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

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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 (CH_4) 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 CO_2 creating corrosion and combustion quality demerits for using of natural gas directly. Therefore, the selective capture of CO_2 from natural gas streams via an energy-efficient adsorption process in porous materials is a mandatory industrial requirement before the distribution and commercialization of CH_4. 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 CO_2/CH_4 and its separation adsorption action were briefly discussed.

Keywords: Nanoporous materials; Natural gas purification; CO2/CH4 separation selectivity; Greenhouse gases; CO_2 capture.

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 (CH_4) 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, CH_4 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 CO_2 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 CO_2 (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 CH_4 in different activities [13-15]. Various materials have been utilized to separate CO_2 over CH_4 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 CO_2 over CH_4 streams [23-30]. I and others have dedicated our research exploring new and chemically stable cost-effective, and efficient porous adsorbents for separating CO_2 over CH_4 and N2 [30-37]. Thus, this review briefly discusses the types of porous adsorbents and synthesis and utilization for separation of CO_2/CH_4.

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].

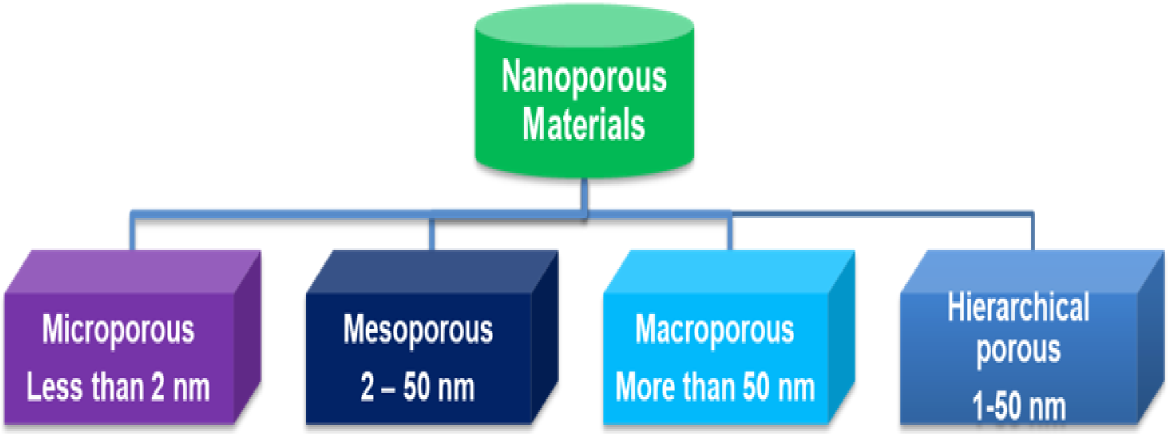

Figure 1: Schematic diagram representing the classes of porous materials based on pore size.

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]. 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]. 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].

3 CO_2/CH_4 separation selectivity

The selection separation of CO_2 from CH_4 stream is the crucial industrial process before the commercialization of CH_4 to afford high safety standards for transportation and process and achieve green and efficient combustion quality in engines. Therefore, various materials were tested for CO_2/CH_4 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. 2).

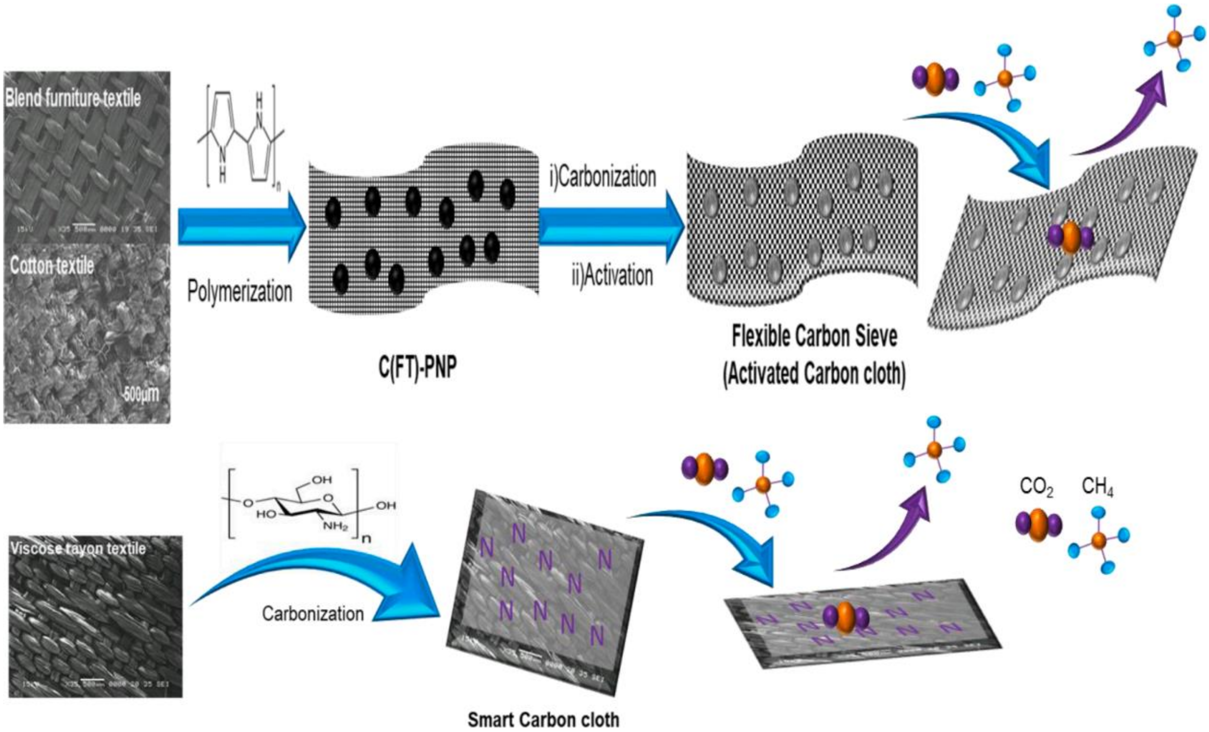

Figure 2: Schematic representation showing the novel synthesis of flexible carbon sieves, reproduced with permission [32]. Copyright 2021, Elsevier.

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. 3 [32]. It was found that the separation selectivity CO_2/CH_4 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 CO_2 over CH_4; the first one is which affords narrow micropores and facilities the adsorption of smaller size CO_2 molecule rather than CH_4 molecule [32,33]. The second is the generation of active basic sites for adsorption of acidic nature CO_2 molecule rather than low polarizability CH_4 [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 CO_2/CH_4 separation selection under different conditions as listed in Table 1. Nevertheless, the separation selectivity value for CO_2/CH_4 is still limited and ranged in 3.5-72.9 [5,26,32-37,46-58].

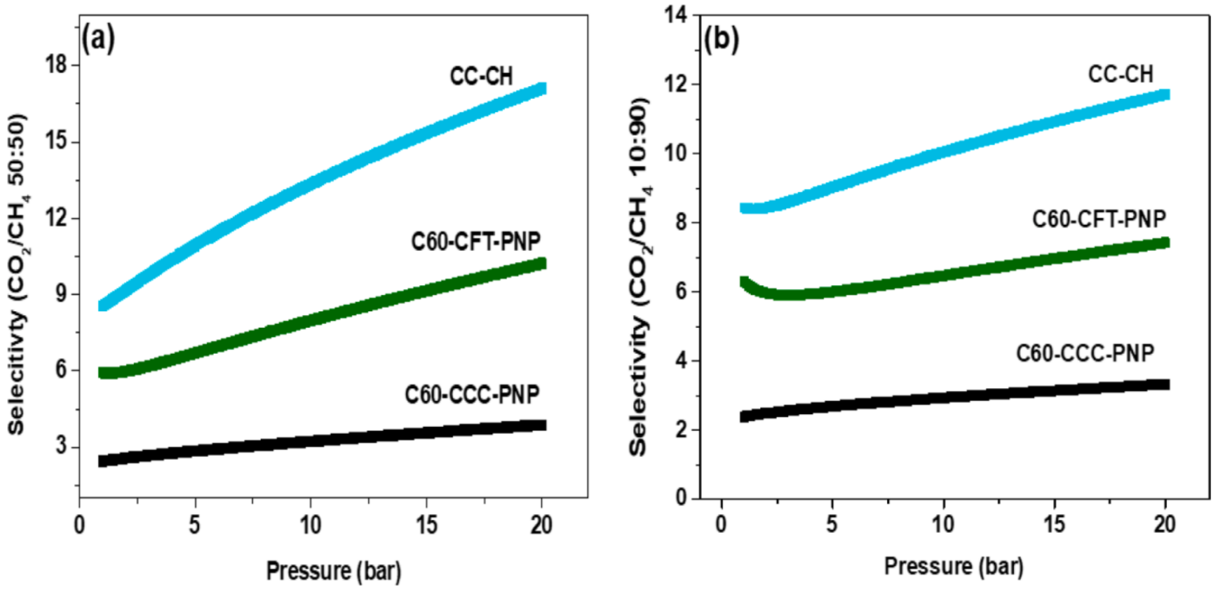

Figure 3: CO_2/CH_4 selectivity based on the ideal adsorbed solution theory method for mixture composition of (a) (50:50), (b) (10:90) for developed flexible carbon sieve, reproduced with permission [32]. Copyright 2021, Elsevier.

Interestingly, recently, after the inclusion of magnetic nickel nanostructures in upwards structure on the surface of porous flexible carbon cloth (Fig. 4), a breakthrough in CO_2/CH_4 separation selectivity was attained (Table 1) [30]. The separation selectivity of CO_2/CH_4 at the binary gas mixture of 50:50 achieved 369.5 and 70 at room temperature (RT) and 20 and 1 bar respectively (Fig. 5). Additionally, the smart filter affords high CO_2/CH_4 separation selectivity at low concentration of CO_2 (binary gas mixture of 10:90 for CO_2:CH_4) 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 CO_2 molecules and Ni/NiO sorption sites situated on flexible porous carbon cloth [30].

Table 1: CO_2/CH_4 (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

[a]The average selectivity value at 298 K.

[b]The selectivity value at 1 bar and 298 K.

[c]The selectivity value at 1 bar and 273 K.

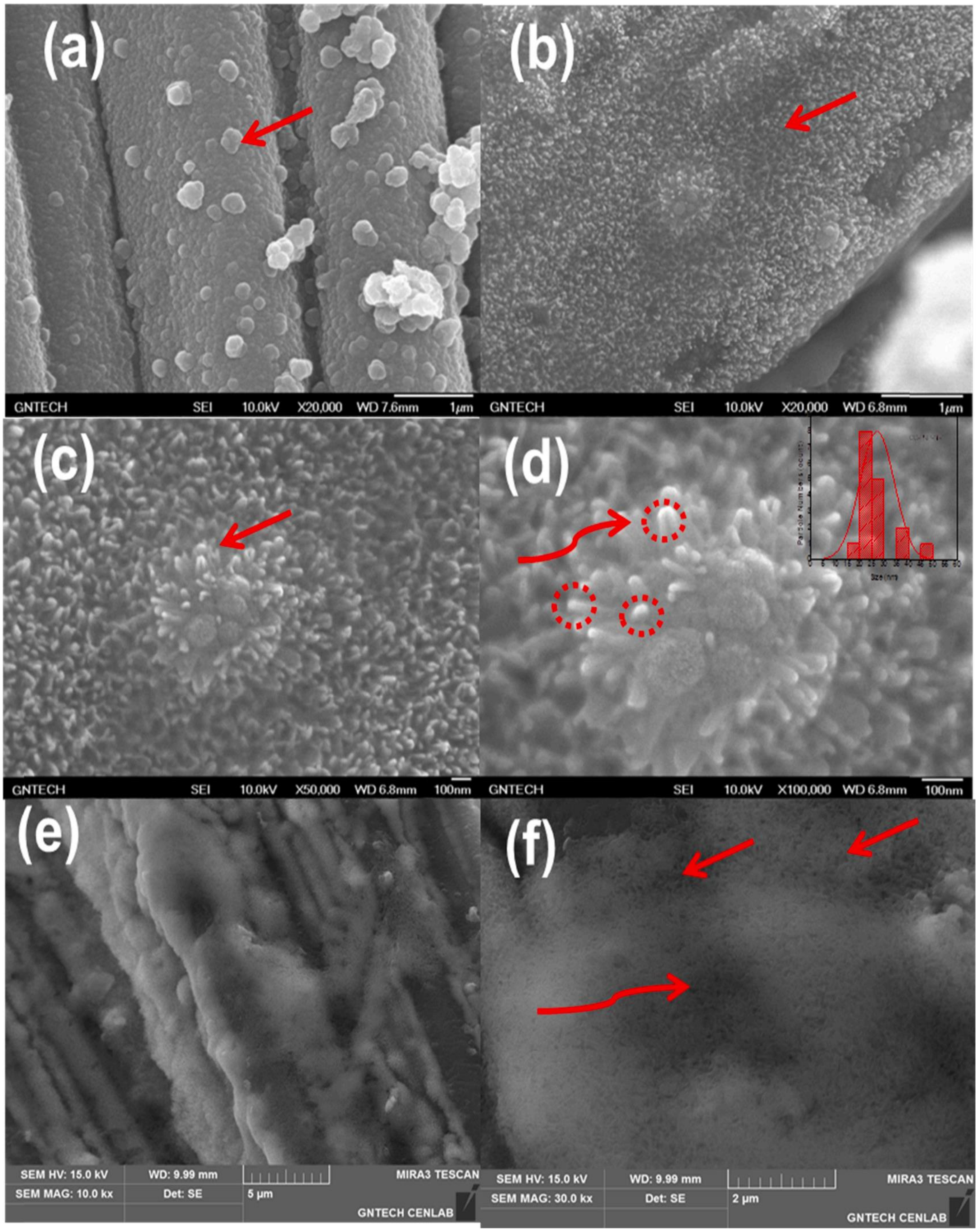

Figure 4: SEM images of (a) CC-PNP, (b) CC-PNP-Ni-7, (c) and (d) CC-PNP-Ni-7 at high magnification, (e) CC-PNP-Ni-10 and (f) CC-PNP-Ni-10 at high magnification, reproduced with permission [30]. Copyright 2021, Elsevier.

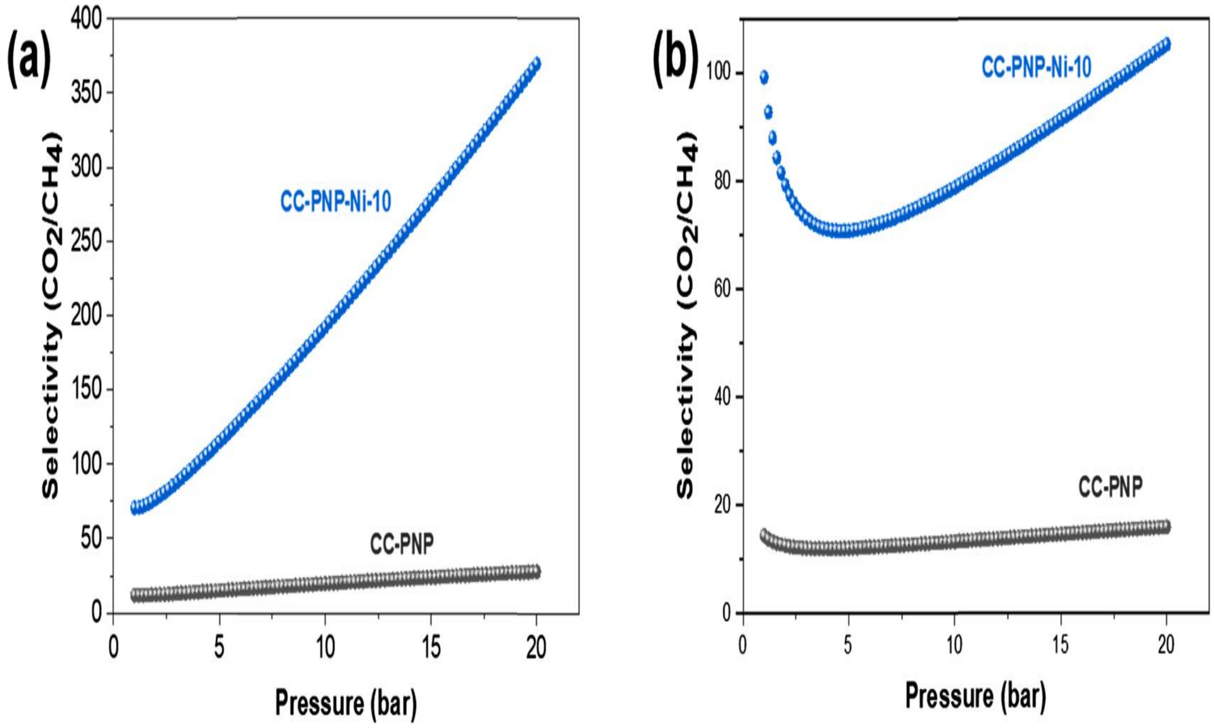

Fig. 5. CO_2/CH_4 selectivity based on the ideal adsorbed solution theory method for mixture composition of (a) (50:50), (b) (10:90) for developed magnetic flexible carbon cloth, reproduced with permission [30]. Copyright 2021, Elsevier.

4 Conclusion

Natural gas (CH_4) 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 CO_2/CH_4 was discussed. Selective capture of CO_2 over CH_4 was studied. Also, the key factors for enhancing the interaction affinity between polarizable CO_2 molecules and micropore walls of porous materials were introduced and reviewed.

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