CARBON letters

Review Articles
Carbon Letters Vol. 17, No. 1, 18-28 (2016)

A review: methane capture by nanoporous carbon materials for automobiles

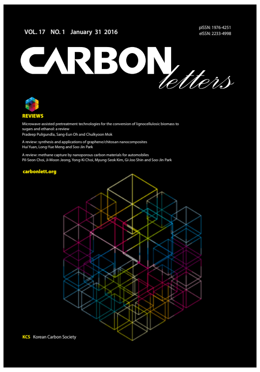
Pil-Seon Choi[1], Ji-Moon Jeong[2], Yong-Ki Choi[2], Myung-Seok Kim[2], Gi-Joo Shin[2] and Soo-Jin Park[2,*]

[1]Fuel & Exhaust Engineering Design Team of Research & Development Division, Hyundai Motor Group, Hwaseong 18280, Korea
[2]Department of Chemistry, Inha University, Incheon 22212, Korea

Article Info
Received 22 May 2015
Accepted 19 June 2015

***Corresponding Author**
E-mail: sjpark@inha.ac.kr
Tel: +82-32-876-7234

DOI: http://dx.doi.org/10.5714/CL.2016.17.1.018



http://carbonlett.org

pISSN: 1976-4251
eISSN: 2233-4998

Abstract

Global warming is considered one of the great challenges of the twenty-first century. In order to reduce the ever-increasing amount of methane (CH_4) released into the atmosphere, and thus its impact on global climate change, CH_4 storage technologies are attracting significant research interest. CH_4 storage processes are attracting technological interest, and methane is being applied as an alternative fuel for vehicles. CH_4 storage involves many technologies, among which, adsorption processes such as processes using porous adsorbents are regarded as an important green and economic technology. It is very important to develop highly efficient adsorbents to realize techno-economic systems for CH_4 adsorption and storage. In this review, we summarize the nanomaterials being used for CH_4 adsorption, which are divided into non-carbonaceous (e.g., zeolites, metal-organic frameworks, and porous polymers) and carbonaceous materials (e.g., activated carbons, ordered porous carbons, and activated carbon fibers), with a focus on recent research.

Key words: methane gas, methane storage, nanomaterial, porous material, carbon adsorbent

1. Introduction

1.1 Global warming and attractive fuels

Over the past 10 y, governments worldwide have been establishing policies to provide renewable and clean energy. Their positions, which have been established from both increasing recognition of environmental problems and from economic demand, have led scientific and industrial communities to study and exploit fresh and useful alternatives to decrease the environmental effects from the use of fossil fuels. For these reasons, the increasing demand for electrical energy and transport fuel has motivated the United States [1] and European Union [2] governments, as well as scientific communities [3], to find new and green energy-carrier resources. Until recently, renewable and clean energy accounted for only a small section of the energy market; however, recent demand has led to growth in this area. Moreover, the abundance of natural gas deposits in some parts of the world will provide a massive resource of energy in the upcoming decades [4].

Natural gas is considered an alternative fuel because of its very low price as an efficient resource [5]. In addition, many researchers and industrial administrators are interested in using universal applications that can be used as alternative fuels for vehicles [6].

The greenhouse effect, which is widely believed to cause global warming, is a result of industrialization and the generation of gases such as methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and so on. Because of the rise in the production of greenhouse gases over the past century, the temperature of the earth has increased by 0.76% and is gradually increasing [7,8]. Many researchers have raised concerns over greenhouse gases and have studied methods directed at their elimination. In particular, CH_4, which is generated by organic waste, cow manure, and industrial waste, is being studied for use as a clean energy. CH_4 is an eco-friendly and generally lower risk energy source that could serve as an alternative, green energy in the international markets for years to come [9-11].

1.2 CH_4 gas and storage for vehicular energy

A large fraction of natural gas is CH_4, which has a low volumetric energy density (VED); however, its use is limited because of storage and transportation issues. For this reason, its compression and storage are of great interest to industrial and scientific communities.

The main challenge is the ability to store natural gas under atmospheric conditions (temperature and pressure) in order to reduce transportation limitations and facilitate its use [12]. In view of this important goal, it is necessary to take into account evaluation of the CH_4 storage capacity, which should reach a target of 150 v/v for the year 2015 [13]. This figure was recently revised to 180 v/v [14-16] (the volume of gas adsorbed at standard temperature and pressure: 298 K, 0.1 MPa, per volume of the storage vessel) or equivalently 35 wt% [17] at 3.5 MPa according to the U.S. Department of Energy.

Currently, CH_4 storage methods involve high-pressure compression in tanks (compressed natural gas [CNG]) [18,19] (the tank mass contributes largely to the storage system mass, significantly decreasing the CH_4 wt% capacity of the entire system) and/or storage in liquid form (liquid natural gas [LNG]) at temperatures down to 120 K (mainly used for intercontinental transportation). Together with the energy density requirements, CH_4 portability has strict requirements in terms of safety, refilling, and delivery. From this perspective, studies on adsorbed natural gas (ANG) and natural gas hydrate (NGH) have been carried out with the aim of representing an efficient alternative solution for CH_4 portability [20].

NGH is solid and has a theoretical volumetric capacity of 164 or 174 v/v, assuming complete filling of the water cages within the clathrate structure, but the formation conditions of NGH are rigorous and its formation rate is low [21]. In addition, the stored gas cannot be released from hydrates by reducing the pressure. Hence, NGH is not suitable as a commercial technique for CH_4 storage.

Compared to pressurization, cryogenic liquefaction, or any other storage method on the market, CH_4 storage through solid materials (ANG) presents advantages according to gravimetric and VED, safety, and energy efficiency. The classification of natural gas adsorption technologies is presented in Fig. 1. It is important to note that the critical issues related to commercialization of ANG storage technology not only include the storage capability of the adsorbent but also the facility costs and the cost of manufacturing. The most important evaluation of the performance of an ANG storage system is the volume of usable gas [22]. This is what scientists frequently call delivery, and it is defined as the volume of gas obtained from the storage vessel when the pressure is reduced from a storage pressure of 35 to 1 bar at room temperature [23]. Despite these issues, ANG technology, where natural gas is adsorbed by a porous adsorbent material at relatively low pressures (35/40 bar), is considered a promising solution in energy storage, especially in the natural-gas fuelled vehicles sector [24]. Within this global energy scenario, it is evident that one of the most important goals for the extensive use of CH_4 is the synthesis of CH_4 storage materials with good adsorption properties under convenient temperature and pressure, but particularly with on-board operating storage capabilities for vehicular applications [25,26].

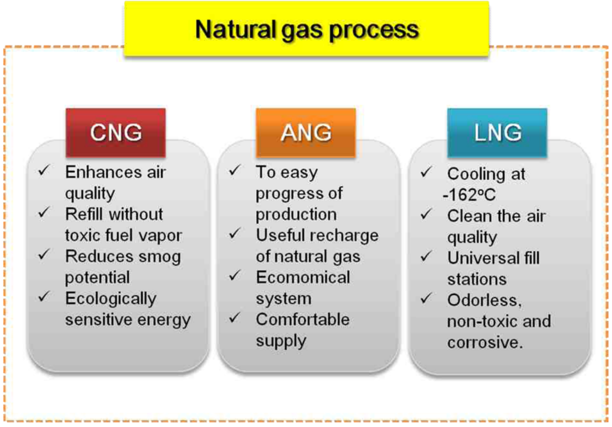


Fig. 1. Classification of natural gas process technologies. CNG, compressed natural gas; ANG, adsorbed natural gas; LNG, liquefied natural gas.

Until now, all available materials present different limitations, especially for on-board storage applications. These limitations include (1) relatively high thermal stability, (2) slow desorption/absorption kinetics, (3) unstable structures [27], (4) high weight, (5) irreversibility upon cycling [28], and (6) high production costs. For these reasons, researchers have focused on the development and analysis of meso- and nano-structured systems with high specific surface areas to exploit CH_4 physisorption.

2. Methane Storage Technology

2.1 Effect of surface treatment on carbonaceous materials for gas adsorption

Much of the previous work in this field has involved the application of adsorbents for CH_4 storage (gas adsorption). Many researchers have studied the use of carbonaceous materials for gas adsorption. Carbonaceous materials have been widely used in industrial applications such as adsorbents [29-31], supercapacitors [32], and batteries. They can be produced from natural materials, including wood, charcoal, petroleum coke, sawdust, and coconut shell. Because of their advantages, carbonaceous materials have been of interest for decades. In particular, we have studied carbonaceous materials as gas adsorbents according to various surface treatments, such as ozone [33], plasma [34], thermal [35], and electrochemical treatment [36].

Park et al. [36] reported the pore structure and surface properties of activated carbons (ACs) for Cr(VI) adsorption enhanced by chemical modifications using acids and bases. Im et al. [37] reported that for hydrogen adsorption, the pore size of electrospun carbon nanofibers was controlled by activation.

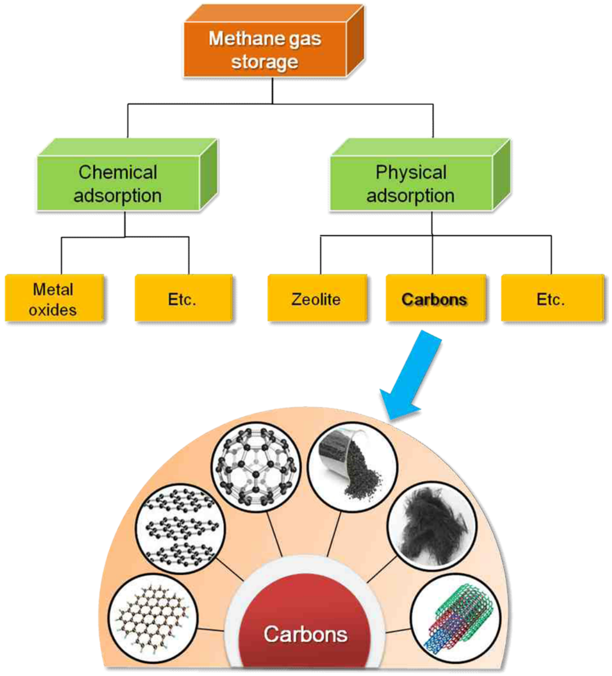


Fig. 2. Classification of application technologies for methane gas storage.

2.2 CH_4 storage technology using porous adsorbents

The process of storing CH_4 through porous adsorbents utilizes the selective adsorption found in gas-solid interactions [38,39]. Typically, common porous adsorbents such as metal-organic frameworks (MOFs), zeolites, ACs, and activated carbon fibers (ACFs) are used in storage tanks. The significant parameters in the adsorption process are (1) the temperature and pressure during the adsorption and (2) the pore size distribution of the adsorbent. The cycle of adsorption and desorption is involved in the CH_4 storage process [40].

The different storage methods are as follows: (1) compression to 200-300 bar at room temperature and (2) liquefaction at low temperature. In these methods, the VED of liquefied CH_4 gas achieves ~64% of the VED of gasoline (34.2 MJ L^{-1}) but it must be stored in high-cost cryogenic vessels and suffers boil-off losses. While CNG necessitates the use of heavy, thick-walled, cylindrical storage tanks and multi-stage compressors to achieve a reasonable VED (9.2 MJ L^{-1}), it achieves only 27 % of the VED of gasoline. In spite of the improvements to cylinders and compressors, the majority of natural gas is stored in CNC tanks [41].

It is necessary to improve the CH_4 storage capacity and adsorption selectivity of porous adsorbents to avoid large amounts of combustion emissions from various sources. CH_4 storage can be stabilized and improved using the pore structure [42-45] and high specific surface area [46] of adsorbents.

In order to achieve a high storage capacity, the establishment of various methods used as CH_4 storage adsorbents is expected to enhance adsorption efficiency for CH_4 storage. Many adsorbents have advantages such as low cost implementation for reproduction and perdu elimination of loss problems.

The process of adsorption is reversible and modification of the adsorbent structure could improve the adsorption efficiency. Moreover, the selection of a suitable adsorbent could improve the CH_4 storage efficiency. At present, the universal adsorbent materials are zeolites [47], porous silicas [48], ACs [49], regular fibers, and so on. These materials have various pore sizes, structures, and specific surface areas, as well as many available fields. Some porous adsorbents for CH_4 storage are listed in Fig. 2 and Table 1 and will be explained in the following section.

3. Porous Non-Carbonaceous Adsorbents

3.1. Metal-organic frameworks and porous polymers

Many MOFs have been prepared by combining organic (ligands) with inorganic units (metal clusters) through strong combination (reticular bond). The functionalities of the components can be varied and the flexibility in size and geometry has progressed toward more than 21,000 various MOFs being studied and announced, with their specific surface areas ranging widely from 1000 to 10,000 m^2/g [50,51]. They have popularized many previous studies because of their excellent adsorption capacities, their specificity for the adsorption of CO_2 [52-54], H_2 [55-57], or hazardous gases, and their great selectivities [58-61]. In addition, they are widely used as chemical catalysts for synthesis. The adsorbents structures of MOF for CH_4 storage are the useful position at the core because of entanglement of molecules. Several structures have a huge adsorbent volume because the pores interact with metallic ions and organic molecules. MOFs are used in gas storage applications because their pore diameters are easily controlled.

Furthermore, conjugated microporous polymers (CMPs) have been of interest because of their porous structures with organic functionalities, for such applications as gas storage, capture, and separation [61-64]. In particular, the committee of CMPs offers novel materials capable of CH_4 storage and their properties can be reduced effectively. Jiang et al. reported that the CH_4 storage efficiencies of Co-CMP and Al-CMP were partially high, although the specific surface areas were lower than those of other MOF materials.

MOFs have excellent CH_4 adsorption capacity at high pressure and low temperature. However, many MOFs have low CH_4 adsorption performance compared to other adsorbents. In order to increase the CH_4 adsorption efficiency, MOFs should be further developed. In addition, the process of preparing MOFs from organic ligands and metal complexes is very expensive and complicated. MOFs accompany many problems because of hindrance during CH_4 adsorption. The use of MOFs in the field of CH_4 adsorption must therefore overcome these limitations.

Kaskel et al. [65] synthesized an MOF (HKUST-1) for CH_4 storage at low pressure. They confirmed that HKUST-1 showed a CH_4 adsorption capacity of 16.5 wt% at 298 K and 35 bar. In addition, the obtained specific surface area was higher than the values of different MOF samples.

Senkovska and Kaskel. [66] prepared an MOF using a porous coordination polymer and evaluated the CH_4 storage capacity.

Table 1. Distribution of porous adsorbents for CH_4 storage

Specimen	Temperature (K)	Pressure (bar)	Specific surface area (m^2/g)	Methane uptake capacity (wt%)	Reference
Zeolite	303	1	692	1.4	[113]
Zeolite-like carbon materials	298	35	-	8.5	[114]
SWCNT	300	40	-	21	[115]
SWNH	303	35	1030	10.6	[116]
SiOC-CDC	298	60	2700	21.5	[117]
PC	273	26	1927	16.5	[118]
MWCNT	298	105	341	11.7	[119]
MOF-CNT	298	18	850	13	[120]
MOF (NU-800)	298	65	3149	21.5	[121]
MOF (IRMOF-6)	298	50	2640	17	[122]
MOF (HKUST-1)	298	35	1850	16.5	[123]
MOF (HKUST-1)	290	35	1748	15.3	[124]
MOF ($Cu_3(btc)_2$)	303	35	1502	14	[125]
MOF (MOF-519)	298	35	2400	13.3	[126]
MOF ($Ni_2(dhtp)$)	298	35	-	12.6	[127]
MOF (UTSA-20)	300	35	1156	11.8	[128]
MCM-41	273	5	-	6.5	[129]
Maxsorb (Grade 30-SPP)	298	3	-	21.1	[130]
GAC (AC3)	298	35	1178	12.7	[131]
Carbide-derived carbon	298	60	3360	18	[132]
Carbon pellets	298	35	2136	8.5	[133]
BC_3 nanosheet (h-BC_3)	298	1	-	18.1	[134]
ACF (Pitch based, A10)	313	3.5	1000	8.3	[135]
ACF (Cellulose based, KF1500)	313	3	1500	8.2	[135]
ACF (CFC54)	298	40	1930	16	[136]
ACF (F-EsACF-5)	298	35	2500	18.1	[137]
ACF (ACF3)	303	35	1397	13.6	[138]
AC (AX21)	243	30	4827	31	[139]
AC (Sugarcane)	293	50	2202	19	[140]
AC (C10)	303	35	2336	19	[141]
AC (Maxsorb III)	298	20	3140	17	[142]
AC (HSAC21)	298	35	1465	16	[143]
AC (RP-20)	303	35	1853	12	[144]
AC (LFC73)	298	35	2400	15.4	[145]
AC (S-800-90-10)	298	50	610	10.7	[146]
AC (CAC-2)	298	30	1141	5.2	[147]

SWCNT, Single-walled carbon nanotube; SWNH, Single-walled carbon nanohorn; SiOC-CDC, Silicon oxycarbide derived carbon; PC, Polycarbonate; MWCNT, Multi-walled carbon nanotube; MOF-CNT, Metal-organic framework-carbon nanotube; MOF, Metal-organic framework; MCM-41, Mobil composite material number 41; GAC, Granular activated carbon; ACF, Activated carbon fiber, AC: activated carbon.

From the results, they confirmed that $Cu_3(btc)_2$ (HKUST-1) (btc = benzene-1,3,5-tricarboxylate) showed the highest CH_4 adsorption capacity at 303 K and 35 bar (15.7 wt%).

3.2. Zeolites

Zeolites exist in natural microporous crystalline silicate framework foams and they can be produced by artificial methods in the lab. They are classified by their pore size, which ranges from 0.5 to 1.2 nm, for the adsorption of gas molecules [67]. They also have been widely applied to gas separation and purification [68-70]. Many researchers have investigated CH_4 storage using zeolites because of the microporous structures between their porosity and CH_4 molecules in the zeolite frameworks. The metal cations in zeolites (i.e., Li, Na, and Al) affect the CH_4 adsorption. CH_4 storage using zeolites has been studied in previous works, mainly with zeolite 5A and zeolite 13X, which show CH_4 storage performance of 2-27 wt% at room temperature and high CH_4 gas pressure [71-74].

Grande and Blom. [75] prepared commercial zeolite 4A and zeolite 13X for efficient adsorption of CH_4 gas. This study was performed with a wide range of pressures (1-10 bar) and flow rates. They reported that zeolite 13X presented an efficiency of 16 wt% at 279 K and 1 bar for CH_4 storage.

Sethia et al. [76] reported that cesium-exchanged zeolite-X could adsorb a natural gas mixture. From the experiments, they reported that the cesium-exchanged zeolite showed a CH_4 adsorption capacity of 14 wt% at 303 K and 1 bar.

3.3. Carbonaceous adsorbents

The carbonaceous adsorbent materials consist of carbon and show good properties such as high strength, heat and electrical conductivities, thermal and chemical stabilities, and eco-affinities [77-82]. They are especially superior for applications in gas storage or adsorption because of their high specific surface areas, large pore volumes, and light weight. Moreover, they have the following advantages for CH_4 storage: (1) carbonaceous materials are not sensitive to wet conditions; (2) the cost of carbonaceous materials is reasonable; (3) the adsorption-desorption temperatures are not particularly good under 373 K; (4) the energy consumption is efficiently low; and (5) they can be applied under atmospheric pressure. All of these conditions affect the studies presently discussed.

3.3.1. Activated carbons

The CH_4 storage capacity is highly influenced by the textural properties. The pore sizes of ACs are classified from micropore to macropore; thus, ACs are not suitable for selective adsorption of a specific gas. Carbonaceous materials as adsorbents generally have low adsorption performance for CH_4, with adsorption heats of less than 45 kJ/mol. The CH_4 storage capacity of an AC is ~14 wt% at 298 K and 35 bar [83]. The textural properties of ACs can be controlled by various activation factors and preparation [84-88]. In particular, the adsorption capacity of ACs as adsorbents for gas storage is influenced by the pore structures.

Sreńscek-Nazzal et al. [140] prepared KOH-AC from sugarcane molasses, which gave a CH_4 adsorption capacity of 19 wt% at 50 bar and 293 K. They emphasized that its remarkable CH_4 storage ability was a result of its preparation involving chemical activation with KOH and carbonization, which led to a good pore structure and thus good CH_4 storage ability. In addition, when prepared by carbonization at 1053 K with a KOH weight ratio of 2.8, the AC demonstrated a high specific surface area (2202 m^2/g) and optimal pore structures.

Bastos-Neto et al. [89] reported ten AC samples prepared using different raw materials. They claimed that the good CH_4 adsorption ability was due to an optimal micropore volume (8-15 Å) and specific surface area (2336 m^2/g). Moreover, they determined the CH_4 adsorption capacity, which was 19 wt% at 303 K and 35 bar. They observed that the AC samples prepared using different raw materials had different textural properties and CH_4 storage capabilities.

Policicchio et al. [114] synthesized high surface activated carbon (HSAC) samples with a pyrolysis temperature and time of 1073 K and 360 min, respectively. The HSAC samples were formed with specific surface areas of up to 1784.36 m^2/g and narrow micropore sizes. The samples were then analyzed by the BET method for surface area and micropore volume measurements. The CH_4 storage capacities of HSAC samples were measured using a Sievert type (*f*-PcT) apparatus at 298 K and 35 bar. They verified that the CH_4 adsorption capacity was 16 wt% and was strongly influenced by the micropore sizes of the adsorbent materials.

Zhou et al. [92] reported the preparation of wet carbon from corncob with tailored pore sizes using a KOH activation agent. The wet carbon had an optimum narrow pore size distribution from 1.6 to 2.8 nm and presented a very high CH_4 storage capacity of 65 wt% at 275 K and 33.5 bar. They emphasized that the high CH_4 storage capacity was attributable to the presence of a tailored pore size distribution, together with a high percentage of optimal pore sizes.

3.3.2. Ordered porous carbons

Ordered porous carbon materials have attracted much research attention due to their wide applications in gas storage, and as electrode materials, supports, catalysts, etc. [93-98]. Many synthetic methods for ordered porous carbon materials have been reported including (1) direct synthesis by organic–organic self-assembly, involving a combination of carbon precursors and block copolymers as soft templates, and (2) nanocasting using silica materials as structural directing hard templates [99-102].

Cao et al. [102] reported that an ordered mesoporous carbon synthesized using a soft-templating method had a CH_4 adsorption capacity of 21 wt% at 300 K and 40 bar. Guan et al. [103] reported that template carbons synthesized using a pyrolysis method had a high specific surface area of ~1,500 m^2/g. Zeolite-template carbon fabricated by carbonization of sucrose had a CH_4 adsorption capacity of 12 wt% at 300 K and 35 bar.

3.3.3. Activated carbon fibers

ACFs are attractive adsorbent materials because they have high specific surface areas and narrow pore size distributions [105-108]. In addition, the fibrous structure of ACFs is easier to handle than granular and powdered carbonaceous materials [109-110].

Shao et al. [111] prepared ACFs by a physical activation

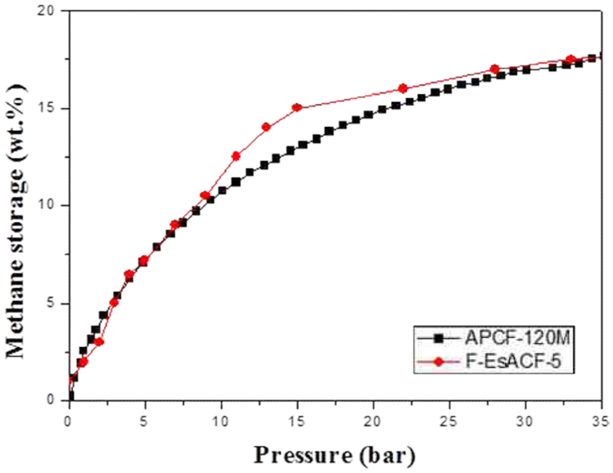


Fig. 3. Methane storage isotherms for APCF-120M and F-EsACF-5 at 298 K and 35 bar. APCF-120M was studied by the present authors. Modified and reproduced from In et al. [137] with permission.

method using pitch-based carbon fibers as a raw material at 1173 K under a flow of H_2O/N_2. The obtained samples showed a CH_4 adsorption capacity of 11 wt% at 298 K and 15 bar. It was found that the pore structure of ACFs could be tuned by controlling the ratio of H_2O/N_2 as the active agent. In addition, the CH_4 adsorption capacity was highly influenced by the narrow micropore size distribution.

Alcañiz-Monge et al. [112] prepared ACFs by CO_2 and steam activation methods using petroleum-pitch based carbon fiber as a raw material. The prepared samples showed a CH_4 storage capacity of 16 wt% at 298 K and 40 bar. It was shown that the CH_4 storage capacity of the ACFs could be enhanced by increasing the micropore sizes.

Im et al. [137] prepared ACFs by fluorination modification using electrospun carbon fibers as a raw material at 1023 K for 3 h in an argon atmosphere. The obtained samples showed a CH_4 adsorption capacity of 17.5 wt% at 298 K and 35 bar. It was found that the pore structure of electrospun ACFs could be tuned by controlling the fluorination surface modification. In addition, the CH_4 adsorption capacity was highly influenced by the synergetic effects of the developed micropore structure and the guiding of methane to carbon pores by fluorine. Fig. 3 shows this data in comparison with other data. The F-EsACF-5 sample showed high methane storage capacity of about 17.5 wt%. Furthermore, the APCF-120M sample showed 17.1 wt% methane storage capacity. The APCF-120M sample was studied by the present authors and prepared by KOH activation using pitch based carbon fibers as a raw material. According to Fig. 3, carbonaceous adsorbent materials, such as AC and ACFs, are suitable for methane storage materials.

4. Conclusions

Useful adsorbents for CH_4 storage technologies should be improved in terms of their storage capacity and adsorption/desorption cycle durability. The study of vastly superior adsorbents for CH_4 storage requires the implementation techno-economical systems. Thus, it is significant that a large body of data has been collected using adsorption reactors and gas storage systems. In addition, because of the progress of nanoporous adsorbents for CH_4 storage, it is expected that improved techno-economical systems will enhance the adsorption performance of CH_4 gas. Furthermore, nanoporous carbonaceous materials as CH_4 storage adsorbents will be extensively developed by researchers and applied to alternative vehicle fuels.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

This study was supported by the Carbon Valley Project of the Ministry of Trade, Industry and Energy, South Korea. This study was also supported by Hyundai Motor Group, Korea.

References

[1] Gallo M, Glossman-Mitnik D. Fuel gas storage and separations by metal-organic frameworks: simulated adsorption isotherms for H_2 and CH_4 and their equimolar mixture. J Phys Chem C, **113**, 6634 (2009). http://dx.doi.org/10.1021/jp809539w.

[2] Rackley SA. Carbon Capture and Storage. Butterworth-Heinemann/Elsevier, Boston (2010).

[3] Hester RE, Harrison RM. Electronic Waste Management. RSC Publishing, Cambridge (2009).

[4] Roosa SA, Ghaveri AG. Carbon Reduction: Policies, Strategies, and Technologies. Fairmont Press, Lilburn, GA (2009).

[5] Wilson EJ, Gerard D. Carbon Capture and Sequestration: Integrating Technology, Monitoring and Regulation. Blackwell Publishing, Ames, IA (2007).

[6] Yang J, Sudik A, Wolverton C, Siegel DJ. High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery. Chem Soc Rev, **39**, 656 (2010). http://dx.doi.org/10.1039/B802882F.

[7] Graetz J. New approaches to hydrogen storage. Chem Soc Rev, **38**, 73 (2009). http://dx.doi.org/10.1039/B718842K.

[8] Murray LJ, Dincă M, Long JR. Hydrogen storage in metal: organic frameworks. Chem Soc Rev, **38**, 1294 (2009). http://dx.doi.org/10.1039/B802256A.

[9] Schlapbach L, Züttel A. Hydrogen-storage materials for mobile applications. Nature, **414**, 353 (2001). http://dx.doi.org/10.1038/35104634.

[10] Lim KL, Kazemian H, Yaakob Z, Daud WRW. Solid-state materials and methods for hydrogen storage: a critical review. Chem Eng Technol, **33**, 213 (2010). http://dx.doi.org/10.1002/ceat.200900376.

[11] Getman RB, Bae YS, Wilmer CE, Snurr RQ. Review and analysis of molecular simulations of methane, hydrogen, and acetylene storage in metal-organic frameworks. Chem Rev, **112**, 703 (2012). http://dx.doi.org/10.1021/cr200217c.

[12] Suh MP, Park HJ, Prasad TK, Lim DW. Hydrogen storage in

metal–organic frameworks. Chem Rev, **112**, 782 (2012). http://dx.doi.org/10.1021/cr200274s.

[13] US Environmental Protection Agency. Inventory of U.S. greenhouse gas emissions and sinks: 1990-2007 (Report No. EPA 430-R-09-004), US Environmental Protection Agency, Washington, DC (2009).

[14] Kayal S, Sun B, Chakraborty A. Study of metal-organic framework MIL-101 (Cr) for natural gas (methane) storage and compare with other MOFs (metal-organic frameworks). Energy, 91, 772 (2015). http://dx.doi.org/10.1016/j.energy.2015.08.096 (1993).

[15] Menon VC, Komarneni S. Porous adsorbents for vehicular natural gas storage: a review. J Porous Mater, **5**, 43 (1998). http://dx.doi.org/10.1023/A:1009673830619.

[16] Collins DJ, Ma S, Zhou HC. Hydrogen and Methane Storage in Metal-Organic Frameworks. In: MacGillivray LR, ed. Metal-Organic Frameworks: Design and Application, John Wiley & Sons, Inc., Hoboken, NJ, 249 (2010).

[17] Düren T, Sarkisov L, Yaghi OM, Snurr RQ. Design of new materials for methane storage. Langmuir, **20**, 2683 (2004). http://dx.doi.org/10.1021/la0355500.

[18] Lin X, Champness NR, Schröder M. Hydrogen, methane and carbon dioxide adsorption in metal-organic framework materials. Top Curr Chem, **293**, 35 (2010). http://dx.doi.org/10.1007/128_2009_21.

[19] Ma S, Sun D, Simmons JM, Collier CD, Yuan D, Zhou HC. Metal-organic framework from an anthracene derivative containing nanoscopic cages exhibiting high methane uptake. J Am Chem Soc, **130**, 1012 (2008). http://dx.doi.org/ 10.1021/ja0771639.

[20] Zhou W. Methane storage in porous metal-organic frameworks: current records and future perspectives. Chem Rec, **10**, 200 (2010). http://dx.doi.org/10.1002/tcr.201000004.

[21] Bousquet P, Ciais P, Miller JB, Dlugokencky EJ, Hauglustaine DA, Prigent C, Van der Werf GR, Peylin P, Brunke EG, Carouge C. Contribution of anthropogenic and natural sources to atmospheric methane variability. Nature, **443**, 439 (2006). http://dx.doi.org/10.1038/nature05132.

[22] Zhou HC, Long JR, Yaghi OM. Introduction to metal-organic frameworks. Chem Rev, **112**, 673 (2012). http://dx.doi.org/10.1021/cr300014x.

[23] Bétard A, Fischer RA. Metal-organic framework thin films: from fundamentals to applications. Chem Rev, **112**, 1055 (2012). http://dx.doi.org/10.1021/cr200167v.

[24] O'Keeffe M, Yaghi OM. Deconstructing the crystal structures of metal-organic frameworks and related materials into their underlying nets. Chem Rev, **112**, 675 (2012). http://dx.doi.org/10.1021/cr200205j.

[25] Yuan D, Lu W, Zhao D, Zhou HC. Highly stable porous polymer networks with exceptionally high gas-uptake capacities. Adv Mater, **23**, 3723 (2011). http://dx.doi.org/10.1002/adma.201101759.

[26] Lin X, Telepeni I, Blake AJ, Dailly A, Brown CM, Simmons JM, Zoppi M, Walker GS, Thomas KM, Mays TJ, Hubberstey P, Champness NR, Schröder M. High capacity hydrogen adsorption in Cu(II) tetracarboxylate framework materials: the role of pore size, ligand functionalization, and exposed metal sites. J Am Chem Soc, **131**, 2159 (2009). http://dx.doi.org/10.1021/ja806624j.

[27] Yuan D, Zhao D, Sun D, Zhou HC. An isoreticular series of metal–organic frameworks with dendritic hexacarboxylate ligands and exceptionally high gas-uptake capacity. Angew Chem Int Ed, **49**, 5357 (2010). http://dx.doi.org/10.1002/anie.201001009.

[28] Kennett JP, Cannariato KG, Hendy IL, Behl RJ. Carbon isotopic evidence for methane hydrate instability during quaternary interstadials. Science, **288**, 128 (2000). http://dx.doi.org/10.1126/science.288.5463.128.

[29] Yoo HM, Lee SY, Kim BJ, Park SJ. Influence of phosphoric acid treatment on hydrogen adsorption behaviors of activated carbons. Carbon Lett, **12**, 112 (2011). http://dx.doi.org/10.5714/CL.2011.12.2.112.

[30] Park SJ, Lee SY, Kim KS, Jin FL. A novel drying process for oil adsorption of expanded graphite. Carbon Lett, **14**, 193 (2013). http://dx.doi.org/10.5714/CL.2013.14.3.193.

[31] Jeon DH, Min BG, Oh JG, Nah C, Park SJ. Influence of nitrogen moieties on CO_2 capture of carbon aerogel. Carbon Lett, **16**, 57 (2015). http://dx.doi.org/10.5714/CL.2015.16.1.057.

[32] Cho EA, Lee SY, Park SJ. Effect of microporosity on nitrogen-doped microporous carbons for electrode of supercapacitor. Carbon Lett, **15**, 210 (2014). http://dx.doi.org/10.5714/CL.2014.15.3.210.

[33] Park SJ, Jin SY. Effect of ozone treatment on ammonia removal of activated carbons. J Colloid Interface Sci, **286**, 417 (2005). http://dx.doi.org/10.1016/j.jcis.2005.01.043.

[34] Meng LY, Park SJ. Effect of heat treatment on CO_2 adsorption of KOH-activated graphite nanofibers. J Colloid Interface Sci, **352**, 498 (2010). http://dx.doi.org/10.1016/j.jcis.2010.08.048.

[35] Park SJ, Park BJ, Ryu SK. Electrochemical treatment on activated carbon fibers for increasing the amount and rate of Cr(VI) adsorption. Carbon, **37**, 1223 (1999). http://dx.doi.org/10.1016/S0008-6223(98)00318-2.

[36] Park SJ, Jang YS. Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr(VI). J Colloid Interface Sci, **249**, 458 (2002). http://dx.doi.org/10.1006/jcis.2002.8269.

[37] Im JS, Park SJ, Kim TJ, Kim YH, Lee YS. The study of controlling pore size on electrospun carbon nanofibers for hydrogen adsorption. J Colloid Interface Sci, **318**, 42 (2008). http://dx.doi.org/10.1016/j.jcis.2007.10.024.

[38] Ma'mun S, Svendsen HF, Hoff KA, Juliussen O. Selection of new absorbents for carbon dioxide capture. Energy Convers Manag, **48**, 251 (2007). http://dx.doi.org/10.1016/j.enconman.2006.04.007.

[39] Balsamo M, Budinova T, Erto A, Lancia A, Petrova B, Petrov N, Tsyntsarski B. CO_2 adsorption onto synthetic activated carbon: kinetic, thermodynamic and regeneration studies. Sep Purif Technol, **116**, 214 (2013). http://dx.doi.org/10.1016/j.seppur.2013.05.041.

[40] Cracknell RF, Gordon P, Gubbins KE. Influence of pore geometry on the design of microporous materials for methane storage. J Phys Chem, **97**, 494 (1993). http://dx.doi.org/10.1021/j100104a036.

[41] Kin KH, Baik KJ, Kim IW, Lee HK. Optimization of membrane process for methane recovery from biogas. Sep Sci Technol, **47**, 963 (2012). http://dx.doi.org/10.1080/01496395.2011.644878.

[42] Biloé S, Goetz V, Guillot A. Optimal design of an activated carbon for an adsorbed natural gas storage system. Carbon, **40**, 1295 (2002). http://dx.doi.org/10.1016/S0008-6223(01)00287-1.

[43] MacDonald JAF, Quinn DF. Carbon absorbents for natural gas storage. Fuel, **77**, 61 (1998). http://dx.doi.org/10.1016/S0016-

2361(97)00128-2.

[44] Sun J, Rood MJ, Rostam-Abadi M, Lizzio AA. Natural gas storage with activated carbon from a bituminous coal. Gas Sep Purif, **10**, 91 (1996). http://dx.doi.org/10.1016/0950-4214(96)00009-6.

[45] Sun J, Brady TA, Rood MJ, Lehmann CM, Rostam-Abadi M, Lizzio AA. Adsorbed natural gas storage with activated carbons made from Illinois coals and scrap tires. Energy Fuels, **11**, 316 (1997). http://dx.doi.org/10.1021/ef960201h.

[46] Pantatosaki E, Pazzona FG, Megariotis G, Papadopoulos GK. Atomistic simulation studies on the dynamics and thermodynamics of nonpolar molecules within the zeolite imidazolate framework-8. J Phys Chem B, **114**, 2493 (2010). http://dx.doi.org/10.1021/jp911477a.

[47] Morris RE, Wheatley PS. Gas storage in nanoporous materials. Angew Chem Int Ed, **47**, 4966 (2008). http://dx.doi.org/10.1002/anie.200703934.

[48] Paraskeva P, Kalderis D, Diamadopoulos E. Production of activated carbon from agricultural by-products. J Chem Technol Biotechnol, **83**, 581 (2008). http://dx.doi.org/10.1002/jctb.1847.

[49] Furukawa H, Cordova KE, O'Keeffe M, Yaghi OM. The chemistry and applications of metal-organic frameworks. Science, **341**, 6149 (2013). http://dx.doi.org/10.1126/science.1230444.

[50] Furukawa H, Ko N, Go YB, Aratani N, Choi SB, Choi E, Yazaydin AÖ, Snurr RQ, O'Keeffe M, Kim J, Yaghi OM. Ultrahigh porosity in metal-organic frameworks. Science, **329**, 424 (2010). http://dx.doi.org/10.1126/science.1192160.

[51] McDonald TM, D'Alessandro DM, Krishna R, Long JR. Enhanced carbon dioxide capture upon incorporation of N,N′-dimethylethylenediamine in the metal–organic framework CuBTTri. Chem Sci, **2**, 2022 (2011). http://dx.doi.org/10.1039/c1sc00354b.

[52] Bao Z, Yu L, Ren Q, Lu X, Deng S. Adsorption of CO_2 and CH_4 on a magnesium-based metal organic framework. J Colloid Interface Sci, **353**, 549 (2011). http://dx.doi.org/10.1016/j.jcis.2010.09.065.

[53] Simmons JM, Wu H, Zhou W, Yildirim T. Carbon capture in metal-organic frameworks: a comparative study. Energy Environ Sci, **4**, 2177 (2011). http://dx.doi.org/10.1039/c0ee00700e.

[54] Caskey SR, Wong-Foy AG, Matzger AJ. Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. J Am Chem Soc, **130**, 10870 (2008). http://dx.doi.org/10.1021/ja8036096.

[55] Qin W, Cao W, Liu H, Li Z, Li Y. Metal-organic framework MIL-101 doped with palladium for toluene adsorption and hydrogen storage. RSC Adv, **4**, 2414 (2014). http://dx.doi.org/10.1039/c3ra45983g.

[56] Anbia M, Sheykhi S. Preparation of multi-walled carbon nanotube incorporated MIL-53-Cu composite metal-organic framework with enhanced methane sorption. J Ind Eng Chem, **19**, 1583 (2013). http://dx.doi.org/10.1016/j.jiec.2013.01.026.

[57] Petit C, Bandosz TJ. MOF-graphite oxide nanocomposites: surface characterization and evaluation as adsorbents of ammonia. J Mater Chem, **19**, 6521 (2009). http://dx.doi.org/10.1039/b908862h.

[58] Glover TG, Peterson GW, Schindler BJ, Britt D, Yaghi O. MOF-74 building unit has a direct impact on toxic gas adsorption. Chem Eng Sci, **66**, 163 (2011). http://dx.doi.org/10.1016/j.ces.2010.10.002.

[59] Liu YY, Leus K, Bogaerts T, Hemelsoet K, Bruneel E, Van Speybroeck V, Van Der Voort P. Bimetallic-organic framework as a zero-leaching catalyst in the aerobic oxidation of cyclohexene. ChemCatChem, **5**, 3657 (2013). http://dx.doi.org/10.1002/cctc.201300529.

[60] Jahan M, Liu Z, Loh KP. A graphene oxide and copper-centered metal organic framework composite as a tri-functional catalyst for HER, OER, and ORR. Adv Funct Mater, **23**, 5363 (2013). http://dx.doi.org/10.1002/adfm.201300510.

[61] Casco ME, Martínez-Escandell M, Gadea-Ramos E, Kaneko K, Silvestre-Albero J, Rodríguez-Reinoso F, High-Pressure Methane Storage in Porous Materials: Are Carbon Materials in the Pole Position? Chem Mater, **27**, 959 (2015). http://dx.doi.org/ 10.1021/cm5042524.

[62] Chen L, Honsho Y, Seki S, Jiang D. Light-harvesting conjugated microporous polymers: rapid and highly efficient flow of light energy with a porous polyphenylene framework as antenna. J Am Chem Soc, **132**, 6742 (2010). http://dx.doi.org/10.1021/ja100327h.

[63] Jiang JX, Wang C, Laybourn A, Hasell T, Clowes R, Khimyak YZ, Xiao J, Higgins SJ, Adams DJ, Cooper AI. Metal-organic conjugated microporous polymers. Angew Chem Int Ed, **50**, 1072 (2011). http://dx.doi.org/10.1002/anie.201005864.

[64] Li A, Sun HX, Tan DZ, Fan WJ, Wen SH, Qing XJ, Li GX, Li SY, Deng WQ. Superhydrophobic conjugated microporous polymers for separation and adsorption. Energy Environ Sci, **4**, 2062 (2011). http://dx.doi.org/10.1039/c1ee01092a.

[65] Senkovska I, Kaskel S. High pressure methane adsorption in the metal-organic frameworks $Cu_3(btc)_2$, $Zn_2(bdc)_2$dabco, and $Cr_3F(H2O)_2O(bdc)_3$. Microporous Mesoporous Mater, **112**, 108 (2008). http://dx.doi.org/10.1016/j.micromeso.2007.09.016.

[66] Chester AW, Derouane EG. Zeolite Characterization and Catalysis: A Tutorial. Springer, New York, NY (2009).

[67] Chałupnik S, Franus W, Wysocka M, Gzyl G. Application of zeolites for radium removal from mine water. Environ Sci Pollut Res, **20**, 7900 (2013). http://dx.doi.org/10.1007/s11356-013-1877-5.

[68] Yang R, Xu Z, Yang S, Michos I, Li LF, Angelopoulos AP, Dong J. Nonionic zeolite membrane as potential ion separator in redox-flow battery. J Membr Sci, **450**, 12 (2014). http://dx.doi.org/10.1016/j.memsci.2013.08.048.

[69] Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. ChemSusChem, **2**, 796 (2009). http://dx.doi.org/10.1002/cssc.200900036.

[70] Cavenati S, Grande CA, Rodrigues AE. Adsorption equilibrium of methane, carbon dioxide, and nitrogen on zeolite 13X at high pressures. J Chem Eng Data, **49**, 1095 (2004). http://dx.doi.org/10.1021/je0498917.

[71] Saha D, Bao Z, Jia F, Deng S. Adsorption of CO_2, CH_4, N_2O, and N_2 on MOF-5, MOF-177, and Zeolite 5A. Environ Sci Technol, **44**, 1820 (2010). http://dx.doi.org/10.1021/es9032309.

[72] Yu L, Gong J, Zeng C, Zhang L. Synthesis of binderless zeolite X microspheres and their CO_2 adsorption properties. Sep Purif Technol, **118**, 188 (2013). http://dx.doi.org/10.1016/j.seppur.2013.06.035.

[73] Brandani F, Ruthven DM. The effect of water on the adsorption of CO_2 and C_3H_8 on type X zeolites. Ind Eng Chem Res, **43**, 8339 (2004). http://dx.doi.org/10.1021/ie040183o.

[74] Li G, Xiao P, Webley P, Zhang J, Singh R, Marshall M. Capture of CO_2 from high humidity flue gas by vacuum swing adsorption with zeolite 13X. Adsorption, **14**, 415 (2008). http://dx.doi.

org/10.1007/s10450-007-9100-y.

[75] Grande CA, Blom R. Cryogenic adsorption of methane and carbon dioxide on zeolites 4A and 13X. Energy Fuels, **28**, 6688 (2014). http://dx.doi.org/10.1021/ef501814x.

[76] Sethia G, Somani RS, Bajaj HC. Sorption of methane and nitrogen on cesium exchanged zeolite-X: structure, cation position and adsorption relationship. Ind Eng Chem Res, **53**, 6807 (2014). http://dx.doi.org/10.1021/ie5002839.

[77] Park SJ, Kim KD. Adsorption behaviors of CO_2 and NH_3 on chemically surface-treated activated carbons. J Colloid Interface Sci, **212**, 186 (1999). http://dx.doi.org/10.1006/jcis.1998.6058.

[78] Seo MK, Park SJ. A kinetic study on the thermal degradation of multi-walled carbon nanotubes-reinforced poly(propylene) composites. Macromol Mater Eng, **289**, 368 (2004). http://dx.doi.org/10.1002/mame.200300303.

[79] Bilalis P, Katsigiannopoulos D, Avgeropoulos A, Sakellariou G. Non-covalent functionalization of carbon nanotubes with polymers. RSC Adv, **4**, 2911 (2014). http://dx.doi.org/10.1039/c3ra44906h.

[80] Bai BC, Cho S, Yu HR, Yi KB, Kim KD, Lee YS. Effects of aminated carbon molecular sieves on breakthrough curve behavior in CO_2/CH_4 separation. J Ind Eng Chem, **19**, 776 (2013). http://dx.doi.org/10.1016/j.jiec.2012.10.016.

[81] Park SJ, Kim BJ. Influence of oxygen plasma treatment on hydrogen chloride removal of activated carbon fibers. J Colloid Interface Sci, **275**, 590 (2004). http://dx.doi.org/10.1016/j.jcis.2004.03.011.

[82] Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A, Quinn DF. Activated carbon monoliths for methane storage: influence of binder. Carbon, **40**, 2817 (2002). http://dx.doi.org/10.1016/S0008-6223(02)00194-X.

[83] Park SJ, Shin JS, Shim JW, Ryu SK. Effect of acidic treatment on metal adsorptions of pitch-based activated carbon fibers. J Colloid Interface Sci, **275**, 342 (2004). http://dx.doi.org/10.1016/j.jcis.2004.01.010.

[84] Kim KS, Park SJ. Synthesis of nitrogen doped microporous carbons prepared by activation-free method and their high electrochemical performance. Electrochim Acta, **56**, 10130 (2011). http://dx.doi.org/10.1016/j.electacta.2011.08.107.

[85] Park SJ, Jang YS, Shim JW, Ryu SK. Studies on pore structures and surface functional groups of pitch-based activated carbon fibers. J Colloid Interface Sci, **260**, 259 (2003). http://dx.doi.org/10.1016/S0021-9797(02)00081-4.

[86] Seo MK, Park SJ. Influence of air-oxidation on electric double layer capacitances of multi-walled carbon nanotube electrodes. Curr Appl Phys, **10**, 241 (2010). http://dx.doi.org/10.1016/j.cap.2009.05.031.

[87] Dreisbach F, Staudt R, Keller JU. High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on activated carbon. Adsorption, **5**, 215 (1999). http://dx.doi.org/10.1023/A:1008914703884.

[88] Jeong JM, Rhee KY, Park SJ. Effect of chemical treatments on lithium recovery process of activated carbons. J Ind Eng Chem, **27**, 329 (2015). http://dx.doi.org/10.1016/j.jiec.2015.01.009.

[89] Bastos-Neto M, Torres AEB, Azevedo DCS, Cavalcante CL Jr. Methane adsorption storage using microporous carbons obtained from coconut shells. Adsorption, **11**, 911 (2005). http://dx.doi.org/10.1007/s10450-005-6045-x.

[90] Sircar S, Golden TC, Rao MB. Activated carbon for gas separation and storage. Carbon, **34**, 1 (1996). http://dx.doi.org/10.1016/0008-6223(95)00128-X.

[91] Liu J, Zhou Y, Sun Y, Su W, Zhou L. Methane storage in wet carbon of tailored pore sizes. Carbon, **49**, 3731 (2011). http://dx.doi.org/10.1016/j.carbon.2011.05.005.

[92] Ma TY, Liu L, Yuan ZY. Direct synthesis of ordered mesoporous carbons. Chem Soc Rev, **42**, 3977 (2013). http://dx.doi.org/10.1039/c2cs35301f.

[93] Sakintuna B, Yurum Y. Templated porous carbons: a review article. Ind Eng Chem Res, **44**, 2893 (2005). http://dx.doi.org/10.1021/ie049080w.

[94] Lee SY, Kim BJ, Park SJ. Influence of KOH-activated graphite nanofibers on the electrochemical behavior of Pt-Ru nanoparticle catalysts for fuel cells. J Solid State Chem, **199**, 258 (2013). http://dx.doi.org/10.1016/j.jssc.2012.12.028.

[95] Lee SY, Park SJ. Synthesis of zeolite-casted microporous carbons and their hydrogen storage capacity. J Colloid Interface Sci, **384**, 116 (2012). http://dx.doi.org/10.1016/j.jcis.2012.06.058.

[96] Moradi SE. Microwave assisted preparation of sodium dodecyl sulphate (SDS) modified ordered nanoporous carbon and its adsorption for MB dye. J Ind Eng Chem, **20**, 208 (2014). http://dx.doi.org/10.1016/j.jiec.2013.04.005.

[97] Ndamanisha JC, Guo L. Ordered mesoporous carbon for electrochemical sensing: a review. Anal Chim Acta, **747**, 19 (2012). http://dx.doi.org/10.1016/j.aca.2012.08.032.

[98] Lee J, Kim J, Hyeon T. Recent progress in the synthesis of porous carbon materials. Adv Mater, **18**, 2073 (2006). http://dx.doi.org/10.1002/adma.200501576.

[99] Ghimbeu CM, Le Meins JM, Zlotea C, Vidal L, Schrodj G, Latroche M, Vix-Guterl C. Controlled synthesis of NiCo nanoalloys embedded in ordered porous carbon by a novel soft-template strategy. Carbon, **67**, 260 (2014). http://dx.doi.org/10.1016/j.carbon.2013.09.089.

[100] Lee SY, Park SJ. Preparation and characterization of ordered porous carbons for increasing hydrogen storage behaviors. J Solid State Chem, **184**, 2655 (2011). http://dx.doi.org/10.1016/j.jssc.2011.07.034.

[101] Karthikeyan S, Viswanathan K, Boopathy R, Maharaja P, Sekaran G. Three dimensional electro catalytic oxidation of aniline by boron doped mesoporous activated carbon. Ind Eng Chem, **21**, 942 (2015). http://dx.doi.org/10.1016/j.jiec.2014.04.036.

[102] Cao D, Zhang X, Chen J, Wang W, Yun J. Optimization of single-walled carbon nanotube arrays for methane storage at room temperature. J Phys Chem B, **107**, 13286 (2003). http://dx.doi.org/10.1021/jp036094r.

[103] Guan C, Su F, Zhao XS, Wang K. Methane storage in a template-synthesized carbon. Sep Purif Technol, **64**, 124 (2008). http://dx.doi.org/10.1016/j.seppur.2008.08.007.

[104] Park SJ, Kim KD. Influence of activation temperature on adsorption characteristics of activated carbon fiber composites. Carbon, **39**, 1741 (2001). http://dx.doi.org/10.1016/S0008-6223(00)00305-5.

[105] Kim BJ, Park SJ. A simple method for the preparation of activated carbon fibers coated with graphite nanofibers. J Colloid Interface Sci, **315**, 791 (2007). http://dx.doi.org/10.1016/j.jcis.2007.07.013.

[106] Park SJ, Kim BJ. Ammonia removal of activated carbon fibers produced by oxyfluorination. J Colloid Interface Sci, **291**, 597 (2005). http://dx.doi.org/10.1016/j.jcis.2005.05.012.

[107] Im JS, Park SJ, Lee YS. Superior prospect of chemically activated electrospun carbon fibers for hydrogen storage. Mater Res Bull, **44**, 1871 (2009). http://dx.doi.org/10.1016/j.materresbull.2009.05.010.

[108] Yoon SH, Lim S, Song Y, Ota Y, Qiao W, Tanaka A, Mochida I. KOH activation of carbon nanofibers. Carbon, **42**, 1723 (2004). http://dx.doi.org/10.1016/j.carbon.2004.03.006.

[109] Park SJ, Seo MK, Lee YS. Surface characteristics of fluorine-modified PAN-based carbon fibers. Carbon, **41**, 723 (2003). http://dx.doi.org/10.1016/S0008-6223(02)00384-6.

[110] Suzuki M. Activated carbon fiber: fundamentals and applications. Carbon, **32**, 577 (1994). http://dx.doi.org/10.1016/0008-6223(94)90075-2.

[111] Shao X, Wang W, Zhang X. Experimental measurements and computer simulation of methane adsorption on activated carbon fibers. Carbon, **45**, 188 (2007). http://dx.doi.org/10.1016/j.carbon.2006.07.006.

[112] Alcañiz-Monge J, De La Casa-Lillo MA, Cazorla-Amoros D, Linares-Solano A. Methane storage in activated carbon fibres. Carbon, **35**, 291 (1997). http://dx.doi.org/10.1016/S0008-6223(96)00156-X.

[113] Dubey SP, Dwivedi AD, Lee C, Kwon YN, Sillanpaa M, Ma LQ. Raspberry derived mesoporous carbon-tubules and fixed-bed adsorption of pharmaceutical drugs. J Ind Eng Chem, **20**, 1126 (2014). http://dx.doi.org/10.1016/j.jiec.2013.06.051.

[114] Antoniou MK, Diamanti EK, Enotiadis A, Policicchio A, Dimos K, Ciuchi F, Maccallini E, Gournis D, Agostino RG. Methane storage in zeolite-like carbon materials. Microporous Mesoporous Mater, **188**, 16 (2014). http://dx.doi.org/10.1016/j.micromeso.2013.12.030.

[115] Cao D, Wu J. Self-diffusion of methane in single-walled carbon nanotubes at sub- and supercritical conditions. Langmuir, **20**, 3759 (2004). http://dx.doi.org/10.1021/la036375q.

[116] Bekyarova E, Murata K, Yudasaka M, Kasuya D, Iijima S, Tanaka H, Kahoh H, Kaneko K. Single-wall nanostructured carbon for methane storage. J Phys Chem B, **107**, 4681 (2003). http://dx.doi.org/10.1021/jp0278263.

[117] Vakifahmetoglu C, Presser V, Yeon SH, Colombo P, Gogotsi Y. Enhanced hydrogen and methane gas storage of silicon oxycarbide derived carbon. Microporous Mesoporous Mater, **144**, 105 (2011). http://dx.doi.org/10.1016/j.micromeso.2011.03.042.

[118] Méndez-Liñán L, López-Garzón FJ, Domingo-García M, Pérez-Mendoza M. Carbon adsorbents from polycarbonate pyrolysis char residue: hydrogen and methane storage capacities. Energy Fuels, **24**, 3394 (2010). http://dx.doi.org/10.1021/ef901525b.

[119] Yulong W, Fei W, Guohua L, Guoqing N, Mingde Y. Methane storage in multi-walled carbon nanotubes at the quantity of 80 g. Mater Res Bull, **43**, 1431 (2008). http://dx.doi.org/10.1016/j.materresbull.2007.06.046.

[120] Xiang Z, Hu Z, Cao D, Yang W, Lu J, Han B, Wang W. Metal-organic frameworks with incorporated carbon nanotubes: improving carbon dioxide and methane storage capacities by lithium doping. Angew Chem Int Ed, **50**, 491 (2011). http://dx.doi.org/10.1002/anie.201004537.

[121] Gomez-Gualdron DA, Gutov OV, Krungleviciute V, Borah B, Mondloch JE, Hupp JT, Yildirim T, Farha OK, Snurr RQ. Computational design of metal-organic frameworks based on stable zirconium building units for storage and delivery of methane. Chem Mater, **26**, 5632 (2014). http://dx.doi.org/10.1021/cm502304e.

[122] Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O'Keeffe M, Yaghi OM. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science, **295**, 469 (2002). http://dx.doi.org/10.1126/science.1067208.

[123] Peng Y, Krungleviciute V, Eryazici I, Hupp JT, Farha OK, Yildirim T. Methane storage in metal–organic frameworks: current records, surprise findings, and challenges. J Am Chem Soc, **135**, 11887 (2013). http://dx.doi.org/10.1021/ja4045289.

[124] He Y, Zhou W, Qian G, Chen B. Methane storage in metal–organic frameworks. Chem Soc Rev, **43**, 5657 (2014). http://dx.doi.org/10.1039/C4CS00032C.

[125] How CK, Khan MA, Hosseini S, Chuah TG, Choong TSY. Fabrication of mesoporous carbons coated monolith via evaporative induced self-assembly approach: effect of solvent and acid concentration on pore architecture. J Ind Eng Chem, **20**, 4286 (2014). http://dx.doi.org/10.1016/j.jiec.2014.01.034.

[126] Gándara F, Furukawa H, Lee S, Yaghi OM. High methane storage capacity in aluminum metal–organic frameworks. J Am Chem Soc, **136**, 5271 (2014). http://dx.doi.org/10.1021/ja501606h.

[127] Wu H, Zhou W, Yildirim T. High-capacity methane storage in metal−organic frameworks M_2(dhtp): the important role of open metal sites. J Am Chem Soc, **131**, 4995 (2009). http://dx.doi.org/10.1021/ja900258t.

[128] Guo Z, Wu H, Srinivas G, Zhou Y, Xiang S, Chen Z, Yang Y, Zhou W, O'Keeffe M, Chen B. A metal–organic framework with optimized open metal sites and pore spaces for high methane storage at room temperature. Angew Chem Int Ed, **50**, 3178 (2011). http://dx.doi.org/10.1002/anie.201007583.

[129] Sloan ED Jr. Fundamental principles and applications of natural gas hydrates. Nature, **426**, 353 (2003). http://dx.doi.org/10.1038/nature02135.

[130] Wegrzyn J, Wiesmann H, Lee T. Low pressure storage of natural gas on activated carbon. Society of Automotive Engineers Proceedings of the Annual Automotive Technology Development Contractor's Coordination Meeting, Warrendale, PA (1992).

[131] Salehi E, Taghikhani V, Ghotbi C, Nemati Lay E, Shojaei A. Theoretical and experimental study on the adsorption and desorption of methane by granular activated carbon at 25°C. J Nat Gas Chem, **16**, 415 (2007). http://dx.doi.org/10.1016/S1003-9953(08)60014-6.

[132] Yeon SH, Osswald S, Gogotsi Y, Singer JP, Simmons JM, Fischer JE, Lillo-Ródenas MA, Linares-Solano Á. Enhanced methane storage of chemically and physically activated carbide-derived carbon. J Power Sources, **191**, 560 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.02.019.

[133] Guan C, Loo LS, Wang K, Yang C. Methane storage in carbon pellets prepared via a binderless method. Energy Convers Manag, **52**, 1258 (2011). http://dx.doi.org/10.1016/j.enconman.2010.09.022.

[134] Moradi M, Peyghan AA. Role of sodium decoration on the methane storage properties of BC_3 nanosheet. Struct Chem, **25**, 1083 (2014). http://dx.doi.org/10.1007/s11224-013-0384-0.

[135] Jiang S, Zollweg JA, Gubbins KE. High-pressure adsorption of methane and ethane in activated carbon and carbon fibers. J Phys Chem, **98**, 5709 (1994). http://dx.doi.org/10.1021/j100073a023.

[136] Cazorla-Amorós D, Alcañiz-Monge J, Linares-Solano A. Characterization of activated carbon fibers by CO_2 adsorption. Langmuir, **12**, 2820 (1996). http://dx.doi.org/10.1021/la960022s.

[137] Im JS, Jung MJ, Lee YS. Effects of fluorination modification on

pore size controlled electrospun activated carbon fibers for high capacity methane storage. J Colloid Interface Sci, **339**, 31 (2009). http://dx.doi.org/10.1016/j.jcis.2009.07.013.

[138] Hattori Y, Konishi T, Kaneko K. XAFS and XPS studies on the enhancement of methane adsorption by NiO dispersed ACF with the relevance to structural change of NiO. Chem Phys Lett, **355**, 37 (2002). http://dx.doi.org/10.1016/S0009-2614(02)00154-9.

[139] Aukett PN, Quirke N, Riddiford S, Tennison SR. Methane adsorption on microporous carbons: a comparison of experiment, theory, and simulation. Carbon, **30**, 913 (1992). http://dx.doi.org/10.1016/0008-6223(92)90015-O.

[140] Sreńscek-Nazzal J, Kamińska W, Michalkiewicz B, Koren ZC. Production, characterization and methane storage potential of KOH-activated carbon from sugarcane molasses. Ind Crops Prod, **47**, 153 (2013). http://dx.doi.org/10.1016/j.indcrop.2013.03.004.

[141] Bastos-Neto M, Canabrava DV, Torres AEB, Rodriguez-Castellón E, Jiménez-López A, Azevedo DCS, Cavalcante CL Jr. Effects of textural and surface characteristics of microporous activated carbons on the methane adsorption capacity at high pressures. Appl Surf Sci, **253**, 5721 (2007). http://dx.doi.org/10.1016/j.apsusc.2006.12.056.

[142] Loh WS, Rahman KA, Chakraborty A, Saha BB, Choo YS, Khoo BC, Ng KC. Improved isotherm data for adsorption of methane on activated carbons. J Chem Eng Data, **55**, 2840 (2010). http://dx.doi.org/10.1021/je901011c.

[143] Policicchio A, Maccallini E, Agostino RG, Ciuchi F, Aloise A, Giordano G. Higher methane storage at low pressure and room temperature in new easily scalable large-scale production activated carbon for static and vehicular applications. Fuel, **104**, 813 (2013). http://dx.doi.org/10.1016/j.fuel.2012.07.035.

[144] Lee JW, Balathanigaimani MS, Kang HC, Shim WG, Kim C, Moon H. Methane storage on phenol-based activated carbons at (293.15, 303.15, and 313.15) K. J Chem Eng Data, **52**, 66 (2007). http://dx.doi.org/10.1021/je060218m.

[145] Lozano-Castelló D, Alcañiz-Monge J, de la Casa-Lillo MA, Cazorla-Amorós D, Linares-Solano A. Advances in the study of methane storage in porous carbonaceous materials. Fuel, **81**, 1777 (2002). http://dx.doi.org/10.1016/S0016-2361(02)00124-2.

[146] Yang W, Feng YY, Jiang CF, Chu W. Synthesis of multi-walled carbon nanotubes using CoMnMgO catalysts through catalytic chemical vapor deposition. Chin Phys B, **23**, 128201 (2014). http://dx.doi.org/10.1088/1674-1056/23/12/128201.

[147] Luo J, Liu Y, Sun W, Jiang C, Xie H, Chu W. Influence of structural parameters on methane adsorption over activated carbon: evaluation by using D–A model. Fuel, **123**, 241 (2014). http://dx.doi.org/10.1016/j.fuel.2014.01.053.