$Zn_3(btc)_2$ AS ADSORBENT FOR GAS CARBON DIOXIDE AND METHANE

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ABSTRACT

Adsorption is a process, which a substance in a gas or liquid becomes attached to a solid. This research is carried out in order to develop the storage from metal organic framework (MOFs) by adsorption application process. MOFs are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. MOFs are capable of storing large amount of gases. $Zn_3(btc)_2$ is one of MOFs and it promising storage materials. During this study, the adsorbent, $Zn_3(btc)_2$ has been developed and characterized as a storage for the carbon dioxide and methane The characteristic of $Zn_3(btc)_2$ as adsorbent was investigated with two parameter which is pressure and time. For the carbon dioxide, the pressures that were used are 2.0 bars, 4 bar and 6.0 bars and for the methane, the pressure that were used are 1.0 bar, 1.5 bars and 2.0 bars. Meanwhile, the parameter of time that used for both gases were same which are 1 hour, 2 hours, 3 hours and 4 hours. From this experiment, it was showed that, the weight of the sample after adsorption for both gases was increased. The experiment result showed that, methane gas was adsorbed more into $Zn_3(btc)_2$ compared to carbon dioxide gas This is because methane has smaller molecule size compare to carbon dioxide molecules which is 108.70 ppm and 116.3 ppm respectively. The rate of adsorption for both gases is low because the $Zn_3(btc)_2$ sample was not in crystallized form. This is as there are no proper autoclaves to synthesis the sample at 393 K and 12 hour. The characteristic of $Zn_3(btc)_2$ was investigated using Scanning Electron Microscope (SEM) in order to observe the structure of the $Zn_3(btc)_2$ before and after adsorption. From the observation, it was showed that the structure of $Zn_3(btc)_2$ was changed after the adsorption occurred. It is shown that the $Zn_3(btc)_2$ structure was expand and the amount of pore was decreased. From the result analysis, it was showed that the adsorption rate was affected more by pressure parameter compare to time parameter. As a conclusion, pressure and time of adsorption will affected the rate of adsorption however; the pore size of sample is still the most essential factor for an effective adsorption.

ABSTRAK

Penyerapan adalah proses dimana gas atau cecair diserapkan ke dalam pepejal. Penyelidikan ini adalah bertujuan untuk mengkaji dan menghasilkan "Metal Organic Frameworks (MOFs)" sebagai simpanan untuk gas dengan mengaplikasikan proses penyerapan. MOFs ialah suatu campuran yang mngandungi ion metal dan kluster koordinat untuk membentuk organik tegap dan menghasilkan struktur dimensi satu, dua, atau tiga yang mempunyai liang. MOFs berupaya untuk menyimpan jumlah gas yang banyak. $Zn_3(btc)_2$ adalah salah satu contoh MOFs dan ia mampu untuk menyimpan gas. Melalui penyelidikan ini ciri-ciri $Zn_3(btc)_2$ sebagai penyimpan gas karbon dioksida dan metana telah dikanal pasti. Ciri-ciri $Zn_3(btc)_2$ sebagai penyimpan gas diuji dengan dua parameter iaitu tekanan dan masa. Untuk karbon dioksida, tekanan yang digunakan ialah 2 bar, 4 bar dan 6 bar manakala untuk gas metana pula adalah 1 bar, 1.5 bar dan 2 bar. Parameter masa yang digunakan pula adalah sama bagi kedua-dua gas ini iaitu 1 jam, 2 jam, 4 jam dan 6 jam. Daripada ekperimen yang telah dijalankan, kedua-dua berat sampel ini bertambah selepas proses penyerapan berlaku. Gas metana menunjukan penyerapan yang paling tinggi berbanding dengan gas karbon dioksida. Ini adalah kerana metana mempunyai saiz molekul yang lebih kecil berbanding dengan saiz molekul karbon doiksida iaitu 108.70 ppm dan 116.3ppm. Kadar penyerapan bagi kedua-dua gas ini rendah kerana sampel yang digunakan dalam penyelidikan ini tidak berada dalam keadaan kristal. Ini kerana ketiadaan "autoclave" yang mampu untuk beroperasi selama 12 jam dan pada suhu 393K. karakter sampel sebelum dan selepas telah diuji dengan menggunakan "Scanning Electron Microscope (SEM)" bagi melihat struktur permukaan dan liang- liang yang terdapat pada sampel itu. Daripada pemerhatian, struktur sampel telah berubah bentuk selepas proses penyerapan berlaku. Ia menunjukkan struktur sampel teleh berkembang dan bilangan liang-liang semakin berkurangan. Parameter tekanan menunjukkan ia memainkan peranan yang paling utama dalam penyerapan ke dalam $Zn_3(btc)_2$ berbanding dengan parameter masa. Sebagai kesimpulan, tekanan dan masa mempengaruhi proses penyerapan namun saiz liang sampel adalah tetap menjadi factor utama kepada penyerapan yang berkesan.

TABLE OF CONTENTS

LIST OF FIGURE

LIST OF TABLES

LIST OF SYMBOLS

CO_2 – Carbon dioxide

CH_4 – Methane

CO – Carbon monoxide

C_2H_4 – Ethylene

C_2H_6 – Ethane

DMF – n,n-dimethylformamide

K – Kelvin

°C – Celsius

tm – Atmosphere

% – Percent

G – Gram

L – Liter

P – Pressure

T – Temperature

Z – Atomic number

hr – Hour

b - Bar

LIST OF ABBREVIATIONS

LNG – Liquefied natural gas

CNG – Compressed natural gas

BSE – Back scattered electrons

SEI – Scanning electron imaging

ppm – Parts per million

nm – Nano meter

Mpa – Mega Pascal

SEM – Scanning Electron Microscope

EDS – Energy dispersive spectrometer

WDS – Wavelength dispersive spectrometer

CRT – Cathode-ray tube

MOFs – Metal Organic-Frameworks

STP – Standard Temperature Pressure

US – United State

HFCs – Hydro fluorocarbons

GWP – Global warming potential

R744 – CO_2 refrigerant

R-12 – Dichlorodifluoromethane

RTECS – Registry of Toxic Effects of Chemical Substances

EINES – European Inventory of Existing Commercial Chemical Substances

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Overview

In recent years, there is a growing demand for light and heavy duty vehicles driven with compressed natural gas (CNG) and in very few cases with liquefied natural gas (LNG). Natural gas (NG) has a considerable advantage over conventional fossil fuels both from an environmental point of view and due to the natural abundance and resources. The main component of natural gas is methane, with a high heat of combustion. The combustion of methane produces the smallest amount of carbon dioxide per unit of heat produced among fossil fuels. Thus a further improvement of natural gas driven vehicles is a key issue for the development of environmentally friendly transportation systems. However, efficient storage and transportation of this source of clean energy is still a key issue. One of the most significant problems to be addressed in this regard is that methane is in a supercritical state near room temperature.

The most common methods of natural gas storage worldwide are liquefaction (due to its supercritical state, it is impossible to liquefy methane at room temperature) and compression of natural gas at room temperature and 200–300 bar (T.L. Cook *et al.*, 1999). LNG offers an energy density comparable to petrol and diesel fuels, but the necessity to store it in expensive cryogenic tanks and the boil-off losses have prevented widespread commercial applications, especially for small vehicles. The main disadvantage of the second method is its lower energy density per unit volume compared to conventional fuels (J.Alcaniz-Monge *et al*., 1997). CNG has a specific volumetric storage capacity about 240 v/v at 200 bars, which represents the volume of stored methane at ambient conditions (1 bar, 303 K) per unit volume of vessel. This is about 2.6 times lower than for natural gas in the liquid state (R.F. Cracknell *et al*., 1993).

Natural gas has a considerable advantage over conventional fossil fuels both from an environmental point of view and due to the natural abundance and resources. The main component of natural gas is methane, with a high heat of combustion. The combustion of methane produces the smallest amount of carbon dioxide per unit of heat produced among fossil fuels. Thus a further improvement of natural gas driven vehicles is a key issue for the development of environmentally friendly transportation systems (J.Alcaniz-Monge. *et al.*, 1997).

But today, engineer find the another way to store the gas that more safety and cheaper. Natural gas is one of the examples of gas that can be store in metal organic such as activated carbons, carbon nanotubes, porous polymers, M41S materials, zeolites and porous ceramics. We know that an efficient material for adsorptive gas storage should have a high specific surface area. Therefore, porous solids are the most promising candidates. However, consideration of the area only is not enough to obtain an efficient material. A key factor determining the interaction of methane with the pore wall is the size of the pore. The methane adsorbent should also have a low heat of adsorption, and high heat capacity (Mota, J. B. P *et al*., 1995).

However, efficient storage and transportation of this source of clean energy is still a key issue. One of the most significant problems to be addressed in this regard is that methane is in a supercritical state near room temperature. An efficient material for adsorptive gas storage should have a high specific surface area. Therefore, porous solids are the most promising candidates. However, consideration of the area only is not enough to obtain an efficient material. A key factor determining the interaction of methane with the pore wall is the size of the pore. Numerical simulations for the adsorption of methane have shown that the maximum density of the adsorbed phase is attained within pores 11.2–11.4 Å in diameter .The methane adsorbent should also have a low heat of adsorption, and high heat capacity

Among these, activated carbons, carbon nanotubes, porous polymers, M41S materials, zeolites and porous ceramics have been regarded as promising media for efficient reversible storage of methane via physisorption Metal-organic frameworks (MOFs) developed recently, have shown promising properties for applications in gas storage due to the large surface areas and well-defined pore sizes. Initial reports for MOFs indicated a high value of gas storage at moderate temperatures and pressures. Recent studies of methane storage in MOFs (35 bar 298 K) report capacities ranging from 213 cm^3 (STP) g^{-1} in $[Cu(O_2CRCO_2)]$ (R = *trans*-$C_6H_4CH{=}CH$) to 240 cm^3 (STP) g^{-1} in IRMOF-6. IRMOFs have the composition $Zn_4O(L)_3$ (L = Linker). In IRMOF-6 benzocyclobutene-3,6-dicarboxylate is used as the linker. Computer simulations for an artificially constructed but until now not synthesized material IRMOF-993 (L = 9,10-anthracenedicarboxylate) show, that this structure should surpass all methane storage capacities reported so far.

1.2 Problem statement

Today application of methane as fuel is increasing drastically due to the application of carbon dioxide also increased. Increasing of demand of gas was producing the problem in storing the gas. Research is being conducted on many fronts in the gas storage field to help identify new improved and more economical ways to store gas. It conducted by the United State, US Energy department is showing that salt formations can be chilled allowing for more gas to be stored. In Sweden a new type of storage facility has been built, called "lined rock cavern”. This storage facility consists of installing a steel tank in a cavern in the rock of a hill and surrounding it with concrete. In transports, it quit dangerous to bring the tank contain methane with high pressure. Today, as a promising method, the storage of carbon dioxide and methane as adsorbed gas in porous materials is discussed. The development of new materials suitable for carbon dioxide and methane gas adsorption is an existing challenge and the research is still running.

MOFs is one of the most effective adsorbent for carbon dioxide and methane gas. Besides it can store high volume of gas and easy to found in the market. The storing of gases in metal organic framework facing problems where it is cannot afford high gas storage capacity. Besides that, methane is in a supercritical state near room temperature and it danger to the consumers. So it is impossible to liquefied methane at room temperature and compression of methane at room temperature is about 200-300 bar.

1.3 Objective

The objectives of this research are:

i. To prepare $Zn_3(btc)_2$ as adsorbent for carbon dioxide and methane gases.
ii. To study the characteristic of $Zn_3(btc)_2$ as adsorbent of carbon dioxide and methane gases.
iii. To study the rate adsorption of carbon dioxide and methane in $Zn_3(btc)_2$ sample.

1.4 Scope of study

The scopes of study for this research are:

i. To identify the impact of using $Zn_3(btc)_2$ as storage medium for carbon dioxide and methane gases.
ii. The characterization of $Zn_3(btc)_2$ as adsorbent of carbon dioxide and methane gases.
iii. To study the performance of $Zn_3(btc)_2$ as adsorbent when changing the pressure and time adsorption.

1.5 Current Research

Porous metal-organic frameworks (MOFs) have recently gained much attention as promising materials for gas adsorption. These materials are synthesized in a self-assembly process in which metal vertices are interconnected by organic linkers. As a result of this building block approach, these materials offer the possibility to tune host / guest interactions and therefore to tailor them rationally for specific adsorption applications. The molecular simulations are used to study carbon dioxide and methane adsorption in $Zn_2(bdc)_2dabco$ MOFs (Gubbins *et al.,* 1997).

Recently, people always talk about environmental protection. Natural gas has a considerable advantage over conventional fossil fuels both from an environmental point of view and due to the natural abundance and resources. The main component of natural gas is methane, with a high heat of combustion. The combustion of methane produces the smallest amount of carbon dioxide per unit of heat produced among fossil fuels. Thus a further improvement of methane driven vehicles is a key issue for the development of environmentally friendly transportation systems. Carbon capture and storage is an approach to mitigate global warming by capturing carbon dioxide from large point sources such as fossil fuel power plants and storing it instead of releasing it into the atmosphere. Although carbon dioxide has been injected into geological formations for various purposes, the long term storage of carbon dioxide is a relatively untried concept and as of 2007, no large scale power plant operates with a full carbon capture and storage system.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

Adsorption is a process, similar to absorption, by which a substance in a gas or liquid becomes attached to a solid. The substance can be a pollutant, called an adsorbate, which is attracted to the surface of a special solid. Adsorption occurs naturally, but industrialists have perfected adsorption methods to clean up hazardous waste or purify drinking water.

Tiny chemical particles suspended in another phase of matter, meaning in the air as a gas or in water as a liquid, are sometimes considered contaminants. These tiny particles can be separated from that phase, called the adsorbent, to enter a different phase. A material of another phase, like the solid carbon, preferentially targets these particles and bonds the adsorbate to its surface. The remaining air or liquid has been purified. This differs from absorption where the particles never change phase, but enter pores of the solid along with the accompanying air or water (Barton *et al*., 1984).

Natural or organic methods of adsorption take place all the time. For example, the ocean adsorbs carbon dioxide in the atmosphere, which effects climate and atmospheric temperature. Early humans observed that if they charred a piece of bone all the way through, they could put the bone in food mixtures, like sugar water, and it would collect polluting particles that weren't edible, thereby purifying the food.

Particles colored in our visible spectrum, as well as those with strong odors, are easiest to adsorb (Komodromos *et al*., 1992).

It is important to harness the power of adsorption in battling modern chemical hazards. Some solids are ideal for adsorption. They have a lot of surface area for their volume because they are pockmarked with micropores. Industrial and commercial uses for adsorption filters vary. For example, carbon makes cold drinking water taste better. A carbon filter can be heated to clean the surface of adsorbates and reused. Activated alumina removes harmful chemicals like fluoride and arsenic from liquids. Synthetic resins can clean up highly hazardous spills, such as nerve gas, in areas that might have high temperatures, like near explosives.

2.2 Natural Gas

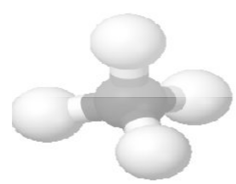
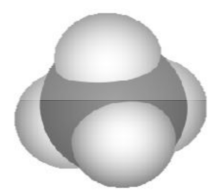
Natural gas is a gaseous fossil fuel consisting primarily of methane but including significant quantities of ethane, propane, butane, and pentane. When heavier hydrocarbons removed it can use as a consumer fuel as well as carbon dioxide, nitrogen, helium and hydrogen sulfide. It is found in oil fields (associated) either dissolved or isolated in natural gas fields (non-associated), and in coal beds kwon as coalbed methane. When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas. Sources of biogas include swamps, marshes, and landfills (landfill gas), as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle (Chen *et al*., 1997).

Since natural gas is not a pure product, when non-associated gas is extracted from a field under supercritical (pressure/temperature) conditions, it may partially condense upon isothermic depressurizing--an effect called retrograde condensation. The liquids thus formed may get trapped by depositing in the pores of the gas reservoir.

One method to deal with this problem is to reinject dried gas free of condensate to maintain the underground pressure and to allow reevaporation and extraction of condensates.

Natural gas is often informally referred to as simply gas, especially when compared to other energy sources such as electricity. Before natural gas can be used as a fuel, it must undergo extensive processing to remove almost all materials other than methane. The by-products of that processing include ethane, propane, butanes, pentanes and higher molecular weight hydrocarbons, elemental sulfur, and sometimes helium and nitrogen.

Table 2.1: Properties of methane gas.

Methane	
	 
Other names	Marsh gas, firedamp
Properties	
Molecular formula	CH_4
Molar mass	16.042 g/mol
Appearance	Colorless gas
Density	0.717 kg/m^3, gas 415 kg/m^3 liquid
Melting point	-182.5 °C, 91 K, -297 °F
Boiling point	-161.6 °C, 112 K, -259 °F
Solubility in water	3.5 mg/100 mL (17 °C)
Hazards	
Main hazards	Highly flammable (**F+**)
Flash point	-188 °C

2.3 Carbon dioxide

Carbon dioxide is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It can found as a gas at standard temperature and pressure and exists in earth's atmosphere in this state. It is currently at a globally averaged concentration of approximately 387 ppm by volume in the earth's atmosphere. Atmospheric concentrations of carbon dioxide fluctuate slightly with the change of the seasons, driven primarily by seasonal plant growth in the Northern Hemisphere. Concentrations of carbon dioxide fall during the northern spring and summer as plants consume the gas, and rise during the northern autumn and winter as plants go dormant, die and decay. Carbon dioxide is a greenhouse gas as it transmits visible light but absorbs strongly in the infrared and near-infrared.

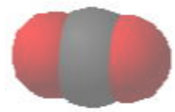
Carbon dioxide is produced by all animals, plants, fungi and microorganisms during respiration and is used by plants during photosynthesis. This is to make sugars which may either be consumed again in respiration or used as the raw material to produce cellulose for plant growth. It is, therefore, a major component of the carbon cycle. Carbon dioxide is generated as a by-product of the combustion of fossil fuels or the burning of vegetable matter, among other chemical processes. Large amounts of carbon dioxide are emitted from volcanoes and other geothermal processes such as hot springs and geysers.

Carbon dioxide has no liquid state at pressures below 5.1 atm, but is a solid at temperatures below -78 °C. In its solid state, carbon dioxide is commonly called dry ice. CO_2 is an acidic oxide if we test with litmus paper with an aqueous solution, it will turns litmus from blue to pink. CO_2 is toxic in higher concentrations, 1% (10,000 ppm) will make some people feel drowsy. Concentrations of 7% to 10% can cause dizziness, headache, visual and hearing dysfunction and unconsciousness within a few minutes to an hour.

Carbon dioxide is used by the food industry, the oil industry, and the chemical industry (Pierantozzi *et al*., 2001). It is used in many consumer products that require pressurized gas because it is inexpensive and nonflammable, and because it undergoes a phase transition from gas to liquid at room temperature at an attainable pressure of approximately 60 bar (870 psi, 59 atm), allowing far more carbon dioxide to fit in a given container than otherwise would. Life jackets often contain canisters of pressured carbon dioxide for quick inflation. Aluminum capsules are also sold as supplies of compressed gas for air guns paintball markers, for inflating bicycle tires, and for making seltzer. Rapid vaporization of liquid carbon dioxide is used for blasting in coal mines. High concentrations of carbon dioxide can also be used to kill pests, such as the comman clothes moth.

Liquid and solid carbon dioxide are important refrigerants, especially in the food industry, where they are employed during the transportation and storage of ice cream and other frozen foods. Solid carbon dioxide is called "dry ice" and is used for small shipments where refrigeration equipment is not practical. Liquid carbon dioxide (industry nomenclature R744 / R-744) was used as a refrigerant prior to the discovery of R-12 and is likely to enjoy a renaissance due to environmental concerns. Its physical properties are highly favorable for cooling, refrigeration, and heating purposes, having a high volumetric cooling capacity. Due to its operation at pressures of up to 130 bars, CO_2 systems require highly resistant components that have been already developed to serial production in many sectors. In car air conditioning, in more than 90% of all driving conditions, R744 operates more efficiently than systems using R-13a. Its environmental advantages (GWP of 1, non-ozone depleting, non-toxic, non-flammable) could make it the future working fluid to replace current HFCs in cars, supermarkets, hot water heat pumps, among others. Some applications: Coca-Cola has fielded CO_2-based beverage coolers and the US Army is interested in CO_2 refrigeration and heating technology (The Coca-Cola Company., 2006 and R744.com., 2007). By the end of 2007, the global car industry is expected to decide on the next-generation refrigerant in car air conditioning.

Table 2.2 : Properties of carbon dioxide gas.

Carbon dioxide	
	
IUPAC name	Carbon dioxide
Other names	Carbonic acid gas; carbonic anhydride; dry ice (solid)
Identifier	
CAS number	[124-38-9]
PubChem	280
EINECS number	204-696-9
RTECS number	FF6400000
Properties	
Molecular formula	CO_2
Molar mass	44.0095(14) g/mol
Appearance	colorless gas
Density	1,600 g/L, solid; 1.98 g/L, gas
Melting point	−57 °C (216 K) (under pressure)
Boiling point	−78 °C (195 K), (sublimes)

2.4 Storage and transport

The major difficulty in the use of natural gas is transportation and storage because of its low density. Natural gas pipelines are economical, but are impractical across oceans. Many existing pipelines in North America are close to reaching their capacity, prompting some politicians representing colder areas to speak publicly of potential shortages.

Liquefied natural gas, LNG carriers can be used to transport liquefied natural gas across oceans, while tank trucks can carry liquefied or compressed natural gas, CNG over shorter distances. They may transport natural gas directly to end-users, or to distribution points such as pipelines for further transport. These may have a higher cost, requiring additional facilities for liquefaction or compression at the production point, and then gasification or decompression at end-use facilities or into a pipeline.

In the past, the natural gas which was recovered in the course of recovering petroleum could not be profitably sold, and was simply burned at the oil field (known as flaring). This wasteful practice is now illegal in many countries. Additionally, companies now recognize that value for the gas may be achieved with LNG, CNG, or other transportation methods to end-users in the future. The gas is now re-injected back into the formation for later recovery. This also assists oil pumping by keeping underground pressures higher. In Saudi Arabia, in the late 1970s, a "Master Gas System" was created, ending the need for flaring. Satellite observation unfortunately shows that some large gas-producing countries still use flaring and venting routinely. The natural gas is used to generate electricity and heat for desalination. Similarly, some landfills that also discharge methane gases have been set up to capture the methane and generate electricity (Malbrunot *et al*., 1996).

Natural gas is often stored in underground caverns formed inside depleted gas reservoirs from previous gas wells, salt domes, or in tanks as liquefied natural gas. The gas is injected during periods of low demand and extracted during periods of higher demand. Storage near the ultimate end-users helps to best meet volatile demands, but this may not always be practicable. With 15 nations accounting for 84% of the world-wide production, access to natural gas has become a significant factor in international economics and politics. In this respect, control over the pipelines is a major strategic factor.

2.5 Materials characterization

2.5.1 Scanning Electron Microscopy, SEM

Scanning Electron Microscopy, SEM is a microscope that uses electrons instead of light to form an image. An optical microscope use lenses to bend the light waves and the lenses are adjusted for focus. In the SEM, electromagnets are used to bend an electron beam which is used to produce the image on screen. By using electromagnets, an observer can have control in how much magnification needed. The electron beam also provides greater clarity in the image produced.

The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electron; back scattered electrons (BSE), characteristic x-ray, light (cathodoluminescence), specimen current and transmitted electrons. These types of signal all require specialized detectors for their detection that are not usually all present on a single machine. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size. Due to the way these images are created, SEM micrographs have a very large depth of field yielding