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Adsorption of Methane and Carbon Dioxide on Activated Carbon and ZIF-8 (Zeolitic Imidazolate Framework)

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Comparative adsorption of methane and carbon dioxide on activated carbon and ZIF-8 (Zeolitic Imidazolate Framework) at 35 °C and up to 100 psi was made. In addition, different ratios of polyvinylidene fluoride (PVDF) with ZIF-8 were also investigated. The textural properties of adsorbents were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), and Quantachrom/Autosorb1-MP. All adsorbents were microporous materials. ZIF-8 has uniform crystalline structure, which is different from the amorphous structure of activated carbon. The result showed the increase in the methane and carbon dioxide adsorption when the pressure increased. ZIF-8 (pure) showed higher methane and carbon dioxide adsorption capacity than the activated carbon corresponding to its surface area, micropore volume, and average pore diameter. The addition of PVDF decreased the methane uptake. Furthermore, ZIF-8 (pure) and activated carbon adsorbed carbon dioxide more than methane, approximately twice due to its preferential adsorption towards carbon dioxide.

1. Introduction

According to problems from global warming by greenhouse gas emission and fluctuation in oil price, alternative energy sources are required to replace the conventional petroleum-based fuels for transportation, especially gasoline and diesel. This attraction leads to study of new clean fuels. One alternative is natural gas because of lower carbon dioxide emission which is the major greenhouse gas emission (Blanco et al., 2016). Normally, natural gas has relatively high H:C ratio (4:1) while other fuels like gasoline and diesel contain long chain hydrocarbon (ratio of C:H typically lower than 2). Thus, less carbon content tends to emit low carbon dioxide upon combustion.

Natural gas is generally composed of up to 90 % of methane and various proportions of impurities such as CO_2, and other heavy hydrocarbons depending on the source of the gas (Rada et al., 2015). Natural gas storage and transportation are essential in utilizing natural gas. Specifically, proper natural gas storage is needed. Potential technological options for natural gas storage include compression under high pressure (CNG), liquefaction under low temperature (LNG), and adsorbed natural gas (ANG).

Although natural gas has gained much interest as an alternative to conventional petroleum for transportation, the most important challenge for the extensive use of natural gas is its limited driving range as a result of its comparatively low volumetric energy storage density. CNG is one of the current technology to solve this problem by storing natural gas as supercritical fluid at 20 - 30 MPa and room temperature in a cylindrical tank. Another technology is LNG. It is usually stored as a boiling liquid at about 113 K in a cryogenic tank and 1MPa (Kayal et al., 2015). For ANG, this technology is to store natural gas by adsorption on porous material at room temperature and modest pressure (3.5 - 4 MPa). Among these technology, ANG technique would be better suited for use in passenger cars because it overcomes disadvantage of CNG and LNG. For instance, the storage tank is cheaper

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and lighter from vessel materials. Moreover, it is safe since ANG operates at room temperature and low pressure compared with CNG and LNG operating conditions (Lozano-Castello et al., 2002).

Enhancement of gas storage density through adsorption depends on types of adsorbent. The requirement of highly effective ANG adsorbent is large adsorption capacity with pores size around 0.8 nm and high packing density. It has to be extremely hydrophobic adsorbents due to non-polar of methane. A good kinetic performance is also needed, such as low heat of adsorption and high heat capacity which prefer for exothermic reaction of adsorption. Additionally, contemplation of inexpensive to the end user is also importance (Lozano-Castello et al., 2002). Many porous materials have been reported in literature including zeolites, activated carbon, and metal organic frameworks (MOFs). Activated carbon materials have a very high surface area, narrow pore size distribution, and high energy densities contribute to high storage capacities. MOFs are a new class of microporous material, which is the most promising to storage methane with high porosity, adjustable pores and variety of factors that can improve their methane storage capacity (Li et al., 2016). Zeolitic imidazolate frameworks-8 is one of the most studied materials owing to their thermal stability and satisfied chemical. The structure of ZIF-8 is sodalite (SOD) zeolitic topology with the formula of Zn(2-methylimidazole)$_2$. ZIF-8 has been extensively used for a variety of application due to its relatively stable material. However, the powder MOFs are generally not appropriate for practical applications such as adsorption. Thus, these materials are shaped for easy controlling and recycling (Abbasi et al., 2017).

This work aims to store the natural gas by increasing volumetric energy storage density of natural gas via ANG technology. Since natural gas consists of mainly methane but it generally has some carbon dioxide, comparative study of methane and carbon dioxide is needed for the effects of carbon dioxide on methane or natural gas storage. The appropriate properties of adsorbents were investigated for designing the porous adsorbents for methane storage. In this work, adsorption of methane and carbon dioxide on activated carbon and ZIF-8 were observed at room temperature and variable pressure (0 - 100 psi) by using static method. Polyvinylidene fluoride (PVDF) was used to fabricate ZIF-8 powder to pellets. Physical properties such as surface area, micropore volume, and pore size distribution were discussed. In addition, fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were analyzed.

2. Experimental procedures

2.1 Chemical

Methane gas (CH_4, 99.99 %) was obtained from Linde Public Company, Thailand. Carbon dioxide gas (CO_2, 99.99 %) was purchased from Labgaz Thailand Co., Ltd. Helium gas (99.99 %) was acquired from Praxair Inc., Thailand.

2.2 Adsorbents

Adsorbents in this study were supported by NANOTEC, Thailand. Samples used in this study were activated carbon, ZIF-8 (pure), 75 wt % ZIF-8, 50 wt % ZIF-8 and 25 wt % ZIF-8 (The percentage in front of ZIF-8 indicates the amount of ZIF-8 mixed with PVDF).

2.3 Characterization

The surface area, micropore volume, and average pore diameter of the adsorbents were measured by a Quantachrom/Autosorb1-MP instrument. The adsorbents were first out gassed to remove the humidity on its surface under vacuum at 250 °C for 16 hours prior to the analysis. After that, nitrogen was purged to adsorb on its surface. The volume-pressure data was used to calculate the BET surface area and micropore volume. The X-ray diffraction (XRD) patterns were carried out with a diffractometer Bruker D8 Advance using Cu radiation (scan range 5 ° to 45 °), supported by NANOTEC, Thailand. The morphology of the adsorbents was investigated by using the scanning electron microscope, Hitachi S-4800, with an accelerating voltage of 5 kV. The adsorbents were coated with platinum under vacuum condition before observation.

2.4 Experimental apparatus

The volumetric apparatus was used to study methane and carbon dioxide adsorption on adsorbents. This apparatus consists of adsorption chamber (1), a gas reservoir (2), a vacuum pump (3), and a pressure transducer (4). The gas reservoir and adsorption chamber were a high pressure stainless steel reactor, and the pressure regulator with 28 MPa maximum limit was installed to control a gas flow rate into the system. A K-type thermocouple was used for measuring the temperature of gas inside the adsorption chamber. The temperature of the adsorption chamber was adjusted and maintained by an internal temperature sensor. The system pressure was measured by a pressure transducer in the range of 0 to 21 MPa with 0.13 % error. The data logger was connected to a computer to record the data. Schematic of the experimental set-up for the equilibrium adsorption of methane is illustrated in Figure 1.

2.5 Adsorption measurement

Adsorption of methane and carbon dioxide on adsorbents was studied at room temperature and variable pressure up to 100 psi. Adsorbent, 0.2 ml, was filled in adsorption chamber. Helium was used as a purge gas in this study. The adsorption processes were carried out using high purity methane gas or carbon dioxide gas. Each experiment was repeated at least 3 times to ensure its reproducibility.

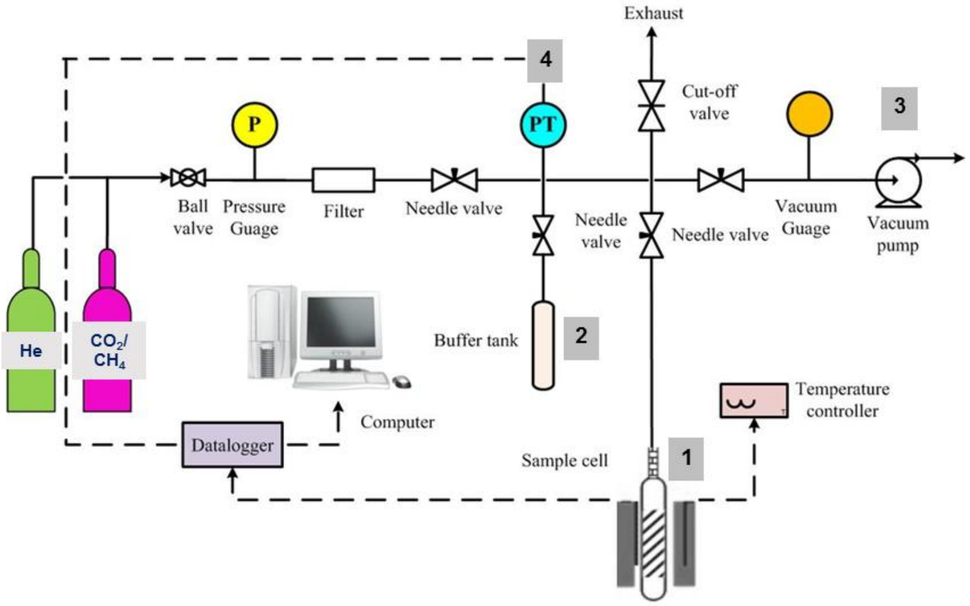

Figure 1: Schematic of the experimental set-up for the equilibrium adsorption of CH_4

3. Results and discussion

3.1 Adsorbent properties

X-ray diffraction was used to investigate the crystallinity of ZIF-8 (pure) as illustrated in Figure 2.

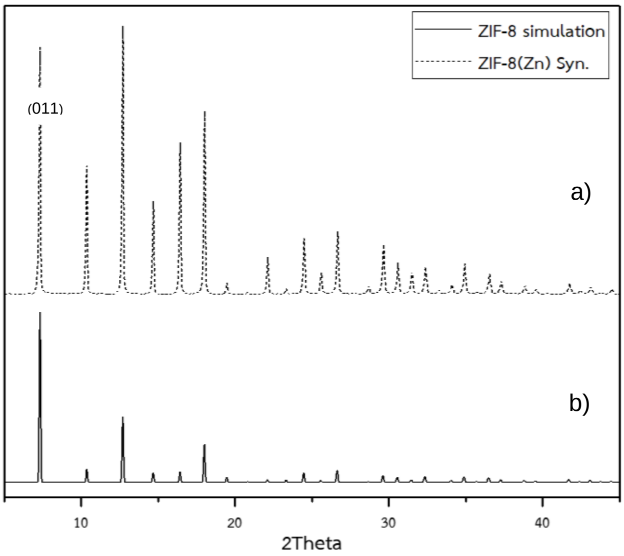

Figure 2: X-ray diffraction (XRD) pattern of ZIF-8 (pure) simulation (a) and ZIF-8 synthetic (pure) (b)

The formation of ZIF-8 (pure) corresponds to ZIF-8 (pure) simulation. The characteristic peak at 2θ = 7.3° associats with the (011) peak of ZIF-8 (pure), as Wee et al. (2014) reported. These characteristics indicate the high crystalline ZIF-8 with no impurities detected. The topology of activated carbon and ZIF-8 (pure) are shown in Figure 3. It confirms the amorphous structure of activated carbon, while ZIF-8 (pure) has a uniform hexagonal shape. From Figure 4, all adsorption-desorption isotherms of adsorbents were obtained by using nitrogen at -196 °C. It can be seen that all adsorbents are type I isotherm conforming to the classification of the IUPAC (Donohue and Aranovich, 1998). This figure indicates micropore structure of all adsorbents. However, the isotherm of activated carbon at a relative pressure lower than 0.2 suggesting the presence of super-micropore in this sample (Blanco et al., 2016). Table 1 lists the physical properties consisting of surface area (S_{bet}), micropore volume (V_{micro}) calculated by Dubinin-Radushkevich (DR) method, and average pore diameter (nm). It can be observed that the larger surface area indicates the higher micropore volume and narrower pore size diameter. ZIF-8 (pure) has the highest surface area and micropore volume among other adsorbents. It also shows the lowest average diameter. Moreover, the surface area and micropore volume of ZIF-8 mixed with PVDF decrease with the increase in the amount of PVDF. However, the unpredictability of some adsorbents was noticed. Even though 75 wt % ZIF-8 has higher surface area and micropore volume than 50 wt % ZIF-8, the average pore diameter of 50 wt % ZIF-8 is lower than 75 wt % ZIF-8. Djeridi et al. (2013) reported that the higher average pore diameter contributed to the lower adsorption capacity. Therefore, the 75 wt % ZIF-8 with the higher average pore size diameter may have lower methane adsorption than the 50 wt % ZIF-8.

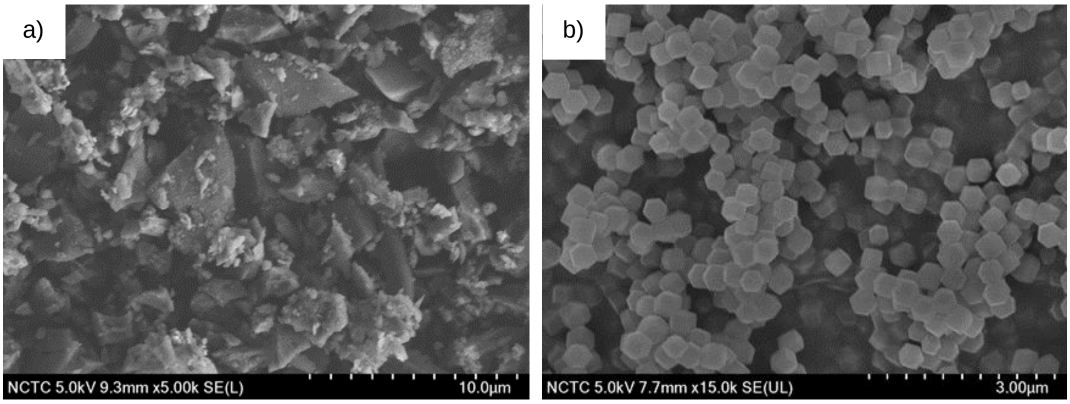

Figure 3: Scanning electron microscope (SEM) of activated carbon (a) and ZIF-8 (pure) (b)

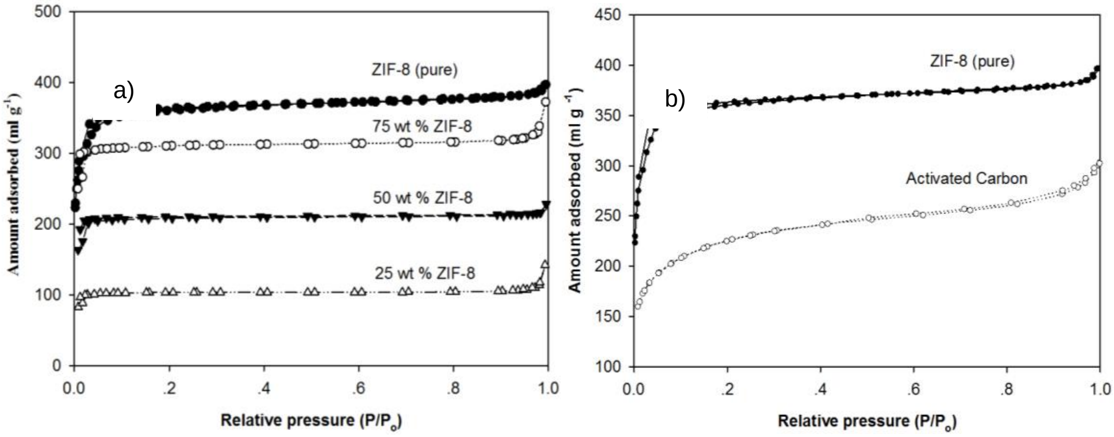

Figure 4: Nitrogen adsorption-desorption isotherm of a) ZIF-8 (pure), 75 wt % ZIF-8, 50 wt % ZIF-8, and 25 wt % ZIF-8 and b) ZIF-8 (pure) and activated carbon at -196.15 °C

Table 1: Physical properties of adsorbents, calculated from N_2 adsorption-desorption isotherms at -196.15 °C

Adsorbent	S_{Bet} (m^2 g^{-1})	V_{micro} DR (ml g^{-1})	D_{avg} (nm)
Activated carbon	719.2	0.41	2.85
ZIF-8	1,182	0.58	1.98
75 wt % ZIF-8	923.2	0.50	2.50
50 wt % ZIF-8	620.6	0.33	2.28
25 wt % ZIF-8	306.9	0.17	2.87

3.2 Methane and carbon dioxide adsorption

Methane and carbon dioxide adsorption on activated carbon and ZIF-8 (pure) are shown in Figure 5. ZIF-8 (pure) has higher methane uptake than activated carbon relating to its relatively high surface area and high micropore volume. Furthermore, the narrowest average pore diameter of ZIF-8 (pure) can support more attraction force between gas molecule and adsorbent, van der Waals forces, resulting in high methane storage capacity (Bagheri and Abedi, 2011). Chemical adsorption was not regarded owing to nonpolar nature of methane molecule. In the same way, the carbon dioxide adsorption of ZIF-8 (pure) is higher than activated carbon. Apart from its physical properties, the chemical properties of ZIF-8 (pure) is also considered. The structure of ZIF-8 (pure) has sodalite (SOD) zeolitic topology with Zn atoms bonded to imidazolate ligands (Navarro et al., 2014). This open metal site of ZIF-8 (pure) has strong interaction with CO_2 due to an electrophile of CO_2 (Hayashi et al., 2007). As the result of physical properties and chemical properties of gas molecules, it is noticeable that the carbon dioxide uptake of ZIF-8 (pure) and activated carbon is twice greater than their methane uptake which is the same trend as reported by Teo et al. (2017). The difference between methane and carbon dioxide adsorption on both activated carbon and ZIF-8 is not significant at low pressure. Figure 6 shows adsorption capacity of ZIF-8 (pure), 75 wt % ZIF-8, 50 wt % ZIF-8 and 25 wt % ZIF-8. The blockage of PVDF inside porous ZIF-8 may cause the decreased in surface area and micropore volume of adsorbents (Table 1). Thus, pure ZIF-8 adsorbs more methane than the 75 wt % ZIF-8, 50 wt % ZIF-8, and 25 wt% ZIF-8, respectively. The average pore sizes of 50 wt % ZIF-8 and 75 wt % ZIF-8, as mentioned before, show no effect on the methane adsorption. In general, the surface area and micropore volume is more influence on the methane adsorption than the average pore size diameter, and it is so in this case.

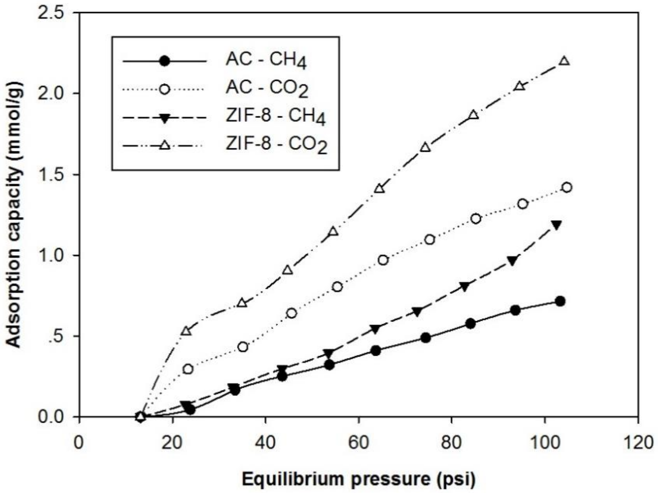

Figure 5: Adsorption of methane and carbon dioxide on activated carbon and ZIF-8 (pure) at 35 °C

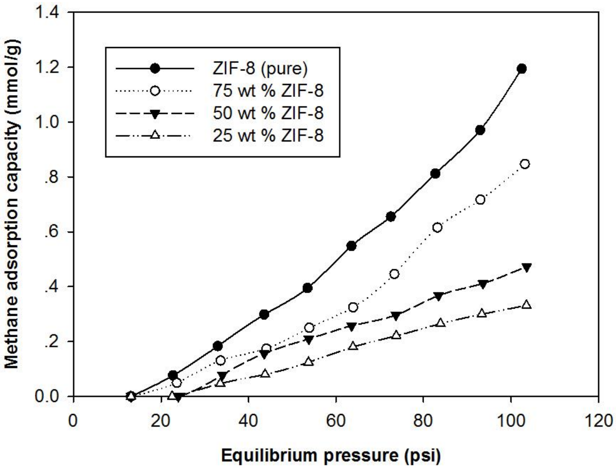

Figure 6: Adsorption of methane on ZIF-8 (pure), 75 wt % ZIF-8, 50 wt % ZIF-8, and 25 wt % ZIF-8 at 35 °C

4. Conclusions

The effects of surface area, micropore volume and pore size diameter must be considered for adsorption capacity of methane and carbon dioxide. When the surface area and micropore volume increased, the methane and carbon dioxide adsorption also increased. Besides physical properties of adsorbents, carbon dioxide adsorbed on ZIF-8 (pure) was higher than activated carbon due to interaction between metal ion and gas molecule. Therefore, the appropriate adsorbent required a high surface area, a high micropore volume, a low average pore size diameter, and extremely hydrophobic to selectively adsorb methane over carbon dioxide. The open metal site should have low interaction towards carbon dioxide, which is a significant challenge in applying MOFs for high methane adsorption with low carbon dioxide adsorption. Additionally, ZIF-8 (pure) was more effective for methane storage than the ZIF-8 mixed with PVDF. Although the PVDF binder reduces the methane adsorption, it is beneficial for further practical applications.

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