2 were measured using volumetric gas sorption analyser (Isorb HP1, Quantachrome). Prior to the measurement, both MFI-1 and MFI-2 were activated at 180 °C for 8 h to ensure that any residual solvents or moisture that could be present in the sample can be removed effectively. The resulting isotherm was measured in the range of 0 – 1 bar at both 25 and 40 °C, which are controlled using water recirculator and isothermal jacket respectively. The porosity properties of MFI-1 and MFI-2 samples were determined using argon (Ar) and nitrogen (N₂) physisorption isotherm, with the samples were degassed under the same condition as mentioned above. The Ar physisorption isotherm were measured at liquid Ar temperature (87 K) using volumetric gas sorption analyser (ASAP2020, Micromeritics). The specific surface area for MFI-1 and MFI-2 was determined using the BET theory from the adsorption branch, which MFI-1 sample which possess solely microporous nature is calculated at the low P/P₀ range between 0.05 to 0.1, whereas MFI-2 sample which possess microporous and mesoporous nature were determined at the P/P₀ range between 0.1 to 0.3, so as to ensure that the assumption of multi-layer adsorption under this range remains valid [162]. The size and volume of micropore and mesopore were calculated using the adsorption branch using HK method and BJH algorithm respectively. As a countercheck, the N₂ physisorption analysis was carried out using volumetric gas sorption analyser (Belsorp-mini II, BEL Japan Inc.) at liquid N₂ temperature (77 K). The crystallinity of the MFI samples was determined using powdered X-ray diffraction (PXRD) using CuK α radiation operated at 40 kV and 40 mA, which was conducted at ambient condition in the range of 2 θ from 2 to 40°, for a

step size of 0.02°. The morphology of the MFI crystals on the other hand were observed with scanning electron microscope (SU-70, Hitachi) at 15 kV acceleration voltage with Pt coating (resolution of 1.0 nm at 15 kV).

3.2.4 Evaluation of SF₆ and N₂ uptake performance

The SF₆ adsorption of the respective MFI adsorbents were modelled using dual-site Langmuir [44]. Dual-site Langmuir-Freundlich model which was typically used in modelling the SF₆ adsorption in MOFs [22, 163] were not used in this case as reasonable accuracy ($R^2 > 0.99$) can be determined using this model. The equation can be defined as follows (**Equation 3-1**):

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

where q is the total quantity of SF₆ adsorbed, p is the partial pressure, $q_{sat,1}$ and $q_{sat,2}$ are defined as the Langmuir parameters for site 1 and 2, respectively. On the other hand, N₂ adsorption data were fitted using single-site Langmuir model (**Equation 3-2**).

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

The saturation capacity of N₂ at ambient temperature and above is generally difficult to be determined as compared to SF₆ in view of its weaker interaction between N₂ and adsorbent. Thus, in this study, it was assumed that the adsorption sites available in the adsorbent is equally accessible to both SF₆ and N₂, which in most circumstances, it is proved to be valid in determining the saturation capacity of weakly-bound adsorbents [44, 163]. On the other hand, the adsorption kinetics of SF₆ was studied under the selection of one dosing pressure (1 bar) at 25 and 40 °C respectively, which can be

described as fractional uptake (**Equation 3-3**). The fractional uptake was plotted against time.

$$\text{Fractional Uptake} = \frac{\text{Amount of uptake at time } t}{\text{Equilibrium uptake}} \dots (3 - 3)$$

The separation performance of SF₆/N₂ under various condition were calculated using ideal adsorbed solution theory (IAST) [164], which can be described as shown (**Equation 3-4**):

$$\text{Selectivity} = \frac{x_1/x_2}{y_1/y_2} \dots (3 - 4)$$

where x_1 and x_2 are the mole fraction of the adsorbed phase for component 1 and 2, with y_1 and y_2 are the mole fraction in the gas phase. The isosteric heat of adsorption (Q_{st}) were calculated using the virial plot (**Equation 3-5**) as shown below:

$$\ln P = \ln N + \left(\frac{1}{T}\right) \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \dots (3 - 5)$$

In this expression, P is the pressure in bar, T is the temperature in Kelvin, N is the total amount adsorbed in mmol/g, a_i and b_i are the virial coefficients that is not a function of temperature, m and n are defined as the number of required coefficients in order to fit the isotherm accurately, which can be determined through trial-and-error. The value of Q_{st} can be determined based on the equation below (**Equation 3-6**) [165, 166]:

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \dots (3 - 6)$$

3.2.5 Vacuum swing adsorption (VSA)

The potential utility of adsorbents in SF₆/N₂ separation process was evaluated via idealized vacuum swing adsorption (VSA) system. The adsorption pressure, P_{ads} and desorption pressure, P_{des} was set at 1 bar and 0.01 bar respectively. Nonetheless, during the desorption process, the total pressure in the column is corresponded to the partial pressure of SF₆ as the SF₆ that was adsorbed in the adsorbent will be released and filled throughout. Hence, the useful capacity or the working capacity of the respective adsorbents can be determined by taking the difference between the total amount of SF₆ adsorbed at the adsorption condition (under the partial pressure of SF₆, 0.1 bar in this study) and the partial pressure of SF₆ in the desorption condition. In general, the applicability of adsorbents in VSA operation can be evaluated based on: (a) SF₆ adsorption under adsorption condition, N_1^{ads} (mmol/g), (b) SF₆ working capacity, ΔN_1 (mmol/g), which is expressed as **Equation 3-7**, (c) regenerability, R , which is expressed as **Equation 3-8** and (d) selectivity under adsorption condition, α_{12}^{ads} , which is expressed as **Equation 3-9**. The mathematical expression can be defined as follows [167]:

$$\Delta N_1 = N_1^{ads} - N_1^{des} \dots (3 - 7)$$

$$R = \frac{\Delta N_1}{N_1^{ads}} \times 100 \dots (3 - 8)$$

$$\alpha_{12}^{ads} = \frac{N_1^{ads}}{N_1^{des}} \times \frac{y_2}{y_1} \dots (3 - 9)$$

3.2.6 Breakthrough measurement

Figure 3-1 Breakthrough system

Breakthrough measurement of MFI samples were conducted under a dynamic flow condition using the experimental set-up as shown in (**Figure 3-1**). The samples were placed in the adsorption cell where the both ends were fixed with glass wool, which were degassed under continuous argon purging at 180 °C for 8 h, using a temperature-controlled system. After the sample cells were cooled to room temperature, an application of binary SF₆/N₂ mixture (1:9 by volume) was supplied in the column at 25 °C. Mass spectrometer was used to identify the gas composition that has passed through the column. The overall analysis can be illustrated with the use of breakthrough plot by taking the normalized partial pressure (P/P_0) against flow gas volume (cc/g sample).

3.3 Results and discussion

3.3.1 Synthesis of hierarchical zeolite MFI

Figure 3-2 PXRD pattern for zeolite MFI crystals

The successful formation of zeolite MFI was first identified using the powdered XRD (**Figure 3-2**). The samples that were prepared using different experimental condition possess identical XRD pattern, which exactly coincides with the reference pattern of the zeolite MFI [168]. Nonetheless, the creation of mesoporosity generally caused a decrease in the peak intensity (MFI-2) which was possibly attributed to a decrease in the total fraction of zeolite MFI domains in the total sample [124]. Despite peak broadening effect for MFI-2 was observed in the XRD pattern which can be possibly attributed to the formation of smaller crystals; however, well-defined morphological shapes were not observed, as shown in **Figure 3-3**.

Figure 3-3 SEM images for zeolite MFI crystals (a) MFI-1; (b) MFI-2

Pore characteristics of the zeolite MFI was identified using Ar physisorption isotherm at 87 K, with N₂ physisorption isotherm at 77 K were provided as a reference so as to ensure that the N₂ sorption of MFI-1 (**Figure 3-4 (b)**) is comparable with the results reported in the literature [161, 169]. As indicated in **Figure 3-4 (a)**, all samples demonstrated large micropore volumes in view of its high Ar uptake at low pressure region. Besides, hysteresis loop that is present between the adsorption-desorption branches in MFI-2 clearly verified the formation of mesoporosity in the sample, with the mesopore diameter was calculated to be 4 nm based on the BJH analysis. Hence, hierarchical structure with the existence of both microporous and mesoporous domains (MFI-2) was created, whereas MFI-1 was purely microporous domains. Based on **Table 3-1**, the BET surface area of MFI-2 is higher than MFI-1, in view of the creation of additional contributions on the mesopore surfaces.

Table 3-1 Surface area and pore volume of zeolite MFI (based on Ar physisorption at 87 K)

Sample	BET surface area (m ² /g)	HK micropore volume (cm ³ g ⁻¹)	HK micropore size (nm)	Average mesopore diameter (nm)
MFI-1	345 ^[a]	0.156	0.49	-
MFI-2	492 ^[b]	0.164	0.51	4

Note: [a] P/P₀ range = 0.05 – 0.1; [b] P/P₀ range = 0.1 – 0.3

Figure 3-4 (a) Ar and (b) N₂ sorption isotherm (adsorption and desorption branches are indicated as closed and open symbols respectively) of MFI-1 and MFI-2; (c) Differential pore volume (dV/dW) and cumulative pore volume of MFI-1 and MFI-2 determined via HK method using Ar sorption isotherm (the value for MFI-2 were offset by 12 cm³ g⁻¹ nm⁻¹ and 0.15 cm³ g⁻¹ respectively); (d) Mesopore size distribution of MFI-1 and MFI-2, which was determined using BJH method using Ar sorption isotherm (the value for MFI-2 was offset by 0.01 cm³ g⁻¹ nm⁻¹)

3.3.2 SF₆ adsorption of zeolite MFI crystals

First, pure component SF₆ and N₂ adsorption isotherm of MFI-1 and MFI-2 crystals were measured at both 25 and 40 °C, as shown in **Figure 3-5**. In general, both zeolite crystals demonstrated decent adsorption properties, in view of its favourable interaction between zeolite framework and SF₆ molecules. This is attributed to the presence of Al³⁺ cations that generates stronger electric field strength for effective dipole-induced-dipole forces by allowing stronger coulombic interaction in view of higher polarizability of SF₆ molecules. Nevertheless, the SF₆ adsorption performance in MFI-2 is generally a little inferior as compared to MFI-1, which indicates the creation of mesoporosity leads to a

slight decrease in the available active sites. However, only marginal decrease in the SF₆ adsorption capacity of MFI-2 was reported at 40 °C.

Figure 3-5 Pure component SF₆ and N₂ isotherm of (a) MFI-1 and (b) MFI-2 at 25 and 40 °C

As reiterated in Section 4.1, improving the overall adsorption kinetics is required for effective processability of adsorbents in the industrial application. Therefore, fractional uptake of MFI-1 and MFI-2 was determined by the measurement of dosing pressure at 1 bar for two different temperatures (**Figure 3-6**). As expected, the presence of mesopore in MFI-2 has led to an increase in SF₆ uptake (c.a. 10 s to reach a fractional uptake of 0.9 as compared to MFI-1 that requires c.a. 3 min to reach the same amount. This result is considerably attractive as compared to the adsorbents that had screened in our previous study (Chapter 3). Hence, the creation of both micropores and mesopores in an adsorbent is an effective way in enhancing the overall SF₆ adsorption kinetics without affecting the SF₆ adsorption significantly.

Figure 3-6 SF₆ adsorption kinetics at the dosing pressure of 1 bar at (a) 25 °C and (b) 40 °C

3.3.3 SF₆/N₂ selectivity and isosteric heat of adsorption of zeolite MFI crystals

The selectivity or separation efficiency that can determine the final product purity is an important factor to be considered. The calculation of SF₆/N₂ selectivities can be determined through IAST, which had demonstrated a strong feasibility and reliability in the prediction of the separation performance of numerous zeolites. The isotherms were fitted using dual site-Langmuir and single-site Langmuir for SF₆ and N₂ isotherm respectively. In this study, the ratio of SF₆ and N₂ was set at 0.1:0.9 as this mixture is commonly incorporated in the industrial process. Then, SF₆/N₂ selectivities were conducted at two different temperatures (25 and 40 °C). The results at the point of interest (1 bar total pressure) are summarized in **Figure 3-7 (a)**. It can be observed that the overall selectivity for MFI-1 exhibit a strong dependence on temperature but a negligible change was observed for MFI-2 which possess both micropore and mesopore. Hence, MFI-2 shows a higher SF₆/N₂ selectivity than MFI-1 at 40 °C.

Figure 3-7 (a) IAST SF_6/N_2 selectivities at 25 °C and 40 °C; (b) Isosteric heat of adsorption of MFI-1 and MFI-2 as a function of SF_6 loading

Besides, isosteric heat of adsorption, Q_{st} were determined as a function of adsorbate loading after the adsorption data was fitted with virial equation. Subsequently, the heats of adsorption as a function of SF_6 loading were calculated and determined (**Figure 3-7 (b)**). As a whole, the isosteric heat of adsorption for MFI-1 and MFI-2 increases with SF_6 loading. This was possibly due to the presence of both adsorbate-adsorbent and adsorbate-adsorbate interaction on the adsorption sites. Notably, MFI-2 which displayed higher SF_6/N_2 selectivity at 40 °C demonstrates lower heat of adsorption as compared to MFI-1, which can be seen from the marginal decrease in SF_6 adsorption of MFI-2 when the temperature increases from 25 to 40 °C (**Figure 3-5**). It is noteworthy that the Q_{st} value is corresponded to the required minimum energy input for the effective regeneration of adsorbent. Hence, based on the analysis, MFI-2 is expected to incur a much lower energy consumption than MFI-1 in practical operation.

3.3.4 Potential applicability in idealized vacuum swing adsorption (VSA)

Adsorption-desorption cycling via temperature or pressure-swing is generally conducted in a realistic industrial operation so as to recover the product as well as to regenerate the media for the next adsorption cycle. Therefore, in this study, the applicability of MFI-1 and MFI-2 were evaluated using idealized VSA as the feed

pressure is close to the ambient condition. In this study, SF₆/N₂ mixture gas at 1 bar was used as the feed pressure into the adsorption column during the adsorption process. The desorption pressure was assumed to be conducted at 0.01 bar. The partial pressure of SF₆ during this process is set at 0.01 bar as the column is expected to be filled with high purity SF₆ which is released from the adsorbents. The results are summarized as shown in **Table 3-2**. It is worth taking note that the performance of MFI-1 and MFI-2 is generally comparable at 40 °C, especially MFI-2 exhibited higher selectivity than that MFI-1. In general, the attractive merits in MFI-2 in terms of its adsorption kinetics, energy penalty was successfully seen in MFI-2 without sacrificing other parameters significantly.

Table 3-2 Evaluation of zeolite MFI adsorbents using idealized VSA model

Sample	Temperature (°C)	N_1^{ads} (mmol/g)	ΔN_1 (mmol/g)	R (%)	α_{12}^{ads}
MFI-1	25	0.855	0.654	76.5	48.5
MFI-2	25	0.690	0.539	78.1	40.2
MFI-1	40	0.584	0.480	82.1	37.5
MFI-2	40	0.546	0.440	80.4	43.7

3.3.5 SF₆ breakthrough analysis

Dynamic flow measurement through breakthrough analysis was also evaluated with the continuous flow of SF₆/N₂ mixture gas. As shown in **Figure 3-8**, a good SF₆/N₂ separation performance was observed for both adsorbents in terms of SF₆ adsorption capacity and SF₆/N₂ selectivity. Nonetheless, a sharper SF₆ breakthrough curves was observed for MFI-2, indicating that the diffusion of SF₆ in MFI-2 is generally much faster than that of MFI-1 under dynamic condition. Therefore, this result is generally consistent with the SF₆ adsorption kinetics (**Figure 3-6**) of MFI-1 and MFI-2.

Figure 3-8 SF₆/N₂ breakthrough curves of (a) MFI-1 and (b) MFI-2 at 1 bar 25 °C

3.4 Conclusion

Zeolite MFI that possess hierarchical porous structure was synthesised and applied for SF₆ capture and recovery. The introduction of mesoporosity in the sample is feasible in facilitating the transport of SF₆ molecules to the active sites, leading to an improvement in SF₆ adsorption kinetics for rapid adsorption-desorption cycling in industrial operation. The performance of hierarchically structured MFI zeolite was further validated with the breakthrough measurement under dynamic condition. It has been observed that hierarchically porous MFI can demonstrate sharp molecular separation in view of the facilitated diffusion of SF₆ within the adsorbent. Moreover, incorporation of hierarchically structured MFI was found to decrease the overall energy penalty, which can be determined from the calculation of isosteric heat of adsorption. These advantages are feasible in compensating the marginal decrease in SF₆ adsorption as compared to the bulk MFI (MFI-1). Besides, the overall SF₆/N₂ selectivity was not affected because a decrease in N₂ uptake was observed for MFI-2 as compared to MFI-1. This result suggests the capability of zeolite MFI in SF₆ adsorption and recovery with the introduction of hierarchical structures.

3.5 Declaration

The work presented in this chapter has been published in Journal of Industrial and Engineering Chemistry.

C. Y. Chuah, S. Yu, K. Na, T-H. Bae, Enhanced SF₆ recovery by hierarchically structured MFI zeolite, **J. Ind. Eng. Chem.**, (2018), 62, 64-71

Chapter 4 Development of Hierarchically Structured HKUST-1

4.1 Introduction

HKUST-1 which contains a large square-shaped pore ($9 \times 9 \text{ \AA}$) has been investigated for its potential application in SF_6 adsorption in view of its kinetic diameter ($5.13 \text{ \AA}$) is suitable for such separation as well as the presence of open-metal sites that favours molecules that possess high polarizability. Comparatively, it is well-noted that MOF-74 which has shown to possess strong SF_6 adsorption capability than that of HKUST-1 possess much weaker hydrolytic stability [170, 171], which limits its potential commercialization of gas adsorption process. Hence, in this chapter, the development of hierarchically structured HKUST-1 that is feasible to perform effective SF_6/N_2 separation and SF_6 recovery was studied. With effective downsizing of particle size and the creation of hierarchical structures with mesoporosity, enhancement in SF_6 adsorption can be expected due to the effective diffusion length into the microporous space can be reduced. Approaches such as templating method using surfactants [69] as well as template-free methods (ligand etching, ball-mill synthesizing and CO_2 -directed assembling) [172-174] has been employed to control the overall crystals size and the creation of hierarchical structures in MOFs. In this study, this synthesis method (refluxing process using ethanol) is comparatively straightforward as compared to the approaches as mentioned above. Based on the results, hierarchically structured HKUST-1 nanocrystals demonstrate enhanced SF_6 adsorption of 4.98 mmol g^{-1} (at 25°C and 1 bar), better SF_6/N_2 selectivity (c.a. 70), faster SF_6 adsorption kinetics and lowest energy penalty for regeneration. Based on the analysis of idealized vacuum swing adsorption (VSA) process, this adsorbent demonstrates better performance in comparison to conventional activated carbon and zeolite 13X in SF_6/N_2 separation.

4.2 Experimental Methods

4.2.1 Materials

Copper(II) nitrate trihydrate, copper(II) acetate monohydrate, trimesic acid, zeolite 13X and activated carbon (activated charcoal, Darco) were purchased from Sigma Aldrich. Absolute ethanol was purchased from VWR. Test gases (SF_6 and N_2) which were used in this work were purchased from Air Liquide. All the chemicals were used as received without additional purifications.

4.2.2 Synthesis of HKUST-1

The synthesis procedure as elaborated below indicates the synthesis of three different types of HKUST-1, namely bulk crystals (HKUST-1a), nanocrystals (HKUST-1b) and nanocrystals with hierarchical structure (HKUST-1c).[69, 174, 175]

HKUST-1a: A copper solution was prepared by dissolving 0.547 g of copper(II) nitrate trihydrate in 7.5 mL of distilled water. In a separate solution, 0.263 g of trimesic acid was added in 7.5 mL of absolute ethanol. The two solutions were eventually mixed and placed in digestion bomb, where the reaction was carried out at 120 °C for 12 h. The resulting precipitate was filtered and washed with copious amount of ethanol/water mixture (1:1).

HKUST-1b: 1.2 g of copper(II) nitrate trihydrate and 0.6 g of trimesic acid was added sequentially into 20 ml of absolute ethanol. The resulting mixture was stirred vigorously for 24 h at room temperature. The precipitate formed is filtered and washed with ethanol/water mixture (1:1).

HKUST-1c: 0.599 g of copper(II) acetate monohydrate and 0.840 g of trimesic acid were added in sequence into the round-bottom flask which contains 40 ml of absolute

ethanol. The solution was heated at 75 °C under reflux for 20 h with continuous Ar flow. The precipitate was collected by repetitive centrifugation-redispersion cycle to remove any residual impurities.

4.2.3 Characterization

SF₆ and N₂ adsorption behaviour of HKUST-1 and commercial adsorbents (zeolite 13X and activated carbon) were determined using volumetric gas sorption analyser as reported in Section 3.2.3, where all the samples were activated at 180 °C under high vacuum for 8 h, except for HKUST-1c which was activated at 150 °C before the measurement. The quantification of surface area and pore volume of HKUST-1 samples were determined volumetric gas sorption analyser (as elaborated in Section 3.2.3) at 77 K, using N₂ as the adsorbate. FT-IR spectra were measured using IR spectrometer (Spectrum One, PerkinElmer) based on the range of 4000 – 500 cm⁻¹ based on the resolution of 4 cm⁻¹. TGA analysis was performed using thermogravimetric/differential thermal analyser (Diamond TG/DTA, PerkinElmer) based on the heating rate of 10 °C/min based on the temperature range of 30 – 800 °C. This measurement was conducted under pure nitrogen purging at 100 ml/min. PXRD was determined at ambient condition under the step size of 0.02° in the range of 2θ from 5 to 35° (D8 Advanced, Bruker). The morphology of HKUST-1 crystals were observed using FE-SEM (JSM6700, Joel).

4.2.4 Evaluation of SF₆ and N₂ uptake performance

The adsorption isotherm of studied adsorbent was determined using dual-site Langmuir-Freundlich model (**Equation 4-1**):

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

where q is the total quantity of SF₆ adsorbed, p is the partial pressure, $q_{\text{sat},1}$ and $q_{\text{sat},2}$ are the saturated loadings for sites 1 and 2; b_1 and b_2 are the Langmuir parameters for site 1 and 2; c and f are the Freundlich parameters for site 1 and 2, respectively. Single-site Langmuir-Freundlich model on the other hand was determined using single-site Langmuir-Freundlich model (**Equation 4-2**). Determination of saturation loading (q_{sat}) of N₂ was conducted using the similar manner as described in Section 3.2.4.

$$q = \frac{q_{\text{sat},1} b_1 p^{1/c}}{1 + b_1 p^{1/c}} \dots (4 - 2)$$

The SF₆ adsorption kinetics of adsorbents were measured at a dosing pressure of 1 bar and 25 °C. This parameter was evaluated as fractional uptake, with the equation is described similarly to the expression as described in Section 3.2.4 (**Equation 3-3**). Besides, SF₆/N₂ selectivity under various condition and isosteric heat of adsorption (Q_{st}) was calculated using IAST (**Equation 3-4**) and virial plot (**Equation 3-5** and **Equation 3-6**) as described in Section 3.2.4. On the other hand, the potential capability of the adsorbents in SF₆/N₂ separation process was determined using an idealized VSA system as described in Section 3.2.5, which are described as **Equation 3-7**, **Equation 3-8** and **Equation 3-9** respectively.

4.3 Results and discussion

4.3.1 Synthesis and characterization of hierarchical HKUST-1 nanocrystals

Figure 4-1 FESEM images and the scheme of HKUST-1 crystals (a) bulk crystal (HKUST-1a), (b) nanocrystal (HKUST-1b) and (c) nanocrystals with hierarchical structures (HKUST-1c)

Conventional micrometre-sized HKUST-1 crystals (HKUST-1a) were conducted using pressurized high-temperature solvothermal reaction. Thus, in this study, by altering the reaction condition, the synthesis of hierarchical nanocrystal HKUST-1 was conducted by altering the reaction conditions (HKUST-1b and c), with the verification from FESEM. As shown in **Figure 4-1**, HKUST-1a possess the lateral dimension of 12 μm , while HKUST-1b and c shows an average crystal size of 300 – 500 and 70 – 120 nm respectively. It can be observed that downsizing of crystals leads to a loss in the defined tetragonal bipyramidal shape based on the images. Nonetheless, FT-IR analysis

confirms the formation of HKUST-1 with the successful coordination of $\text{Cu}_2(\text{COO})_4$ unit in the sample (**Figure 4-2 (a)**). Besides, as observed in the PXRD measurement, the pattern remains intact, meaning that the physiochemical properties are not compromised during the downsizing synthesis.

Figure 4-2 (a) FTIR; (b) PXRD; (c) N_2 physisorption at 77 K and (d) pore size distribution of HKUST-1 crystals

The pore characteristics of HKUST-1 that are synthesised in this work were determined using N_2 physisorption method that was conducted at 77 K. In general, all samples demonstrate a large micropore volumes in view of its high N_2 adsorption at low-pressure region (**Figure 4-2 (c)**). Meanwhile, the presence of mesoporosity within the HKUST-1a and c was identified through this analysis, with the formation of hysteresis loop in between adsorption and desorption branches. The mesopore size that was estimated through BJH method is estimated to be around 4 nm for HKUST-1a and c (**Figure 4-2 (c) and (d)**). The calculation of surface areas and pore volumes were summarized as

shown in **Table 4-1**. It was observed that the BET surface area of HKUST-1c is higher than that of HKUST-1a, indicating that an increase in surface area can be observed during the transition from bulk crystal to nanocrystal. Besides, HKUST-1c also demonstrates higher micropore surface area and volume, indicating that downsizing the particle size is feasible in the creation of more accessible surface areas. Similar values of micropore volumes in HKUST-1b and c also indicates that the generation of mesopores in HKUST-1c does not reduce the overall microporosity and crystallinity of HKUST-1c.

Table 4-1 Surface area and pore volumes of HKUST-1 samples

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) [a]	S_{Lang} ($\text{m}^2 \text{g}^{-1}$) [a]	S_{micro} ($\text{m}^2 \text{g}^{-1}$) [b]	V_{micro} ($\text{m}^3 \text{g}^{-1}$) (cc/g)
HKUST-1a	1090	1626	951	0.498
HKUST-1b	1135	1727	1093	0.580
HKUST-1c	1328	1699	1279	0.585

Note: [a] BET (S_{BET}) and Langmuir (S_{Lang}) surface area are obtained at $P/P^\circ = 0.05 - 0.3$. [b] Micropore surface area (S_{micro}) and volume (V_{micro}) are obtained using t -plot method at the pressure range of $P/P^\circ = 0.4 - 0.6$

4.3.2 SF_6 adsorption and capacities of HKUST-1 crystals

The pure component SF_6 adsorption isotherm of HKUST-1 crystals that were synthesised in this work is measured at 25 and 40 °C, using two commercial adsorbents (zeolite 13X and activated carbon) as the reference for effective benchmarking. As a whole, all HKUST-1 crystals demonstrate better adsorption properties as compared to zeolite 13X and activated carbon (**Figure 4-3 (a, b)**). Besides, the SF_6 performance of HKUST-1 samples was comparatively better than zeolite MFI as reported in Chapter 3, under the same measurement condition (**Figure 3-5**). This is possibly attributed to the presence of the coordinatively open metal sites (Cu paddle wheel of HKUST-1) that allows favourable interaction with SF_6 molecules. HKUST-1b shows favourable SF_6

uptake as compared to the bulk crystal (HKUST-1a) in view of its higher surface area and micropore volume. Interestingly, SF₆ adsorption HKUST-1c demonstrates more remarkable performance as compared to HKUST-1b despite the surface area and micropore volume of the crystals are comparable. Hence, the presence of mesopore in HKUST-1c might allow and facilitate the transport of SF₆ molecules to the active sites more readily with the reducing of the diffusion length of SF₆.

Figure 4-3 Pure component SF₆ adsorption of measured adsorbents at (a) 25 °C and (b) 40 °C; SF₆ adsorption kinetics of (c) HKUST-1 crystals and (d) zeolite 13X and activated carbon (with HKUST-1c as the reference), under the temperature of 25 °C with 1 bar as the dosing pressure.

On the other hand, adsorption-desorption kinetics which is an important parameter to investigate the overall processing rate of adsorbents in industrial operation is investigated in this work. Thus, SF₆ adsorption kinetics was determined at 25 °C at the dosing pressure of 1 bar, which can be evaluated as fractional uptake (ratio of gas uptake

at a given time with respect to the equilibrium uptake). As shown in **Figure 4-3 (c)**, all HKUST-1 samples demonstrate rapid SF₆ adsorption rate at the specified condition. Despite the mass transport model predicts that the uptake rate decreases with the size of adsorbent, it was observed that HKUST-1a shows comparable rate of SF₆ adsorption as compared to HKUST-1b in view of the presence of mesoporosity in HKUST-1a that allows rapid distribution of SF₆ molecules to the micropore domains. HKUST-1b, the absence of mesoporosity can be compensated with creation of small crystal size. Hence, the rate of SF₆ uptake for both HKUST-1a and HKUST-1b are almost comparable. Without a doubt, HKUST-1c shows the best performance in the evaluation of adsorption kinetics as a result of the synergistic effect of both downsizing the HKUST-1 crystal size and the introduction of mesoporosity into the nanocrystals. As a comparison, the uptake rate of HKUST-1c was benchmarked with the commercial adsorbents (zeolite 13X and activated carbon). As shown in **Figure 4-3 (d)**, the required equilibration time for both commercial adsorbents were much longer than that of HKUST-1c. Thus, the results obtained from the SF₆ isotherm and adsorption kinetics indicates that creating a hierarchically microporous and mesoporous materials provides an efficient way to enhance SF₆ adsorption and decrease the required time for SF₆ adsorption to reach equilibrium.

4.3.3 SF₆/N₂ selectivity and isosteric heat of adsorption

Selectivity or separation efficiency is also an important parameter to quantify the purity of the recovered products. Therefore, for this reason, N₂ adsorption of all adsorbents were measured and calculated using IAST which has been demonstrated to be feasible in predicting the separation performance of zeolites and MOFs adsorbents. The isotherm of SF₆ and N₂ were fitted with dual-site Langmuir-Freundlich model and single-site Langmuir-Freundlich model respectively, with the R² values greater than 0.99. In this

work, the SF₆/N₂ selectivities were calculated based on the SF₆/N₂ ratio of 1:9, which is the mixture that is used readily in the industry, calculated at two different temperatures (25 and 40 °C). The result is displayed as shown in **Figure 4-4 (a)**. Among the three HKUST-1 samples, HKUST-1a crystals shows the lowest SF₆/N₂ selectivity. HKUST-1b on the other hand demonstrates improved SF₆/N₂ selectivity in view of increased SF₆ uptake at 25 and 40 °C (**Figure 4-4 (a, b)**). With both downsize and the introduction of mesoporosity into the HKUST-1 crystals (HKUST-1c), the overall SF₆/N₂ selectivity improves from 50 to 70 at 25 °C, thus providing a competitive advantage over zeolite 13X and activated carbon. In general, the increased in accessibility of SF₆ molecules to the active sites in HKUST-1c which can be evident by the increase in SF₆ uptake at low pressure range has results in improved SF₆/N₂ selectivity.

Figure 4-4 (a) SF₆/N₂ selectivities calculated by IAST at 25 °C and 40 °C (Partial pressure of SF₆ and N₂ were 0.1 and 0.9 bar respectively) **(b)** Isosteric heat of adsorption as a function of loading for all adsorbents

Isosteric heat of adsorption (Q_{st}) which is a measure of binding energy between the adsorbent and adsorbate was determined after fitting the SF₆ isotherm using virial equation. The overall Q_{st} values as a function of SF₆ loading for all adsorbents tested were summarized as shown in **Figure 4-4 (b)**. Surprisingly, HKUST-1c which possess the highest SF₆ adsorption, maintains the lowest Q_{st} as the loading increases. This

behaviour can be observed from the marginal decrease (c.a. 5%) of the SF₆ adsorption as the loading increases, indicating this adsorbent possess low SF₆ binding energy. On the other hand, the decrease in SF₆ uptake for both HKUST-1a and b is more significant as the temperature increases (**Figure 4-3 (a, b)**). Therefore, HKUST-1c demonstrates its advantages for the application with a slight elevation in the feed temperature. This result may indicate that the presence of mesopores within the HKUST-1c nanocrystals besides shortening the diffusion length to enhance the effective transport of SF₆ molecules to the active sites, it increases the number of active sites that are readily accessible for SF₆ molecules.

4.3.3 Potential utility in idealized vacuum swing adsorption

In the realistic industrial operation, an adsorption-desorption cycle can be conducted either by temperature (TSA) or pressure (PSA) swing adsorption. In this work, the potential utility of the HKUST-1 crystals and commercial adsorbents were evaluated using idealized VSA, which utilizing the same working principle as PSA. Conventional PSA where the desorption pressure is conducted at ambient pressure is generally not suitable for HKUST-1 in view of the SF₆ adsorption under this condition is almost saturated. Thus, in order to evaluate for its feasibility for PSA, the feed gas has to be compressed at high pressure in order to ensure positive working capacity. This leads to high energy penalty for compression, which resulting in the process to be not economical. Thus, in this VSA model, the feed pressure was set at 1 bar SF₆/N₂ mixture (1:9, that is SF₆ partial pressure of 0.1 bar), with the desorption was carried out at 0.01 bar. During the desorption condition, it was assumed that the adsorption cell will be filled with SF₆ gas during the desorption process which is released from the adsorbent, thus 0.01 bar of SF₆ was set as the desorption condition. As shown in **Table 4-2**, hierarchically structured HKUST-1 nanocrystals show the highest potential utility

among all the tested adsorbents. For instance, the working capacity and SF₆/N₂ selectivity of HKUST-1c is 45% and 111% higher than HKUST-1a, indicating that the creation of hierarchically structured HKUST-1 crystals demonstrates its competitive advantage, besides outperforming zeolite 13X and activated carbon. This is further proven by its attractive performance as compared to zeolite MFI as reported in **Table 3-2** in Chapter 3.

Table 4-2 Evaluation of zeolite MFI adsorbents using idealized VSA model

Sample	N_1^{ads} (mmol/g)	ΔN_1 (mmol/g)	R (%)	α_{12}^{ads}
HKUST-1a	0.981	0.868	88.5	38.2
HKUST-1b	1.196	1.067	89.2	48.3
HKUST-1c	1.372	1.256	91.5	80.6
Zeolite 13X	0.923	0.861	93.3	51.2
Activated Carbon	1.006	0.8585	85.3	30.3

4.4 Conclusion

In this study, hierarchically structured HKUST-1 nanocrystals that demonstrate improved SF₆ adsorption, SF₆/N₂ selectivity, SF₆ adsorption kinetics and reduced energy penalty for regeneration as compared to conventional HKUST-1. Through modification of the synthesis procedure and temperature, downsizing and the introduction of mesoporosity can be generated in the HKUST-1 crystals. Creation of nanosize crystals offers an increase in surface area, whereas creation of mesoporosity allows the facilitation of SF₆ molecular transport into and out of the active sites in the micropores of HKUST-1. Thus, hierarchically structured HKUST-1 not only possess enhanced performance in SF₆ capture and recovery, but it shows remarkable

performance in an idealized VSA process. More importantly, our scalable synthesis method highlights its potential promising of nanoscale engineering to synthesize porous materials for enhanced SF₆ recovery

4.5 Declaration

The work presented in this chapter has been published in Journal of Industrial and Engineering Chemistry.

C. Y. Chuah, K. Goh, T-H. Bae, Hierarchically structured HKUST-1 nanocrystals for enhanced SF₆ capture and recovery, **J. Phys. Chem. C**, (2017), 121 (12), 6758-6755

Chapter 5 Development of Hierarchically Porous Co-MOF-74 Hollow Nanorods

5.1 Introduction

MOFs in general hold a great promise in comparison to other nanoporous materials particularly in the application of gas storage and separation in view of their high accessible surface area and porosity together with tuneable functionalities [90, 176-179]. Indeed, it has been well reported that several MOFs possess functional groups that can allow reversible interaction with CO₂ possess reasonably high equilibrium CO₂ uptake capacity as well as selectivity. Nonetheless, such performance cannot guarantee the success in realistic operation as the gas separation is typically carried out in a dynamic condition where the diffusion of adsorbate within the adsorbent also plays the critical role. Hence, the key to the successful application in practical gas capture technologies is to enhance the dynamic capacity by engineering the structure of MOFs including morphology and nanoarchitecture. In essence, the hollow-structured nanomaterial is a desired platform to facilitate adsorption-desorption cycling by shortening the diffusion distance [180-182]. There are several publications which hollow MOFs were synthesised either by hard or soft template methods [183, 184] or by post-synthetic modification [185, 186]. These methods require the removal of templates or additional treatments, resulting in the increased complexity of processing steps and amount of chemicals used. Recently, the synthesis of hollow ZIF-67 nanorods by using self-sacrificing template has been reported [181]. Nonetheless, it still remains difficult to develop a facile method to fabricate hierarchically porous, hollow nanocrystalline MOFs with open metal sites. Herein, self-sacrifice template strategy based on nanoscale Kirkendall effect to form novel Co-MOF-74 hollow nanorods with granular shell is developed, which such structure enables a rapid adsorption-desorption gas adsorption

in dynamic condition. In this study, Co-MOF-74 has been chosen as the model MOF in this study as MOF-74 generally possess high density of open metal sites (ca. 3.3 sites per 1 nm²) with one-dimensional large pore channels, leading to a high adsorption capacity of guest molecule [187, 188]. Note that despite Mg-MOF-74 has been reported to possess the best CO₂ adsorption capacity under dry condition, Co-MOF-74 generally exhibited higher retention of the uptake capacity and better regenerability than Mg-MOF-74 in the presence of moisture, despite the CO₂ uptake of Co-MOF-74 is comparatively lower, thus suggesting a better applicability of Co-MOF-74 in practical operation.

5.2 Experimental Methods

5.2.1 Materials

2,5-dihydroxyterephthalic acid (H₄dobdc) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) were purchased from Alfa Aesar. Cobalt acetate tetrahydrate ((CoCH₃COO)₂·4H₂O), dimethylformamide (DMF, HCON(CH₃)₂), ethanol 200 proof (C₂H₅OH), methanol (CH₃OH), polyvinylpyrrolidone (PVP, M_w = 55,000) and zeolite 5A were purchased from Sigma Aldrich and were used as received without further purification.

5.2.2 Synthesis of adsorbent

Synthesis of Co-MOF-74 bulk rods: The Co-MOF-74 bulk rods were prepared by following the procedure as described in the reference. In a beaker, 0.144 g of H₄dobdc and 0.713 g of Co(NO₃)₂·6H₂O were dissolved in 60 ml of 1/1/1 (v/v/v) mixture of DMF/C₂H₅OH/H₂O, with the aid of sonication. The clear solution was eventually transferred into a Teflon-lined stainless-steel autoclave, where the autoclave was placed in the oven at 100 °C for 24 h. After cooling the solution to room temperature, the mother

liquid was decanted. The bulk crystals were washed two times with DMF, followed by solvent exchange with methanol for six times over three days. Finally, the Co-MOF-74 bulk rods were dried at room temperature overnight under vacuum.

Synthesis of Co precursor nanorods ($\text{Co}_3(\text{OH})(\text{CH}_3\text{COO})_5$): In a typical synthesis procedure, 1.0 g of PVP and 0.64 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 200 ml of ethanol at room temperature so as to form a clear solution. The pink solution was refluxed under strong agitation at 85 °C for 2 h. The resulting precipitate was collected via centrifugation and precipitation with ethanol to remove the residual PVP residues that was attached on the surface. The Co precursor was dried at 60 °C overnight under vacuum.

Synthesis of Co-MOF-74 hollow nanorods: First, 0.118 g of H_4dobdc (0.60 mmol) were dissolved into 30 ml of DMF to form a clear dark brown solution (Solution A). In a separate vial, 0.1 g of Co precursor (0.12 mmol) was dispersed in 20 ml of DMF (Mixture B). In the next step, Mixture B was poured into solution A under strong agitation at 85 °C, which the resulting solution was stirred for an additional of 2 h. The Co-MOF-74 hollow nanorods was collected via centrifugation and redispersion with DMF. In order to ensure that the final products were free of impurities, the resulting precipitate was re-dispersed with DMF, which was heated at 50 °C for 6 h. Further purifications were conducted by utilizing solvent exchange with methanol, which this process was repeated for about 5 times. Finally, the Co-MOF-74 hollow nanorods were dried at 60 °C overnight under vacuum.

Synthesis of Co-MOF-74 nanoparticles: The procedures for the synthesis of Co-MOF-74 nanoparticles were similar to the synthesis of Co-MOF-74 hollow nanorods except that the solution A was poured into the mixture B under strong agitation at 85 °C.

5.2.3 Characterization

The adsorption behaviour of CO₂ and N₂ in Co-MOF-74 were measured using volumetric gas sorption analyser (Quantachrome, isorbHP1). Prior to the analysis, the adsorbents were activated at 180 °C for 10 h to ensure that the residual solvent or moisture that are present in the samples can be effectively removed. The isotherms were conducted at 25 °C under the pressure range of 0 – 1 bar, which the temperature was controlled using water circulator. The porosity properties of Co-MOF-74 samples were conducted using volumetric gas sorption analyser (Micromeritics, ASAP 2020). Prior to the measurement, the samples were activated at the same condition as mentioned above. The pore size distribution of Co-MOF-74 were analysed from N₂ desorption branch using the non-linear density functional theory (NLDFT) method. The crystallinity of Co-MOF-74 samples were determined using powdered X-ray diffraction (PXRD, Rigaku Miniflex) which is operating at 40 kV and 15 mA using CuK α radiation (λ = 0.15406 nm), which was conducted at ambient condition in the range of 2θ from 2 to 50°, for a step size of 0.02°. The morphological properties of Co-MOF-74 samples were examined under Field Emission-Scanning Electron Microscopy (FE-SEM, Thermo Scientific, FEI SEM Quanta 200F) and Transmission Electron Microscopy (TEM, Thermo Scientific, FEI TEM Tecnai T20). The thermal stability of Co-MOF-74 samples were performed using thermogravimetric/differential thermal analyser (PerkinElmer, Diamond TG/DTA) under the heating rate of 10 °C/min under N₂ purging (flow rate of 200 ml/min), with the temperature scan from 30 to 800 °C. The initial weight loss due to the presence of residual solvents can be determined by controlling the temperature of the adsorbent at 180 °C for 5 h under N₂ purging.

5.2.4 Breakthrough and Chromatographic Separation

The breakthrough measurement of Co-MOF-74 were conducted using the custom-built set-up as described in **Figure 3-1**. The samples were first placed in the adsorption cell with both ends were enclosed with glass wool. The samples were activated under continuous argon purging for 180 °C for 8 h so as to ensure that the residual solvents and water that are potentially present in the samples were completely removed. The temperature was precisely controlled using heating tape that was equipped with temperature controller. Then CO₂/N₂ binary mixture (20:80) was supplied into the adsorption column at 25 °C, where the outlet gas composition was analysed using mass spectrometer (Hiden, HPR20). The CO₂ and N₂ breakthrough pots were demonstrated by taking the plot of normalized concentration (C/C_o) against time. On the other hand, the chromatographic separation was also conducted using the same set-up, with some modifications in the experimental procedures. The adsorption cell was set at the specified temperature (80 °C) after the samples were fully activated. Once the temperature of the adsorption cell was maintained at a steady value, a pulse injection of CO₂/N₂ binary mixture was sent to the adsorption cell to observe the CO₂ and N₂ peaks from the mass spectrometer for the course of 10 minutes. The composition of the outlet was detected using mass spectrometer. Similarly, a plot of intensity against time was plotted for effective comparison across different samples. Similarly, zeolite 5A was used as the reference material for the analysis of chromatographic separation of CO₂ and N₂.

5.3 Results and discussion

5.3.1 Synthesis of Co-MOF-74

Figure 5-1 Schematic of formation and unique architecture of Co-MOF-74 hollow nanorods; FT-IR curves of PVP and Co precursor nanorods (NR) after washing with ethanol

The schematic diagram for the formation of Co-MOF-74 hollow nanorod and its architecture were described in **Figure 5-1**. The as-prepared Co precursor nanorods of Co₃(OH)(CH₃COO)₅ were transformed to Co-MOF-74 hollow nanorods in the DMF solution containing H₄dobdc. The reaction during this chemical conversion process can be described as shown in equation (1). In this reaction, the Co precursor nanorods served as not only the self-sacrificing templates but also the deprotonation agents. The mechanism behind the formation of the hollow nanorods can be explained with the nanoscale Kirkendall effect which is a consequence of the difference in the diffusion rates between the two-ion species. Such effect has proven its feasibility in creating the hollow structure during the chemical transformation [181, 189, 190].

The Co precursor nanorods (Co₃(OH)(CH₃COO)₅) were first synthesised with a PVP-assisted hydrolysis method in ethanol [181]. Based on the PXRD pattern, the phase of Co precursor has been identified as the cobalt hydroxide acetate of Co₃(OH)(CH₃COO)₅ (**Figure 5-2 (a)**). As a whole, prior to the synthesis of Co-MOF-74 hollow nanorods, the

FT-IR analysis was conducted to verify that PVP was not present in the Co-precursor nanorods (**Figure 5-2 (b)**) The characteristic -C-N peak (1280 cm^{-1}) in PVP was not detected in Co precursor nanorods, indicates that residual PVP is not present.

Figure 5-2 (a) PXRD pattern of Co precursor nanorods and Co-MOF-74 hollow nanorods; (b) FT-IR curves of PVP and Co precursor nanorods (NR) after ethanol washing

On the other hand, **Figure 5-3 (a)** and **(d)** demonstrates FE-SEM and TEM images of Co precursor nanorods respectively, indicating the solid core with a diameter and length of ca. 100 nm and ca. 500 nm. It can be observed that the peaks of the Co precursor were not observed after the transformation of the Co-MOF-74 nanorods, indicating a full conversion of the Co precursors (**Figure 5-2 (a)**). The corresponding FESEM images (**Figure 5-3 (b, c)**) showed that the overall rod-like shape is well-maintained after the transformation and the surface is constructed by numerous interconnected rod-like subunits (nanorods with a diameter and length of ca. 5 nm and ca. 20 nm), which is in good agreement with the crystallite size estimated from the PXRD pattern (average crystallite size of Co-MOF-74 hollow nanorods was determined to be ca. 13 nm based on Scherrer's equation). TEM images (**Figure 5-3 (e, f)**) also clearly reveals the hollow nature of the Co-MOF-74 nanorods with the sharp contrast between the granular shell

(ca. 40 nm) and the central void space. The interparticle pores formed by the rod-like subunits can provide fast diffusion pathway for incoming guest molecules in and out of MOF crystals. In addition, the thin shells could further significantly reduce the gas diffusion distance to facilitate adsorption/desorption of gas molecules as compared to the bulk crystals.

Figure 5-3 FE-SEM images of (a) Co precursor nanorods and (b, c) Co-MOF-74 hollow nanorods; TEM images of (d) Co precursor nanorods and (e, f) Co-MOF-74 hollow nanorods

Hence, in order to gain more insights into the formation process of the hollow structure, time-dependent experiments were conducted, with the results are summarized in **Figure 5-4 (a-f)**. The deprotonated ligand anion is typically expected to have a bigger ionic size than the Co^{2+} cation, thus it is expected that the diffusion rate of Co^{2+} cations is faster than the ligand anions. After 2-minute reaction, *in-situ* formation of Co-MOF-74 shell was formed on the surface of the Co precursors (**Figure 5-4 (b)**). Such robust shell is functioned to maintain the rod-like morphology as well as the limit the inward diffusion rate of the ligand anion. Within 5 minutes of the transformation reaction (**Figure 5-4**

(c)), the appearance of voids in the centre of Co precursors were formed, thus revealing the outward diffusion of the smaller ions (Co^{2+} cations) from the Co solid precursors that dominates the growth of the Co-MOF-74 shell. This is further verified with the formation of shell that was constructed with Co-MOF-74 (**Figure 5-4 (i)**). TEM image of the product after 30 minutes of conversion (**Figure 5-4 (d)**) shows that the unreacted Co precursors still exists at the core of the nanorods and the corresponding PXRD pattern (**Figure 5-4 (g)**) confirms the existence of Co precursors. After 2 hours, the conversion reaction was completed (**Figure 5-4 (f)**), which is consistent with the PXRD results (**Figure 5-2 (a)**). Besides, it has been observed that the sequence of mixing between the linker and the precursor solution is critical to maintain the morphology of the rod-like structure. This is conducted by adding the linker solution to the Co precursor (solution A added to mixture B). Based on the FE-SEM image, dissolution of Co precursors was occurred, leading to the recrystallization of Co-MOF-74, forming the Co-MOF-74 nanoparticles (**Figure 5-4 (h)**).

Figure 5-4 TEM images that shows the evolution of Co precursor nanorods to Co-MOF-74 hollow nanorods at **(a-f)** 0 minutes, 2 minutes, 5 minutes, 30 minutes, 60 minutes and 120 minutes respectively. **(g)** PXRD pattern of the product after 30 minutes of conversion; **(h)** FESEM of Co-MOF-74 nanoparticles; **(i)** TEM images of Co-MOF-74 nanorods after 5 minutes transformation reaction, that was washed with methanol; **(j)** FE-SEM image of Co-MOF-74 bulk rods

As a control study, Co-MOF-74 bulk rods were prepared via conventional solvothermal reaction as described in previous work [179]. The corresponding FE-SEM image shows that the bulk rod possesses the diameter and length of ca. 10 μm and ca. 40 μm respectively. The thermal stability of Co-MOF-74 hollow nanorods and bulk rods at 180 $^{\circ}\text{C}$ was confirmed by PXRD pattern (**Figure 5-5 (a, b)**). TGA was also performed to study the thermal stability of the as-prepared MOFs (**Figure 5-5 (c, d)**). Based on the figure, Co-MOF-74 bulk rods start to decompose at ca. 300 $^{\circ}\text{C}$, exhibiting better thermal stability than Co-MOF-74 hollow nanorods (ca. 250 $^{\circ}\text{C}$). It is reasonable that bulk materials have better thermal stability than nanomaterials due to low surface energy and defects. Nonetheless, it is worth noting that the regeneration temperature for CO_2 capture is lower than 180 $^{\circ}\text{C}$, indicating that both Co-MOF-74 crystals can be regenerated without any decomposition issue.

Figure 5-5 (a, b) PXRD patterns of Co-MOF-74 bulk rods and hollow nanorods treated at 30 °C and 180 °C overnight under vacuum; (c, d) TGA curves of bulk Co-MOF-74 bulk rods and hollow nanorods

N₂ physisorption analysis was further conducted at 77 K to investigate the pore characteristics of the synthesised Co-MOF-74. As shown in **Figure 5-6** (a), both samples exhibit a high N₂ uptake at low pressure region, indicating the presence of large amount of micropores. However, Co-MOF-74 hollow nanorods show a hysteresis loop between adsorption and desorption branches, revealing the presence of mesopores that are contributed by the interparticle pores of granular shell (**Figure 5-4** (c, e)). The corresponding pore size distribution curve of Co-MOF-74 hollow nanorods that was calculated using NLDFT method show the size of these pores to be ranged in 0.8 – 10 nm, indicating the co-existence of hierarchical micropores and mesopores. On the contrary, only micropores (0.8 – 2 nm) were observed on Co-MOF-74 bulk crystals. As

shown in **Table 5-1**, both Co-MOF-74 bulk rods and hollow nanorods possess a high BET surface area of 1049 m²/g and 804 m²/g respectively, further confirming the high crystallinity of the as-prepared Co-MOF-74 as revealed by the PXRD (**Figure 5-2 (a, b)**). We infer that Co-MOF-74 hollow nanorods that was prepared at a lower temperature with a shorter reaction time may have slightly lower crystallinity than Co-MOF-74 bulk rods that was synthesised solvothermally, giving rise to a lower surface area than bulk rods.

Table 5-1 Surface area and pore volume of Co-MOF-74 bulk rods and hollow nanorods

	S_{BET} (m ² /g) [a]	S_{Lang} (m ² /g) [a]	V_{total} (cc/g) [b]
Co-MOF-74 bulk rods	1049	1303	0.464
Co-MOF-74 hollow nanorods	804	1035	0.433

Note: [a] BET (S_{BET}) and Langmuir (S_{Lang}) surface area are obtained at $P/P^{\circ} = 0.05 - 0.15$. [b] Total pore volume (V_{total}) is calculated at $P/P^{\circ} = 0.95$

Figure 5-6 (a) N₂ adsorption and desorption curve of Co-MOF-74; **(b)** Pore size distribution of Co-MOF-74 bulk and Co-MOF-74 hollow nanorods

5.3.2 Gas adsorption behaviour of Co-MOF-74

Subsequently, CO₂ and N₂ adsorption properties of Co-MOF-74 crystals at the static equilibrium condition were investigated. The pure component isotherms which were measured at 25 °C are displayed in **Figure 5-7 (a)**. In general, both Co-MOF-74 samples demonstrated strong affinity for CO₂ over N₂, which is attributed to the presence of

coordinatively unsaturated open metal sites. It is well known that open metal sites allow reversible interaction between the framework and CO₂ which has a higher polarizability and quadrupole moment than N₂. Nonetheless, Co-MOF-74 hollow nanorods exhibited a decreased CO₂ uptake capacity at equilibrium as compared to that of bulk rods (ca. 4.10 mmol/g vs. ca. 6.5 mmol/g at 25 °C and 1 bar), presumably due to the decreased in specific surface area (**Table 5-1**) [191]. However, in practical operations, gas separations are conducted in the dynamic flow condition in which the diffusion of gases within the adsorbents can limit the overall performance [120, 191]. Thus, to study the behaviour of adsorbents under dynamic condition, breakthrough measurements were conducted using binary mixture of CO₂/N₂ at 25 °C, with the result is depicted in **Figure 5-7 (b)**. In contrast to the equilibrium measurement, the CO₂ breakthrough occurs slightly earlier for the bulk Co-MOF-74 as compared to the hollow nanorods. More importantly, the shape of the breakthrough curve has become slightly sharper by changing the morphology of MOF-74 crystals from the bulk rods to hollow nanorods, which is further implied from the adsorption-desorption cycling profile (**Figure 5-7 (c, d)**). These results imply that the dynamic separation of gas molecules is no more limited by the slow mass transfer within the adsorbent for the case of Co-MOF-74 hollow nanorods. Such improved performance of Co-MOF-74 hollow nanorods under a dynamic condition is attributed to the shortened diffusion distance for gas molecules within the adsorbent by reducing the particle size and removing the core area that requires the elongated diffusion time to be saturated with adsorbate.

Figure 5-7 CO₂ and N₂ (a) adsorption isotherm and (b) dynamic breakthrough measurement of Co-MOF-74 bulk and hollow nanorods at 25 °C; (c, d) Multiple adsorption-desorption cycling of Co-MOF-74 bulk and hollow nanorods at 25 °C. The feed gas for the breakthrough measurement is composed of 20% CO₂ and 80% N₂

Improved dynamic separation performance of Co-MOF-74 hollow nanorods was further validated by a chromatographic separation where adsorption-desorption behaviour is expressed as intensity (of the peak) vs. the elution time plot (**Figure 5-8 (a, b)**) [121]. For an effective benchmarking, the same chromatographic separation analysis was conducted with zeolite 5A, which is widely used as the column material for gas chromatography (**Figure 5-8 (c)**). As a whole, the CO₂ peak for Co-MOF-74 hollow nanorods is much narrower than that of the bulk counterpart, indicating that adsorption-desorption behaviour of CO₂ is significantly facilitated in the hollow nanorods where the core areas that limits the mass transfer is removed. Note that zeolite 5A exhibited a

much longer tail in the CO₂ peak than the Co-MOF-74 because the size of the pore of zeolite 5A (0.48 nm) is much smaller than that of the Co-MOF-74 (1.1 nm), resulting in a lower diffusivity of the gas molecules. Forgoing results demonstrates the potential utility of Co-MOF-74 hollow nanorod in high-performance chromatographic molecular separation.

Figure 5-8 Chromatographic separation of CO₂ and N₂ for (a) Co-MOF-74 bulk nanorods; (b) Co-MOF-74 hollow nanorods and (c) zeolite 5A. The feed gas is composed of 20% CO₂ and 80% N₂. The signals for CO₂ were intensified by factor of 10 to improve the visibility.

5.4 Conclusion

In summary, Co-MOF-74 hollow nanorods with a granular shell were successfully synthesised by a self-sacrifice template method in a facile and efficient way. The time dependent experiments revealed that the nanoscale Kirkendall effect as a consequence

of the difference in diffusion rate of Co^{2+} and ligand ions are responsible for the formation of hollow nanostructures. We also found that the sequence of mixing the reactants is crucial to maintain the rod-like morphology. Although Co-MOF-74 hollow nanorods exhibited a decreased surface area, leading to a decreased CO_2 adsorption capacity at equilibrium, it showed a better CO_2 separation performance than the bulk crystals under a dynamic flow condition. Such enhanced performance was further validated by a chromatographic separation where the peak of CO_2 was significantly narrowed for the hollow nanorod crystals due to the facilitated adsorption and desorption benefited from its unique hierarchical architecture.

5.5 Declaration

The work presented in this chapter has been submitted, with the manuscript is under review.

X. Zhang¹, C. Y. Chuah¹, Panpan Dong, Young-Hwan Cha, Tae-Hyun Bae, Min-Kyu Song, Hierarchically porous Co-MOF-74 hollow nanorods for enhanced dynamic CO_2 separation, *ACS Appl. Mater. Interfaces* **2018**, 10, 50, 43316-43322

Chapter 6 Hierarchically Porous Polymers Containing Triphenylamine for Enhanced SF₆ Separation

6.1 Introduction

In recent years, microporous organic polymer (MOPs) had gained its interest as adsorbents in view of their large accessible surface area, strong chemical tenability as well as structural robustness. MOPs are generally developed and constructed based on the small molecular precursors that are made up of light elements (H, B, C, N and O) via the covalent bonding [192]. As compared to MOFs which have been utilized readily as adsorbents for adsorptive-based separation, MOPs are generally less susceptible towards chemical degradation and humidity [120, 193]. Hence, it can be expected during the repetitive adsorption-desorption cycling, its porosity as well as pore size distribution will remain intact during operation. Furthermore, similar to MOFs, the chemical functionalities of MOPs can be tuned readily as a way to enhance the adsorption performance of polarizable molecules (namely CO₂ and SF₆), as emphasised in several studies [98, 122]. Nevertheless, additional considerations such as adsorption-desorption kinetics, SF₆ binding energy, SF₆/N₂ selectivity should be evaluated adequately so that the potential capability of MOPs in SF₆/N₂ separation can be readily accessed, in view of a large kinetic diameter SF₆ molecules as compared to CO₂. As emphasised in previous chapters (Chapter 3 and 4), improvement in the SF₆ adsorption kinetics can be demonstrated with the introduction of mesoporosity into the adsorbents. Thus, by taking the motivation obtained from the analysis of these observations, MOPs which can be synthesized with the creation of both microporosity and mesoporosity were conducted in this work. Based on a simple MOP structure synthesized using dichloroxylylene (DCX), amine-incorporated POPs that possesses hierarchically porous structure by co-condensation of DCX and triphenylamine (TPA) was developed. TPA-containing POPs

which possess high accessible surface area and good thermal stability showed the enhanced SF₆ separation performance owing to the improved affinity towards SF₆. The enhanced performance of TPA-containing porous polymer was further validated by the dynamic breakthrough and chromatographic measurements.

6.2 Experimental Methods

6.2.1 Materials

Triphenylamine (TPA), α,α' -dichloro-*p*-xylene (DCX), anhydrous FeCl₃, 1,2-dichloroethane (DCE) and zeolite 13X were purchased from Sigma Aldrich. Tetrahydrofuran and methanol were purchased from VWR. All chemicals were used as received without additional purifications. SF₆, N₂ and SF₆/N₂ binary mixture (1:9) were supplied by Airliquide.

6.2.2 Synthesis of adsorbents

Figure 6-1 Reaction scheme of PPN_x

Amine-incorporated MOPs were synthesised based on a previous work with modification. As depicted from **Figure 6-1**, PPN0, PPN1 and PPN2 were developed

using TPA and DCX as the starting materials. For the synthesis of PPN0, 0.875 g of DCX was added into 30 mL of DCE under inert atmosphere. In the next step, 1.07 g of FeCl₃ was incorporated into the solution, where the resulting mixture was stirred for 24 h at 80 °C. The resulting solid precipitate was obtained by washing with substantial amount of methanol and tetrahydrofuran until a clear filtrate is formed. The final product was eventually dried in vacuum oven at 60 °C. The synthesis of PPN1 and PPN2 were similarly conducted by using 0.525 g of DCX and 0.245 g as well as 0.175 g of DCX and 0.735 g of TPA in 30 ml of DCE respectively.

6.2.3 Porosity and morphology characterization

The adsorption behaviour of SF₆ and N₂ in PPN_x series were determined using volumetric gas sorption analyser as reported in Section 3.2.3. Prior to the analysis, the adsorbents were activated at 120 °C for 8 h to ensure that the residual solvent or moisture that are present in the samples can be effectively removed. The porosity properties of PPN_x samples (surface area and pore size distribution) were conducted using volumetric gas sorption analyser as described in Section 3.2.3. FT-IR spectra were measured using IR spectrometer (PerkinElmer, Spectrum One) in the range of 4000 to 400 cm⁻¹ under the resolution of 4 cm⁻¹. The morphological properties of PPN_x adsorbents were examined under FE-SEM (JOEL, JSM6700) at 5 kV acceleration voltage with Au coating. The composition of PPN_x were measured using CHNS elemental analyzer (Elementar) and energy-dispersive X-ray spectroscopy (EDX) equipped to the FE-SEM system. Thermogravimetric analysis (TGA) was performed using thermogravimetric analyzer (TA instrument, SDT Q600 TGA) at the temperature range from 40 – 800 °C under pure nitrogen purging (100 ml/min) at the heating rate of 10 °C/min.

6.2.4 SF₆/N₂ adsorption behaviour of PPN_x copolymers

The SF₆ adsorption of the respective PPN_x copolymers were modelled using single-site Langmuir model (**Equation 3-2**). In this study, dual-site Langmuir-Freundlich [22, 191] or dual-site Langmuir model [44] which was commonly adopted for the identification of fitting parameters for SF₆ isotherms in MOFs and zeolites were not utilized in view of reasonable accuracy ($R^2 > 0.99$) can be determined. Determination of saturation loading (q_{sat}) of N₂ was conducted using the similar manner as described in Section 3.2.4. The adsorption kinetics of SF₆ and SF₆/N₂ selectivity on PPN_x sample on the other hand was evaluated in the similar manner as described in Section 3.2.4 by using **Equation 3-3** and **Equation 3-4** respectively. Meanwhile, the isosteric heat of adsorption (Q_{st}) were calculated using the Clausius-Clapeyron equation as shown below (**Equation 6-1**):

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \dots (6 - 1)$$

In this expression, p is the pressure (bar), T is the temperature (Kelvin) and q is the SF₆ adsorption amount (mmol g⁻¹). The explicit analytical expression of p as a function of q can be developed readily using single-site and dual-site Langmuir equation [194, 195]. Besides, it has been observed that the isosteric heat of adsorption does not differ substantially at different temperatures. The potential capability of the adsorbents in SF₆/N₂ separation process was determined using an idealized VSA system as described in Section 3.2.5, which are described as **Equation 3-7**, **Equation 3-8** and **Equation 3-9** respectively.

6.2.5 Breakthrough and chromatographic separation

The breakthrough measurement under dynamic flow condition was conducted using the custom-built set-up as described in **Figure 3-1**. The samples were first placed in the

adsorption cell with both ends were enclosed with glass wool. The samples were activated under continuous argon purging for 120 °C for 8 h (zeolite 13X on the other hand was activated at 180 °C for 8 h) to ensure that the residual solvents and water were completely removed. The temperature was precisely controlled using heating tape that was equipped with temperature controller. Then, SF₆/N₂ binary mixture (1:9) was supplied into the adsorption column at both 25 and 40 °C, where the outlet gas composition was analysed using mass spectrometer (HPR20, Hiden). The SF₆ and N₂ breakthrough plot was demonstrated by taking the plot of normalized concentration (C/C₀) against flow gas volume per unit mass of sample. The SF₆ uptake and SF₆/N₂ selectivity were determined by taking the onset of SF₆ and N₂ breakthrough as the breakthrough time, without integrating the breakthrough curve. On the other hand, the chromatographic separation of PPN_x copolymers and zeolite 13X was also conducted using the same set-up, with the method is described similarly in Section 5.2.4, with the exception that the feed gas is SF₆/N₂ gas mixture.

6.3 Results and discussion

6.3.1 Synthesis of PPN_x adsorbents

As verified using Fourier-transform infrared (FT-IR) spectroscopy, successful synthesis of amine-incorporated POPs (PPN_x) was performed through the copolymerization reaction between DCX and TPA using FeCl₃ as the catalyst (**Error! Reference source not found.**). Based on the FT-IR analysis, the presence of the unsaturated -C=C- vibration (1500 to 1600 cm⁻¹) was clearly determined on all PPN_x series owing to the presence of aromatic ring. For the case of PPN1 and PPN2, the presence of both 2900 cm⁻¹ and 1300 cm⁻¹ which corresponds to C-H stretching in DCX and N-C stretching in TPA was clearly identified on the spectrum. On the other hand, the presence of C-H

stretching in PPN0 was observed, indicating the successful synthesis of PPN x series. Elemental analysis (C, H and N) of the PPN x on the other hand indicates the successful incorporation of tertiary amine on PPN1 and PPN2 (**Table 6-1**). Further analysis with the EDX indicates that the residual FeCl₃ catalyst was successfully removed by copious washing with solvents after the synthesis, which is evident from the absence of iron in the samples (**Figure 6-2 (b), (c), (d)**). Thus, the Cl peak that was detected in the EDX spectra of PPN x are mainly developed from unreacted chloromethyl group in DCX. Thus, the overall composition of the PPN x samples were determined from both CHNS elemental analysis and EDX measurement. The calculated C-Cl conversion of all PPN x samples were found to be in the range of 92.7 – 94.9 % (**Table 6-2**).

Figure 6-2 (a) FT-IR spectra of PPNx copolymers; FE-SEM; EDX analysis of (b) PPN0, (c) PPN1 and (d) PPN2

Table 6-1 Elemental analysis of PPNx sample

Sample	C	H	N	Cl
PPN0	79.84	4.440	0.109	3.030
PPN1	81.41	4.272	1.123	3.760
PPN2	84.78	4.288	4.288	1.590

Note: Residual chlorine (Cl) can be calculated by the following procedures:

- (1) Determine the C, H and N content in the copolymers using elemental analysis
- (2) Determine the ratio of C/Cl based on the EDX data of copolymers
- (3) Cl content was computed by taking the product of C content from elemental analysis and C/Cl ratio (from the EDX data)

Table 6-2 Summary of reacted and unreacted C-Cl moiety in PPNx sample

Sample	Total reacted C-Cl moiety (mol)	Total unreacted (residual) C-Cl moiety (mol)	Ratio of reacted to unreacted C-Cl moiety	% C-Cl conversion
PPN0	1.58	0.085	18.5	94.9
PPN1	1.34	0.106	12.7	92.7
PPN2	0.764	0.0448	17.1	94.8

TGA analysis on all PPN_x samples revealed their reasonably high thermal stability, up till 500 °C. It was observed that the thermal stability of PPN2 is slightly profound as compared to PPN0 and PPN1, which is presumably because of the aromatic rings that possess high thermal stability as compared to the methylene linkers that are abundant in PPN0 and PPN1. This observation is consistent with the finding in previous work [111]. Through the FE-SEM analysis, the morphology of PPN0 samples typically made up of irregular small particles, meanwhile irregular particles with fibrous-like structures were observed on both PPN1 and PPN2 without well-defined morphologies [111] (**Figure 6-3**).

Figure 6-3 (a) TGA curve of PPN_x copolymers; FE-SEM images of (b) PPN0, (c) PPN1 and (d) PPN2

Next, N₂ physisorption isotherms at 77 K were studied, which is generally critical and important to identify the pore characteristics of PPN_x. As shown in **Figure 6-4** (a), all

PPN_x samples displayed type 1 isotherm in view of its high N₂ uptake at low pressure region, indicating large micropore volume. Unlike PPN0, a clear hysteresis loop between adsorption and desorption branches in PPN1 and PPN2 were observed, indicating the formation of mesoporosity as determined to be approximately 4 nm using the BJH analysis (**Figure 6-4 (b)**). Thus, the creation of hierarchical structures with both microporous and mesoporous domains were verified in PPN1 and PPN2, whereas pure microporous domains were observed in PPN0. On the other hand, the average size of micropores were found to be about 1.2 nm for all PPN_x (**Figure 6-4 (c)**). The surface areas and pore volumes were calculated and summarized in (**Table 6-3**). In general, the trend of BET surface area, Langmuir surface area and total pore volume decreases with the increase in TPA content in the copolymers. Nonetheless, the micropore surface area and volume of PPN1 was the highest as compared to PPN0 and PPN2, which is similar to the trend observed in previous work [111, 120]. Thus, this result indicates that the overall porosity of the final copolymer can be tuned readily by altering the ratio of TPA and DCX.

Table 6-3 Surface areas and pore volumes of PPN_x copolymers based on N₂ physisorption at 77 K

Sample	S _{BET} (m ² /g) ^[a]	S _{Lang} (m ² /g) ^[a]	S _{micro} (m ² /g) ^[b]	V _{micro} (cc/g) ^[b]	V _{total} (cc/g) ^[c]
PPN0	1480	1985	866	0.402	2.60
PPN1	1392	1859	946	0.442	1.87
PPN2	1081	1439	717	0.336	1.09

Note: [a] BET (S_{BET}) and Langmuir (S_{Lang}) surface area are obtained at P/P^o = 0.05 – 0.20; [b] Micropore surface area (S_{micro}) and volume (V_{micro}) are determined using *t*-plot method at the pressure range of P/P^o = 0.4 – 0.6; [c] Total pore volume (V_{total}) were obtained at P/P^o = 0.99.

Figure 6-4 (a) N_2 sorption isotherm (adsorption and desorption branches are indicated as closed and open symbols respectively); (b) Mesopore size distribution (using BJH method) and (c) Micropore size distribution (using HK method) of PPN0, PPN1 and PPN2

6.3.2 SF_6 and N_2 adsorption of PPN x

The pure component isotherms of SF_6 and N_2 isotherms in PPN x copolymers which were measured at both 25 and 40 $^{\circ}C$ are summarized in **Figure 6-5**. All PPN x copolymers demonstrated favourable interaction with SF_6 as compared to N_2 . The possible reason for this observation is the presence of tertiary amines and chloride atoms in the PPN x copolymers, which allows dipole-induced-dipole interaction with SF_6 . Such interactions also lead to favourable interaction between CO_2 in view of both SF_6 and CO_2 has a much higher polarizability than N_2 . In this study, it was observed that PPN0 exhibit the highest SF_6 adsorption at ambient condition as compared to PPN1 and PPN2 in view of its high BET and Langmuir surface area. Nonetheless, by comparing the SF_6

adsorption at the point of interest (0.1 bar), which is typically used in industrial operation, the SF₆ adsorption of both PPN0 and PP1 were found to be comparable. Notably, the SF₆ adsorption of PPN0 at ambient condition (25 °C and 1 bar, 34.3 wt%) in general was comparable with the SF₆ adsorption on porous organic cages (CC3 α , 33.6 wt%) [196]. Meanwhile, the performance of PPN0 at ambient condition is generally much higher than conventional zeolite MFI (22.0 wt%) [197].

Figure 6-5 SF₆ and N₂ uptake of (a) PPN0; (b) PPN1 and (c) PPN2; (d) SF₆ adsorption kinetics of PPN0, PPN1, PPN2 and zeolite 13X at 25 °C

Moreover, we have investigated the adsorption kinetics of adsorbents, by calculating the fractional uptake against time (**Figure 6-5 (d)**). The kinetic study of zeolite 13X which is a widely-used commercial adsorbents was also conducted to benchmark the performance of produced adsorbents. It was observed that all PPN_x copolymers demonstrates rapid SF₆ uptake at 25 °C, where it takes less than 10 s to achieve 90 % of

the total fractional uptake. In contrast, commercial zeolite 13X merely showed 80% of the total fractional uptake even after 4 minutes. For the case of PPN0, it was observed that the fractional uptake is slightly inferior as compared to PPN1 and PPN2 as it does not possess any significant mesoporosity that allows the rapid diffusion of SF₆ molecules into the active sites. However, the enhancement in adsorption kinetics with the introduction of mesoporosity was marginal as compared to the zeolite MFI in our previous work. This is because PPN_x has a larger micropore (1.2 nm) than that of zeolite MFI (0.54 nm) [197].

6.3.3 SF₆/N₂ selectivity and isosteric heat of adsorption of porous polymers

Figure 6-6 (a) IAST SF₆/N₂ selectivities of PPN_x copolymers as a function of pressure at 25 °C; (b) Isosteric heat of adsorption of PPN_x copolymers as a function of SF₆ loading

The SF₆/N₂ selectivity or separation efficiency is also an important criterion that determines the purity (or quality) of the product gas. Thus, N₂ adsorption isotherm was measured and the selectivity was calculated by employing IAST, which has been proven to be useful in modelling the selectivity behaviour in MOF and POP system previously [120]. Thus, to conduct this analysis, the isotherms were fitted using single-site Langmuir model, where for this analysis, the SF₆/N₂ ratio was fixed at the ratio of 1:9 as this composition is commonly used in the industrial operations. The calculation of

SF₆/N₂ selectivities under this composition were conducted at 25 °C (**Figure 6-6 (a)**). In general, SF₆ isotherms of PPN_x copolymers can be fitted with single-site Langmuir equation with reasonably high accuracy ($R^2 > 0.99$), indicating the active sites residing in the adsorbent are distributed homogeneously. Thus, the selectivity behaviour of all produced adsorbents remained practically unchanged as a function of pressure, as compared to zeolites and MOFs, which demonstrate a much stronger dependence of pressure in the overall selectivity [191, 197]. Particularly, the incorporation of tertiary amines into the porous polymer structures was very effective in improving SF₆/N₂ selectivity. Interestingly, PPN1 exhibited the highest SF₆/N₂ selectivity among porous polymers tested. It may imply that further increasing amine content from the amount in PPN1 gives a marginal or no effect in improving the affinity towards SF₆. Rather, the decrease in the accessible micropore surface area (946 to 717 m²/g) and the micropore volume (0.442 to 0.336 cm³/g) led to a poorer performance of PPN2 as compared to PPN1.

The role of tertiary amine is further investigated by calculating the isosteric heat of adsorption, Q_{st} which is a measure of binding energy between adsorbent and adsorbate. The calculated heat of adsorption for different adsorbents are shown in **Figure 6-6 (b)**. It was found that PPN1 and PPN2 have a higher Q_{st} value (28.1 and 24.2 kJ mol⁻¹ respectively) than PPN0 (22.3 kJ mol⁻¹), indicating the incorporation of tertiary amines enhance the interactions between the adsorbent and SF₆ molecules. Furthermore, the order in the heat of adsorption of PPN_x copolymers matched to the order in selectivity exactly. Thus, this implies that optimum amine loading while keeping a high microporosity is critical factor leading to a high affinity to SF₆, resulting in a high SF₆/N₂ selectivity.

6.3.4 Potential utilization of PPNx in idealized VSA

The potential application of PPNx copolymer in SF₆/N₂ separation was verified using idealized VSA. To obtain the desired product and regenerate for the subsequent cycle, the adsorption-desorption cycling via pressure- or temperature-swing adsorption was commonly performed. Nevertheless, as the feed pressure is typically present at a near-ambient condition where SF₆/N₂ separation is needed, the behaviour of PPNx copolymer was evaluated using the idealized VSA model. For this illustration, it is assumed that the feed pressure is typically present at near ambient condition (1 bar), with the SF₆/N₂ ratio of 1:9. The gases were flowed through the adsorption column. In the next step, the desorption was occurred at 0.01 bar. It is expected that during the desorption process, the column is expected to be filled with mainly SF₆ which is released from the adsorption, where the partial pressure of SF₆ at the desorption process is set at 0.01 bar. This analysis prevents overestimations and allow us to reach a more accurate depiction with regards to the working capacity.

Table 6-4 Evaluation of PPNx adsorbents in an idealized VSA model

Sample	Temperature (°C)	N_1^{ads} (wt%)	ΔN_1 (wt%)	R (%)	α_{12}^{ads}
PPN0	25	9.75	8.53	87.4	34.2
PPN1	25	9.47	8.17	86.2	38.2
PPN2	25	5.77	5.10	88.5	39.8
PPN0	40	6.89	6.08	88.3	35.9
PPN1	40	6.31	5.53	87.7	36.9
PPN2	40	3.82	3.40	89.1	41.9

Table 6-4 summarizes the four main criteria used for the investigation of the overall feasibility of VSA model as described in the literature. As given from the table, the

performance of PPN0 and PPN1 are generally comparable in terms of the total amount of SF₆ adsorbed, SF₆ working capacity and SF₆ regenerability at both conditions, nonetheless the latter demonstrates higher SF₆/N₂ selectivity at both condition. The core reason behind this observation is presumably the additional adsorption sites provided by the tertiary amines, which help segregate SF₆ from SF₆/N₂ mixture. Besides, it is worth emphasising that the observation of an attractive SF₆ adsorption kinetics is encouraging. This is because an effective adsorption-desorption cycling behaviour as well as decent energy penalty increases the potential of PPN1 for practical applications.

5.3.5 Breakthrough and chromatographic measurements

Figure 6-7 SF₆/N₂ breakthrough curves for PPN_x copolymers at (a) 25 °C and (b) 40 °C. The breakthrough curves for zeolite 13X was served as a reference.

In practical gas separation applications, the actual operation mode is generally conducted in dynamic flow rather than static equilibrium condition. Thus, the SF₆/N₂ separation performance of PPN_x copolymers was evaluated under dynamic flow condition using a custom-built breakthrough system. To effectively demonstrate the potential of produced adsorbents, zeolite 13X was also studied under the studied experimental conditions. As shown in **Figure 6-7**, all PPN_x copolymers demonstrated a sharp breakthrough of SF₆, indicating the overall performance was not limited by the slow diffusion of SF₆ in the adsorbents. In contrast, the breakthrough of SF₆ occurred

earlier for zeolite 13X in spite of its higher equilibrium uptake than PPN_x. It implies that the slow mass transfer of zeolite 13X is the limiting factor determining the performance in the dynamic flow condition which is more industrially relevant than the static equilibrium condition.

Figure 6-8 SF₆/N₂ chromatographic separation of (a) PPN0, (b) PPN1, (c) PPN2 and (d) zeolite 13X at 60 °C. The intensity of SF₆ for PPN_x copolymers and zeolite 13X was intensified for 50 and 200 times respectively for clarity purpose.

Besides, chromatographic separation of SF₆/N₂ where the adsorption-desorption behaviour is expressed as a peak was also conducted on both PPN_x samples and zeolite 13X at 60 °C. As shown in **Figure 6-8**, all PPN_x copolymers exhibited sharp peaks owing to the rapid adsorption and desorption of gas molecules. In contrast, zeolite 13X showed a significantly broadened SF₆ peak, indicating that the repetitive adsorption-desorption cycling of zeolite 13X is time-consuming as well as potentially energy

intensive. More importantly, PPN1 was the only sample that can perfectly segregate SF₆ and N₂ (no overlap in two peaks) in this operation condition owing to its higher SF₆/N₂ selectivity than PPN0 and PPN2. Altogether, mesoporosity and the tertiary amines in PPN1 provided a significant advantage for dynamic SF₆/N₂ separation processes.

6.4 Conclusion

PPN_x copolymer that possess large accessible surface area with high affinity towards polarizable molecules was synthesised and investigated for its potential application in SF₆ capture and recovery. The introduction of tertiary amine groups into the DCX-based POP frameworks provided a large performance improvement. We observed that amine-incorporated POPs (PPN_x copolymers) exhibits better SF₆/N₂ selectivity without sacrificing the SF₆ adsorption at the desired partial pressure (0.1 bar) with marginal increase in isosteric heat of adsorption. Besides, PPN_x copolymers generally shows rapid SF₆ adsorption kinetics, indicating their suitability in rapid adsorption-desorption cycling. Importantly, we have also demonstrated the superior performance of PPN_x copolymers than zeolite 13X, which this adsorbent is commonly exploited in industrial gas separation processes. Thus, the PPN_x copolymers are promising for effective SF₆ capture and recovery.

6.5 Declaration

The work presented in this chapter has been published in Microporous and Mesoporous Materials.

C. Y. Chuah¹, Y. Yang¹, T-H. Bae, Hierarchically porous polymers containing triphenylamine for enhanced SF₆ separation, **Micropor. Mesopor. Mater.**, (2018), 272, 232-240

Chapter 7 Development of HKUST-1 nanocrystals in increasing the permeability of polymeric membrane in O₂/N₂ and CO₂/CH₄ separation

7.1 Introduction

Permeability-selectivity trade-off in polymeric membrane has been well demonstrated in the Robeson plot in view of the solution-diffusion is the dominant gas transport mechanism. Thus polymer chains that allows rapid diffusion of gas molecules will inevitably lead to a drastic decrease in the membrane selectivity [42, 43]. MMM on the other hand is the most technical viable option in order to account for the limitation of the molecular sieve membrane that does not demonstrate high scalability. Based on the porous materials that was elaborated in previous chapters (Chapter 3 to 6), MOFs as a whole has attracted vast research interest as the fillers in MMM in view of its large surface area and pore volume, where the functionalities can be tuned via pre- or post-synthetic functionalization [198, 199]. Furthermore, as compared to zeolites, MOFs typically demonstrate better compatibility in the interface between filler and polymer in view of the presence of organic moieties, thus eliminating the needs to use the compatibilizer for the case of zeolites [151, 200]. In this work, we will focus on the effect of utilizing HKUST-1 nanocrystals, which shows reasonable performance in SF₆/N₂ separation in mixed-matrix membrane so as to evaluate the overall membrane performance for O₂/N₂ and CO₂/CH₄ separation. In general, the synthesis of HKUST-1 has been commercially available under the trade name Basolite C300. Nonetheless, its crystal size is considerably large for the fabrication of thin dense mixed-matrix membrane. Thus, HKUST-1 nanocrystals which has been synthesised elsewhere will be utilized in the fabrication of mixed-matrix membrane. Conventional polymeric membrane (polysulfone) which suffers from low gas permeability in spite of their decent gas selectivities were chosen as the polymer matrix. It has been observed that the

utilization of HKUST-1 nanocrystal as the filler materials has demonstrated an increase in gas permeability, without compromising the selectivity. Thus, with the enhancement in gas permeability without compromise the selectivity significantly, the economic feasibility of the gas separation process can be improved drastically.

7.2 Experimental Methods

7.2.1 Materials

Copper(II) nitrate trihydrate and trimesic acid were purchased from Sigma Aldrich. Absolute ethanol and chloroform were purchased from VWR. Polysulfone polymer were purchased from Solvay Special Chemicals. All chemicals were used as received without further purifications.

7.2.2 Synthesis of HKUST-1 Nanocrystals

The synthesis of HKUST-1 nanocrystals was conducted based on the procedure as described elsewhere [175]. 1.2 g of copper(II) nitrate trihydrate was added into 20 ml of absolute ethanol, followed by the addition of 0.6 g of trimesic acid. The resulting mixture was stirred at ambient condition for 24 h. The resulting precipitate was filtered and washed using ethanol:water mixture (1:1) and dried in the vacuum oven at 60 °C overnight.

7.2.3 Membrane Fabrication

Dense film of mixed-matrix membrane was fabricated via solution casting technique. The nanocrystal HKUST-1 was first dispersed in chloroform using sonication horn. Then, the polymers were subsequently added into the solution while stirring vigorously. The mixture was allowed to stir for at least one day so as to allow the solution to be homogenized. Then, the dope solution was casted onto the glass plate via the usage of

casting knife, with the membranes were placed in the glove bag with the environment that is filled with chloroform vapor so as to prevent rapid solvent evaporation. The resulting membrane was eventually annealed in vacuum oven at 160 °C for 24 h before permeation testing.

7.2.4 Characterization of HKUST-1 nanocrystals

O₂, N₂, CO₂ and CH₄ adsorption properties of HKUST-1 nanocrystals were measured using volumetric gas sorption analyser (Quantachrome, Isorb HP1). Prior to the measurement, HKUST-1 nanocrystal was activated at 160 °C for 8 h under high vacuum to ensure that the residual solvents that are present in the sample can be removed effectively. The isotherm measurement was conducted at 35 °C under the pressure range of 0 to 1 bar, with the temperature was controlled precisely with water recirculator. Powdered X-ray diffraction (PXRD) data was obtained using Bruker D2 phaser that was equipped with CuK α radiation. The analysis was conducted under ambient condition under the range of 2θ from 5 to 40°, using the step size of 0.02°. The morphology of HKUST-1 was observed using field-emission scanning electron microscope (FESEM, Joel, JSM6701) under the acceleration voltage of 5 kV.

7.2.5 Characterization of mixed-matrix membrane

The cross-section of mixed-matrix membranes containing HKUST-1 nanocrystals were observed using FESEM under the acceleration voltage of 5 kV. Prior to the observation, the membranes were cryogenically fractured in liquid nitrogen before gold coating. The properties of the pure polymeric membranes were verified using Fourier Transform Infrared Spectroscopy (FT-IR) spectra with a resolution of 4 cm⁻¹ between 4000 and 500 cm⁻¹ (PerkinElmer, Spectrum One). The thermal properties of the membranes were measured using thermogravimetric analyser (SDT Q600 TGA, TA instrument) at a

heating rate of 10 °C/min under the temperature range from 40 to 800 °C under pure nitrogen purging of 100 ml/min. The densities of the pure polymeric and mixed-matrix membrane were determined based on the Archimedes principle by measuring the mass of sample in air and auxiliary liquid (ethanol) using an analytical balance (Mettler Toledo, ME204) equipped with a density kit.

7.2.6 Mixture gas permeation test

Gas permeation test was carried out using a constant pressure-variable volume system that was developed by GTR Tec Corporation. Compressed air ($O_2/N_2 = 21/79$), carbon dioxide/methane mixture ($CO_2/CH_4 = 50/50$) and helium, which were used in the system were purchased from Airliquide. After the membrane was mounted onto the permeation cell, the upstream and downstream sides were subjected to compressed air and helium gas respectively. The flow rate was controlled using mass flow controller respectively. The downstream gas that was permeated through the membrane was swept by helium at a periodic time interval until the concentration of O_2 and N_2 (or CO_2 and CH_4) reached a steady state (i.e. no significant fluctuation of their respective concentrations). The concentration of O_2 and N_2 (or CO_2 and CH_4) gas were determined from gas chromatography. The temperature of the permeation cell was set at 35 °C. The reproducibility of the permeation results was further tested by repeating the measurement for at least three samples of each polymeric and mixed-matrix membrane.

7.2.7 Gas adsorption analysis

To calculate the solubility-diffusivity behaviour in mixed-matrix membrane, gas adsorption analysis of pure polymer and mixed-matrix membrane was conducted using volumetric gas sorption analyser as described in Section 6.2.4. All membranes were measured and activated under the same condition as described above. The O_2 , N_2 , CO_2

and CH₄ adsorption was determined by interpolation of the isotherm. The solubility of O₂, N₂, CO₂ and CH₄ in the membrane, S was computed by using the relationship as described below (**Equation 7-1**):

$$S = \frac{q\rho}{p} \dots (7 - 1)$$

Here, q is the gas sorption per mass of membrane, p is the pressure and ρ is the density of membrane. The calculation of diffusivity, D was computed by dividing the permeability, P by solubility, S . The unit of P and S are expressed as $\text{mol} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{bar}$ and $\text{mol}/\text{m}^3 \cdot \text{bar}$, respectively.

7.3 Results and discussion

7.3.1 Synthesis of HKUST-1 nanocrystals

Figure 7-1 (a) PXRD pattern, (b) FT-IR, (c) TGA and FESEM image of nanocrystal HKUST-1

The successful synthesis of HKUST-1 was first verified using PXRD as shown in **Figure 7-1 (a)**. In general, the XRD pattern is comparable with the results from the literature [175]. This is further verified with the FT-IR analysis, where the coordination of trimesic acid into the $\text{Cu}_2(\text{COO})_4$ paddle wheel (**Figure 7-1 (b)**). The thermal stability of the framework was further verified with the sample remains stable up till 350 °C (**Figure 7-1 (c)**). As mentioned in the introduction, it is required for the sample to be sufficiently small enough for the fabrication of thin-dense mixed-matrix membrane. Thus, verification from the FESEM image is required to determine the overall morphology. Based on the **Figure 7-1 (d)**, the average particle size is estimated to be in the range from 100 – 200 nm.

7.3.2 O_2 , N_2 , CO_2 and CH_4 adsorption of HKUST-1 nanocrystals

Figure 7-2 (a) O_2 , N_2 and **(b)** CO_2 , CH_4 adsorption isotherm of HKUST-1 nanocrystal that was measured at 35 °C

O_2 and N_2 adsorption isotherm of nanocrystal HKUST-1 were measured at 35 °C, with the results are summarized in **Figure 7-2 (a)**. Large square pore windows (9 x 9 Å) in HKUST-1 allows both adsorbates to access the adsorption sites into the adsorbent without any resistance. In general, in view of the weak interactions between both adsorbates and HKUST-1 nanocrystals, linear adsorption isotherms were observed for both O_2 and N_2 at the pressure range tested. Slightly higher N_2 adsorption was

observed as compared to O₂ uptake because of its higher polarizability of N₂ ($17.6 \times 10^{-25} \text{ cm}^3$) than that of O₂ ($15.4 \times 10^{-25} \text{ cm}^3$) [201]. Nevertheless, the O₂/N₂ sorption selectivity of HKUST-1 can be considered negligible. On the other hand, CO₂ and CH₄ adsorption isotherm of nanocrystal HKUST-1 were also measured at 35 °C (**Figure 7-2 (b)**). Despite it is expected that its large pore size allows a better accessibility towards CO₂ and CH₄, it was observed that higher CO₂ adsorption was observed as compared to CH₄. This is attributed to the presence of the coordinatively unsaturated open metal sites that allows favourable interaction with CO₂ which possess higher polarizability ($29.11 \times 10^{-25} \text{ cm}^3$) and quadrupole moment ($4.30 \times 10^{-26} \text{ esu cm}^2$) as compared to CH₄ ($25.93 \times 10^{-25} \text{ cm}^3$ and 0 esu cm^2) [3, 201]. Nonetheless, based on the linear isotherm profile of CO₂ and CH₄ based on the entire tested pressure range, it can be inferred that the binding sites available in HKUST-1 is still not sufficiently strong enough to affect the diffusion of CO₂ in the HKUST-1 nanocrystals.

7.3.3 Fabrication of mixed-matrix membrane

Figure 7-3 (a) FT-IR spectra of polysulfone polymer; (b) TGA analysis of 10 wt% and 20 wt% HKUST-1 nanocrystal in polysulfone polymer

In this work, polysulfone membrane which are commonly used as the gas separation were used as the polymer matrix for the fabrication of mixed-matrix membrane. The properties of the pure polymer was verified using FT-IR spectroscopy

to compare the polymer properties with those reported in the literature [202, 203] (**Figure 7-3 (a)**). Mixed-matrix membranes containing 10 wt% and 20 wt% HKUST-1 nanocrystals were then fabricated, and the morphologies of these membranes were observed using FESEM (**Figure 7-4**). As a whole, a typical *sieve-in-a-cage* morphology which is commonly observed in zeolite-based mixed-matrix membrane was not observed in this study [151, 200, 204]. The presence of organic moieties in nanocrystal HKUST-1 allows a better compatibility between the filler and polymer chain. Furthermore, the utilization of nanocrystals allows an increase in the accessible surface area between the polymer and filler, thus leading to better dispersion of filler in the polymer matrix. The TGA analysis of the mixed-matrix membrane in comparison with the pure polymeric membranes indicated that the presence of the fillers did not affect the thermal stability of the polymer (**Figure 7-3 (c, d)**).

Figure 7-4 FESEM images of mixed-matrix membranes **(a, b)** 10 wt% HKUST-1 in polysulfone; **(c, d)** 20 wt% HKUST-1 in polysulfone

7.3.4 Gas permeation properties

Table 7-1 Permeation results of pure polymer and mixed-matrix membrane under 1 bar of upstream pressure with air ($O_2/N_2 = 21/79$) at 35 °C

Membrane	O_2 permeability (barrer)	O_2/N_2 selectivity
Polysulfone	2.01 ± 0.12	4.23 ± 0.25
Polysulfone + 10 wt% HKUST-1	3.80 ± 0.12	4.85 ± 0.10
Polysulfone + 20 wt% HKUST-1	9.62 ± 0.58	4.71 ± 0.08

Table 7-2 Permeation results of pure polymer and mixed-matrix membrane under 1 bar upstream pressure with CO_2/CH_4 mixture (50/50) at 35 °C

Membrane	CO_2 permeability (barrer)	CO_2/CH_4 selectivity
Polysulfone	9.34 ± 1.13	25.7 ± 4.20
Polysulfone + 10 wt% HKUST-1	17.6 ± 3.47	25.9 ± 0.36
Polysulfone + 20 wt% HKUST-1	39.4 ± 3.14	19.5 ± 1.25

Table 7-1 and **Table 7-2** summarizes the gas permeation properties of the membrane which are measured at 35 °C under 1 bar upstream pressure with an O_2/N_2 (21:79) and CO_2/CH_4 (50:50) binary mixture. In general, it has been observed that the incorporation of HKUST-1 increases the O_2 and CO_2 permeability drastically significantly without affecting the O_2/N_2 and CO_2/CH_4 selectivity of the nascent membrane. The best performance was observed for the case of 20 wt% HKUST-1/polysulfone membrane, where the O_2 permeability and O_2/N_2 selectivity increased by 379% and 11% respectively over the performance of pure polysulfone membrane as well as for the case of 20 wt% HKUST-1/polysulfone membrane, where the CO_2

permeability increased by 321.8%. This was presumably attributed to the fact that the incorporation of HKUST-1 nanocrystals that possess large pore windows and well-defined pore channels allow the rapid transport of both O₂ and N₂ molecules in the mixed-matrix membrane.

Figure 7-5 Pure component (O₂, N₂, CO₂ and CH₄) adsorption isotherms of pure polymer and mixed-matrix membranes for (a, b) polysulfone, (c, d) polysulfone + 20 wt% HKUST-1

With this, additional evaluation of the improved membrane performance was then evaluated by quantify the diffusivity and solubility of O₂, N₂, CO₂ and CH₄ in mixed-matrix membrane. Thus, in this analysis, O₂, N₂, CO₂ and CH₄ adsorption of pure polymeric and 20 wt% HKUST-1 in mixed-matrix membranes were measured at 35 °C, with the results are demonstrated in **Figure 7-5**. This analysis reveals that HKUST-1 nanocrystals dramatically improved the diffusivities of both gases in the membranes. Hence, the increase in permeability in mixed-matrix membrane is ascribed to the increase in both the solubility and diffusivity upon incorporation of HKUST-1

nanocrystals. Based on the O₂ and N₂ adsorption isotherm, it was observed that the O₂/N₂ sorption selectivity decreases marginally in the mixed-matrix membrane, which is consistent with the gas uptake property of the HKUST-1 nanocrystals (**Figure 7-5**), which preferentially take up N₂ over O₂. However, HKUST-1 nanocrystals have proven to be capable of improving the diffusion selectivity, leading to an increase in O₂/N₂ permselectivity. Similar trend was also observed for the solubility-diffusivity calculation for the case of CO₂/CH₄ separation.

Table 7-3 O₂ and N₂ solubility and diffusivity data for pure polymer and mixed-matrix membrane at 35 °C

Membrane	Density (g/cm ³)	O ₂ solubility (mol/m ³ -bar)	O ₂ diffusivity, x 10 ⁻¹³ (m ² /s)	N ₂ solubility (mol/m ³ -bar)	N ₂ diffusivity x 10 ⁻¹³ (m ² /s)
Polysulfone	1.24	19.1	7.98	14.3	2.53
Polysulfone + 20 wt% HKUST-1	1.25	29.0	23.6	24.2	6.01

Table 7-4 CO₂ and CH₄ solubility and diffusivity data for pure polymer and mixed-matrix membrane at 35 °C

Membrane	ρ (g/cm ³)	CO ₂ solubility (mol/m ³ -bar)	CO ₂ diffusivity, x 10 ⁻¹³ (m ² /s)	CH ₄ solubility (mol/m ³ -bar)	CH ₄ diffusivity x 10 ⁻¹³ (m ² /s)
Polysulfone	1.24	261	2.72	17	1.61
Polysulfone + 20 wt% HKUST-1	1.25	516	5.81	70	2.17

7.4 Conclusion

HKUST-1 nanocrystals, which have well-defined pore channels is selected as the filler to improve O₂/N₂ and CO₂/CH₄ separation performance in polymeric membranes. It was found out that the incorporation of HKUST-1 nanocrystals dramatically improved the O₂ and CO₂ permeability of polysulfone, which is a widely used membrane polymers

that was suffered from poor permeability. In general, the overall O₂/N₂ and CO₂/CH₄ selectivity does not decrease substantially, indicating that the formation of defects at polymer-filler interfaces was effectively restricted owing to the good adhesion between the two phases. Detailed analysis reveals that the HKUST-1 nanocrystals effectively increased both solubility and diffusivity of gases in mixed-matrix membrane.

7.5 Declaration

Part of the work presented in this chapter has been published under BMC Chemical Engineering.

C. Y. Chuah, T-H. Bae, Incorporation of HKUST-1 nanocrystals to increase the permeability of polymeric membranes in O₂/N₂ separation, *BMC Chem. Eng.*, **2019**, 1:2

Chapter 8 Effect of incorporating amine-functionalized HKUST-1 in polymeric membrane for CO₂/N₂ separation

8.1 Introduction

As mentioned in Chapter 7, trade-off relationship in the polymeric membrane has been well reported in the Robeson plot as the transport of gas molecules are conducted via solution-diffusion mechanism. In comparison to other membrane categories, MMM on the other hand is considered to be the most technical viable option as molecular sieve membranes which are mainly made up of nanoporous materials suffers limitations in scaling up into large membrane modules. Thus, based on the varieties of nanoporous materials that have been reported thus far, MOFs generally attracted vast research interest as the fillers in MMM in view of its large surface area and pore volume, where the functionalities can be tuned via pre- or post-synthetic functionalization [198, 199]. On the other hand, MOFs generally demonstrate better compatibility in the interface between filler and polymer as compared to inorganic zeolites in view of the presence of organic moieties, thus eliminating the needs to use of additional compatibilizers to increase the overall compatibility between filler/polymer interface [151, 200]. In the previous chapter, it has been observed that HKUST-1 nanocrystals are feasible in improving CO₂ permeability without sacrificing the overall selectivity. Thus, in this work, we have incorporated amines which can be readily feasible via post-synthetic functionalization of amines, which generally demonstrates enhancement in CO₂ adsorption particularly at low partial pressure. With the addition of amine-functionalized HKUST-1 nanocrystals in the membranes, enhancement in CO₂/N₂ selectivity can be observed.

8.2 Experimental Methods

8.2.1 Materials

Matrimid 5218 polymer was purchased from Huntsman Corporation. 3-picolylamine ($C_6H_8N_2$), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) and trimesic acid ($C_9H_6O_6$) were purchased from Sigma Aldrich. Absolute ethanol, chloroform, *n*-hexane and toluene were purchased from VWR. All other chemicals were used as received without further purifications.

8.2.2 Synthesis of HKUST-1 and amine-functionalized HKUST-1

Figure 8-1 Structure of ODPA-TMPDA polymer

Nanocrystal HKUST-1 were synthesised based on the procedures as described in Section 7.2.1. Amine-functionalized HKUST-1 were developed based on the method as described elsewhere (**Figure 8-1**) [198]. First, 0.50 g of nanocrystal HKUST-1 were first activated at 160 °C under argon purging for 24 h to ensure that any residual solvents that could be potentially present in the samples can be removed. After the resulting reaction flask are cooled to room temperature, 30 ml of toluene was added to create a suspension. In the next step, 3-picolylamine with different volume was added into the solution, which can be done by altering the ratio between Cu and amine. The resulting suspension was conducted under argon purging for 12 h under reflux at 110 °C. The

solid products were washed copiously with *n*-hexane to remove any unreacted substituents. The product was summarized based on the following notation: HKUST-1- x NH₂ ($x = 0, 25, 50, 75, 100$), which x denotes the percentage of amine that was added into the suspension with 1 mole of Cu as the basis. HKUST-1- x -NH₂ with the most optimal performance is eventually selected for the subsequent analysis (membrane fabrication and gas permeation analysis).

8.2.3 Membrane fabrication

The formation of dense-film membranes can be conducted via solution casting technique. First, the dispersion of HKUST-1 and amine-functionalized HKUST-1 nanocrystals was dispersed in chloroform with the aid of sonication horn and vigorous stirring. Then, Matrimid polymers were subsequently added into the solution with the aid of vigorous stirring. In order to ensure that the solution remains homogeneous, the mixture was agitated overnight. Next, casting knife was used to develop the flat-sheet membrane, which the dope solution was poured onto the glass plate. Rapid solvent evaporation was prevented by ensuring that the casting environment (in the glove bag) was filled with chloroform vapor. After sufficient evaporation time was provided, the resulting membranes were annealed at 160 °C (mixed-matrix membrane containing HKUST-1 nanocrystals) and 120 °C (mixed-matrix membrane containing amine-functionalized HKUST-1 nanocrystals) overnight in the vacuum oven.

8.2.4 Characterization of HKUST-1 and amine-functionalized HKUST-1 nanocrystals

CO₂ and N₂ adsorption properties of HKUST-1 and amine-functionalized HKUST-1 nanocrystals were conducted using volumetric gas sorption analyser (Quantachrome, NOVATouch LX2). The HKUST-1 and amine-functionalized

HKUST-1 nanocrystals were first outgassed at 160 °C and 120 °C for 24 hours respectively under high vacuum condition so as to confirm that any residual solvents that could be possibly present in the samples can be removed effectively. The respective isotherms are measured in the range of 0 – 1 bar at 35 °C, which the temperature was precisely controlled by water recirculator. The isotherms were fitted using dual-site and single-site Langmuir equation respectively as demonstrated in **Equation 3-1 and 3-2**. On the other hand, CO₂/N₂ selectivity of HKUST-1 and amine-functionalized HKUST-1 was determined via Ideal Adsorbed Solution Theory (IAST) [164], as described in **Equation 3-3**.

The porosity properties of HKUST-1 and amine-functionalized HKUST-1 nanocrystals were determined using N₂ physisorption analysis at 77 K using volumetric gas sorption analyser (Quantachrome, Autosorb-6B) by adopting the same activation condition as mentioned above. The crystallinity of the HKUST-1 and amine-functionalized HKUST-1 nanocrystals were determined using powdered X-ray diffraction, PXRD (Bruker, D2 phaser) that was equipped with CuK α (1.5418 Å) radiation. The measurement was analysed in the range of 2θ from 5 to 40°, at the step size of 0.02°, which was conducted under ambient condition. The morphology of HKUST-1 and amine-functionalized HKUST-1 nanocrystals was observed using field-emission scanning electron microscope, FESEM (Joel, JSM6701) under the acceleration voltage of 5 kV. The amine contents in HKUST-1 and amine-functionalized HKUST-1 nanocrystals were determined using elemental analysis (Elementar). The thermal stabilities of HKUST-1 and amine-functionalized HKUST-1 nanocrystals were determined using thermogravimetric analyser (TA Instrument, SDT Q600 TGA). The ramping rate was set at 10 °C/min under the temperature scan that ranges from 40 to 800

°C. Throughout the measurement, 100 ml/min of pure nitrogen was supplied to the sample.

8.2.5 Characterization of mixed-matrix membranes containing HKUST-1 and amine-functionalized HKUST-1 nanocrystals

The overall morphologies of the mixed-matrix membranes were determined by observing the cross-section using field-emission scanning electron microscope (Joel, JSM6701) under the acceleration voltage of 5 kV. In order to preserve the membrane morphology, the membranes were cryogenically fractured under liquid nitrogen prior to gold coating. The properties of pure polymeric membrane were confirmed from Fourier transform-infrared spectroscopy (FTIR) spectra, which the resolution was set at 4 cm^{-1} under the range of $4000\text{ to }450\text{ cm}^{-1}$ (PerkinElmer, Spectrum One). Similarly, the thermal stabilities of the respective membrane were determined using thermogravimetric analyser (TA Instrument, SDT Q600 TGA). The heating rate was set at 10 °C/min under the temperature range from $40\text{ to }800\text{ °C}$ under the pure nitrogen purging at 100 ml/min . The respective densities of pure polymeric and mixed-matrix membrane were determined using the Archimedes principle as described in Section 7.2.5. The mechanical test of the pure polymer and mixed-matrix membrane was conducted using tensile force tester (Zwick/Roell Z0.5) under ambient humidity ($R_H \approx 80\%$), which follows ASTM D 882 as the testing protocol for the flat sheet membrane.

8.2.6 Mixture gas permeation test and gas adsorption analysis

The mixture gas permeation test was conducted using constant pressure-variable volume system that was developed by GTR Tec Corporation. All the measurement conditions and procedures remain the same as described in Section 7.2.6, with the feed gas used in this study is CO_2/N_2 mixture (20:80) which was purchased from Airliquide.

On the other hand, the solubility-diffusivity behaviour of the polymeric membrane and mixed-matrix membrane was determined by measuring the CO₂ and N₂ adsorption isotherm, by using the volumetric gas sorption analyser (Quantachrome, isorbHP1). Similarly, the membranes were activated at the same condition (annealing condition) as described above. The CO₂ and N₂ adsorption at specified pressure (0.2 bar and 0.8 bar respectively) can be determined via interpolation. The solubility and diffusivity of CO₂ and N₂ of the respective membranes, S can be calculated by using the method as described in Section 7.2.7 (**Equation 7-1**).

8.3 Results and discussion

8.3.1 Synthesis of HKUST-1 and amine-functionalized HKUST-1 nanocrystals

Figure 8-2 (a) PXRD; (b) N₂ physisorption isotherm (adsorption and desorption branch are indicated as open and closed symbol respectively); (c) FTIR and (d) TGA of HKUST-1 and amine-functionalized HKUST-1

The overall crystallinity of HKUST-1 nanocrystals was first identified using powdered X-ray diffraction (PXRD), as shown in **Figure 8-2 (a)**. The corresponding diffraction peaks are generally identical to the results reported in the literature [175]. After such verification, amine-functionalization of HKUST-1 was conducted using a post-synthetic approach (as indicated in the experimental section). As observed from the PXRD pattern, amine-functionalization process does not destroy the overall crystallinity of the sample, although the overall peak intensity decreased as the amine content increased. The N₂ physisorption measurement at 77 K (**Figure 8-2 (b)**) shows that pristine HKUST-1 nanocrystals demonstrate high N₂ sorption at low-pressure region. This results also indicates the presence of large micropore volume in the HKUST-1 nanocrystal sample, as shown in **Table 8-1**. However, after incorporating amines into the framework, the overall porosity can be expected to decrease. Indeed, according to the N₂ physisorption measurement, the overall porosity of the HKUST-1-*x*NH₂ decreases upon introducing the amine group. In particular, when the percentage of amine that added into the suspension exceeds 50%, N₂ molecules hardly entered the pores of the resulting amine-HKUST-1. As evidenced by the elemental analysis in **Table 8-2**, the amount of amine did not increase after this level of loading. It can be observed that the overall structure (presence of Cu₂(COO)₄ paddle wheel) remains intact after amine was added, based on the FT-IR spectrum (**Figure 8-2 (c)**). However, the thermal stability of HKUST-1 nanocrystals indicates that the structure is thermally stable up till 350 °C. Incorporating the amines led to a small decline in the thermal stability (300 °C) (**Figure 8-2 (d)**). As mentioned in the introduction, fabricating thin, dense mixed-matrix membranes requires the utilization of small crystals. Thus, the morphologies of the HKUST-1-*x*NH₂ crystals was observed through the FESEM images (**Figure 8-3**). As expected, the particle size of the HKUST-1-*x*NH₂ synthesised was estimated to be

approximately 200 to 300 nm. Thus, selecting the most appropriate amine-functionalized filler for gas separation process were conducted by verifying the CO₂ and N₂ adsorption of HKUST-1-*x*NH₂ crystals.

Table 8-1 Surface areas and pore volumes of HKUST-1 and amine-functionalized HKUST-1 nanocrystals (HKUST-1-*x*NH₂) computed based on N₂ physisorption at 77 K

Sample	S _{BET} ^[a] (m ² /g)	S _{LANG} ^[a] (m ² /g)	S _{micro} ^[b] (m ² /g)	V _{micro} ^[b] (cc/g)
HKUST-1-0NH ₂	1165	1722	1114	0.580
HKUST-1-25NH ₂	567	597	548	0.216
HKUST-1-50NH ₂	19	28	10	0.005
HKUST-1-75NH ₂	18	35	13	0.002
HKUST-1-100-NH ₂	15	23	12	0.002

Note: [a] BET (S_{BET}) and Langmuir (S_{LANG}) surface area are obtained at P/P^o = 0.05 – 0.3. [b] Micropore surface area (S_{micro}) and volume (V_{micro}) are obtained using *t*-plot method at the pressure range of P/P^o = 0.4 – 0.6

Figure 8-3 FESEM images of (a) HKUST-1-0NH₂; (b) HKUST-1-25NH₂; (c) HKUST-1-50NH₂; (d) HKUST-1-75NH₂; (e) HKUST-1-100NH₂

Table 8-2 Elemental analysis of HKUST-1 and amine-functionalized HKUST-1 nanocrystals

Sample	C (%)	H (%)	N (%)
HKUST-1-0NH₂	35.81	3.368	0.323
HKUST-1-25NH₂	41.50	2.448	3.752
HKUST-1-50NH₂	43.82	2.649	5.015
HKUST-1-75NH₂	44.06	2.634	4.198
HKUST-1-100-NH₂	42.11	2.590	5.485

8.3.2 CO₂ and N₂ adsorption of HKUST-1 and amine-functionalized HKUST-1 nanocrystals

Figure 8-4 (a) CO₂ and (b) N₂ adsorption of HKUST-1-*x*NH₂ nanocrystals at 35 °C; (c) IAST CO₂/N₂ selectivity at 35 °C under 1 bar CO₂/N₂ feed pressure under the ratio of 20/80.

The CO₂ and N₂ adsorption isotherm of HKUST-1 and amine-functionalized HKUST-1 nanocrystals were conducted at 35 °C, which the result are summarized as shown in **Figure 8-3 (a, b)**. Based on the adsorption isotherm, both the pristine and amine-functionalized HKUST-1 preferentially adsorb CO₂ over N₂ due to its higher polarizability and quadrupole moment [3]. The coordinatively unsaturated open metal sites or amines in the HKUST-1-*x*NH₂ crystals could serve as binding sites for CO₂. Adding the amine group is feasible for CO₂ adsorption at low partial pressure, as reported in several studies [16, 198, 205]. Nevertheless, incorporating amines sacrificed

the surface area (**Table 8-1**) of the HKUST-1 crystals, resulting in a decreased CO₂ adsorption in the high-pressure region. Meanwhile, N₂ uptake was gradually decreased as amine loading increased. Overall, the results suggest that amine-functionalized HKUST-1 crystals have the potential utility in low pressure CO₂/N₂ separation, such as post-combustion CO₂ capture. Further evaluation using IAST selectivity analysis, plotted in **Figure 8-3 (c)**, indicated the superior CO₂/N₂ selectivity of HKUST-1 compared to the bare framework (HKUST-1-0NH₂). Hence, based on these results, two different fillers (HKUST-1-0NH₂ and HKUST-1-25NH₂) were selected to be incorporated in the mixed-matrix membrane so as to investigate the gas permeation performance, based on the selection of the most optimal amine loading into the HKUST-1 framework in terms of CO₂ adsorption (at 0.2 bar) and CO₂/N₂ selectivity.

8.3.3 Fabrication of mixed-matrix membrane

Figure 8-5 FESEM images of mixed-matrix membrane for (a, b) 10 wt% HKUST-1-0NH₂ with Matrimid; (c, d) 20 wt% HKUST-1-0NH₂ with Matrimid; (e, f) 10 wt% HKUST-1-25NH₂ with Matrimid; (g, h) 20 wt% HKUST-1-25NH₂ with Matrimid

In this work, a commercial polymer (Matrimid), that has been utilized in the gas separation membrane was used as the polymer matrices for the fabrication of mixed-matrix membrane. Mixed-matrix membranes containing 10 wt% and 20 wt% HKUST-1-0NH₂ and HKUST-1-25NH₂ were developed and the morphologies of the respective membranes were observed using FESEM (**Figure 8-5**). In general, typical morphology that was commonly identified in mixed-matrix membranes containing zeolites (*sieve-in-a-cage*) was not detected in this work [151, 200, 204]. In general, the presence of organic moieties and amines in the HKUST-1-*x*NH₂ allows for a better compatibility between the filler and polymer. This is further assisted with the creation of small particle size to increase the interfacial area between the filler and polymer. The properties of the mixed-matrix membranes were further analysed using TGA analysis. The incorporation

of the fillers does not affect the thermal stability of the polymer (**Figure 8-6**). However, a mechanical test of the mixed-matrix membrane has clearly verified by its feasibility of amine-impregnated HKUST-1 in enhancing the mechanical strength as compared to its bare framework (HKUST-1-0NH₂), despite the overall mechanical stability being a slightly lower than that of its nascent polymer (**Table 8-3**).

Figure 8-6 TGA analysis of 10 wt% and 20 wt% (a) HKUST-1-0NH₂ and (b) HKUST-1-25NH₂, using Matrimid as the polymer matrix

Table 8-3 Mechanical test of pure polymer and mixed-matrix membrane

Sample	Tensile Strength (MPa)	Young Modulus (MPa)	Elongation at break (%)
Matrimid	2321 ± 35	93 ± 4	6.42 ± 0.75
Matrimid + 10 wt% HKUST-1-0NH ₂	2201 ± 207	69 ± 4	4.34 ± 0.30
Matrimid + 20 wt% HKUST-1-0NH ₂	2292 ± 141	58 ± 5	3.45 ± 0.04
Matrimid + 10 wt% HKUST-1-25NH ₂	2243 ± 118	79 ± 6	4.99 ± 0.74
Matrimid + 20 wt% HKUST-1-25NH ₂	2184 ± 195	65 ± 6	3.14 ± 0.09

8.3.4 Gas permeation properties

Table 8-4 Permeation results of pure polymer and mixed-matrix membrane under 1 bar CO₂/N₂ mixture (20/80) at 35 °C

Membrane	CO ₂ permeability (barrer)	CO ₂ /N ₂ selectivity
----------	---------------------------------------	---

Matrimid	10.4 ± 0.06	31.0 ± 2.95
Matrimid + 10 wt% HKUST-1-0NH₂	15.5 ± 1.70	32.3 ± 0.20
Matrimid + 20 wt% HKUST-1-0NH₂	22.2 ± 3.40	33.8 ± 3.37
Matrimid + 10 wt% HKUST-1-25NH₂	12.3 ± 0.47	39.4 ± 0.83
Matrimid + 20 wt% HKUST-1-25NH₂	13.0 ± 0.17	42.7 ± 0.97

The gas permeation properties of membranes were measured at 35 °C under 1 bar upstream pressure containing CO₂/N₂ in a 20/80 mixture, as shown in **Table 8-4**. In general, the incorporation of HKUST-1-0NH₂ enhances the overall CO₂ permeability compared to CO₂/N₂ selectivity. This can be observed through the incorporation of 20 wt% HKUST-1 in mixed-matrix membrane, which induces a 113% and 9% increase in CO₂ permeability and CO₂/N₂ selectivity. This is attributed to the presence of large pore windows (9 x 9 Å) in HKUST-1 that allows the ease of transport of gas molecules with minimized resistance, where this result is consistent with the study as described in Chapter 7 where the HKUST-1 nanocrystals is feasible in improving O₂ permeability and CO₂ permeability in mixed-matrix membranes. Nevertheless, the overall CO₂/N₂ selectivity of mixed-matrix membrane is generally comparable to the nascent membrane, indicating that incorporating HKUST-1 is unable to enhance the sufficiently enhance the overall performance in a favourable direction. Thus, amine-functionalized HKUST-1 (HKUST-1-25NH₂) was incorporated into the Matrimid membrane to verify its performance. Based on the gas permeation data, CO₂/N₂ selectivity improved by 38% compared to that of the pristine membrane. This result is consistent with the increase in CO₂/N₂ selectivity with the incorporation of amines into the framework (**Figure 8-3 (c)**).

Subsequently, the improvement in the CO₂/N₂ separation of the mixed-matrix membranes were conducted further with the quantifications of the diffusivity and solubility of CO₂ and N₂ in mixed-matrix membranes. Hence, the CO₂ and N₂ adsorption properties of pure polymeric membrane and mixed-matrix membrane were determined at 35 °C, as shown in **Figure 8-6 (a-c)**. The overall calculation of CO₂ and N₂ diffusivity and solubility were calculated and summarized in **Table 8-5**. The isotherm profile shows that at the point of interest (0.2 bar of CO₂), the CO₂ adsorption of the mixed-matrix membrane that contains 20 wt% HKUST-1-0NH₂ is comparatively higher than its nascent membranes, whereas the CO₂ adsorption of mixed-matrix membrane that contains 20 wt% HKUST-1-25NH₂ were remained comparable. This can be shown by its marginal (4.5%) change in CO₂ solubility in comparison to pure polymeric membrane. This is possibly attributed to a drastic decrease in the accessible surface area as amine was incorporated into HKUST-1 nanocrystals which exhibits high porosities (**Figure 8-2 (b)**). Nevertheless, substantial decrease in N₂ diffusivity and solubility of mixed-matrix membrane that utilized amine-functionalized HKUST-1 nanocrystals can be observed, leading to an increase in CO₂/N₂ diffusion selectivity by 38%.

Figure 8-7 CO₂ and N₂ adsorption isotherm of (a) Matrimid; (b) Matrimid + 20 wt% HKUST-1-0NH₂; (c) Matrimid + 20 wt% HKUST-1-25NH₂ at 35 °C

Table 8-5 CO₂ and N₂ solubility and diffusivity data for pure polymer and mixed-matrix membranes at 35 °C under 1 bar of total feed pressure (0.2 bar for CO₂ and 0.8 bar for N₂)

Membrane	Density (g/cm ³)	CO ₂ solubility, (mol/m ³ -bar)	CO ₂ diffusivity, $\times 10^{-13}$ (m ² /s)	N ₂ solubility (mol/m ³ -bar)	N ₂ diffusivity, $\times 10^{-13}$ (m ² /s)
Matrimid	1.22	841	0.940	15.2	1.68
Matrimid + 20 wt% HKUST-1-0NH ₂	1.29	970	1.74	19.2	2.61
Matrimid + 20 wt% HKUST-1-25NH ₂	1.33	803	1.23	14.6	1.59

8.4 Conclusion

Amine-functionalized HKUST-1 nanocrystals were synthesized via a post-synthetic approach and used to fabricate mixed-matrix membranes for CO₂/N₂ separation. Incorporating pristine HKUST-1 nanocrystals escalated CO₂ permeability significantly without having any positive effect on CO₂/N₂ selectivity. In contrast, the amine-functionalized HKUST-1 nanocrystals enhanced the CO₂/N₂ selectivity (by as much as 38%) along with the gas permeability, which is a highly desirable performance enhancement. According to the detailed solubility-diffusivity analysis, the incorporation

of HKUST-1 nanocrystals increased the overall diffusivity and solubility of CO₂ and N₂ in mixed-matrix membrane in a non-selective manner. However, the amine-functionalized HKUST-1 was able to suppress the diffusivity and solubility of N₂ while increasing CO₂ diffusivity substantially. Our findings demonstrate that amine-functionalized HKUST-1 is feasible in improving the CO₂/N₂ separation performance of polymeric membrane while utilizing a facile, scalable membrane fabrication method.

8.5 Declaration

The work presented in this chapter has been submitted, with the manuscript is under review.

C. Y. Chuah, W. Li, S.A.S.C Samarasinghe, G. S. M. D. P. Sethunga, T-H. Bae, Enhancing the CO₂ separation performance of polymer membranes via the incorporation of amine-functionalized HKUST-1 nanocrystals, *manuscript under review*.

Chapter 9 Conclusions

9.1 Overview

Nanoporous materials and membranes has been well-presented as one of the feasible methods that can be utilized in gas adsorption and separation processes in view of the unique physiochemical and structural properties in these materials. Thus, research on these categories has demonstrated considerable interest among researchers worldwide. As a summary, this thesis presents the potential application of nanoporous materials and membranes in gas separation process, where the main empirical findings and future work are summarized in the subsequent section.

9.2 Summary of empirical findings

The major findings and conclusions were summarized and concluded as follows. A comparison of porous materials and membranes that is reported in this thesis is summarized in **Table 9-1**.

- (1) The creation of hierarchical microporous-mesoporous structure is capable of improving the overall adsorption kinetics, particularly for the case of SF₆ which possess larger kinetic diameter (5.13 Å) as compared to CO₂ (3.30 Å). Hence, addition of mesoporosity into the adsorbents facilitates the transport of SF₆ molecules effectively to the available active sites, thus allowing a shorter equilibration time during the adsorption process.
- (2) While the creation of mesoporosity allows an enhancement of the SF₆ adsorption kinetics, such effect will be much more substantial if the micropore size is comparable to the kinetic diameter of SF₆. For instance, the incorporation of mesoporosity in zeolite MFI (with the micropore size of about 5 Å) accelerates the equilibration process, from ca. 3 minutes in bulk zeolite MFI (MFI-1) to ca.

10 s in hierarchical zeolite MFI (MFI-2). The effect of mesoporosity can be less pronounced if the micropore size is sufficiently large (e.g. HKUST-1 (9 x 9 Å) and PPN framework (12 Å)).

- (3) It has been well-presented that permeability-selectivity trade-off in polymeric membrane has limited the enhancement in the overall gas separation process. This is attributed to the fact that the gas transport properties of gases are mainly dominated by solution-diffusion mechanism. In view of the development of molecular sieve membranes that are made up of pure zeolite and metal-organic framework is difficult to be scaled up into large membrane modules, mixed-matrix membrane using nanoporous materials as the filler is considered to be the most feasible option. In this study, we have observed that the incorporation of nanoporous materials is feasible in enhancing the overall gas permeability without sacrificing the intrinsic membrane selectivity of selected gas pair (O₂/N₂, CO₂/CH₄, CO₂/N₂).

Table 9-1 Summary of the major properties of the microporous materials and membranes that is reported in this thesis

Parameters Chapter	Major Findings	Merits	Limitations
Chapter 3 (Hierarchical Zeolite MFI)	<ul style="list-style-type: none"> Two types of zeolite MFI (MFI-1 and MFI-2) with high crystallinity have been developed. 	<ul style="list-style-type: none"> MFI-2 shows improved adsorption kinetics (short saturation time). MFI-2 shows lower SF₆ binding energy. 	<ul style="list-style-type: none"> MFI-2 shows lower SF₆ adsorption as compared to MFI-1 under same condition. SF₆ adsorption of MFI is lower than HKUST-1 (in Chapter 4)
Chapter 4 (Hierarchical HKUST-1)	<ul style="list-style-type: none"> Three types of HKUST-1 structure (with different pore size and particle size) have been developed 	<ul style="list-style-type: none"> HKUST-1c shows improved adsorption kinetics and highest SF₆ adsorption HKUST-1c shows lower SF₆ binding energy as compared to other HKUST-1 series 	<ul style="list-style-type: none"> The SF₆ equilibration time of HKUST-1c is longer than MFI-2. HKUST-1c is generally shows weaker hydrolytic stability than zeolite, despite the presence of water is minimal in SF₆/N₂ separation.
Chapter 5 (Co-MOF-74 Hollow Nanorods)	<ul style="list-style-type: none"> Two types of Co-MOF-74 (bulk and hollow nanorods) have been developed 	<ul style="list-style-type: none"> Co-MOF-74 hollow nanorods show improved performance in dynamic CO₂/N₂ 	<ul style="list-style-type: none"> Co-MOF-74 hollow nanorods show reduced crystallinity and porosity than Co-MOF-74 bulk rods.

		<p>separation process (breakthrough and chromatographic separation).</p> <ul style="list-style-type: none"> • Creation of hollow Co-MOF-74 is verified from FESEM and TEM images 	<ul style="list-style-type: none"> • Co-MOF-74 hollow nanorods show reduced CO₂ adsorption as compared to Co-MOF-74 bulk rods.
<p>Chapter 6 (Hierarchical Porous Polymers)</p>	<ul style="list-style-type: none"> • Three types of hierarchical porous polymers with various porosities have been developed. 	<ul style="list-style-type: none"> • PPN1 shows improved SF₆/N₂ selectivity as compared to PPN0 and PPN2. • PPN1 shows clear segregation between SF₆ and N₂ in chromatographic separation process. • PPN_x possess stronger stability towards chemical degradation and humidity as compared to MOFs (Chapter 4, 5) 	<ul style="list-style-type: none"> • SF₆ adsorption performance of PPN_x series is generally lower than zeolite MFI and HKUST-1. • PPN1 shows reduced porosity properties as compared to PPN0
<p>Chapter 7 (MMM containing HKUST-1)</p>	<ul style="list-style-type: none"> • HKUST-1 nanocrystals have been successfully synthesised. • MMM with improved gas separation performance has been reported. 	<ul style="list-style-type: none"> • HKUST-1 nanocrystals are feasible in improving O₂ and CO₂ permeability in MMM without sacrificing membrane's selectivity. 	<ul style="list-style-type: none"> • Large pore size of HKUST-1 nanocrystals has led to its difficulty in improving membrane's selectivity. • The overall membrane performance is difficult to surpass the upper bound limit due to the intrinsic properties of the polymers that is selected in this work.
<p>Chapter 8 (MMM containing amine-functionalized HKUST-1)</p>	<ul style="list-style-type: none"> • Amine functionalized HKUST-1 nanocrystals have been successfully synthesised. • MMM with desirable performance has been reported. 	<ul style="list-style-type: none"> • HKUST-1-0NH₂ in MMM is feasible in improving CO₂ permeability. • HKUST-1-25NH₂ in MMM is feasible in improving CO₂/N₂ selectivity. 	<ul style="list-style-type: none"> • The presence of amines in HKUST-1-25NH₂ reduces the overall CO₂ adsorption substantially as compared to HKUST-1-0NH₂. • The overall membrane performance is difficult to surpass the upper bound limit due to the intrinsic properties of the polymers that is selected in this work.

9.3 Recommendations and future works

The quest of developing suitable nanoporous materials and membranes for gas separation process has been the major focus of attention as these materials has shown its capability in the eventual utilization for the industrial operation. As research progresses, the application of nanoporous materials and membranes has been expanded to other gas separation processes. Thus, the following sections are aimed to provide several insights for subsequent researches to expand the potential of these materials on other gas separation application.

- (1) The utilization of nanoporous materials as a filler in mixed-matrix membrane has been generally considered to be the most technically viable option at current stage due to the fabrication of large-scale as well as high packing density of membrane module is much more feasible as compared to the molecular sieve membranes that are made up of purely nanoporous materials. As a whole, mixed-matrix membrane is an effective way to alter the transport behaviour of the polymer matrix with a simple concept of dispersing the filler into the polymer phase. Depending the properties of the filler, the enhancement in either permeability, selectivity or both can be expected, leading to its propensity to eliminate the trade-off relation between permeability-selectivity relation in pure polymeric membrane as described by Robeson [42, 43] (**Figure 9-1**). Nonetheless, it is important to note that the fabrication of thin-dense mixed-matrix membranes or ultra-thin skin layer for the composite membrane fabrication requires the filler to be on a nanoscale range to as to reduce the propensity of particle agglomeration and non-ideal interfacial morphologies. Besides, it has been observed that leveraging the filler materials into other shapes or morphologies is feasible in opening new opportunities for scalable fabrication

of composite membranes. For instance, the usage of two-dimensional (2D) nanomaterials (e.g. layered silicate, 2D MOFs) are feasible to enhance the gas selectivity because tortuous diffusion pathway for the gas molecules can be expected. With the correct choice of the polymeric membrane and 2D nanomaterials, the overall performance can be compelling enough to drive the performance to exceed the upper bound limit (Strategy 2, **Figure 9-1 (b)**).

Figure 9-1 (a) Permeability-selectivity plot that highlights the performance of different types of membrane; **(b)** CO_2/CH_4 Robeson plot demonstrates plausible strategies in realizing the membranes with industrially attractive performance. Conventional polymers are membranes that demonstrate potential in terms of effective commercialization for large-scale industrial use for gas separation process.

(2) Nevertheless, despite results have shown that composite membranes for gas separation process has been promising based on the gas separation performance, no commercial products that is related to composite membrane is available in the market at present time. This is attributed to its technical challenges in developing high quality filler materials (which must be developed into large-scale with minimal batch-by-batch variation) together with the development of thin film composite membranes or dual-layer hollow fiber membranes without appreciable defects. On the other hand, the stability of the fillers under long-term operation is still generally lacking in literature studies. Thus, despite the chasing of the membrane separation performance beyond the Robeson upper bound is

important, it is still necessary to address the current hurdles that have been facing, that is developing composite membranes into large-scale modules.

- (3) On the other hand, the capability of nanoporous materials to allow preferential adsorption towards polarizable gases has been expanded to hydrocarbon separations (olefin/paraffin or acetylene-based separation) separation in view of its high polarizabilities in these gases. However, in this aspect, studies on conventional MOFs such as M-MOF-74, HKUST-1 and others which contains coordinatively unsaturated open metal sites that is capable of performing reversible interaction with polarizable molecules is generally difficult to achieve an extraordinary high selectivity as compared to CO_2/N_2 or SF_6/N_2 separation, where clear distinction in terms of polarizabilities can be expected. Till date, there have been limited nanoporous materials that is feasible in demonstrating high selectivity (ca. 5 or less), as shown in **Table 9-2**. In recent study, the study of UTSA-300a has demonstrated promising gas separation performance in view of its high $\text{C}_2\text{H}_2/\text{CO}_2$ and $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ selectivity [79]. It has been postulated that the strong hydrogen bonding between UTSA-300a and C_2H_2 allows the structural change to be triggered to an open structure during C_2H_2 adsorption, while other gases (CO_2 and C_2H_4) are to be remained in a closed position. Nonetheless, in general, calculation of gas selectivity through IAST calculation should be taken extra care as the gate opening behaviour which has been observed in this framework may not reflect the actual separation behaviour in the dynamic breakthrough condition due to the gate opening behaviour through flexible MOF structure when gas mixture was subjected to the adsorbents.

Table 9-2 Comparison of C_2H_2 , CO_2 and C_2H_4 adsorption across commonly reported MOFs [80]

Sample	C ₂ H ₂ (cc/g)	CO ₂ (cc/g)	C ₂ H ₄ (cc/g)	V _{C₂H₂} / V _{CO₂}	V _{C₂H₂} / V _{C₂H₄}	Condition	Ref.
HKUST-1	201	113	-	1.78	-		[206]
JCM-1	76.5	38.1	35.7	2.01	2.14		[80]
MAF-2	70	19	-	3.68	-		[207]
MFM-188	232.6	120.7	-	1.93	-	C ₂ H ₂ : 295 K; CO ₂ : 298 K	[208]
Mg(HCOO) ₂	66	45	-	1.47	-		[209]
Mg-MOF-74	184.4	179.2	-	1.03	-		[179, 210]
M'-MOF-3a	42.6	-	9.0	-	4.73		[211]
NOTT-300	142	95.9	-	1.48	-	293 K	[212]
PCP-33	121.8	58.6	86.8	2.08	1.40		[213]
SIFSIX-1-Cu	190.4	107.9	92.1	1.74	2.07		[214]
SIFSIX-Cu- <i>i</i>	90.0	108.4	49.1	1.21	1.84		[214]
SIFSIX-3-Zn	81.5	57.0	50.2	1.43	1.62		[214]
UTSA-74-Zn	108.2	70.9	-	1.53	-	296 K	[215]
UTSA-100a	95.6	-	37.2	-	2.57	296 K	[216]
UTSA-300a	68.9	3.25	0.92	21.2	74.9		[79]
ZJU-8	194.7	103.9	-	1.87	-		[217]
ZJU-40	216.2	87.6	-	2.47	-		[218]

Note: All conditions are compared at 1 bar and 298 K except otherwise stated.

(4) Other than the application of nanoporous materials on other gas separation process, it is important to study the mixture gas adsorption under dynamic condition, particularly for the case post combustion CO₂ capture where water vapor was present in the feed. In general, a more generally accepted approach in the evaluation of the separation performance of mixture gas with two or more components under dynamic condition should be conducted via breakthrough measurement. It is determined by subjecting the interested test gas to the system where the outlet composition is monitored as a function of time, which can be detected using mass spectrometer or gas chromatography. Despite the performance of adsorbents under humid condition can be evaluated directly by subjecting the humid test gas, the breakthrough measurement can provide

misleading results if the measurement was not conducted appropriately. Particularly, the conclusion should not be drawn by conducting the breakthrough analysis based on the first cycle without repetitive adsorption-desorption cycling. This is because the initial position of the adsorbent can serve as the “drying agent” that will desiccate the humid gas mixture, leaving only the dry test gas to propagate through the adsorption cell [120, 193, 219-221]. Nevertheless, it should be well noted that even though the porous materials that had been screened using the current measurement protocol demonstrated reasonable performance in terms of CO₂ adsorption and stability in humid condition, a detailed cost analysis should be conducted so as to verify the practical feasibility of these materials in terms of replacing the conventional technologies (e.g. cryogenic distillation, swing adsorption) for gas adsorption process.

9.4 Outlook

All in all, nanoporous materials and membranes have showcased itself as the promising materials for gas separation processes. Despite this, the potential challenges in utilizing these materials in industrial gas separation process is still challenging by numerous practical limitations, namely the presence of H₂O as the impurities in the post-combustion CO₂ capture that can serve as the competitive adsorption with CO₂, limitation of the extraordinary desorption condition for effective removal of adsorbate during the repetitive adsorption-desorption cycling process as well as limited selectivity for molecules with similar polarizabilities. Hence, with the careful address of these challenges, the potential of nanoporous materials and membranes in industrial gas adsorption process can be realized in a not-too-distant future.

Chapter 10 List of References

- [1] C. J. King, *Separation processes*, 2nd ed.: Mineola, New York : Dover Publications, 2013.
- [2] R. T. Yang, *Adsorbents: fundamentals and applications*: New York : Wiley-Interscience, 2003.
- [3] 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.
- [4] D. S. Sholl and R. P. Lively, "Seven chemical separations: to change the world: purifying mixtures without using heat would lower global energy use, emissions and pollution--and open up new routes to resources," *Nature*, vol. 532, pp. 435-438, 2016.
- [5] B. Metz, O. Davidson, H. de Coninck, M. Loos, and L. Meyer, *IPCC special report on carbon dioxide capture and storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change* vol. 4: IPCC, Cambridge University Press: Cambridge, United Kingdom and New York, USA, 2005.
- [6] X. Fang, X. Hu, G. Janssens-Maenhout, J. Wu, J. Han, S. Su, *et al.*, "Sulfur hexafluoride (SF₆) emission estimates for China: an inventory for 1990–2010 and a projection to 2020," *Environ. Sci. Technol.*, vol. 47, pp. 3848-3855, 2013.
- [7] K. Tignor, A. M. SK Boschung, J. Nauels, Y. A. Xia, Bex, *et al.*, *The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change*: IPCC Climate Change, 2013.
- [8] P. Forster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. W. Fahey, *et al.*, "Changes in atmospheric constituents and in radiative forcing. Chapter 2," in

Climate Change 2007. The Physical Science Basis, ed New York: Cambridge University Press, 2007.

- [9] A. Ravishankara, S. Solomon, A. A. Turnipseed, and R. Warren, "Atmospheric lifetimes of long-lived halogenated species," *Science*, vol. 259, pp. 194-199, 1993.
- [10] D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon dioxide capture: prospects for new materials," *Angew. Chem. Int. Ed.*, vol. 49, pp. 6058-6082, 2010.
- [11] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, *et al.*, "Carbon dioxide capture in metal–organic frameworks," *Chem. Rev.*, vol. 112, pp. 724-781, 2011.
- [12] F. Bauer, T. Persson, C. Hulteberg, and D. Tamm, "Biogas upgrading–technology overview, comparison and perspectives for the future," *Biofuels, Bioprod. Biorefin.*, vol. 7, pp. 499-511, 2013.
- [13] G. Ankit and S. B. Aditya. (2017, May 18, 2019). *Carbon Capture And Storage Market Size By Technology*. Available: <https://www.gminsights.com/industry-analysis/carbon-capture-and-storage-market>
- [14] V. Scott, S. Gilfillan, N. Markusson, H. Chalmers, and R. S. Haszeldine, "Last chance for carbon capture and storage," *Nature Clim. Chang.*, vol. 3, p. 105, 2013.
- [15] 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.

- [16] Y. Yang, C. Y. Chuah, and T.-H. Bae, "Polyamine-appended porous organic polymers for efficient post-combustion CO₂ capture," *Chem. Eng. J.*, vol. 358, pp. 1227-1234, 2019.
- [17] H. M. Lee, M. B. Chang, and K. Y. Wu, "Abatement of sulfur hexafluoride emissions from the semiconductor manufacturing process by atmospheric-pressure plasmas," *J. Air Waste Manag. Assoc.*, vol. 54, pp. 960-970, 2004.
- [18] S. Sircar and T. Golden, "Purification of hydrogen by pressure swing adsorption," *Sep. Sci. Technol.*, vol. 35, pp. 667-687, 2000.
- [19] O. Yamamoto, T. Takuma, and M. Kinouchi, "Recovery of SF₆ from N₂/SF₆ gas mixtures by using a polymer membrane," *IEEE Electr. Insul. Mag.*, vol. 18, pp. 32-37, 2002.
- [20] K. Inami, Y. Maeda, Y. Habuchi, M. Yoshimura, S. Hamano, and H. Hama, "Problems of the application of N₂/SF₆ mixtures to gas - insulated bus," *Electr. Eng. Jpn.*, vol. 137, pp. 25-31, 2001.
- [21] I. Cha, S. Lee, J. D. Lee, G.-w. Lee, and Y. Seo, "Separation of SF₆ from gas mixtures using gas hydrate formation," *Environ. Sci. Technol.*, vol. 44, pp. 6117-6122, 2010.
- [22] M.-B. Kim, S.-J. Lee, C. Y. Lee, and Y.-S. Bae, "High SF₆ selectivities and capacities in isostructural metal-organic frameworks with proper pore sizes and highly dense unsaturated metal sites," *Micropor. Mesopor. Mater.*, vol. 190, pp. 356-361, 2014.
- [23] U.S. Energy Information Administration. (2016, January 29). *International Energy Outlook 2016*. Available: [http://www.eia.gov/forecasts/ieo/pdf/0484\(2016\).pdf](http://www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf)

- [24] British Petroleum (BP). (2017, January 27). *BP Statistical Review of World Energy June 2016*. Available: <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full-report.pdf>
- [25] 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.
- [26] C. E. Baukal Jr, *Oxygen-enhanced combustion*: CRC press, 2010.
- [27] A. Beltrame, P. Porshnev, W. Merchan-Merchan, A. Saveliev, A. Fridman, L. Kennedy, *et al.*, "Soot and NO formation in methane–oxygen enriched diffusion flames," *Combust. Flame*, vol. 124, pp. 295-310, 2001.
- [28] J. J. Murphy and C. R. Shaddix, "Combustion kinetics of coal chars in oxygen-enriched environments," *Combust. Flame*, vol. 144, pp. 710-729, 2006.
- [29] E. F. Da Silva and H. F. Svendsen, "Computational chemistry study of reactions, equilibrium and kinetics of chemical CO₂ absorption," *Int. J. Greenh. Gas Con.*, vol. 1, pp. 151-157, 2007.
- [30] E. Blanchon le Bouhelec, P. Mougin, A. Barreau, and R. Solimando, "Rigorous modeling of the acid gas heat of absorption in alkanolamine solutions," *Energy Fuels*, vol. 21, pp. 2044-2055, 2007.
- [31] A. Takase, H. Kanoh, and T. Ohba, "Wide carbon nanopores as efficient sites for the separation of SF₆ from N₂," *Sci. Rep.*, vol. 5, p. 11994, 2015.
- [32] R. Cornelissen and G. Hirs, "Exergy analysis of cryogenic air separation," *Energy Convers. Manag.*, vol. 39, pp. 1821-1826, 1998.

- [33] Y. Kansha, A. Kishimoto, T. Nakagawa, and A. Tsutsumi, "A novel cryogenic air separation process based on self-heat recuperation," *Sep. Purif. Technol.*, vol. 77, pp. 389-396, 2011.
- [34] R. Boehme, J. Parise, and R. P. Marques, "Simulation of multistream plate-fin heat exchangers of an air separation unit," *Cryogenics*, vol. 43, pp. 325-334, 2003.
- [35] A. Sandeep, S. James, and S. Ganesan, "Emerging and Existing Oxygen Production Technology Scan and Evaluation," COSIA, GHG Working Group 2018.
- [36] C. W. Skarstrom, "Method and apparatus for fractionating gaseous mixtures by adsorption," United States of America Patent 2,944,627, 1960.
- [37] M. P. G. De and D. Daniel, "Process for separating a binary gaseous mixture by adsorption," United States of America Patent 3,155,468, 1964.
- [38] 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.
- [39] D. Ruthven and S. Farooq, "Air separation by pressure swing adsorption," *Gas Sep. Purif.*, vol. 4, pp. 141-148, 1990.
- [40] 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.
- [41] D. Cao and S. Sircar, "Heat of adsorption of pure sulfur hexafluoride on micro-mesoporous adsorbents," *Adsorption*, vol. 7, pp. 73-80, 2001.

- [42] L. M. Robeson, "The upper bound revisited," *J. Membr. Sci.*, vol. 320, pp. 390-400, 2008.
- [43] L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes," *J. Membr. Sci.*, vol. 62, pp. 165-185, 1991.
- [44] 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.
- [45] J. Seader, E. J. Henley, and D. K. Roper, *Separation process principles: chemical and biochemical operations*: John Wiley and Sons, Inc, 2011.
- [46] E. R. Parnham and R. E. Morris, "Ionothermal synthesis of zeolites, metal–organic frameworks, and inorganic–organic hybrids," *Acc. Chem. Res.*, vol. 40, pp. 1005-1013, 2007.
- [47] N. Takako, I. Takuji, A. Chie, H. Yasuhisa, K. Yoshimichi, and H. Takaaki, "Solvothermal Synthesis of LIT-type Zeolite," *Cryst Growth Des.*, vol. 12, pp. 1752-1761, 2012.
- [48] L. Ren, Q. Wu, C. Yang, L. Zhu, C. Li, P. Zhang, *et al.*, "Solvent-free synthesis of zeolites from solid raw materials," *J. Am. Chem. Soc.*, vol. 134, pp. 15173-15176, 2012.
- [49] C. S. Cundy and P. A. Cox, "The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism," *Micropor. Mesopor. Mater.*, vol. 82, pp. 1-78, 2005.
- [50] S. M. Auerbach, K. A. Carrado, and P. K. Dutta, *Handbook of zeolite science and technology*: CRC press, 2003.

- [51] 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. 1910-1917, 2009.
- [52] S. Prodinger, R. S. Vemuri, T. Varga, B. P. McGrail, R. K. Motkuri, and M. A. Derewinski, "Impact of chabazite SSZ-13 textural properties and chemical composition on CO₂ adsorption applications," *New J. Chem.*, vol. 40, pp. 4375-4385, 2016.
- [53] A. Zukal, J. Pawlesa, and J. Čejka, "Isosteric heats of adsorption of carbon dioxide on zeolite MCM-22 modified by alkali metal cations," *Adsorption*, vol. 15, pp. 264-270, 2009.
- [54] G. Calleja, J. Pau, and J. Calles, "Pure and multicomponent adsorption equilibrium of carbon dioxide, ethylene, and propane on ZSM-5 zeolites with different Si/Al ratios," *J. Chem. Eng. Data*, vol. 43, pp. 994-1003, 1998.
- [55] J. Shang, G. Li, R. Singh, Q. Gu, K. M. Nairn, T. J. Bastow, *et al.*, "Discriminative separation of gases by a “molecular trapdoor” mechanism in chabazite zeolites," *J. Am. Chem. Soc.*, vol. 134, pp. 19246-19253, 2012.
- [56] M. Taramasso, G. Perego, and B. Notari, "Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides," United States of America Patent 4,410,501, 1983.
- [57] S. Mirajkar, A. Thangaraj, and V. Shiralkar, "Sorption properties of titanium silicate molecular sieves," *J. Phys. Chem.*, vol. 96, pp. 3073-3079, 1992.
- [58] S. M. Kuznicki, "Large-pored crystalline titanium molecular sieve zeolites," United States of America Patent 4,853,202, 1989.

- [59] 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," *Prog. Polym. Sci.*, vol. 39, pp. 817-861, 2014.
- [60] S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacubinas, C. M. Braunbarth, *et al.*, "A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules," *Nature*, vol. 412, p. 720, 2001.
- [61] Z. Lin, J. Rocha, A. Navajas, C. Téllez, J. n. Coronas, and J. Santamaría, "Synthesis and characterisation of titanosilicate ETS-10 membranes," *Micropor. Mesopor. Mater.*, vol. 67, pp. 79-86, 2004.
- [62] R. Marathe, S. Farooq, and M. Srinivasan, "Modeling gas adsorption and transport in small-pore titanium silicates," *Langmuir*, vol. 21, pp. 4532-4546, 2005.
- [63] S. Park, S. Cho, W. Ahn, and W. Kim, "Adsorption characteristics of divalent cation-exchanged ETS-4s pretreated at different temperature," *Micropor. Mesopor. Mater.*, vol. 145, pp. 200-204, 2011.
- [64] I. Tiscornia, I. Kumakiri, R. Bredesen, C. Téllez, and J. Coronas, "Microporous titanosilicate ETS-10 membrane for high pressure CO₂ separation," *Sep. Purif. Technol.*, vol. 73, pp. 8-12, 2010.
- [65] G. Bellussi, R. Millini, P. Pollesel, and C. Perego, "Zeolite science and technology at Eni," *New J. Chem.*, vol. 40, pp. 4061-4077, 2016.
- [66] 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?," *J. Am. Chem. Soc.*, vol. 134, pp. 15016-15021, 2012.

- [67] K. C. Stylianou and W. L. Queen, "Recent advances in carbon capture with metal–organic frameworks," *CHIMIA Int. J. Chem.*, vol. 69, pp. 274-283, 2015.
- [68] J. Qian, F. Sun, and L. Qin, "Hydrothermal synthesis of zeolitic imidazolate framework-67 (ZIF-67) nanocrystals," *Mater. Lett.*, vol. 82, pp. 220-223, 2012.
- [69] L. G. Qiu, T. Xu, Z. Q. Li, W. Wang, Y. Wu, X. Jiang, *et al.*, "Hierarchically Micro - and Mesoporous Metal – Organic Frameworks with Tunable Porosity," *Angew. Chem. Int. Ed.*, vol. 47, pp. 9487-9491, 2008.
- [70] M. Li and M. Dinca, "Reductive electrosynthesis of crystalline metal–organic frameworks," *J. Am. Chem. Soc.*, vol. 133, pp. 12926-12929, 2011.
- [71] 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," *J. Am. Chem. Soc.*, vol. 131, pp. 16000-16001, 2009.
- [72] W.-J. Son, J. Kim, J. Kim, and W.-S. Ahn, "Sonochemical synthesis of MOF-5," *Chem. Commun.*, pp. 6336-6338, 2008.
- [73] M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann, and F. Emmerling, "Mechanochemical synthesis of metal-organic frameworks: a fast and facile approach toward quantitative yields and high specific surface areas," *Chem. Mater.*, vol. 22, pp. 5216-5221, 2010.
- [74] O. M. Yaghi, M. O'keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, and J. Kim, "Reticular synthesis and the design of new materials," *Nature*, vol. 423, p. 705, 2003.

- [75] B. Chen, X. Wang, Q. Zhang, X. Xi, J. Cai, H. Qi, *et al.*, "Synthesis and characterization of the interpenetrated MOF-5," *J. Mater. Chem.*, vol. 20, pp. 3758-3767, 2010.
- [76] P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, *et al.*, "Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation," *Nature*, vol. 495, p. 80, 2013.
- [77] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'keeffe, *et al.*, "Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage," *Science*, vol. 295, pp. 469-472, 2002.
- [78] C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, *et al.*, "An explanation for the very large breathing effect of a metal–organic framework during CO₂ adsorption," *Adv. Mater.*, vol. 19, pp. 2246-2251, 2007.
- [79] R.-B. Lin, L. Li, H. Wu, H. Arman, B. Li, R.-G. Lin, *et al.*, "Optimized Separation of Acetylene from Carbon Dioxide and Ethylene in a Microporous Material," *J. Am. Chem. Soc.*, vol. 139, pp. 8022-8028, 2017.
- [80] J. Lee, C. Y. Chuah, J. Kim, Y. Kim, N. Ko, Y. Seo, *et al.*, "Separation of Acetylene from Carbon Dioxide and Ethylene by a Water Stable Microporous Metal - organic Framework with Aligned Imidazolium Groups inside the Channels," *Angew. Chem. Int. Ed.*, vol. 130, pp. 7955-7999, 2018.
- [81] S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, *et al.*, "Adsorption properties of HKUST-1 toward hydrogen and other small molecules monitored by IR," *Phys. Chem. Chem. Phys.*, vol. 9, pp. 2676-2685, 2007.

- [82] S. S.-Y. Chui, S. M.-F. Lo, J. P. Charmant, A. G. Orpen, and I. D. Williams, "A chemically functionalizable nanoporous material $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$," *Science*, vol. 283, pp. 1148-1150, 1999.
- [83] A. O. z. r. Yazaydın, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, *et al.*, "Screening of metal–organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach," *J. Am. Chem. Soc.*, vol. 131, pp. 18198-18199, 2009.
- [84] S. Couck, J. F. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An amine-functionalized MIL-53 metal–organic framework with large separation power for CO_2 and CH_4 ," *J. Am. Chem. Soc.*, vol. 131, pp. 6326-6327, 2009.
- [85] J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. van Klink, and F. Kapteijn, "Amino-based metal-organic frameworks as stable, highly active basic catalysts," *J. Catal.*, vol. 261, pp. 75-87, 2009.
- [86] T. M. McDonald, D. M. D'Alessandro, R. Krishna, and J. R. Long, "Enhanced carbon dioxide capture upon incorporation of $\text{N,N}'$ -dimethylethylenediamine in the metal – organic framework CuBTtri," *Chem. Sci.*, vol. 2, pp. 2022-2028, 2011.
- [87] T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong, and J. R. Long, "Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal–organic framework mmen- $\text{Mg}_2(\text{dobpdc})$," *J. Am. Chem. Soc.*, vol. 134, pp. 7056-7065, 2012.
- [88] M. Aubrey, R. Ameloot, B. M. Wiers, and J. R. Long, "Metal–organic frameworks as solid magnesium electrolytes," *Energy Environ. Sci.*, vol. 7, pp. 667-671, 2014.

- [89] 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," *Proc. Natl. Acad. Sci. USA*, vol. 103, pp. 10186-10191, 2006.
- [90] M. S. Denny Jr, J. C. Moreton, L. Benz, and S. M. Cohen, "Metal–organic frameworks for membrane-based separations," *Nat. Rev. Mater.*, vol. 1, p. 16078, 2016.
- [91] 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.*, vol. 47, pp. 2071-2073, 2011.
- [92] B. Chen, Z. Yang, Y. Zhu, and Y. Xia, "Zeolitic imidazolate framework materials: recent progress in synthesis and applications," *J. Mater. Chem. A*, vol. 2, pp. 16811-16831, 2014.
- [93] H. Hayashi, A. P. Cote, H. Furukawa, M. O’Keeffe, and O. M. Yaghi, "Zeolite A imidazolate frameworks," *Nat. Mater.*, vol. 6, p. 501, 2007.
- [94] N. T. Nguyen, H. Furukawa, F. Gándara, H. T. Nguyen, K. E. Cordova, and O. M. Yaghi, "Selective capture of carbon dioxide under humid conditions by hydrophobic chabazite - type zeolitic imidazolate frameworks," *Angew. Chem. Int. Ed.*, vol. 53, pp. 10645-10648, 2014.
- [95] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, *et al.*, "Targeted synthesis of a porous aromatic framework with high stability and exceptionally high surface area," *Angew. Chem.*, vol. 121, pp. 9621-9624, 2009.
- [96] D. Yuan, W. Lu, D. Zhao, and H. C. Zhou, "Highly stable porous polymer networks with exceptionally high gas - uptake capacities," *Adv. Mater.*, vol. 23, pp. 3723-3725, 2011.

- [97] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, *et al.*, "Conjugated microporous poly (aryleneethynylene) networks," *Angew. Chem. Int. Ed.*, vol. 46, pp. 8574-8578, 2007.
- [98] J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. Jones, *et al.*, "Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks," *J. Am. Chem. Soc.*, vol. 130, pp. 7710-7720, 2008.
- [99] A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'keeffe, A. J. Matzger, and O. M. Yaghi, "Porous, crystalline, covalent organic frameworks," *Science*, vol. 310, pp. 1166-1170, 2005.
- [100] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'keeffe, *et al.*, "Designed synthesis of 3D covalent organic frameworks," *Science*, vol. 316, pp. 268-272, 2007.
- [101] J.-Y. Lee, C. D. Wood, D. Bradshaw, M. J. Rosseinsky, and A. I. Cooper, "Hydrogen adsorption in microporous hypercrosslinked polymers," *Chem. Commun.*, pp. 2670-2672, 2006.
- [102] C. D. Wood, B. Tan, A. Trewin, H. Niu, D. Bradshaw, M. J. Rosseinsky, *et al.*, "Hydrogen storage in microporous hypercrosslinked organic polymer networks," *Chem. Mater.*, vol. 19, pp. 2034-2048, 2007.
- [103] B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, *et al.*, "A new strategy to microporous polymers: knitting rigid aromatic building blocks by external cross-linker," *Macromolecules*, vol. 44, pp. 2410-2414, 2011.
- [104] N. B. McKeown, S. Makhseed, and P. M. Budd, "Phthalocyanine-based nanoporous network polymers," *Chem. Commun.*, pp. 2780-2781, 2002.

- [105] P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, and C. E. Tattershall, "Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials," *Chem. Commun.*, pp. 230-231, 2004.
- [106] Y. Yang, Q. Zhang, Z. Zhang, and S. Zhang, "Functional microporous polyimides based on sulfonated binaphthalene dianhydride for uptake and separation of carbon dioxide and vapors," *J. Mater. Chem. A*, vol. 1, pp. 10368-10374, 2013.
- [107] B. S. Ghanem, N. B. McKeown, P. M. Budd, and D. Fritsch, "Polymers of intrinsic microporosity derived from bis (phenazyl) monomers," *Macromolecules*, vol. 41, pp. 1640-1646, 2008.
- [108] F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe, and O. M. Yaghi, "A crystalline imine-linked 3-D porous covalent organic framework," *J. Am. Chem. Soc.*, vol. 131, pp. 4570-4571, 2009.
- [109] P. Kuhn, M. Antonietti, and A. Thomas, "Porous, Covalent Triazine - Based Frameworks Prepared by Ionothermal Synthesis," *Angew. Chem. Int. Ed.*, vol. 47, pp. 3450-3453, 2008.
- [110] J. Schmidt, J. Weber, J. D. Epping, M. Antonietti, and A. Thomas, "Microporous conjugated poly (thienylene arylene) networks," *Adv. Mater.*, vol. 21, pp. 702-705, 2009.
- [111] Y. Yang, Q. Zhang, S. Zhang, and S. Li, "Synthesis and characterization of triphenylamine-containing microporous organic copolymers for carbon dioxide uptake," *Polymer*, vol. 54, pp. 5698-5702, 2013.

- [112] Y. Yang, Q. Zhang, J. Zheng, and S. Zhang, "Synthesis and characterization of pyrrole-containing microporous polymeric networks," *Polymer*, vol. 54, pp. 3254-3260, 2013.
- [113] P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp, *et al.*, "A "click-based" porous organic polymer from tetrahedral building blocks," *J. Mater. Chem.*, vol. 21, pp. 1700-1703, 2011.
- [114] J. Weber and A. Thomas, "Toward stable interfaces in conjugated polymers: microporous poly (p-phenylene) and poly (phenyleneethynylene) based on a spirobifluorene building block," *J. Am. Chem. Soc.*, vol. 130, pp. 6334-6335, 2008.
- [115] Q. Zhang, Y. Yang, and S. Zhang, "Novel Functionalized Microporous Organic Networks Based on Triphenylphosphine," *Chem. Eur. J.*, vol. 19, pp. 10024-10029, 2013.
- [116] J. Germain, J. M. Fréchet, and F. Svec, "Hypercrosslinked polyanilines with nanoporous structure and high surface area: potential adsorbents for hydrogen storage," *J. Mater. Chem.*, vol. 17, pp. 4989-4997, 2007.
- [117] A. P. Cote, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, and O. M. Yaghi, "Reticular synthesis of microporous and mesoporous 2D covalent organic frameworks," *J. Am. Chem. Soc.*, vol. 129, pp. 12914-12915, 2007.
- [118] A.-H. Lu and S. Dai, *Porous Materials for Carbon Dioxide Capture.*: Berlin, Heidelberg: Springer Berlin Heidelberg: Imprint: Springer, 2014., 2014.
- [119] A. I. Cooper, "Conjugated microporous polymers," *Adv. Mater.*, vol. 21, pp. 1291-1295, 2009.

- [120] Y. Yang, C. Y. Chuah, H. Gong, and T.-H. Bae, "Robust microporous organic copolymers containing triphenylamine for high pressure CO₂ capture application," *J. CO₂ Util.*, vol. 19, pp. 214-220, 2017.
- [121] C. Y. Chuah, Y. Yang, and T.-H. Bae, "Hierarchically porous polymers containing triphenylamine for enhanced SF₆ separation," *Micropor. Mesopor. Mater.*, vol. 272, pp. 232-240, 2018.
- [122] R. Dawson, D. J. Adams, and A. I. Cooper, "Chemical tuning of CO₂ sorption in robust nanoporous organic polymers," *Chem. Sci.*, vol. 2, pp. 1173-1177, 2011.
- [123] W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei, and H. C. Zhou, "Polyamine - Tethered Porous Polymer Networks for Carbon Dioxide Capture from Flue Gas," *Angew. Chem. Int. Ed.*, vol. 51, pp. 7480-7484, 2012.
- [124] 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. 455-461, 2016.
- [125] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, *et al.*, "Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores," *Science*, vol. 279, pp. 548-552, 1998.
- [126] M. Morey, A. Davidson, and G. Stucky, "Silica-based, cubic mesostructures: synthesis, characterization and relevance for catalysis," *J. Porous Mater.*, vol. 5, pp. 195-204, 1998.
- [127] J. A. Schwarz, C. I. Contescu, and K. Putyera, *Dekker encyclopedia of nanoscience and nanotechnology*: New York : M. Dekker, c2004., 2004.

- [128] B. D. Reid, F. A. Ruiz-Trevino, I. H. Musselman, K. J. Balkus, and J. P. Ferraris, "Gas permeability properties of polysulfone membranes containing the mesoporous molecular sieve MCM-41," *Chem. Mater.*, vol. 13, pp. 2366-2373, 2001.
- [129] S. Kulprathipanja, *Zeolites in industrial separation and catalysis*: Weinheim : Wiley-VCH, [2010], 2010.
- [130] M. R. Mello, D. Phanon, G. Q. Silveira, P. L. Llewellyn, and C. M. Ronconi, "Amine-modified MCM-41 mesoporous silica for carbon dioxide capture," *Micropor. Mesopor. Mater.*, vol. 143, pp. 174-179, 2011.
- [131] H. Y. Huang, R. T. Yang, D. Chinn, and C. L. Munson, "Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas," *Ind. Eng. Chem. Res.*, vol. 42, pp. 2427-2433, 2003.
- [132] A. Galarneau, H. Cambon, F. Di Renzo, R. Ryoo, M. Choi, and F. Fajula, "Microporosity and connections between pores in SBA-15 mesostructured silicas as a function of the temperature of synthesis," *New J. Chem.*, vol. 27, pp. 73-79, 2003.
- [133] S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, *et al.*, "Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure," *J. Am. Chem. Soc.*, vol. 122, pp. 10712-10713, 2000.
- [134] G. Zhang, P. Zhao, L. Hao, and Y. Xu, "Amine-modified SBA-15 (P): A promising adsorbent for CO₂ capture," *J. CO₂ Util.*, vol. 24, pp. 22-33, 2018.
- [135] A. C. Chang, S. S. Chuang, M. Gray, and Y. Soong, "In-situ infrared study of CO₂ adsorption on SBA-15 grafted with γ -(aminopropyl) triethoxysilane," *Energy Fuels*, vol. 17, pp. 468-473, 2003.

- [136] R. A. Khatri, S. S. Chuang, Y. Soong, and M. Gray, "Carbon dioxide capture by diamine-grafted SBA-15: A combined Fourier transform infrared and mass spectrometry study," *Ind. Eng. Chem. Res.*, vol. 44, pp. 3702-3708, 2005.
- [137] M. Bhagiyalakshmi, L. J. Yun, R. Anuradha, and H. T. Jang, "Synthesis of chloropropylamine grafted mesoporous MCM-41, MCM-48 and SBA-15 from rice husk ash: their application to CO₂ chemisorption," *J. Porous Mater.*, vol. 17, pp. 475-484, 2010.
- [138] F. Zheng, D. N. Tran, B. J. Busche, G. E. Fryxell, R. S. Addleman, T. S. Zemanian, *et al.*, "Ethylenediamine-modified SBA-15 as regenerable CO₂ sorbent," *Ind. Eng. Chem. Res.*, vol. 44, pp. 3099-3105, 2005.
- [139] N. Hiyoshi, K. Yogo, and T. Yashima, "Adsorption characteristics of carbon dioxide on organically functionalized SBA-15," *Micropor. Mesopor. Mater.*, vol. 84, pp. 357-365, 2005.
- [140] J. Jammaer, T. S. van Erp, A. Aerts, C. E. Kirschhock, and J. A. Martens, "Continuous Synthesis Process of Hexagonal Nanoplates of P6m Ordered Mesoporous Silica," *J. Am. Chem. Soc.*, vol. 133, pp. 13737-13745, 2011.
- [141] J. Jammaer, A. Aerts, J. D'Haen, J. W. Seo, and J. A. Martens, "Convenient synthesis of ordered mesoporous silica at room temperature and quasi-neutral pH," *J. Mater. Chem.*, vol. 19, pp. 8290-8293, 2009.
- [142] A. L. Khan, S. P. Sree, J. A. Martens, M. T. Raza, and I. F. Vankelecom, "Mixed matrix membranes comprising of matrimid and mesoporous COK-12: Preparation and gas separation properties," *J. Membr. Sci.*, vol. 495, pp. 471-478, 2015.

- [143] J. G. Wijmans and R. W. Baker, "The solution-diffusion model: a review," *J. Membr. Sci.*, vol. 107, pp. 1-21, 1995.
- [144] C. E. Powell and G. G. Qiao, "Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases," *J. Membr. Sci.*, vol. 279, pp. 1-49, 2006.
- [145] G. Dong, H. Li, and V. Chen, "Challenges and opportunities for mixed-matrix membranes for gas separation," *J. Mater. Chem. A*, vol. 1, pp. 4610-4630, 2013.
- [146] T. T. Moore and W. J. Koros, "Non-ideal effects in organic–inorganic materials for gas separation membranes," *J. Mol. Struct.*, vol. 739, pp. 87-98, 2005.
- [147] M. Aroon, A. Ismail, T. Matsuura, and M. Montazer-Rahmati, "Performance studies of mixed matrix membranes for gas separation: a review," *Sep. Purif. Technol.*, vol. 75, pp. 229-242, 2010.
- [148] H. Vinh-Thang and S. Kaliaguine, "Predictive models for mixed-matrix membrane performance: a review," *Chem. Rev.*, vol. 113, pp. 4980-5028, 2013.
- [149] R. W. Baker, *Membrane technology and applications*, 2nd ed.: John Wiley & Sons, Ltd, 2004.
- [150] R. D. Noble, "Perspectives on mixed matrix membranes," *J. Membr. Sci.*, vol. 378, pp. 393-397, 2011.
- [151] H. Gong, S. S. Lee, and T.-H. Bae, "Mixed-matrix membranes containing inorganically surface-modified 5A zeolite for enhanced CO₂/CH₄ separation," *Micropor. Mesopor. Mater.*, vol. 237, pp. 82-89, 2017.

- [152] 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.
- [153] T. T. Moore, R. Mahajan, D. Q. Vu, and W. J. Koros, "Hybrid membrane materials comprising organic polymers with rigid dispersed phases," *AIChE J.*, vol. 50, pp. 311-321, 2004.
- [154] 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," *Prog. Polym. Sci.*, vol. 32, pp. 483-507, 2007.
- [155] R. Mahajan, R. Burns, M. Schaeffer, and W. J. Koros, "Challenges in forming successful mixed matrix membranes with rigid polymeric materials," *J. Appl. Polym. Sci.*, vol. 86, pp. 881-890, 2002.
- [156] T.-H. Bae and J. R. Long, "CO₂/N₂ separations with mixed-matrix membranes containing Mg₂(dobdc) nanocrystals," *Energy Environ. Sci.*, vol. 6, pp. 3565-3569, 2013.
- [157] A. Ismail, T. Kusworo, and A. Mustafa, "Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Amino silane agent," *J. Membr. Sci.*, vol. 319, pp. 306-312, 2008.
- [158] H. H. Yong, H. C. Park, Y. S. Kang, J. Won, and W. N. Kim, "Zeolite-filled polyimide membrane containing 2,4,6-triaminopyrimidine," *J. Membr. Sci.*, vol. 188, pp. 151-163, 2001.
- [159] R. Mahajan and W. J. Koros, "Factors controlling successful formation of mixed-matrix gas separation materials," *Ind. Eng. Chem. Res.*, vol. 39, pp. 2692-2696, 2000.

- [160] R. Mahajan, "Formation, characterization and modeling of mixed matrix membrane materials," Ph. D. Thesis, University of Texas, 2000.
- [161] M. Choi, H. S. Cho, R. Srivastava, C. Venkatesan, D.-H. Choi, and R. Ryoo, "Amphiphilic organosilane-directed synthesis of crystalline zeolite with tunable mesoporosity," *Nat. Mater.*, vol. 5, p. 718, 2006.
- [162] K. S. Walton and R. Q. Snurr, "Applicability of the BET method for determining surface areas of microporous metal-organic frameworks," *J. Am. Chem. Soc.*, vol. 129, pp. 8552-8556, 2007.
- [163] P.-J. Kim, Y.-W. You, H. Park, J.-S. Chang, Y.-S. Bae, C.-H. Lee, *et al.*, "Separation of SF₆ from SF₆/N₂ mixture using metal-organic framework MIL-100 (Fe) granule," *Chem. Eng. J.*, vol. 262, pp. 683-690, 2015.
- [164] A. Myers and J. M. Prausnitz, "Thermodynamics of mixed - gas adsorption," *AIChE J.*, vol. 11, pp. 121-127, 1965.
- [165] L. Czepirski and J. JagieŁŁo, "Virial-type thermal equation of gas—solid adsorption," *Chem. Eng. Sci.*, vol. 44, pp. 797-801, 1989.
- [166] R.-J. Li, M. Li, X.-P. Zhou, D. Li, and M. O'Keeffe, "A highly stable MOF with a rod SBU and a tetracarboxylate linker: unusual topology and CO₂ adsorption behaviour under ambient conditions," *Chem. Commun.*, vol. 50, pp. 4047-4049, 2014.
- [167] Y. S. Bae and R. Q. Snurr, "Development and evaluation of porous materials for carbon dioxide separation and capture," *Angew. Chem. Int. Ed.*, vol. 50, pp. 11586-11596, 2011.

- [168] K. Na, M. Choi, and R. Ryoo, "Cyclic diquaternary ammoniums for nanocrystalline BEA, MTW and MFI zeolites with intercrystalline mesoporosity," *J. Mater. Chem.*, vol. 19, pp. 6713-6719, 2009.
- [169] R. Srivastava, M. Choi, and R. Ryoo, "Mesoporous materials with zeolite framework: remarkable effect of the hierarchical structure for retardation of catalyst deactivation," *Chem. Commun.*, pp. 4489-4491, 2006.
- [170] 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," *J. Mater. Chem. A*, vol. 4, pp. 5176-5183, 2016.
- [171] J. B. DeCoste, G. W. Peterson, B. J. Schindler, K. L. Killops, M. A. Browe, and J. J. Mahle, "The effect of water adsorption on the structure of the carboxylate containing metal–organic frameworks Cu-BTC, Mg-MOF-74, and UiO-66," *J. Mater. Chem. A*, vol. 1, pp. 11922-11932, 2013.
- [172] Y. Mao, D. Chen, P. Hu, Y. Guo, Y. Ying, W. Ying, *et al.*, "Hierarchical Mesoporous Metal–Organic Frameworks for Enhanced CO₂ Capture," *Chem. Eur. J.*, vol. 21, pp. 15127-15132, 2015.
- [173] L. Peng, J. Zhang, Z. Xue, B. Han, X. Sang, C. Liu, *et al.*, "Highly mesoporous metal–organic framework assembled in a switchable solvent," *Nat. Commun.*, vol. 5, p. 4465, 2014.
- [174] M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann, and F. Emmerling, "Mechanochemical synthesis of metal–organic frameworks: a fast and facile approach toward quantitative yields and high specific surface areas," *Chem. Mater.*, vol. 22, pp. 5216-5221, 2010.

- [175] L. H. Wee, M. R. Lohe, N. Janssens, S. Kaskel, and J. A. Martens, "Fine tuning of the metal–organic framework Cu₃(BTC)₂ HKUST-1 crystal size in the 100 nm to 5 micron range," *J. Mater. Chem.*, vol. 22, pp. 13742-13746, 2012.
- [176] A. Cadiau, K. Adil, P. Bhatt, Y. Belmabkhout, and M. Eddaoudi, "A metal-organic framework–based splitter for separating propylene from propane," *Science*, vol. 353, pp. 137-140, 2016.
- [177] R. Kumar, D. Raut, U. Ramamurty, and C. Rao, "Remarkable improvement in the mechanical properties and CO₂ uptake of MOFs brought about by covalent linking to graphene," *Angew. Chem. Int. Ed.*, vol. 128, pp. 7988-7992, 2016.
- [178] W. Zhang, D. Banerjee, J. Liu, H. T. Schaef, J. V. Crum, C. A. Fernandez, *et al.*, "Redox - Active Metal - Organic Composites for Highly Selective Oxygen Separation Applications," *Adv. Mater.*, vol. 28, pp. 3572-3577, 2016.
- [179] 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," *J. Am. Chem. Soc.*, vol. 130, pp. 10870-10871, 2008.
- [180] S. Hwang, W. S. Chi, S. J. Lee, S. H. Im, J. H. Kim, and J. Kim, "Hollow ZIF-8 nanoparticles improve the permeability of mixed matrix membranes for CO₂/CH₄ gas separation," *J. Membr. Sci.*, vol. 480, pp. 11-19, 2015.
- [181] L. Yu, J. F. Yang, and X. W. Lou, "Formation of CoS₂ nanobubble hollow prisms for highly reversible lithium storage," *Angew. Chem. Int. Ed.*, vol. 55, pp. 13422-13426, 2016.
- [182] Y. V. Kaneti, J. Tang, R. R. Salunkhe, X. Jiang, A. Yu, K. C. W. Wu, *et al.*, "Nanoarchitected Design of Porous Materials and Nanocomposites from Metal - Organic Frameworks," *Adv. Mater.*, vol. 29, p. 1604898, 2017.

- [183] L. Peng, J. Zhang, J. Li, B. Han, Z. Xue, B. Zhang, *et al.*, "Hollow metal–organic framework polyhedra synthesized by a CO₂–ionic liquid interfacial templating route," *J. Colloid Interface Sci.*, vol. 416, pp. 198-204, 2014.
- [184] F. Zhang, Y. Wei, X. Wu, H. Jiang, W. Wang, and H. Li, "Hollow zeolitic imidazolate framework nanospheres as highly efficient cooperative catalysts for [3+ 3] cycloaddition reactions," *J. Am. Chem. Soc.*, vol. 136, pp. 13963-13966, 2014.
- [185] Z. Zhang, Y. Chen, X. Xu, J. Zhang, G. Xiang, W. He, *et al.*, "Well - Defined Metal - Organic Framework Hollow Nanocages," *Angew. Chem. Int. Ed.*, vol. 53, pp. 429-433, 2014.
- [186] X. Xu, Z. Zhang, and X. Wang, "Well - Defined Metal - Organic - Framework Hollow Nanostructures for Catalytic Reactions Involving Gases," *Adv. Mater.*, vol. 27, pp. 5365-5371, 2015.
- [187] D. Britt, H. Furukawa, B. Wang, T. G. Glover, and O. M. Yaghi, "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites," *Proc. Natl. Acad. Sci.*, vol. 106, pp. 20637-20640, 2009.
- [188] A. C. Kizzie, A. G. Wong-Foy, and A. J. Matzger, "Effect of humidity on the performance of microporous coordination polymers as adsorbents for CO₂ capture," *Langmuir*, vol. 27, pp. 6368-6373, 2011.
- [189] S. Xiong and H. C. Zeng, "Serial ionic exchange for the synthesis of multishelled copper sulfide hollow spheres," *Angew. Chem. Int. Ed.*, vol. 51, pp. 949-952, 2012.

- [190] W. Wang, M. Dahl, and Y. Yin, "Hollow nanocrystals through the nanoscale Kirkendall effect," *Chem. Mater.*, vol. 25, pp. 1179-1189, 2012.
- [191] 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.
- [192] L. Tan and B. Tan, "Hyperscrosslinked porous polymer materials: design, synthesis, and applications," *Chem. Soc. Rev.*, vol. 46, pp. 3322-3356, 2017.
- [193] G. D. Pirngruber, L. Hamon, S. Bourrelly, P. L. Llewellyn, E. Lenoir, V. Guillerm, *et al.*, "A method for screening the potential of MOFs as CO₂ adsorbents in pressure swing adsorption processes," *ChemSusChem*, vol. 5, pp. 762-776, 2012.
- [194] 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 Environ. Sci.*, vol. 4, pp. 3030-3040, 2011.
- [195] P. M. Mathias, R. Kumar, J. D. Moyer, J. M. Schork, S. R. Srinivasan, S. R. Auvil, *et al.*, "Correlation of multicomponent gas adsorption by the dual-site Langmuir model. Application to nitrogen/oxygen adsorption on 5A-zeolite," *Ind. Eng. Chem. Res.*, vol. 35, pp. 2477-2483, 1996.
- [196] T. Hasell, M. Miklitz, A. Stephenson, M. A. Little, S. Y. Chong, R. Clowes, *et al.*, "Porous organic cages for sulfur hexafluoride separation," *J. Am. Chem. Soc.*, vol. 138, pp. 1653-1659, 2016.

- [197] C. Y. Chuah, S. Yu, K. Na, and T.-H. Bae, "Enhanced SF₆ recovery by hierarchically structured MFI zeolite," *J. Ind. Eng. Chem.*, vol. 62, pp. 64-71, 2018.
- [198] C. Montoro, E. García, S. Calero, M. A. Pérez-Fernández, A. L. López, E. Barea, *et al.*, "Functionalisation of MOF open metal sites with pendant amines for CO₂ capture," *J. Mater. Chem.*, vol. 22, pp. 10155-10158, 2012.
- [199] N. Planas, A. L. Dzubak, R. Poloni, L.-C. Lin, A. McManus, T. M. McDonald, *et al.*, "The mechanism of carbon dioxide adsorption in an alkylamine-functionalized metal–organic framework," *J. Am. Chem. Soc.*, vol. 135, pp. 7402-7405, 2013.
- [200] T.-H. Bae, J. Liu, J. A. Thompson, W. J. Koros, C. W. Jones, and S. Nair, "Solvothermal deposition and characterization of magnesium hydroxide nanostructures on zeolite crystals," *Micropor. Mesopor. Mater.*, vol. 139, pp. 120-129, 2011.
- [201] S. Sircar, "Basic research needs for design of adsorptive gas separation processes," *Ind. Eng. Chem. Res.*, vol. 45, pp. 5435-5448, 2006.
- [202] M. Rahmani, A. Kazemi, and F. Talebnia, "Matrimid mixed matrix membranes for enhanced CO₂/CH₄ separation," *J. Polym. Eng.*, vol. 36, pp. 499-511, 2016.
- [203] Ł. Ewa, W. Cezary, C. Andrzej, D. Konrad, S. Stanisława, C. Anna, *et al.*, "Preparation of sulfonated polysulfone membrane for enzymes immobilisation," *Biocybern. Biomed. Eng.*, vol. 32, pp. 77-86, 2012.
- [204] P. Goh, A. Ismail, S. Sanip, B. Ng, and M. Aziz, "Recent advances of inorganic fillers in mixed matrix membrane for gas separation," *Sep. Purif. Technol.*, vol. 81, pp. 243-264, 2011.

- [205] 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," *J. Membr. Sci.*, vol. 569, pp. 149-156, 2019.
- [206] M. Fischer, F. Hoffmann, and M. Fröba, "New microporous materials for acetylene storage and C₂H₂/CO₂ separation: insights from molecular simulations," *ChemPhysChem*, vol. 11, pp. 2220-2229, 2010.
- [207] J.-P. Zhang and X.-M. Chen, "Optimized acetylene/carbon dioxide sorption in a dynamic porous crystal," *J. Am. Chem. Soc.*, vol. 131, pp. 5516-5521, 2009.
- [208] F. Moreau, I. Da Silva, N. H. Al Smail, T. L. Easun, M. Savage, H. G. Godfrey, *et al.*, "Unravelling exceptional acetylene and carbon dioxide adsorption within a tetra-amide functionalized metal-organic framework," *Nat. Commun.*, vol. 8, pp. 14085-14093, 2017.
- [209] D. G. Samsonenko, H. Kim, Y. Sun, G. H. Kim, H. S. Lee, and K. Kim, "Microporous magnesium and manganese formates for acetylene storage and separation," *Chem. Asian J.*, vol. 2, pp. 484-488, 2007.
- [210] S. Xiang, W. Zhou, Z. Zhang, M. A. Green, Y. Liu, and B. Chen, "Open metal sites within isostructural metal-organic frameworks for differential recognition of acetylene and extraordinarily high acetylene storage capacity at room temperature," *Angew. Chem.*, vol. 122, pp. 4719-4722, 2010.
- [211] S.-C. Xiang, Z. Zhang, C.-G. Zhao, K. Hong, X. Zhao, D.-R. Ding, *et al.*, "Rationally tuned micropores within enantiopure metal-organic frameworks for highly selective separation of acetylene and ethylene," *Nat. Commun.*, vol. 2, p. 204, 2011.

- [212] S. Yang, A. J. Ramirez-Cuesta, R. Newby, V. Garcia-Sakai, P. Manuel, S. K. Callear, *et al.*, "Supramolecular binding and separation of hydrocarbons within a functionalized porous metal–organic framework," *Nat. Chem.*, vol. 7, p. 121, 2015.
- [213] J. Duan, W. Jin, and R. Krishna, "Natural gas purification using a porous coordination polymer with water and chemical stability," *Inorg. Chem.*, vol. 54, pp. 4279-4284, 2015.
- [214] X. Cui, K. Chen, H. Xing, Q. Yang, R. Krishna, Z. Bao, *et al.*, "Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene," *Science*, vol. 353, pp. 141-144, 2016.
- [215] F. Luo, C. Yan, L. Dang, R. Krishna, W. Zhou, H. Wu, *et al.*, "UTSA-74: A MOF-74 isomer with two accessible binding sites per metal center for highly selective gas separation," *J. Am. Chem. Soc.*, vol. 138, pp. 5678-5684, 2016.
- [216] T.-L. Hu, H. Wang, B. Li, R. Krishna, H. Wu, W. Zhou, *et al.*, "Microporous metal–organic framework with dual functionalities for highly efficient removal of acetylene from ethylene/acetylene mixtures," *Nat. Commun.*, vol. 6, p. 7328, 2015.
- [217] J. Cai, H. Wang, H. Wang, X. Duan, Z. Wang, Y. Cui, *et al.*, "An amino-decorated NbO-type metal–organic framework for high C₂H₂ storage and selective CO₂ capture," *RSC Adv.*, vol. 5, pp. 77417-77422, 2015.
- [218] H.-M. Wen, H. Wang, B. Li, Y. Cui, H. Wang, G. Qian, *et al.*, "A microporous metal–organic framework with lewis basic nitrogen sites for high C₂H₂ storage and significantly enhanced C₂H₂/CO₂ separation at ambient conditions," *Inorg. Chem.*, vol. 55, pp. 7214-7218, 2016.

- [219] S. J. Datta, C. Khumnoon, Z. H. Lee, W. K. Moon, S. Docao, T. H. Nguyen, *et al.*, "CO₂ capture from humid flue gases and humid atmosphere using a microporous coppersilicate," *Science*, vol. 350, pp. 302-306, 2015.
- [220] J. A. Mason, T. M. McDonald, T.-H. Bae, J. E. Bachman, K. Sumida, J. J. Dutton, *et al.*, "Application of a high-throughput analyzer in evaluating solid adsorbents for post-combustion carbon capture via multicomponent adsorption of CO₂, N₂, and H₂O," *J. Am. Chem. Soc.*, vol. 137, pp. 4787-4803, 2015.
- [221] G. Li, P. Xiao, P. Webley, J. Zhang, R. Singh, and M. Marshall, "Capture of CO₂ from high humidity flue gas by vacuum swing adsorption with zeolite 13X," *Adsorption*, vol. 14, pp. 415-422, 2008.