



Nanoporous Materials as Tool for Natural Gas Purity Upgrading

Nour F. Attia

Gas Analysis and Fire Safety Laboratory, National Institute of Standards

Corresponding author's email: nour.fathi@nis.sci.eg

Article Type: Review article

Received on 6 August 2022, Accepted on 15 August 2022

Abstract

The extensive usage of fossil fuels associated with the huge emission of greenhouse gases accelerates the global warming effect and its associated climate change phenomena. Natural gas (CH₄) is considered as an environmentally friendly combustion fuel and is a good alternative to alleviate this phenomenon. However, the natural gas streams contain huge concentrations of CO₂ creating corrosion and combustion quality demerits for using of natural gas directly. Therefore, the selective capture of CO₂ from natural gas streams via an energy-efficient adsorption process in porous materials is a mandatory industrial requirement before the distribution and commercialization of CH₄. In this review, a brief review of porous materials, classification, synthesis, and exploitation of porous materials in natural gas purification was studied. Moreover, recent advances in the separation selectivity of CO₂/CH₄ and its separation adsorption action were briefly discussed.

Keywords: Nanoporous materials; Natural gas purification; CO₂/CH₄ separation selectivity; Greenhouse gases; CO₂ capture.

1. Introduction

The huge emission of greenhouse gases due to the rapid consumption of fossil fuels in various activities, including transportation and generation of electricity in power plants, accelerated its negative impact on the environmental pollution crisis [1] This is in conjunction with the high fossil fuel price and their limited stock worldwide. On the contrary, methane (CH₄) as natural gas presents clean combustion in the energy generation process rather than in other fossil fuel products, thus, affording a green and environmentally friendly energy source. Moreover, CH₄ exist in huge stock in many places worldwide as landfill gas and is also generated from renewable sources such as farming product (biogas) [2-3]. Nevertheless, the purity of natural gas from both sources is considered as a technical dilemma due to the acidic impurities (gases), causing low combustion efficiency and correction issues to pipe and processing equipment [4-11]. The landfill gas and biogas streams which are the main sources of natural gas contain a high concentration of acidic CO₂ gas which was found to be 35-50 % in landfill gas and 25-45 % in biogas [4-7]. Additionally, minor concentrations of H₂S and SO₂ also existed. Thus, efficient methane purification should be done, affording high purity of methane gas of 98%,

which achieves the permissible level of CO₂ (less than 2%) based on the safety level of transportation pipes [12]. Hence, selective separation of CO₂ (purity upgrading) from natural gas streams has to be implemented before distribution and commercial usage of CH₄ in different activities [13-15]. Various materials have been utilized to separate CO₂ over CH₄ gas such as organic membranes which are extensively used [16]. However, some other organic hydrocarbons and H₂S contaminants negatively affect the separation and permeability of organic membranes [20-22]. Recently, variety of porous materials such as nanoporous carbons, metal-organic frameworks (MOFs) and porous polymers have been tested for selective capture of CO₂ over CH₄ streams [23-30]. I and others have dedicated our research exploring new and chemically stable cost-effective, and efficient porous adsorbents for separating CO₂ over CH₄ and N₂ [30-37]. Thus, this review briefly discusses the types of porous adsorbents and synthesis and utilization for separation of CO₂/CH₄.

2. Porous materials

2.1 Types of porous materials

Nanoporous materials (NPMs) are a unique type of materials that own special features called pores on their surface [38]. The nanoporous materials can be fabricated and constructed from different natures. However, NPMs are usually evaluated based on some textual parameters such as specific surface area (SSA), total pore volume (TPV), and pore size distributions (PSDs) which evaluates the average pore size and which category exist [39]. Then, there are three classes of NPMs were defined based on the pore size as presented in Fig.1. The first class denoted as microporous materials when the pore sizes are less and equal to 2 nm, mesoporous materials when the pore size situated between 2 and 50 nm and then macroporous materials when the pore sizes are higher than 50 nm (Fig.1) [40]. Moreover, the fourth category was reported in the literature which is denoted as hierarchical materials which is micro-mesoporous materials (contain micro and meso pores) [27,30] (Fig. 1). Interestingly, NPMs are classified into three types based on chemical composition (nature). Hence, an example for organic NMPs is porous polymers [41-42], and for inorganic NPMs are zeolites, porous carbons, and nanoporous silica [27-31,43]. Finally, the last type is hybrid NPMs such metal-organic frameworks [1].

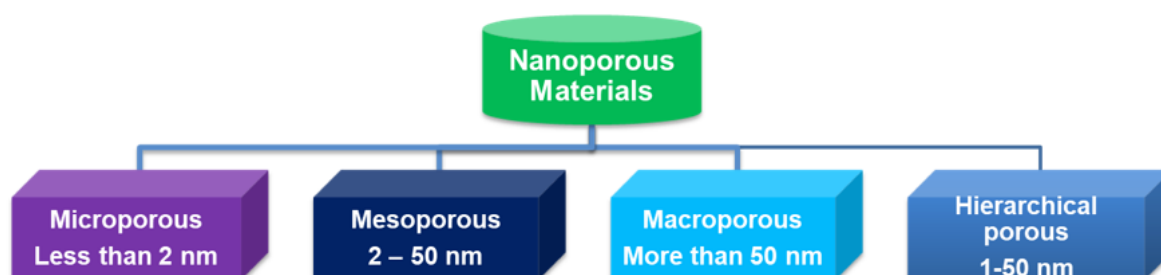


Figure 1: Schematic diagram representing the classes of porous materials based on pore size.

2.2 Synthesis of porous materials approaches

The NPMs synthesis routes depend on the types of NPMs in terms of composition and pore size class. Therefore, for organic NPMs (nanoporous polymers) usually started from a monomer and in this aspect, the monomer, crosslinker, and solvents were precisely selected to afford special environment such as functional group, pore size, and SSAs inside the pore for specific application [41-42] as depicted in Fig.2. For inorganic NPMs, the mainly used are activated porous carbons which have two routes of synthesis; the first one is the utilization of porous silica and zeolites as a template and then infiltrate with organic precursors and then carbonization was executed. Afterward, the template was removed leaving NPMs with an almost similar pore size of the template used [43]. The second one, is direct carbonization of biomass waste and then followed by a chemical/ physical activation process yielding high SSA NPMs [27,38] (Fig. 2). This approach is mainly used due to the sustainable and cost-effective merits of carbon precursors [28], however, the obtained pore sizes are hard to be tune [27-29]. Hybrid NPMs which are denoted as MOFs and are defined as crystalline porous materials and are mainly yielded from the reaction of the organic linkers with metal clusters [1]. MOF is characterized by interesting features such as high SSA, TPV, easier surface functionalization, and tunable pore sizes [3,4,13].

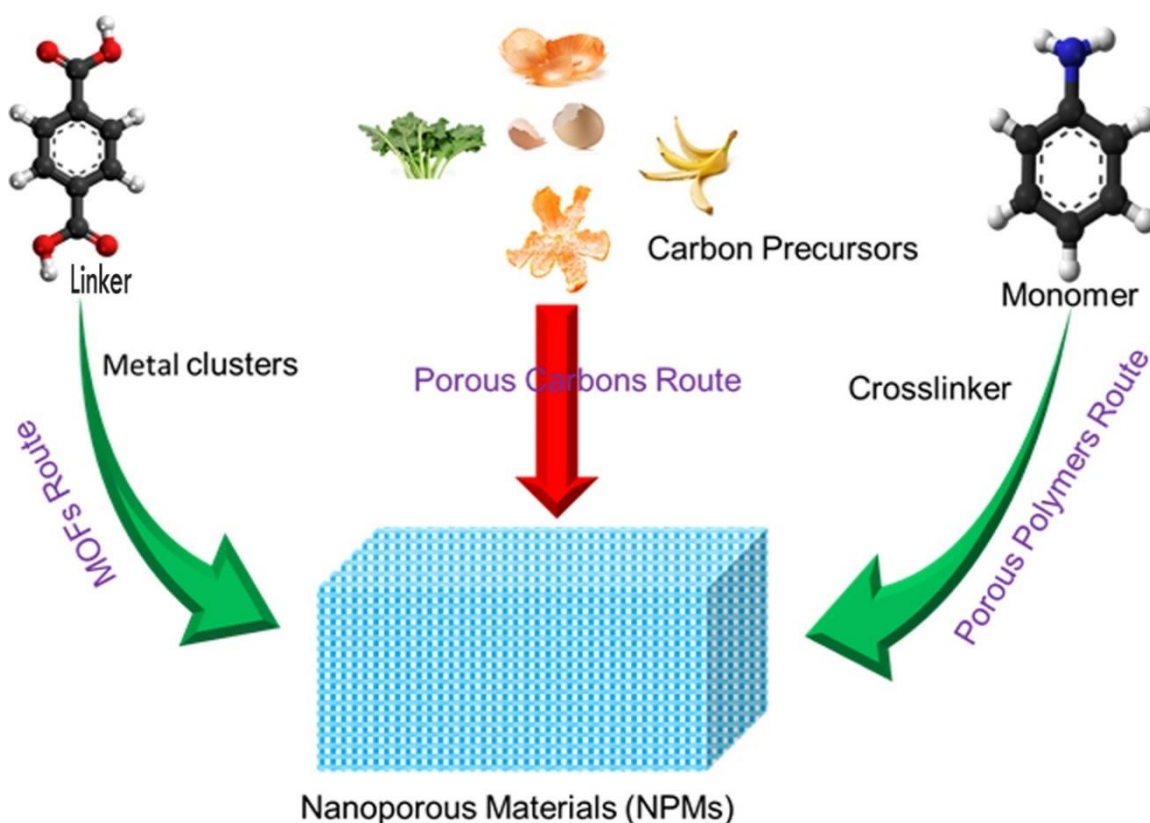


Figure 2: Schematic diagram representing brief synthesis routes of nanoporous materials.

3. CO₂/CH₄ separation selectivity

The selection separation of CO₂ from CH₄ stream is the crucial industrial process before the commercialization of CH₄ to afford high safety standards for transportation and process and achieve green and efficient combustion quality in engines. Therefore, various materials were tested for CO₂/CH₄ separation to address this raised issue and the separation selectivity values presented in the review were evaluated using the ideal adsorbed solution theory (IAST) model. In this regard, in our recent studies, flexible porous carbon cloths were developed from different textile fabric precursors decorated with spherical porous carbon nanoparticles rich with nitrogen species (Fig. 3).

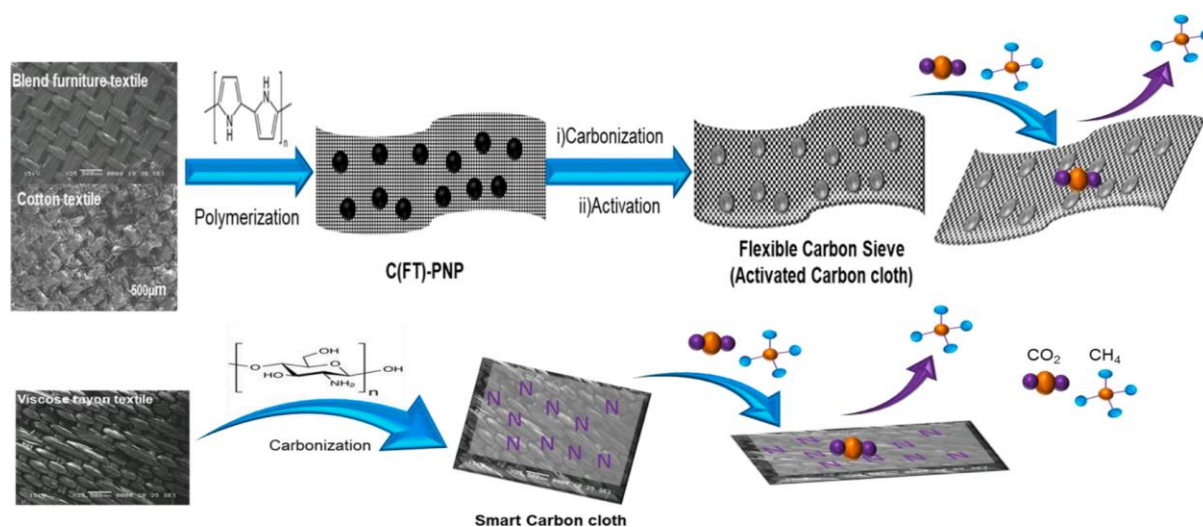


Figure 3: Schematic representation showing the novel synthesis of flexible carbon sieves, reproduced with permission [32]. Copyright 2021, Elsevier.

The developed flexible cloth (CH-CC) achieved higher separation selectivity for CO₂/CH₄ of 17.1 and 11.7 (Table1) at 20 bar and ambient temperature for a binary gas mixture of 50:50 and 10:90, respectively as indicated in Fig. 4 [32]. It was found that the separation selectivity CO₂/CH₄ is primary depend on the intrinsic texture structure properties of the textile fabrics precursor used [32]. Actually, there are two key points for selective of CO₂ over CH₄; the first one is which affords narrow micropores and facilities the adsorption of smaller size CO₂ molecule rather than CH₄ molecule [32,33]. The second is the generation of active basic sites for adsorption of acidic nature CO₂ molecule rather than low polarizability CH₄ [44-45]. Thus, the design of NPMs with rich basic active sites (high electron density elements) with narrow pores size are preferable for efficient CO₂/CH₄ separation [30,32]. Therefore, adhering to this fabrication approach variety of NPMs were prepared and implemented in CO₂/CH₄ separation selection under different conditions as listed in Table 1. Nevertheless, the separation selectivity value for CO₂/CH₄ is still limited and ranged in 3.5-72.9 [5,26,32-37,46-58].

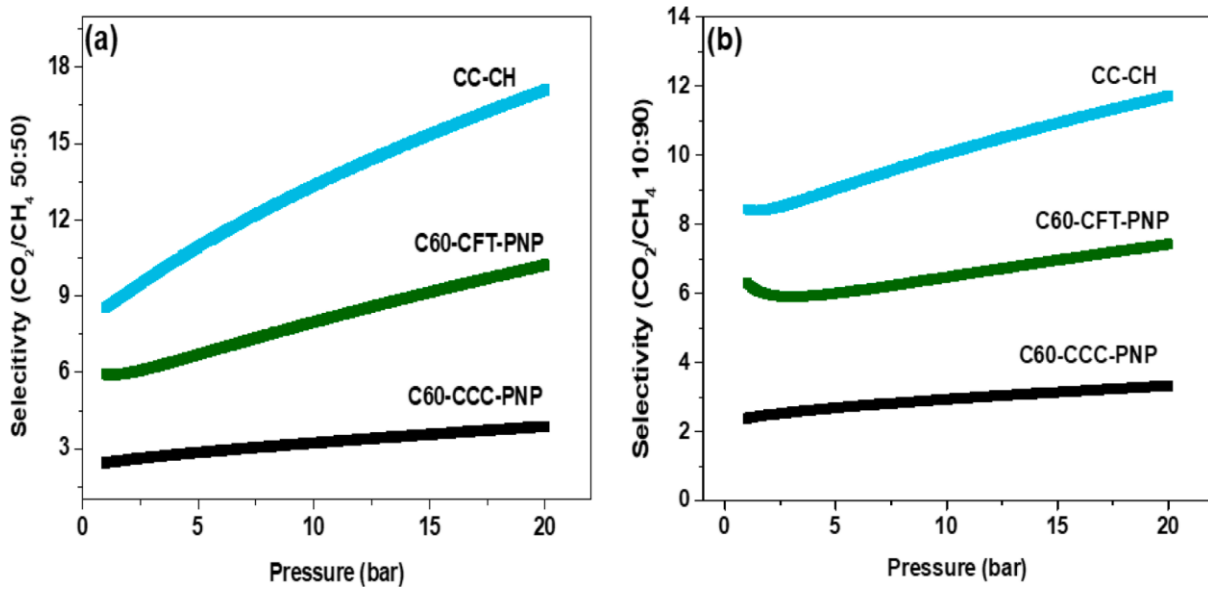


Figure 4: CO₂/CH₄ selectivity based on the ideal adsorbed solution theory method for mixture composition of (a) (50:50), (b) (10:90) for developed flexible carbon sieve, reproduced with permission [32]. Copyright 2021, Elsevier.

Interestingly, recently, after the inclusion of magnetic nickel nanostructures in upwards structure on the surface of porous flexible carbon cloth (Fig. 5), a breakthrough in CO₂/CH₄ separation selectivity was attained (Table 1) [30]. The separation selectivity of CO₂/CH₄ at the binary gas mixture of 50:50 achieved 369.5 and 70 at room temperature (RT) and 20 and 1 bar respectively (Fig. 6). Additionally, the smart filter affords high CO₂/CH₄ separation selectivity at low concentration of CO₂ (binary gas mixture of 10:90 for CO₂:CH₄) recording 105 and 77 at RT and 20 and 1 bar, respectively (Table 1). This significant separation selectivity was attributed to improved interaction affinity between polarizable CO₂ molecules and Ni / NiO sorption sites situated on flexible porous carbon cloth [30].

Table 1: CO₂/CH₄ (50:50) selectivity various reported porous materials.

Sample	CO ₂ /CH ₄ (50:50)	Reference
CC-CH	17.1 (13.3) ^a (8.6) ^b	32
CBF-1273-CO ₂ -1h	3.5	26
SC700P	7.0 ^b	5
ACC (cloth)	5.0 ^b	34
FIPC (cloth)	14.0 ^c	35
Activated carbon monoliths	2.2	36
Ordered Mesoporous Carbon	3.0 ^b	46
BILP-10	12.0	47
PCN-222	4.5	48
MOF-505@5GO	8.6 ^b	37
Glc-C-4	4.5	49
UMCM-2	4.4	50
MKPOP-4	4.5 ^b	51
CC-PNP-Ni-10	369.5 (70) ^a	30
CC-PNP	27.9	33
SIFSIX-2-Cu-i	33 ^a	52
MIP-202	72.9 ^a	53
Ni@ZrOF	12.65 ^a	54
LCU-102a	20	55
SU-AC-700	14.4	56
IN	15.3	57
NAHA-4	20a	58

^aThe average selectivity value at 298 K.

^bThe selectivity value at 1 bar and 298 K.

^cThe selectivity value at 1 bar and 273 K.

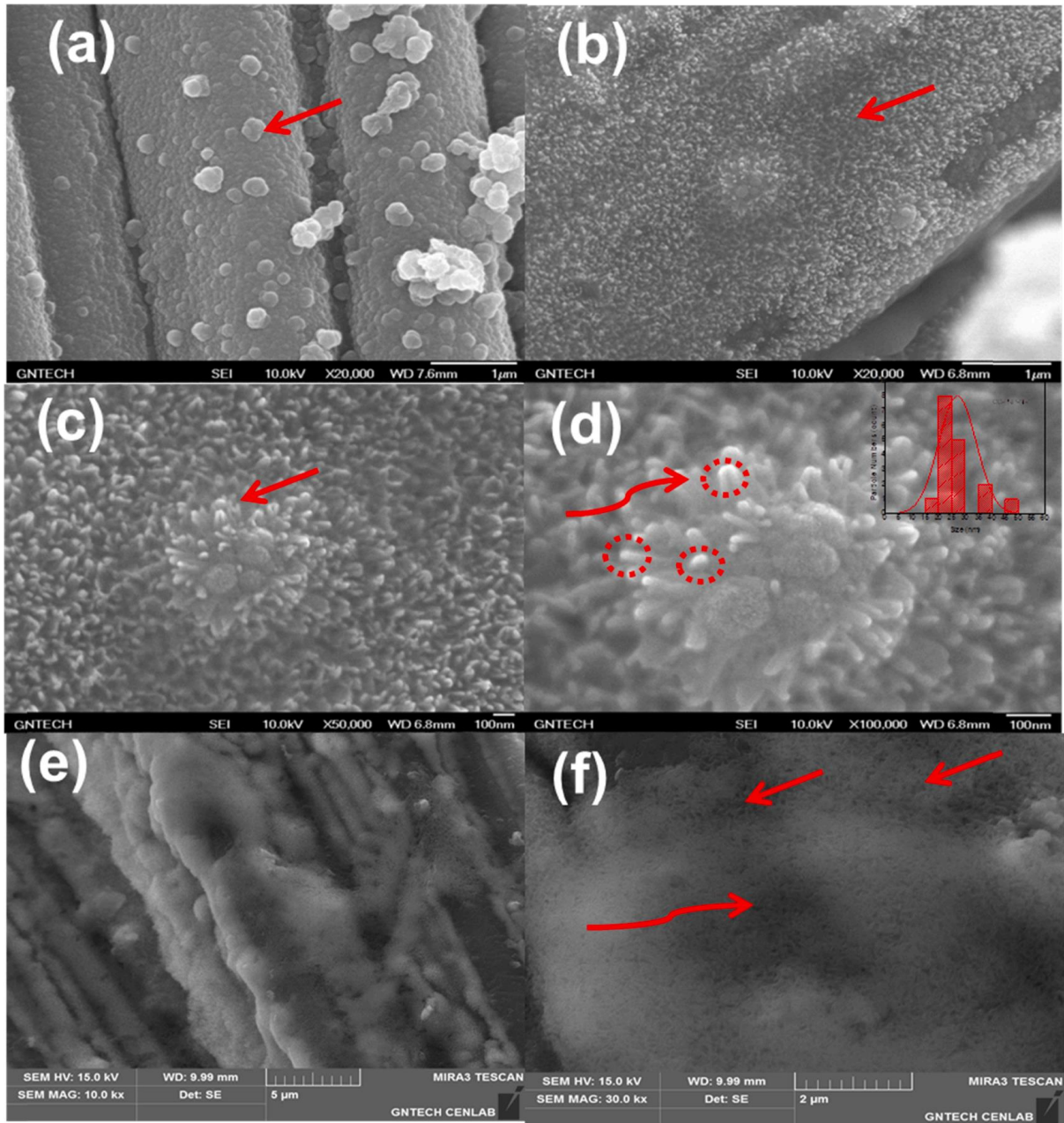


Figure 5: SEM images of (a) CC-PNP, (b) CC-PNP-Ni-7, (c) and (d) CC-PNP-Ni-7 at high magnification, (e) CC-PNP-Ni-10 and (f) CC-PNP-Ni-10 at high magnification, reproduced with permission [30]. Copyright 2021, Elsevier.

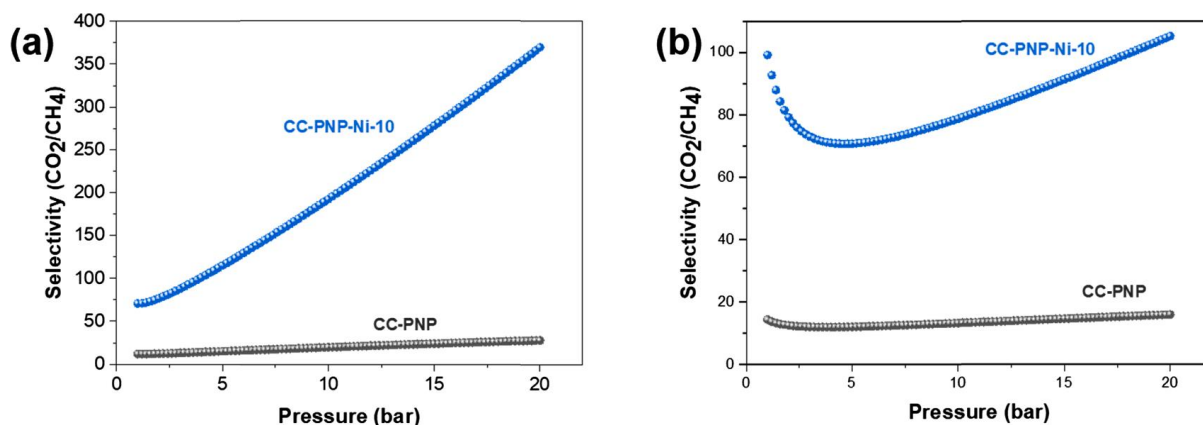


Fig. 6. CO₂/CH₄ selectivity based on the ideal adsorbed solution theory method for mixture composition of (a) (50:50), (b) (10:90) for developed magnetic flexible carbon cloth, reproduced with permission [30]. Copyright 2021, Elsevier.

4. Conclusion

Natural gas (CH₄) is considered a clean combustion fuel and is a promising alternative to gasoline to mitigate the climate change phenomenon. Hence, in this review, porous materials definition, classification, and synthesis routes were reviewed. Moreover, the utilization of various nanoporous adsorbents for the adsorption separation of CO₂/CH₄ was discussed. Selective capture of CO₂ over CH₄ was studied. Also, the key factors for enhancing the interaction affinity between polarizable CO₂ molecules and micropore walls of porous materials were introduced and reviewed.

References

1. Ma S. and Zhou H.-C. Gas storage in porous metal–organic frameworks for clean energy applications. *Chem. Commun.*, 46. 44-53 (2010).
2. Yang S. H. B., Babu P., Chua S. F. S. and Linga P. Carbon dioxide hydrate kinetics in porous media with and without salts. *Appl. Energy*, 162. 1131-1140 (2016).
3. He Y., Zhou W., Qian G. and Chen B. Methane storage in metal–organic frameworks. *Chem. Soc. Rev.* 43. 5657- 5678 (2014).
4. Bao Z., Yu L., Ren Q., Lu X. and Deng S. Adsorption of CO₂ and CH₄ on a magnesium-based metal organic framework. *J. Colloid Interface Sci.* 353. 549-556 (2011).
5. Mestre A. S., Freire C., Pires J., Carvalho A. P. and Pinto M. L. High performance microspherical activated carbons for methane storage and landfill gas or biogas upgrade. *J. Mater. Chem. A*, 2. 15337-15344 (2014).
6. Coromina H. M. and Walsh D. A. Biomass-derived activated carbon with simultaneously enhanced CO₂ uptake for both pre and post-combustion capture applications. *J. Mater. Chem. A*, 4. 280-289 (2016).

7. Delgado J. A., Uguina M. A., Sotelo J. L., Ruiz B. and Gomez J. M. Fixed-bed adsorption of carbon dioxide/methane mixtures on silicalite pellets. *Adsorption*, 12. 5-18 (2006).
8. Zhang Y., Sunarso J., Liu S. and Wang R. Current status and development of membranes for CO₂/CH₄ separation: A review. *Int. J. Greenhouse Gas Control*, 12. 84-107 (2013).
9. Baker R. W. and Lokhandwala K. Natural Gas Processing with Membranes: An Overview. *Ind. Eng. Chem. Res.*, 47. 2109-2121 (2008).
10. Cavenati S., Grande C. A. and Rodrigues A. E. Removal of carbon dioxide from natural gas by vacuum swing adsorption. *Energy Fuel*, 20. 2648-2659 (2006).
11. Bao Z., Yu L., Ren Q., Lu X. and Deng S. Adsorption of CO₂ and CH₄ on a magnesium-based metal organic framework. *J. Colloid Interface Sci.*, 353. 549-556 (2011).
12. Othman M.R., Tan S.C. and Bhatia, S. Separability of carbon dioxide from methane using MFI zeolite-silica film deposited on gamma-alumina support. *Micro. Meso. Mater.*, 121. 138-144 (2009).
13. Chen K. J., Madden D. G., Pham T., Forrest K. A., Kumar A., Yang- Q. Y., Xue W., Space B., Perry J. J. T., Zhang J. P., Chen X. M. and Zaworotko M. Tuning pore size in square-lattice coordination networks for size-selective sieving of CO₂. *J. Angew. Chem., Int. Ed.* 55. 10268-10272. (2016).
14. [14] Li L., Wang Y., Yang J., Wang X., Li J. Targeted capture and pressure/temperature- responsive separation in flexible metal-organic frameworks. *J. Mater. Chem. A* , 3. 22574-22583 (2015).
15. Yang H., Xu Z., Fan M., Gupta R., Slimane R.B., Bland A. E. and Wright I. Progress in carbon dioxide separation and capture: a review. *J. Environ. Sci.* 20, 14-27 (2008).
16. Han S. H., Lee J. E., Lee K. J., Park H. B. and Lee Y.M. Highly gas permeable and microporous polybenzimidazole membrane by thermal rearrangement. *J. Memb. Sci.*, 357, 143-151 (2010).
17. Rasi S., Läntelä J. and Rintala J. Upgrading landfill gas using a high-pressure water absorption process. *Fuel*, 115. 539-543 (2014).
18. Baker R.W. and Lokhandwala K. Natural gas processing with membranes: An Overview. *Ind. Eng. Chem. Res.* 47. 2109-2121 (2008).
Wind J. D., Paul D. R. and Koros W. J. Natural gas permeation in polyimide membranes. *J. Membr. Sci.* 228. 227-236 (2004).
19. Nemestóthy N., Bakonyi P., Lajtai-Szabó P. and Bélafi-Bakó K. The impact of various natural gas contaminant exposures on CO₂/CH₄ separation by a polyimide Membrane. *membranes* 10. 324 (2020). doi:10.3390/membranes10110324
20. Xiao Y., Low B.T., Hosseini S. S., Chung T. S. and Paul D. R. The strategies of molecular architecture and modification of polyimide-based membranes for CO₂ removal from natural gas-A review. *Prog. Polym. Sci.*, 34. 561-580 (2009).
21. L.S. White, T.A. Blinka, H.A. Kloczewski, I-F. Wang. Properties of a polyimide gas separation membrane in natural gas streams. *J. Membr. Sci.* 103. 73- 82 (1995).

22. Chen Y., Wu H., Liu Z., Sun X., Xia Q. and Li Z. Liquid-Assisted mechanochemical synthesis of copper based MOF-505 for the separation of CO₂ over CH₄ or N₂. *Ind. Eng. Chem. Res.* 57. 703-709 (2018) .
23. Arab P., Rabbani M. G., Sekizkardes A. K., İslamoğlu T. and El-Kaderi H. M. Copper (I)-catalyzed synthesis of nanoporous azo-linked polymers: impact of textural properties on gas storage and selective carbon dioxide capture. *Chem. Mater.* 263. 1385-1392 (2014).
24. Bera R., Ansari M., Alam A. and Das N. Nanoporous azo polymers (NAPs) for selective CO₂ uptake. *J. CO₂ Util.*, 28. 385-392 (2018).
25. Arami-Niya A., Rufford T. E. and Zhu Z. Nitrogen-doped carbon foams synthesized from banana peel and zinc complex template for adsorption of CO₂, CH₄, and N₂. *Energy Fuel*, 30.7298-7309 (2016).
26. Jung M., Park J., Lee K., Attia N. F., Oh H. Effective synthesis route of renewable nanoporous carbon adsorbent for high energy gas storage and CO₂/N₂ selectivity. *Rene. Energy*, 161. 30-42 (2020).
Park J., Jung M., Jang H., Lee K., Attia N. F., Oh H. A facile synthesis tool of nanoporous carbon for promising H₂, CO₂, and CH₄ sorption capacity and selective gas separation. *J. Mater. Chem. A.* 6. 23087-23100 (2018).
27. Park J., Attia N. F., Jung M., Lee M. E., Lee K., Chung J., Oh H. Sustainable nanoporous carbon for CO₂, CH₄, N₂, H₂ adsorption and CO₂/CH₄ and CO₂/N₂ separation. *Energy*, 158. 9-16 (2018) .
28. Kim S., Cho S. Y., Son K., Attia N. F., Oh H. A metal-doped flexible porous carbon cloth for enhanced CO₂/CH₄ separation. *Sep. Purif. Technol.*, 277. 119511 (2021).
29. Park J., Cho S. Y., Jung M., Lee K., Nah Y.-C., Attia N. F., Oh H. H. Efficient synthetic approach for nanoporous adsorbents capable of pre-and post-combustion CO₂ capture and selective gas separation, *J. CO₂ Util.*, 45. 101404 (2021).
30. Jung M., Park J., Cho S. Y., Elashery S. E. A., Attia N. F., Oh H. Flexible carbon sieve based on nanoporous carbon cloth for efficient CO₂/CH₄ separation, *Surf. Interf.*, 23. 100960 (2021).
31. Attia N. F., Jung M., Park J., Jang H., Lee K., Oh H. Flexible nanoporous activated carbon cloth for achieving high H₂, CH₄, and CO₂ storage capacities and selective CO₂/CH₄ separation. *Chem. Eng. J.* 379. 122367 (2020).
32. Sayantan C., Sudip B., Piyali B., and Asim B. Porous organic–inorganic hybrid materials for catalysis, energy and environmental applications. *Chem. Comm.* 58 (2022) 3429-3460.
Rodríguez-Blanco G., Giraldo L. and Moreno-Piraján J. C. Carbon molecular sieves from carbon cloth: Influence of the chemical impregnant on gas separation properties. *Appl. Surf. Sci.*, 256. 5221-5225 (2010).
33. Arami-Niya A., Rufford T. E. and Zhu Z. Activated carbon monoliths with hierarchical pore structure from tar pitch and coal powder for the adsorption of CO₂, CH₄ and N₂. *Carbon*, 103. 115-124 (2016).
34. Chen Y., Lv D., Wu J., Xiao J., Xi H., Xia Q. and Li Z. A new MOF-505@GO composite with high selectivity for CO₂/CH₄ and CO₂/N₂ separation. *Chem. Eng. J.* 308. 1065-1072 (2017).

35. Sevilla M. and Fuertes A. B. Sustainable porous carbons with a superior performance for CO₂ capture, *Energy Environ. Sci.*, 4: 1765-1771 (2011).
36. Sevilla M., Parra J. B. and Fuertes A. B. Assessment of the role of micropore size and N-doping in CO₂ capture by porous carbons. *ACS Appl. Mater. Interf.*, 5. 6360-6368 (2013).
37. Sing K. S. W., Everett D. H., Haul R. A. W., Moscou L., Pierotti R. A., Rouquerol J. and Siemieniewska T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure Appl. Chem.*, 57. 603-611 (1985).
38. Attia N. F., Lee S. M., Kim H. J. and Geckeler K. E. Nanoporous polypyrrole: preparation and hydrogen storage properties, *Int. J. Energy Res.*, 38. 466-476 (2014).
39. Germain J., Hradil J., Frechet J. M. J. and Svec F. High surface area nanoporous polymers for reversible hydrogen storage. *Chem. Mater.*, 18. 4430-4435 (2006).
40. Attia N. F., Lee S. M., Kim H. J. and Geckeler K. E. Nanoporous carbon-templated silica nanoparticles: Preparation, effect of different carbon precursors, and their hydrogen storage adsorption. *Micro. Meso. Mater.* 173. 139-146 (2013).
41. Sevilla M., Sangchoom W., Balahmar N., Fuertes A. B. and Mokaya R. Highly porous renewable carbons for enhanced storage of energy-related gases (H₂ and CO₂) at high pressures. *ACS Sustain. Chem. Eng.*, 4. 4710-4716 (2016).
42. Sevilla M., Parra J. B. and Fuertes A. B. Assessment of the role of micropore size and N-doping in CO₂ capture by porous carbons. *ACS Appl. Mater. Interf.* 5. 6360-6368 (2013).
43. Yuan B., Wu X., Chen Y., Huang J., Luo H. and Deng S. Adsorption of CO₂, CH₄, and N₂ on ordered mesoporous carbon: approach for greenhouse gases capture and biogas upgrading. *Environ. Sci. Technol.*, 47. 5474-5480 (2013).
44. Rabbani M. G., Sekizkardes A. K., El-Kadri O. M., Kaafarani B. R. and El-Kaderi H. M. Pyrene-directed growth of nanoporous benzimidazole-linked nanofibers and their application to selective CO₂ capture and separation. *J. Mater. Chem.*, 22. 25409-25417 (2012).
45. Lv D., Shi R., Chen Y., Chen Y., Wu H., Zhou X., Xi H., Li Z. and Xia Q. Selective adsorptive separation of CO₂/CH₄ and CO₂/N₂ by a water resistant zirconium-porphyrin metal-organic framework. *Ind. Eng. Chem. Res.* 57. 12215-12224 (2018).
46. Wang X., Yuan B., Zhou X., Xia Q., Li Y., An D. and Li Z. Novel glucose-based adsorbents (Glc-Cs) with high CO₂ capacity and excellent CO₂/CH₄/N₂ adsorption selectivity. *Chem. Eng. J.* 327. 51-59 (2017).
47. Peng X., Cheng X. and Cao D. Computer simulations for the adsorption and separation of CO₂/CH₄/H₂/N₂ gases by UMCM-1 and UMCM-2 metal organic frameworks. *J. Mater. Chem.* 21. 11259-11270 (2011).
48. Li H., Ding X., Zhao Y.-C. and Han B.-H. Preparation of mannitol-based ketal-linked porous organic polymers and their application for selective capture of carbon dioxide. *Polymer* 89. 112-118 (2016).
49. Nugent P., Belmabkhout Y., Burd S.D., Cairns A.J., Luebke R., Forrest K., Pham T., Ma S., Space B., Wojtas L., Eddaoudi M. and Zaworotko M.J. Porous materials with

- optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature* 495. 80–84 (2013).
50. Lv D., Chen J., Yang K., Wu H., Chen Y., Duan C., Wu Y., Xiao J., Xi H., Li Z. and Xia Q. Ultrahigh CO₂/CH₄ and CO₂/N₂ adsorption selectivities on a cost-effectively L-aspartic acid-based metal-organic framework. *Chem. Eng. J.* 375. 122074 (2019).
 51. Singh M., Solanki P., Patel P., Mondal A. and Neogi S. Highly active ultrasmall Ni nanoparticle embedded inside a robust metal–organic framework: remarkably improved adsorption, selectivity, and solvent-free efficient fixation of CO₂. *Inorg. Chem.* 58. 8100-8110 (2019).
 52. Li Y.W., Yan H., Hu T. L., Ma H. Y., Li D. C., Wang S. N., Yao Q. X., Dou J. M., Xu J., Bu H. Two microporous Fe-based MOFs with multiple active sites for selective gas adsorption. *Chem. Commun.* 53. 2394-2397 (2017).
 53. He J., To J.W.F., Psarras P.C., Yan H., Atkinson T., Holmes R.T., Nordlund D., Bao Z. and Wilcox J. Tunable polyaniline-based porous carbon with ultrahigh surface area for CO₂ capture at elevated pressure. *Adv. Energy Mater.*, 6. 1502491 (2016).
 54. Saleh M., Lee H. M., Kemp K. C. and Kim K. S. Highly stable CO₂/N₂ and CO₂/CH₄ selectivity in hyper-cross-linked heterocyclic porous polymers. *ACS Appl. Mater. Interfaces* 6. 7325-7333 (2014).
 55. Yuan B., Wang J., Chen Y., Wu X., Luo H. and Deng S. Unprecedented performance of N-doped activated hydrothermal carbon towards C₂H₆/CH₄, CO₂/CH₄, and CO₂/H₂ separation. *J. Mater. Chem. A* 4. 2263-2276 (2016).