Doctoral Dissertation

博士論文

Preparation and Modification of Hollow Fiber Type Carbon Molecular Sieve Membranes for Gas Separation

（ガス分離用中空糸型分子ふるい炭素膜の作製と改質）

2022 年 9 月

NIE JING

聶 静

山口大学大学院創成科学研究科

Abstract

Rapid population growth and economic progress over the past decades have triggered a sharp increase in the global demand for fossil fuels thereby resulting in an energy crisis. The problem may be alleviated by upgrading and producing gaseous energy, but one of the major challenges associated with gaseous energy is to separate it effectively from other less desirable gases. Thus, energy-saving and high-efficiency separation technology is needed. In the past three decades, gas separation membranes, including polymeric membranes and inorganic membranes, have attracted much attention due to their advantages in terms of energy efficiency, operational simplicity, cost competitiveness, and small footprint. Although polymeric membranes have been utilized in practical gas separation, their separation performance is not sufficient for widespread practical application. Carbon molecular sieve (CMS) membranes, one of the inorganic porous membranes, can be prepared by pyrolyzing polymeric precursors. Their pore structures provide molecular sieving ability and possess good thermal and chemical resistance. Especially, the separation properties of the CMS membranes for a variety of gas pairs have exceeded the upper bound of polymeric membranes. These characteristics have made them attractive candidates for gas separation.

The pore structures, separation properties, and transport mechanism of the CMS membranes depend critically on the type of the polymeric precursors, pyrolysis conditions and pre- and post-treatments. Thus, in this thesis, I prepared CMS membranes derived from different polymeric precursors and investigated the effect of pyrolysis conditions and post-treatment on the gas permeation properties.

In Chapter 2, toluene vapor addition was performed for the first time during the pyrolysis process to prepare highly selective CMS membranes. Adding toluene vapor in the pyrolysis process was a simple method to improve the selectivity compared with

the traditional chemical vapor deposition post-treatment technique. Additionally, the use of toluene can avoid the high transportation costs of gaseous hydrocarbons. The results indicated that toluene vapor addition increased selectivities of the H_2-related gas pairs compared with CMS membranes without toluene vapor addition. This could not be realized simply by increasing the pyrolysis temperature without toluene vapor addition. The CMS membrane with toluene vapor addition also showed higher permeance with a moderate selectivity compared with the CMS membrane with gaseous hydrocarbon addition reported in the literature. Furthermore, the gas permeance and selectivity could be readily controlled by adjusting the pyrolysis temperature and duration of the addition. The optimal preparation conditions of the CMS membrane with toluene vapor addition depend on the targeted gas pair to be separated. This study indicated that adding liquid hydrocarbon vapor in the pyrolysis process can be a simple and effective method for preparing highly selective CMS membranes.

In Chapter 3, the mechanism of achieving high selectivity for the CMS membranes prepared by adding toluene vapor was further investigated. The physical and chemical properties of CMS membrane with adding toluene vapor were characterized using some sophisticated characterization techniques. It was found that toluene vapor addition formed carbon deposition on the outer surface region of the CMS membrane, which agreed with the previous report. The gas adsorption experiment suggested that toluene vapor addition also resulted in the loss and the narrowing of ultramicroporosity. Additionally, I preliminary analyzed the mechanism of achieving high selectivity for the CMS membrane with toluene vapor addition.

In Chapter 4, a novel porous carbon fiber (PCF) was investigated to prepare supported CMS membranes derived from wood tar solution, as the development of wood tar-derived CMS membranes has been limited by the availability of porous supports in recent years. Moreover, the CMS membranes supported on commercially available porous ceramic tubes were also prepared under the same conditions for comparison purposes. The PCF consisted of interconnected pore structures, which provide additional paths and channels for gas transport, whereas the porous structure of the ceramic support consisted of voids between the alumina particles. It was found that for both supports, 70 wt% wood tar solution was the optimal solution for preparation of CMS membranes. The PCF-supported CMS membranes exhibited higher gas permeance and selectivity than the NA3-supported membranes. Furthermore, a series of PCF-supported CMS membranes from 70 wt% wood tar solution were prepared at different pyrolysis temperatures, the membrane pyrolyzed at 600 °C exhibited the highest H_2 selectivity. This study demonstrated that PCF can be used for supported CMS membranes derived from wood tar solution. Additionally, PCF is also a promising support for the supported CMS membranes derived from other polymeric precursors.

Finally, Chapter 5 summarized the main contents of this thesis.

要旨

過去数十年にわたる急速な人口増加と経済発展は、化石燃料に対する世界的な需要の急激な増加を引き起こし、それによってエネルギー危機をもたらしている。この問題は、燃料ガスの転換と製造方法の改善によって軽減することができるが、他のガスとの分離を高効率で行うことが一つの課題である。そのため、消費エネルギーが少なく高効率な分離技術が必要とされている。過去 30 年、高分子膜や無機膜を用いる膜ガス分離は、エネルギー効率、操作の単純さ、コスト競争力、および小さな設置面積などの利点により多くの注目を集めてきた。高分子膜は実際の商業ガス分離に利用されているが、その分離性能は実用範囲を広げるには十分ではない。無機多孔質膜の 1 つである分子ふるい炭素（CMS）膜は、高分子前駆体の熱分解で製造できる。その細孔構造は、分子ふるい能力を有し、優れた耐熱性および化学的耐性も備える。CMS 膜の分離特性は高分子膜の性能上限を超えている。このことから CMS 膜は膜ガス分離において必要な分離膜の魅力的な候補である。

CMS 膜の細孔構造、分離性能、およびガス透過機構は、高分子前駆体の種類、熱分解条件、および前処理と後処理に依存する。この論文では、市販のポリイミド中空糸膜と木タールを前駆体とした CMS 膜を作製し、熱分解条件と後処理がガス透過特性に及ぼす影響を調べている。

第 2 章では、熱分解プロセスにおけるトルエン蒸気の添加が高分離性 CMS 膜の作製に用いることができることを初めて報告した。 熱分解プロセスにおいてトルエンのような炭素源を添加する方法は、従来の化学気相成長法に比べて簡便な方法である。 また、トルエンの使用は、炭化水素ガスを炭素源と

して用いる場合のような高コストの供給方法を回避することができる。トルエン蒸気の添加は CMS 膜の H2 分離性を大きく増加した。この分離性の増加はトルエン蒸気を加えずに熱分解温度だけを調節する方法では達成できないものであった。トルエン蒸気を添加して作製した CMS 膜は、文献で報告されている炭化水素ガスを添加した CMS 膜と比較して、より高い透過速度と適度な分離性を示すことが分かった。 熱分解温度と添加時間を調節することで、ガス透過速度や分離性を容易に制御することができた。その最適な条件は分離したい対象ガスによって異なる。 本研究は、熱分解プロセスに液体炭化水素を蒸気として加えることで、高分離性 CMS 膜を容易かつ効率的に調製できることを示した。

第 3 章では、トルエン蒸気を添加して作製した CMS 膜の高分離性達成のメカニズムについて、さらに検討を行った。トルエン蒸気を添加した CMS 膜の物理的および化学的特性について、いくつかの高度な特性評価技術を使用して評価した。トルエン蒸気の添加により、CMS 膜の外表面領域に炭素が堆積されることがわかったが、これは以前の報告と一致した。また、ガス吸着実験から、トルエン蒸気の添加により、超微細孔の消失と狭窄が起こることが示唆された。これらの結果を踏まえてトルエンを添加した CMS 膜の高選択性達成のメカニズムを考察した。

第 4 章では、新規な多孔質炭素繊維（PCF）を用いて担持型の木タール由来 CMS 膜の作製方法を検討した。近年、CMS 膜の開発に必要な多孔質支持体の入手が困難であり、新規な支持体が切望されている。そこで、従来からよく使われている市販の多孔質セラミック管を用いた CMS 膜と同じ条件で作製し、

その特性を比較検討した。PCF は相互に連結した細孔からなり、ガス輸送のための追加の経路とチャネルを提供するのに対し、セラミック支持体の多孔質構造はアルミナ粒子間の空隙から構成されている。どちらの支持体も、70%木タール溶液が CMS 膜の調製に最適な溶液であることがわかった。PCF を用いた CMS 膜は、セラミックス多孔質支持体を用いた CMS 膜よりも高いガス透過速度と分離性を示した。さらに、異なる熱分解温度で炭素化した一連の PCF 担持 CMS 膜を作製したところ、600℃で熱分解した膜が最も高い H2 選択性を示した。この研究により、PCF が木タール溶液由来の担持型 CMS 膜に使用できることを示すことができた。PCF は他の高分子前駆体から得られる担持型 CMS 膜の支持体としても有望と考えられる。

　最後に第 5 章で、本論文の要約をまとめる。

Contents

Chapter 1 Introduction

1.1 Membrane for gas separation

Membrane technologies have received increasing attention in the field of gas separation, as their applications exhibit significant advantages in terms of low environmental impacts, high energy efficiency, and simple equipment [1-3]. Membrane-based gas separation can be traced back to the 19th. Mitchell was a pioneer in observing the phenomenon that the rubber membranes had the perm-selectivity for gases [4]. Fick proposed a mathematical theory of gas permeation through polymers, called Fick's first law [5]. Thomas Graham described the basic principle and theory in terms of gas transport through natural rubber, which aroused tremendous interest in the study of gas separation [6]. These works provided the foundation for the development of membrane-based gas separation technologies.

Before the 20th century, membrane-based gas separation was only used as a tool to develop physical/chemical theories in the laboratory. Until 1943, the microporous ceramic membranes were used to separate uranium isotopes [7]. However, this project was used for military purposes, thus it was not allowed to announce. In the 1960s, Sidney Loeb and Sirivasan Sourirajan made a great contribution to membrane preparation that they successfully prepared high flux asymmetric cellulose acetate membranes using for water desalination [8]. Furthermore, reverse osmosis membranes can be produced on a large scale and be assembled into large-area modules. This great progress provided a basis for the development of gas separation membranes from the laboratory to industrial scale. Monsanto Co. built the first membrane plant for H_2 purification, marking that membrane-based gas separation had achieved the commercial application [9].

Membrane separation has developed from assistive toward competitive technologies relative to the conventional technologies (amine adsorption, cryogenic distillation, and pressure swing adsorption) in the past three decades. Presently, they have been widely applied in many fields, including hydrogen recovery, nitrogen production, and natural gas treatment [1-3]. Besides, their potential applications also include olefin/paraffin separation in hydrocarbon processing [10] and removing NH_3 from recycling streams in ammonia synthesis [11]. Membrane separation performance can be affected by membrane materials and preparation techniques. According to materials, the membrane can be classified into polymer membrane, inorganic membrane, and mixed matrix membrane. The characteristics of various membrane are summarized as follow:

1.1.1 Polymeric membrane

Polymeric membranes are the earliest commercial membranes used for gas separation because of their excellent processability, high flexibility and scalability, and excellent cost effectiveness [12]. Their commercial applications are inseparable from the effort of the major chemical/plastic companies (e. g. DuPont, Monsanto, General Electric, Dow). Polymers can be classified into two categories based on the glass transition temperatures [13]. One is rubber polymers, such as poly(dimethylsiloxane), silicone rubber, nitrile butadiene, etc. The other category is glass polymers, such as cellulose acetate, polyamides, polyimides, polyetherimides, polypropylene, poly(vinyl chloride), etc. However, polymeric membranes always encounter a compromise problem between permeability and selectivity: the membranes with high permeability generally display low selectivity and vice versa [14,15]. In the past decades, researchers have made great efforts in membrane materials and preparation technologies and hope to overcome the tradeoff problem. Unfortunately, pure polymeric membranes have not been able to solve this problem until now. The other challenge for polymer membranes is their poor resistance to the harsh operating environment, such as high temperature, high pressure, and chemical corrosion. In order to improve separation performance, some researchers shifted attention to co-polymeric materials [16-18]. Although the co-polymeric materials have been used to prepare membranes, significant progress in the tradeoff of the separation performance was still difficult to achieve.

1.1.2 Mixed matrix membrane

Considering the trade-off limitation of polymeric membranes, some researchers switched their attention toward mixed matrix membranes (MMMs). MMMs are prepared by blending porous fillers in a polymer matrix [19-20]. For ideal MMMs, porous fillers that have special shapes, surface chemistry, and mechanical strength, are uniformly dispersed in the continuous polymer phase. Moreover, no interface defects exist in ideal MMMs. MMMs are believed to combine the easy processability of a polymer membrane with the superior selectivity of porous additives. However, such ideal morphology is almost not achieved owing to imperfect adhesion between polymer and porous additives. Imperfect adhesion can form different types of interface defects, thus nonideal MMMs are more complex. Besides, the performance of the MMMs also depends properties of the fillers and polymers.

1.1.3 Inorganic membrane

Inorganic membranes are another promising gas separation tool in the membrane field after the polymeric membranes due to their high permeation and good stability. Although the inorganic membranes are developed earlier than those non-natural polymeric membranes, the relevant results are not allowed to be made public because they were studied for military purposes. [21]. The booming development of inorganic membranes started at the beginning of the 1980s [22]. Membralox, Carbosep, and Ceraflo are all products of that period. According to the membrane structures, the inorganic membranes could be divided into porous (mesoporous and microporous) and dense (non-porous) membranes. Compared with porous membranes, the applications of dense membranes are generally limited by their low permeability.

Currently, the dominant inorganic membranes for commercial applications are porous membranes [21,22]. Commonly used porous membrane materials include glass, metal, alumina, zirconia, silica, zeolite, and carbon. For the membrane preparation, the membrane configuration also is a very important role. Both asymmetric and symmetric configurations, including hollow fiber membranes and supported membranes, have been recognized as suitable configurations for commercial applications [23,24]. The performance of porous membranes mainly depends on their pore structures. The pore structures of silica, zeolite, and carbon membranes display sieving properties for large molecules. It is based on the difference in the diameters of gas molecules, where relatively small gas can selectively pass through the pores and move across the membrane whereas larger gas is obstructed from the pores [25]. Silica membranes are suitable for separating hydrogen gas from larger gas molecules, but they have insufficient perm-selectivity for purifying H_2 from similar-sized molecules (O_2 and N_2) [26]. For zeolite membranes, they have been used for CO_2/CH_4 separation [27,28], isomers separation [29,30], and hydrogen purification [31,32]. However, one of the greatest challenges they face to produce the large size and defect-free membranes. Among inorganic porous membranes, the carbon membranes show significant advantages in terms of their rapid adsorption and desorption characteristics, high adsorption capacity, pore-size controllability, as well as thermal and chemical resistance [24,33,34]. In recent years, carbon membranes particularly carbon molecular sieving (CMS) membranes have received increasing attention in the field of membrane-based gas separation and have also been considered a promising candidate to replace the polymeric membrane, as their separation properties for a variety of gas pairs have exceeded the upper bound limit of polymeric membranes. Below, we will focus on carbon membranes.

The pioneering work on carbon membranes was performed in 1955 when Barrer et al. attempted to prepare a plug by compressing graphite carbon powder and called it a carbon membrane [35]. In 1973, Ash et al. used the membrane obtained by large area compressed carbon powder to separate single gases and binary gas mixtures [36].

Although Bird and Trimm [37] prepared unsupported and supported CMS membranes from poly (furfuryl alcohol) (PFA) in 1983, they did not completely control the factors determining the properties of carbon. The membrane shrinkage in carbonization always resulted in cracks and discontinuities, thus, gas transport properties of similar samples prepared separately had significant differences. During the same period, Soffer and Koresh successfully prepared CMS membrane by pyrolyzing polymeric precursors [38,39]. Currently, most carbon membranes reported in the literature are prepared by pyrolyzing polymeric precursors.

According to different separation mechanisms, the carbon membrane can be classified into adsorption-selective carbon (ASC) membranes and CMS membranes. ASC membranes can separate the gas component depending on the difference in adsorption properties for gas molecules, e.g., the non-adsorbable or weakly adsorbable components (i.e., N_2, H_2, O_2) can be separated from the more strongly adsorbable components (i.e., hydrocarbons, NH_3, SO_2, H_2S) [24,40]. Whereas, the CMS membranes separate gas molecules through the molecular sieving function of pore structures. From a structural point of view, micropores of ASC membranes are slightly wider than those of CMS membranes [41], which makes ASC membranes less selective than CMS membranes. Therefore, today's carbon membrane research focuses on the CMS membranes [42,43].

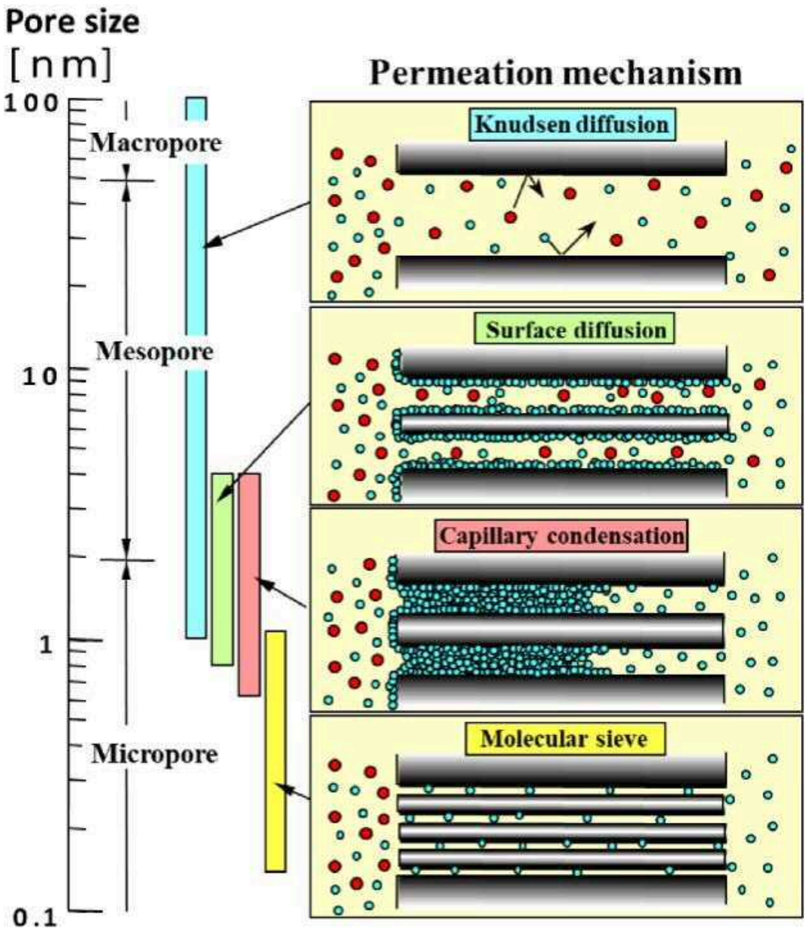

Figure 1-1. Gas transport mechanism.

1.2 Permeation mechanism

The transport behavior of gas passing through the membrane is determined by both the physical/chemical properties of membrane materials and gas molecules. Gas transport mechanisms consist of surface diffusion, Knudsen diffusion, capillary condensation, and molecular sieving [44,45], as shown in Figure 1-1.

1.2.1 Knudsen diffusion

When the pore dimension of the membrane is smaller than the mean-free path of gas, the degree of collision between gas and pore walls is higher than the collision between gases. The gas transport mechanism through membrane materials is Knudsen diffusion. In general, the pore diameter of around 5 to 10 nm under pressure and 5 to 50 nm under nonpressure conditions, respectively, Knudsen diffusion dominates [46]. This diffusion mechanism is dependent on the differences in the molecular weights of feed gases. Light gases move and diffuse faster because they collide with the pore wall much more. The selectivity factor is inversely proportional to the square root of the molecular weight of separated gas components [45]. The resulting selectivity is rather low and doesn’t suit for the actual separation process.

1.2.2 Surface diffusion

Surface diffusion is based on the adsorption properties of gases in pore structures rather than pore size [44,47]. It can not be neglected in the membrane when one component has an affinity to the membrane. The component is preferentially adsorbed on the pore wall relative to other components, then passes through the pore and diffuses along the surface of the pore wall. With the number of gas mixtures increasing on the pore surface, if the adsorbed or more strongly adsorbed gas diffuses faster than non-adsorbed or poorly adsorbed gases, indicating that the surface diffusion mechanism occurs.

The surface diffusivity of the adsorbable gas is very fast because this process requires relatively low activation energy. Furthermore, the adsorbable component can prevent the small non-absorbable or weakly adsorbable component from moving through the non-surface space of the pore.

1.2.3 Capillary condensation

For the gas of favorable condensability or strong affinity, it adsorbs on the membrane surface and condenses in the pores, thereby blocking the pore and preventing non-condensable components from permeating into the pore [48]. This behavior occurs in the hydrogen sulfide/hydrogen and sulfur dioxide/hydrogen separation processes, where H_2S and SO_2 are separated depending on capillary condensation, and their condensation phenomenon prevents the H_2 from permeating through the pores [44,46]. Additionally, capillary condensation is possible to improve the permeability and selectivity of the membrane.

1.2.4 Molecular sieving

When pore size is located in between diameters of two gas molecules in targeted gas pairs, the gas separation is dominated by molecular sieving. In this transport process, relatively small gas can pass through pores and move across pore structure, while large gas is obstructed from the pore [24,49]. These membranes exhibit superior gas permeability and selectivity for smaller gas.

1.2.5 Sorption and diffusion

Gas transport behavior in membranes obeys the sorption-diffusion mechanism. Gas molecules firstly adsorb on the high-pressure side of the membrane, then diffuse from the high-pressure side to the low-pressure side, and finally desorb on the low-pressure region. Figure 1-2 shows a schematic diagram of gas transport through the membrane.

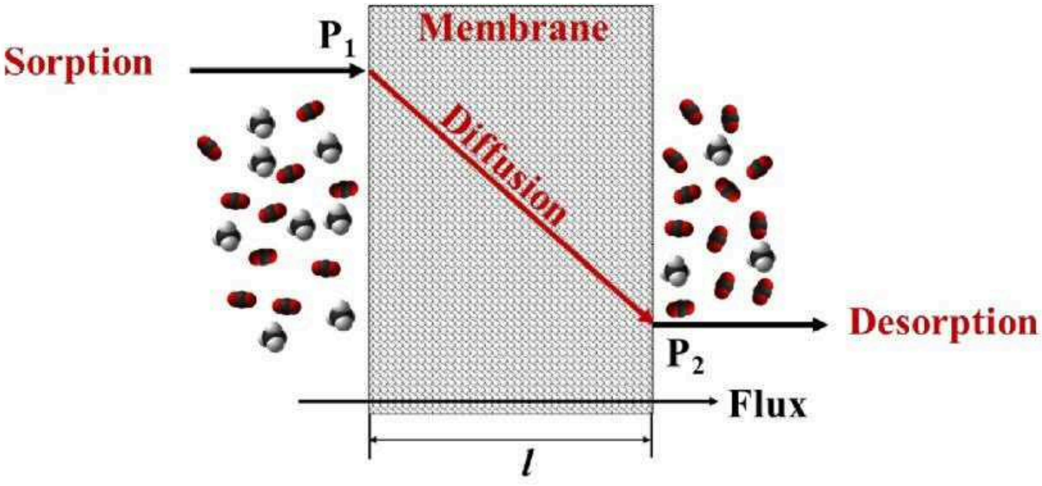

Figure 1-2. The schematic diagram of gas transport through the membrane.

Permeability and selectivity are usually calculated to determine the gas separation performance of membrane. The former (P_i) is used to measure the productivity of gas passing through the membrane:

$$P_i = \frac{N_i l}{\Delta p_i} \tag{1}$$

Where N_i is steady state flux of gas transport through membrane with thickness l, the pressure difference of the upstream side and downstream is Δp_i.

For asymmetric hollow-fiber-type membranes, the membrane thickness is difficult to measure, so their productivity is defined as the permeance (P_i/l)

$$P_i/l = \frac{N_i}{\Delta p_i} \tag{2}$$

The selectivity ($\alpha_{i/j}$) decides separation efficiency of the target gas pair, which is the ratio of gas i permeability and gas j permeability:

$$\alpha_{i/j} = \frac{P_i}{P_j} \tag{3}$$

According to the Fick's first law, the permeability of the gas passing through membrane can further be defined as the product of solubility (S_i) and diffubility (D_i):

$$P_i = D_i\, S_i \tag{4}$$

For the CMS membranes, the solubility is the normalized pressure of the equilibrium concentration of gas, which is related to the gas condensability and the interaction between gas and membrane materials. The solubility can be calculated by Langmuir isotherm,

$$S_i = \frac{C_i}{P_i} = \frac{C'_{Hi}\, b_i}{1+b_i\, p_i} \tag{5}$$

C_i is the equilibrium uptake of gas i by the membrane, p_i is the partial pressure, C'_{Hi} and b_i is the Langmuir hole filling capacity and Langmuir affinity constant for gas i, respectively.

Diffusion of gases in CMS membrane depends on molecular sieve function of pore size. Two gases, having small difference in molecular diameter, can be separated according to a substantial difference in their activation energy. Furthermore, the ultramicropores of CMS membrane display 'entropic selectivity' feature due to their rigid nature, which can constrain the rotation and vibration of the molecules.

1.3 Carbon molecular sieve membrane

Soffer and Koresh pioneered preparing CMS membrane by pyrolyzing polymeric precursors [37,38]. They demonstrated that the pyrolysis temperature and atmosphere can affect the pore aperture size of the CMS membrane. During the following ten years, research into the CMS membrane for gas separation has made significant progress. Carbon Membranes Ltd. (Israel) commercialized cellulose-based carbon membranes at the end of the 1990s to be the first and only manufacturer of CMS membrane, but the company closed in 2001. Since then, researchers continued to work on the commercial development of carbon membranes, including the pilot-scale system for carbon membranes manufacturing [50] and fabrication technique for large-scale carbon membrane modules [42,43].

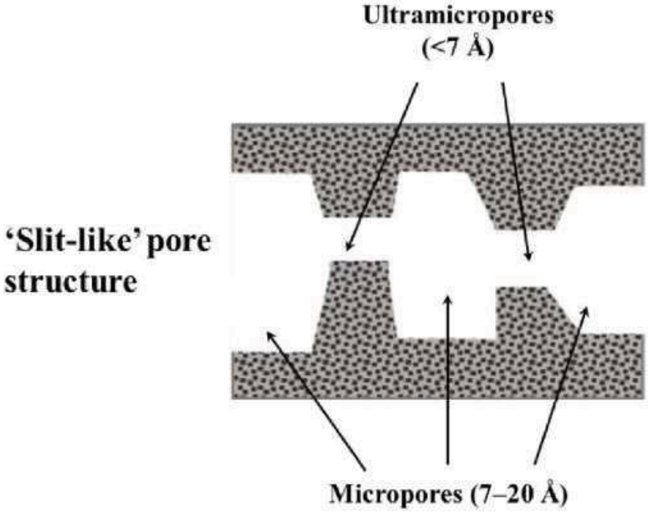

Figure 1-3. 'Slit-like' pore structre of CMS membranes.

In general, CMS membranes are prepared by pyrolyzing/carbonizing a polymeric precursor at a high temperature (500–800 °C) in an inert atmosphere or vacuum [51]. As shown in Figure 1-3, a rigid, slit-like pore structure is formed during the pyrolysis process, which is composed of micropores (7–20 Å) and ultramicropores (<7 Å) that exhibit a strong size exclusion capability and good thermal and chemical stabilities. However, their structure, separation properties, and transport mechanism depend critically on the type of the precursor materials, pyrolysis conditions, and pre- and post-treatment technologies [52-54].

1.3.1 Configuration

CMS membranes can be categorized generally into two classes: supported and unsupported membranes. The membranes are supported on porous materials such as carbon and ceramic, named supported CMS membrane. Figure 1-4 shows two different shapes of supported membranes: disk shape and tubular shape, which have good mechanical strength. They can be prepared by a simple coating or deposition process. In order to obtain good performance, CMS membranes are prepared as thin as possible.

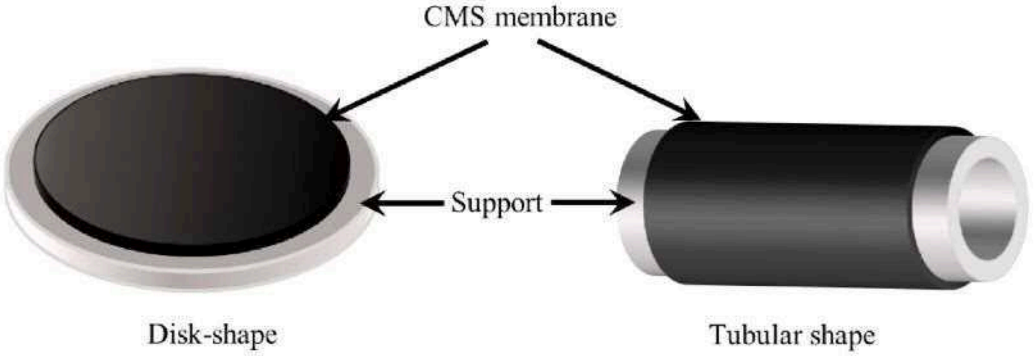

Figure 1-4. Schematic of suppoted CMS membranes.

Compared with supported membranes, the unsupported carbon membranes are brittle and uneasy to handle. Their configurations have flat type and hollow fiber type. Among them, flat type is usually used to analyze materials properties. Whereas hollow-fiber-type CMS membranes possess a large surface-area-to-volume ratio, which is beneficial for assembling membrane modules with high separation performances. Furthermore, hollow-fiber-type membranes can also be divided into two configurations: symmetric and asymmetric configurations, as shown in Figure 1-5.

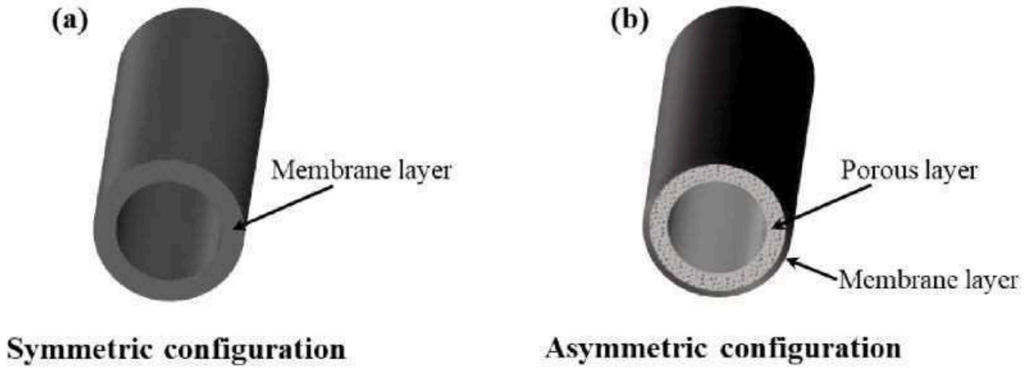

Figure 1-5. Hollow-fiber-type CMS membranes: (a) symmetric and (b) asymmetric configurations.

1.3.2 Precursor materials

The selection of precursor materials is the first and the most important step in the CMS preparation because the pyrolysis of different precursors will produce CMS membranes with different properties [52]. Over the past three decades, a variety of polymeric materials, including polyimide (PI) and its derivatives [55,56], poly (furfuryl alcohol) (PFA) [57], cellulose acetate (CA) [49,58], poly (phenylene oxide) (PPO) [59,60], polyacrylonitrile (PAN) [61], polyetherimide (PEI) [62], phenolic resins

[63,64], polymer blends [65,66] and other materials, have been used to prepare CMS membranes.

From the view of separation and mechanical properties, the best CMS membranes are prepared from the carbonization of aromatic polyimides [49]. Fu and Koros prepared CMS membranes using four novel types of polyimide precursors and reported the effect of the fractional free volume (FFV) of the polyimides on permeation performance of CO_2, CH_4, O_2, and N_2 passing through the membranes [67]. The permeability of polyimide membranes increases with increasing FFV of polymer structure, and the resultant CMS membranes also maintain high permeability. The effect of the bulky side-groups leads to an increase in FFV for polyimide, which decreases the packing density of the chains and enlarges the activation zone and available free volume. Furthermore, CMS membranes derived from co-polyimides, such as 6FDA/PMDA-TMMDA [68] and P84 co-polyimides [69], have also exhibited excellent gas separation performances. Blending polymers are also viewed as an approach to alter the properties of polymeric precursors, and have been used to prepare high-quality CMS membranes. However, the production of most synthetic polyimides and derivatives exists the drawbacks of low yield, complex production process, and high cost. Therefore, using commercialized precursors, such as Kaption, and Matrimid, is critical for the large-scale production of CMS membranes.

1.3.3 Pyrolysis conditions

Pyrolysis is the key stage in the preparation of CMS membranes. The pyrolysis results in the decomposition of the organic compounds and the evolution of gas molecules, a stiff and cross-linked carbon matrix form progressively during the process [70]. The carbon matrix is a disordered structure with a large number of porosities rather than graphitizing carbon. The pyrolysis parameters include atmosphere, heating rate, pyrolysis temperature, and soaking time. He and Hägg [71] prepare the hollow-fiber-type CMS membranes derived from deacetylated cellulose acetate and built a calculation model base on the experimental results to predict the importance of each factor. The result indicates that the pyrolysis atmosphere played the most important role, followed by pyrolysis temperature, heating rate, and thermal soaking time.

1.3.3.1 pyrolysis atmosphere

Commonly used pyrolysis atmospheres include vacuum and inert gases such as N_2 and Ar. Geiszler and Koros found that the CMS membranes derived from the same precursor but pyrolyzed under different atmospheres exhibited different separation performances [51]. More specifically, the membrane obtained under the inert gas condition displays higher permeance and lower selectivity than that obtained under the vacuum. This may be because the pyrolysis mechanisms produced under the two atmospheres are different [72]. Carbonization under a vacuum, the sample may be decomposed by the decomposition mechanism in a single molecule. Whereas the inert atmosphere can accelerate carbonization reaction through increasing gas-phase heat and mass transfer, the inert gas molecules seem to form a more ‘open’ porous matrix in the CMS membranes thereby obtaining higher permeance and lower selectivity. Additionally, the effect of He, Ar, and CO_2 atmosphere on the CMS membrane performance is similar at low pyrolysis temperature (550 °C). When the pyrolysis was carried out at a temperature above 800 °C under the CO_2 atmosphere, the obtained product was a highly porous, non-selective carbon membrane. Furthermore, the inert gas can also prevent unwanted burnout and chemical damage to the precursor. The double-component gases containing a certain amount of O_2 and inert gas (He and Ar) was also used to prepare the CMS membrane [52]. The study indicated that there is a strong correlation between the amount of oxygen and the resultant membrane performance.

1.3.3.2 Pyrolysis temperature

Pyrolysis temperature has a significant effect on pore structure and separation performance of the resultant membranes. In a certain temperature range, increasing the pyrolysis temperature decreases gas permeability but increases the ideal selectivity [73,74]. Koresh et al. studied the effect of pyrolysis temperature on the evolution of the pore structure of CMS [75,76]. More specifically, pyrolysis can remove the surface group of the precursor and burn off part of skeletal carbon elements, leading to the opening of the pore structure. For the CMS carbonized at above 800 °C, the pores are closed due to the vast extent of sintering. Besides, increasing the pyrolysis temperature results in a more compact and turbulent structure, an increase in crystallinity and density, and a decrease in the average interplanar spacing of the graphite layer of carbon [77].

Additionally, the optimum temperature is determined by precursor material used and gas pairs separated. For the polyimide used as a precursor, membranes obtained at the pyrolysis temperature range of 700–850 °C display excellent H_2/CH_4 performance [56], whereas membranes obtained at 600–630 °C display excellent C_3H_6/C_3H_8 and C_4H_6/C_4H_{10} separation properties [73]. When cellulose acetate is used as the precursor, CMS membranes pyrolyzed at 550 °C showed superior performance for CO_2 capture [78] and CO_2/CH_4 separation [79]. Furthermore, Cellulose acetate derived asymmetric CMS membranes pyrolyzed at 700 and 850 °C showed excellent H_2/CO_2 separation performance [80]. Sulfonated poly (phenylene oxide) (SPPO) derived flexible CMS membranes pyrolyzed at 600 °C showed good mechanical stability and excellent performance for O_2/N_2 and CO_2/CH_4 separation [60]. When the pyrolysis temperature increased to 700 °C, the CMS membrane became less flexible and somewhat brittle. The CMS membranes derived from PEI/PVP polymer blends and pyrolyzed at 800 °C showed good separation performance for CO_2/CH_4 and CO_2/N_2 [81].

1.3.3.3 Thermal soaking time

Thermal soaking time is the stage of time that keep membranes at pyrolysis peak temperature, which can be determined by the final pyrolysis temperature [70]. Vu and Koros [82] indicated that decreasing soaking time was the most effective method to increase CO_2 permeance without sacrificing CO_2/CH_4 selectivity. They suspected that only rearrangement of microstructure appears in this stage, resulting in reduction of the mean pore size distribution and the number of pores for the diffusible molecules. David and Ismail [83] studied the effect of soaking time from 10 to 180 min on performance of the CMS membranes. The results showed that the O_2 permeability first increased in the soak time of 10 min to 120 min, and decreased after soaking for more than 120 min. Moreover, the long soaking time tended to form the CMS membrane with high selectivity. Porosity change at different soak times was caused by the dynamic conversion of amorphous porous carbon to crystalline graphite. Long-time soaking study of 2h to 8h indicated that increasing soaking time tends to increase the selectivity and decrease permeability [84], which agrees with other reports [83, 85].

1.3.3.4 Heating rate

The heating rate is also not ignored factor, which determines the release rate of volatile components produced during the pyrolysis process [86]. The applicable heating rate for the CMS membranes is generally in the range of 1-10 °C/min, which depends on the polymeric precursor materials [87]. The CMS membranes prepared at a lower heating rate display better separation performance. Higher heating rates may cause pinholes, microcracks, blisters, and deformation, and extreme cases may make the membrane useless for gas separation [86].

1.3.4 Pre and post treatments

The most commonly pre-treatment method is oxidation in the temperature range of 100 to 400 °C under an air atmosphere. Oxidizing precursor materials before pyrolysis can improve their stability because polymeric precursors are hydrogenated in the process thereby forming C=C bonds and oxygen-containing groups. Furthermore, oxidation can also prevent excessive evaporation of the gas products during the pyrolysis stage, thereby maximizing the carbon yield of the resulting membrane. Asymmetric polyimide hollow fiber precursor without pre-oxidation will soften in the pyrolysis stage and the resulting membrane display rather poor gas separation performance [56]. The duration and the temperature of the oxidation process have a decisive influence on the morphological characteristics and performance of the final membrane [88]. When the oxidation temperature is above 550°C, an irregular outer surface was observed due to the substantial degradation of the polymeric precursor.

On the other hand, physical and chemical pre-treatments have attracted considerable attention in the preparation of CMS membranes. Bhuwania and Koros [89] develop a sol-gel crosslinking reaction to prevent morphological collapse in the carbonization process. The technology (referred as V-treatment) applied a sol-gel crosslinking reaction to induce vinyl crosslinked silica on the precursor fiber pore wall, which prevented the porous layer from collapsing during the carbonization process and increased the permeability of the CMS membrane.

The post-treatment methods, including chemical vapor deposition (CVD) [54,90,91], post-activation [92-95], hyperaging/super-hyperaging [96,97], and coating [98] have applied to adjust pore size of CMS membranes and improve their separation performance. Among them, post-treatment of the membrane through CVD is the most preferred method because it allows one to effectively control the pore size and thus remarkably improves the selectivity. The main advantages of using CVD are its simple operation and remarkable effects on the membrane properties. Recently, Yoshimune [90] also confirm this result through investigating the propylene volume fraction and CVD time on the performance of CMS membrane. Qiu and Koros [96] indicated that the hyperaging technology can improve H_2/C_2H_4 selectivity and stabilize the CMS membrane against physical aging. Furthermore, they also indicated that super-hyperaging can recover the separation performance for a physically aged CMS membrane [97]. The coating technology is usually used to modify membrane defects to prevent gas flow through defect parts [98].

1.4 Current challenges and possible solutions in CMS membranes

Although CMS membranes have been viewed as promising candidates in the gas separation community, their investigation have been still remaining at the laboratory scale. The most suitable membrane configurations for practical applications are hollow-fiber type and tubular-supported type due to their high surface area to volume ratio. The main problems faced by both CMS membranes are the inability to meet the separation requirements for specific gas pairs and the availability of suitable porous supports.

It is well-known that post-treatments can effectively improve the separation performance of CMS membranes. Hayashi [54] and Yoshimula [90] have used CVD method to perpare the CMS membranes with high selectivity, where they used propylene as a carbon source. However, the use of a gaseous carbon source in the CVD process is not easy to operate and the unused carbon source can't be trapped. Another important point is high price and transportation costs of the propylene. According to the literature [99-102], CVD methods using liquid hydrocarbons as the carbon source have been widely used for the preparation of CMS adsorbents, where the adsorption selectivity was improved by decreasing pore size of adsorbents, as shown in Figure 1-6. However, the liquid hydrocarbons such as benzene and toluene have not been used to prepare the CMS membrane. Compared with the gaseous carbon source, liquid hydrocarbons were easily added during the CVD process, and the hydrocarbons can be trapped by a cooling device and recycled. Therefore, the use of liquid hydrocarbons as a CVD carbon source may be a promising approach to improve CMS membrane separation performance.

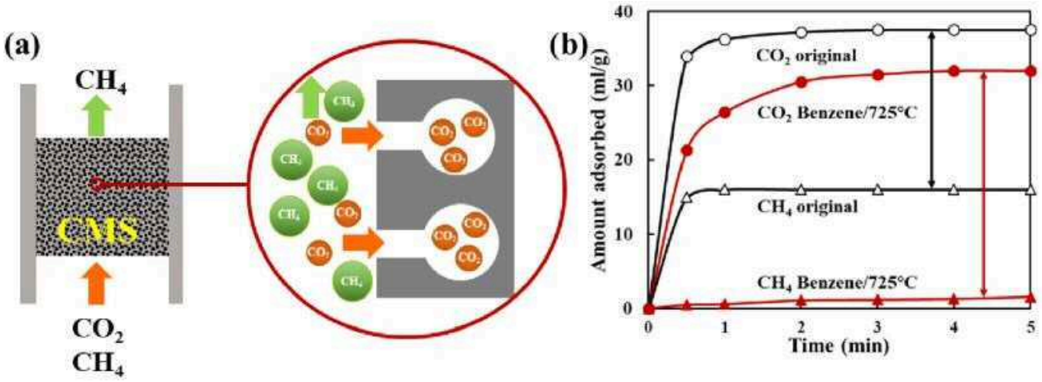

Figure 1-6. (a) Adsorption schematic diagram of CMS adsorbent and (b) adsorption profiles of CO_2 and CH_4 over orginal adsorbent and benzene treated adsorbent [101].

Recent years, the research and development of tubular-supported CMS membranes have been limited by availability of suitable porous supports. Toray Industries, Inc.

developed a thin and light porous carbon fiber (PCF) in 2018, as shown in Figure 1-7. The PCF is composed of carbon and has good flexibility and chemical stability. Moreover, its interconnected pore structures provid more paths or channels for gas permeation. Thus, it is considered as a promising support for CMS membranes.

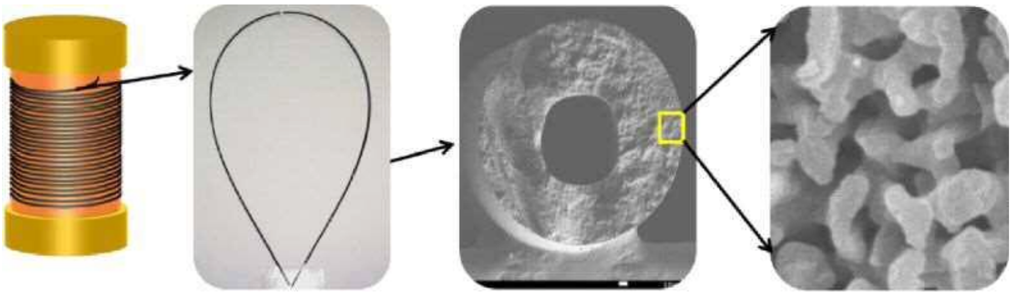

Figure 1-7. Photo and microstructure of porous carbon fiber.

1.5 Content of dissertation

As was mentioned above, CMS membranes have been viewed as promising candidates in the gas separation community. Their unique ‘slit-like’ pore structures provide molecular sieving ability and possess good thermal and chemical resistance. Moreover, the performance of CMS membranes can be changed by adjusting the pore structures. In this dissertation, I prepared highly selective CMS membranes derived from polyimide fiber by varying the pyrolysis parameters and using the post-treatment technology. In addition, I also prepared wood tar derived CMS membranes on novel porous carbon fiber and investigated the effects of wood tar concentration and pyrolysis temperature on gas separation performance.

From the view of the large-scale gas separation applications, available commercial materials selected as the precursors of CMS membranes are necessary. Based on this point, I used polyimide hollow fiber produced by Ube Industries, Ltd. as the precursor to prepare the CMS membranes in Chapter 2. Although the obtained CMS membranes showed high gas selectivities, the selectivities for some targeted gas pairs have not met the requirement for practical application. To improve the selectivity, a simple chemical vapor deposition (CVD) addition was carried out in the pyrolysis process. Herein, toluene was used for the first time as a carbon source of CVD to prepare the CMS membranes. In this case, the toluene vapor was introduced into the furnace by mixing with the N_2 stream through a bubbling process. Moreover, the effects of pyrolysis temperature and addition time of toluene vapor on the gas separation performance was investigated. This work has been published in an international journal [103].

The research in Chapter 2 indicated that toluene vapor added membranes showed higher selectivities of H_2-related gas pairs compared to non-added membranes pyrolyzed at higher temperatures with similar H_2 permeance. Moreover, the pyrolysis temperature and addition time of toluene vapor can adjust the gas separation performance, the optimum pyrolysis temperature and addition time were determined by desired separation gas pair. However, the mechanism of achieving high selectivity by toluene vapor addition was unclear. In Chapter 3, the physical and chemical properties of CMS membranes with toluene vapor addition were characterized using XPS, DRIFT, XRD, TEM, and adsorption experiments of N_2 and CO_2.

In addition to commercial precursor materials, using natural and renewable resources as the precursor materials have attracted more and more attention for the CMS membrane preparation due to their wide availability and low cost. These materials, such as lignin and wood tar, are generally not suitable for preparing hollow-fiber-type membranes, thus, porous supports are necessary. However, the current availability of suitable porous supports is limited. Recently, a new porous carbon fiber (PCF), which is considered a promising candidate for porous support, has been prepared for commercialization. In Chapter 4, I used PCF as the support and prepared supported CMS membranes derived from wood tar solution. For comparison, CMS membranes supported on commercially available porous ceramic tubes (NA3) were also prepared under the same conditions. The effects of the concentration of wood tar solution, the support, and the pyrolysis temperature on the gas separation performances are investigated. This work has also been published in an international journal [104].

Finally, Chapter 5 summarized the research work described in this dissertation and proposed the ideas for future work.

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Chapter 2 Effect of Chemical Vapor Deposition of Toluene on Gas Separation Performance of Carbon Molecular Sieve Membranes

2.1. Introduction

The current gas separation technologies include amine absorption, cryogenic distillation, pressure swing adsorption (PSA), and membrane separation, all of which have achieved ‘commercial products’ status. Among them, amine adsorption for CO_2 capture is based on the strong chemical reaction between amine solution and CO_2, therefore, the desorption process is relatively difficult, leading to high operating costs and environmental harm [1]. Cryogenic distillation and PSA are generally high energy consumption gas separation technologies [2]. Low operational cost and good environmental compatibility of membrane technology could make it a potentially more attractive substitute for conventional gas separation technologies [3]. Based on the synthetic materials, gas separation membranes are generally divided into two broad categories: polymeric membranes and inorganic membranes. Among these membranes, polymeric membranes have been utilized in practical gas separation due to their good mechanical properties and excellent processabilities, such as N_2 separation from the air, CO_2 separation from biogas, and H_2 recovery from oil refinery plants. However, their separation performance is not sufficient for their widespread practical application, and the challenge in improving the separation performance lies in breaking the trade-off relationship between the permeability and selectivity [4].

Carbon molecular sieve (CMS) membranes are considered to be the most potential gas separation tool due to their rapid adsorption and desorption characteristics, high adsorption capacity, pore-size controllability, as well as thermal and chemical resistance [5,6]. Soffer and Koresh pioneered preparing CMS membrane by pyrolyzing polymeric precursors [7,8]. They demonstrated that the pyrolysis temperature and atmosphere can affect the pore aperture size of the CMS membrane. During the following ten years, research into the CMS membrane for gas separation has made significant progress. Carbon Membranes Ltd. (Israel) commercialized cellulose-based carbon membranes at the end of the 1990s to be the first and only manufacturer of CMS membrane, but the company closed in 2001. Since then, researchers continued to work on the commercial development of carbon membranes, including the pilot-scale system for carbon membranes manufacturing [9] and fabrication technique for large-scale carbon membrane modules [10].

In general, CMS membranes are prepared by pyrolyzing a polymeric precursor at a high temperature (500–800 °C) in an inert atmosphere or vacuum [11]. Their structure, separation properties, and transport mechanism depend critically on the type of the precursor materials [12,13], pyrolysis conditions [14,15], and pre- and post-treatment methods [16-19]. Thus, many approaches have been used to develop high-performance CMS membranes, which include increasing the fractional free volume of the polyimide (PI) precursor to enhance permeability [20], pre-oxidizing the polymeric precursor to stabilize the carbon chains and thus prevent excessive volatilization of elemental carbon [21], increasing the pyrolysis temperature to improve the selectivity of the membrane [22], conducting pyrolysis in an inert atmosphere to accelerate the carbonization process and increase the membrane permeability [11,22], and employing post-treatment techniques such as CVD method to control the pore size and improve the selectivity [17-19]. Among them, post-treatment of the membrane through CVD is the most preferred method because it allows one to effectively control the pore size and thus remarkably improve the selectivity. The main advantages of using CVD are its simple operation and remarkable effects on the membrane properties. For instance, propylene was used as a carbon source for CVD to modify carbon membranes. Specifically, Hayashi et al. [17] prepared CMS membranes supported on porous ceramic tubes with high permselectivity via CVD using propylene as the carbon source. They mixed propylene with argon gas at 650 °C for up to 20 min after pyrolyzing a tubular PI composite membrane at 700–800 °C, and observed that the He, CO_2, O_2, and N_2 permeances decreased with time. The CVD treatment under the optimum conditions made O_2/N_2 and CO_2/N_2 separation properties overcome the tradeoff of polyimide membrane. Recently, Haider et al. [18] conducted CVD with propylene after the oxidation and reduction of carbon hollow fiber membranes prepared from cellulose-based precursors to tailor the membrane pore structure. Yoshimune and Haraya [19] also performed the CVD treatment through propylene as a carbon source on carbon membranes derived from sulfonated poly(phenylene oxide) (SPPO). They conducted CVD during the membrane pyrolysis process, and mixed propylene with the inert gas at the final stage of carbonization. Such a process is a very useful membrane treatment method because of its simple one-step operation. They demonstrated that the volume fraction of propylene and deposition period can be modulated to effectively control the pore size, and reported that the resulting CMS hollow fiber membrane exhibited the best H_2/CH_4 selectivity of 29940.

It is well known that the CVD method has been widely used for preparing the CMS adsorbents [23-28]. These CMS adsorbents have the pore size in the Ångstrom level can be used to separate gas pairs, which are similar to the CMS membranes. Additionally, the CMS adsorbents with Ångstrom level also can be obtained through pyrolyzing specially designed precursor materials [29-30]. Compared with gaseous carbon sources, liquid hydrocarbons are more favored in the preparation of CMS adsorbents. They are introduced into the furnace through mixing with an inert gas by a bubbling process. Moreover, they can also be readily trapped at the outlet of the reactor to prevent the release of unused hydrocarbons into the atmosphere. A patent has described the use of liquid hydrocarbons to prepare carbon molecular sieves through CVD method [23]. The CVD of benzene [24-26] also was used to modify the activated carbons for improving their kinetics of gas separation. Horikawa et al. [27] controlled the pore size of phenol–formaldehyde resin char by the CVD of different hydrocarbons (benzene, toluene, o-, m-, and p-xylene), and demonstrated that the pore size can be effectively tailored by varying the amount of the adsorbed hydrocarbon vapor. They also elucidated the mechanism of pore size modulation through CVD; they suggested that the hydrocarbon vapor first adsorbed to the pore surface and then underwent pyrolysis to carbon in the pore. Through computational simulations and experiments, Yamane et al. [28] demonstrated that the structure of the pyrolyzed carbon deposited on the activated carbon depends on the type of the carbon source used in CVD. They reported that CMS specimens produced using benzene and toluene as carbon sources for CVD have similar amorphous pyrolyzed carbon structures, and that toluene is suitable as a CVD source for preparing high-performance air-separation CMS adsorbents.

To our knowledge, liquid hydrocarbons such as benzene and toluene have not been used to modify CMS membrane. Toluene is a relatively low-toxic organic solvent, which is different from the carcinogenicity of benzene. In this study, we investigated the effect of the simple incorporation of toluene vapor into the nitrogen gas stream at the final pyrolysis temperature on the gas permeance and selectivity of CMS membranes. The final pyrolysis temperature ranged from 625 to 700 °C, and the duration of toluene vapor addition ranged from 10 to 50 min. A commercial asymmetric hollow fiber membrane made of PI was used as the polymeric membrane precursor because it is easily available and is also of interest from the perspective of practical application.

2.2. Experimental

2.2.1. Preparation of CMS membrane

In this study, commercial PI hollow fiber membranes (UMS-A2(V) series, 887 $/m^2, Ube Industries, Ltd., Yamaguchi, Japan) produced for air dryers were used as the precursor to prepare CMS membranes because of their good permeation properties and easy availability. The precursor membranes were thermostabilized at 320 °C for 30 min in the air atmosphere with relative humidity (RH) of 30–40% before pyrolysis and toluene vapor modification. The resultant thermostabilized PI precursors were heated under a nitrogen gas flow. Figure 2-1 shows the polyimide hollow fiber precursors and the preparation of CMS membrane.

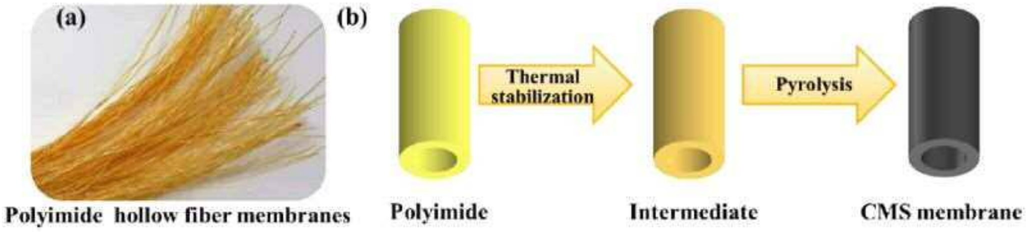

Figure 2-1. Polyimide hollow fiber precursors (a) and the preparation of CMS membrane (b).

Pyrolysis was carried out between 625 and 700 °C for 120 min. Toluene vapor was incorporated in the flowing nitrogen gas after 1 h of reaching the final pyrolysis temperature. Figure The duration of toluene vapor addition was varied from 10 to 50 min. Figure 2-2 shows the thermal protocol of CMS membrane with toluene vapor modification. The samples are designated as CMS-x/y, where 'x' is the pyrolysis temperature and 'y' is the duration of toluene vapor addition. For example, a CMS membrane pyrolyzed at 700 °C with toluene vapor addition for 30 min is denoted as CMS-700/30. For comparison, the PI precursors were pyrolyzed at different temperatures using the same method, but without introducing toluene vapor. These samples are denoted as CMS-x.

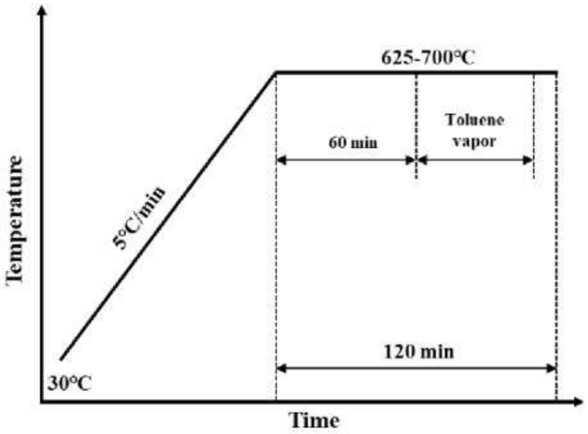

Figure 2-2. Thermal protocol for the preparation of carbon molecular sieve membranes through toluene vapor modification. The duration of toluene vapor addition ranged from 10 to 50 min.

Figure 2-3 shows a schematic of the setup used for membrane pyrolysis and toluene vapor modification. A ceramic tube (inner diameter: 24 mm, length: 500 mm) was placed in an electric tube furnace (ARF-30KC, Asahi Rika Manufacturing Co., Ltd., Chiba, Japan) with a 300 mm long heating zone. In the furnace, the 100 mm long central zone, wherein the thermostabilized PI precursor of ~ 0.01 g was placed, was maintained at a preset temperature. Nitrogen gas was flown through two tubes into the ceramic tube. One tube was connected directly to the ceramic tube. This nitrogen gas flow line was kept open during the pyrolysis process until the furnace was cooled to a temperature below 200 °C. The other tube was connected to a bubbling bottle containing toluene and then to the ceramic tube. The temperature of the toluene bubbling is around ~20 °C. The gas line with the nitrogen/toluene vapor mixture, which contains 2 vol.% of the toluene vapor (The estimated value from saturation vapor pressure: 3 vol.%), was opened after 1 h of reaching the final pyrolysis temperature. The volume fraction of toluene vapor was calculated from the weight change of toluene before and after bubbling for the toluene vapor modification period. The flow rate of nitrogen in each tube was maintained at 300 mL/min.

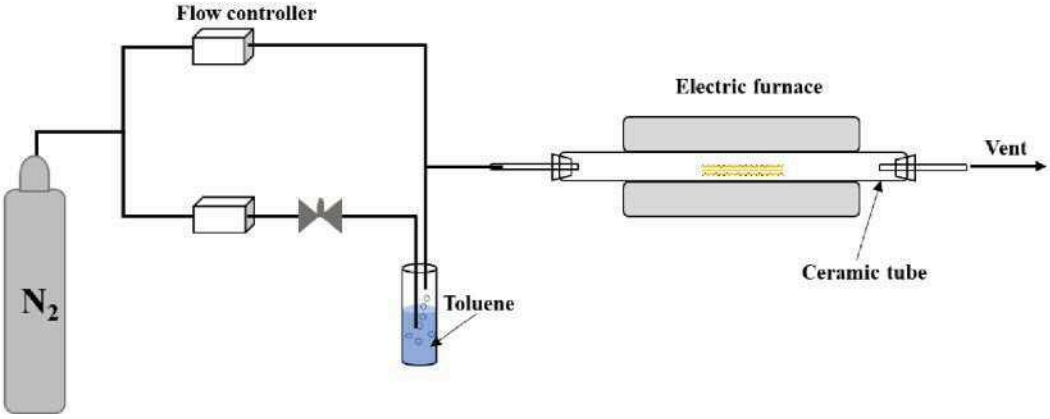

Figure 2-3. Schematic of the setup used for membrane pyrolysis and toluene vapor modification.

2.2.2. Characterization and gas transport properties

Thermogravimetry was carried out on a TG-8120 instrument (Rigaku Co., Tokyo, Japan) at a heating rate of 5 °C/min under the flow of helium gas at 100 mL/min rate. The microstructure of the membrane was analyzed by scanning electron microscopy (SEM; JSM-7600F, JEOL Ltd., Tokyo, Japan). The samples were sputter-coated (Auto Fine Coater, JFC-1600, JEOL Ltd., Tokyo, Japan) with platinum for 60 s before SEM observation.

A custom-built constant volume/variable pressure apparatus (Figure 2-4), which contained an absolute capacitance manometer with a full-scale range of 10 Torr (Baratron 627F11TBC2B, MKS Instruments, Inc., United States) in the downstream, was used to test the separation performance of the CMS membranes. The downstream part of the apparatus was connected to the bore side of the hollow fiber membrane, while a single test gas (H_2, CO_2, O_2, N_2, and CH_4) was introduced at a constant pressure at the shell side of the membrane. The permeation experiment was conducted at 35 °C and 1 atm pressure. The membrane was degassed at 135 °C for 2 h before the gas permeation experiments.

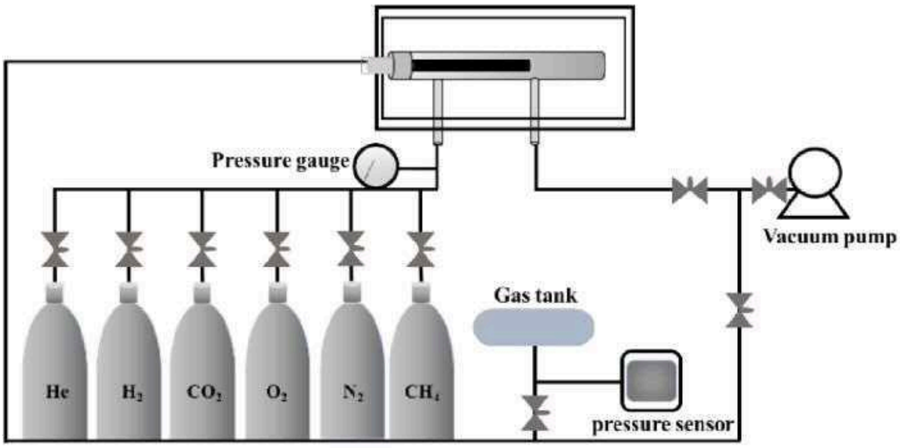

Figure 2-4. Single-gas permeation system for testing separation performance of CMS membrane.

For an asymmetric hollow fiber membrane, it is difficult to determine the membrane skin layer thickness. The separation efficiency of the CMS membranes in this study was evaluated by pressure-normalized steady-state flux or permeance. The gas permeance, *P*, was calculated as follows:

$$P = 10^6 \cdot \frac{273}{760} \cdot \frac{V}{\Delta p \cdot A \cdot T} \cdot (\frac{d_p}{d_t}) \quad (1)$$

where *V* and *T* are the volume (cm^3) and temperature (K) of the downstream region of the chamber, respectively, *A* is the effective transport area of the CMS membrane (cm^2), Δp is the pressure difference between the upstream and downstream regions (cmHg), and *dp/dt* is the pressure rate in the steady state (Torr/s). The unit of *P* used here is GPU, which is 10^{-6} cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1} (1 GPU = 3.35×10^{-10} mol m^{-2} s^{-1} Pa^{-1}). The ideal selectivity, $\alpha_{A/B}$ was calculated as

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

where P_A and P_B are the permeances of gases A and B, respectively.

2.3. Results and discussion

2.3.1. Characterization of the precursor membrane

Figure 2-5 shows the thermogravimetric curve of the precursor, PI hollow fiber membrane. Weight loss occurred in two stages at temperatures below 800 °C. The precursor began to decompose at 430 °C, and yielded a first peak at 500 °C. The second stage of weight loss began at 550 °C, when the first stage was not completed, resulting in a peak at 610 °C. The weight loss in the second stage was larger than that in the first stage. The weight losses at 600 and 700 °C were 25 and 40%, respectively.

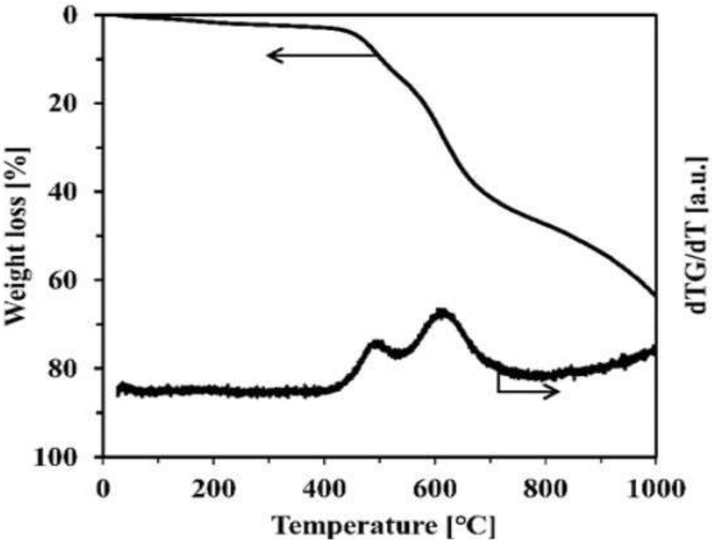

Figure 2-5. Thermogravimetric curve of the precursor, polyimide hollow fiber membrane, recorded under He flow at 100 mL/min. Heating rate: 5 °C/min.

2.3.2. Microstructure of CMS membrane

Figure 2-6 shows the cross-sectional SEM images of the region around the outer surface of the CMS membrane for CMS-700 (Figure 2-6a) and CMS-700/30 (Figure 2-6b). The SEM images indicate that both the CMS membranes have similar asymmetric structures. The membranes appear to have carbonized skin layers on their outer surfaces. The thickness of the skin layer was found to be less than 200 nm. Beneath the carbonized skin layer, sponge-like porous structures are observed. Notably, no remarkable difference was observed on the outer surface for both types of CMS membrane during SEM observation.

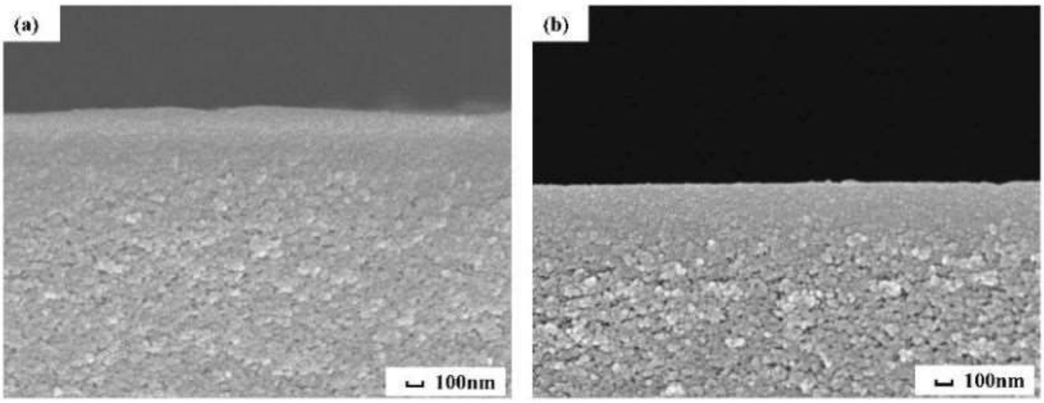

Figure 2-6. Cross-sectional SEM images of CMS membranes pyrolyzed at 700 °C without toluene vapor addition (a) and with 30 min of toluene vapor addition (b).

2.3.3. Gas permeation properties

2.3.3.1 Effect of pyrolysis temperature

Figure 2-7 shows the effect of the pyrolysis temperature on the gas separation performance of the CMS membranes pyrolyzed with and without using toluene vapor.

As the pyrolysis temperature was increased from 625 to 700 °C, the gas permeance of the membrane pyrolyzed without using toluene vapor decreased, while its H_2 selectivity increased monotonously. This is because of the densification of the carbonized skin layer with increasing pyrolysis temperature. A similar change of permeation properties was observed in a previous study, which reported the carbon membranes obtained using asymmetric 3,3′,4,4′-biphenyltetracarboxylic dianhydride-based PI hollow fibers as the precursor [31]. It is well known that a higher pyrolysis temperature tends to yield a higher H_2 selectivity, while causing a decrease in the H_2 permeance to some extent. However, the CMS-725 membrane showed lower H_2/CH_4 and H_2/N_2 selectivities than the CMS-700 sample. A few attempts to prepare CMS-725 membrane with higher selectivity membrane were failed. A similar result was reported by Yoshino et al. [14], where they prepared carbon membrane at 700 °C, which showed a lower H_2/CH_4 selectivity than their carbon membrane pyrolyzed at 650 °C.

The permeances of the CMS membranes pyrolyzed between 625 and 700 °C and subjected to 10 min of toluene vapor modification were lower than those of the membranes pyrolyzed between 625 and 700 °C without using toluene vapor. That is, the gas permeance of the CMS membranes decreased upon toluene vapor modification. The reduction in the H_2 permeance was similar and relatively small for samples pyrolyzed between 650 and 700 °C in the presence of toluene vapor, while the permeance of less permeable gases decreased significantly. This result suggests that toluene vapor modification more effectively inhibited the permeation of less permeable gases. The largest reduction in permeance was observed at 650 °C for CH_4, 675 °C for

N_2, and 700 °C for O_2 and CO_2. That is, H_2 selectivities were enhanced by toluene vapor modification for the membranes pyrolyzed between 650 and 700 °C, with the exception of the H_2/CH_4 selectivity for the sample pyrolyzed at 700 °C using toluene vapor. Thus, the proposed toluene vapor modification can serve as a simple and effective method for enhancing the H_2 separation performance of a CMS membrane.

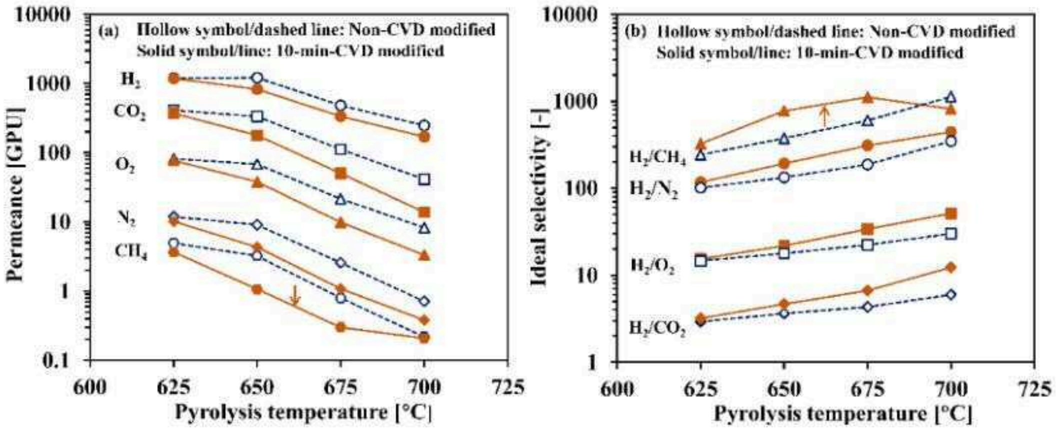

Figure 2-7. Separation performance of CMS membranes pyrolyzed with and without toluene vapor at 35 °C and 1 atm: (a) gas permeances and (b) ideal selectivities. The hollow symbol/dashed line and solid symbol/line represent non-CVD modified and 10-min-CVD modified membranes, respectively. The upward arrow and downward arrow represent the selectivity improvement and permeance reduction due to toluene vapor modification, respectively.

2.3.3.2 Modification time on gas permeance

Figure 2-8 shows the change in the gas permeance with the modification time. The H_2 and CO_2 permeances (Figure 2-8a and b) of the CMS membranes pyrolyzed at lower temperatures of 625, 650, and 675 °C decreased monotonously with increasing modification time. The permeances of the CMS membranes pyrolyzed at 700 °C decreased significantly with the increase in the modification time up to 20 min, and then plateaued or decreased at a slower rate. The reduction in CO_2 permeance is consistent with the observations made by Hayashi et al. for the carbonized polyimide membrane modified by CVD of propylene [17]. Further, the reduction in the CO_2 permeance with the modification time was larger than the reduction in the H_2 permeance. Although the N_2 permeance (Figure 2-8c) of the membranes pyrolyzed at lower temperatures (625–675 °C) also decreased monotonously with increasing modification time, it increased slowly after 30 min of modification at the higher temperature of 700 °C. A similar increase in the CH_4 permeance (Figure 2-8d) with the modification time was observed for the membrane pyrolyzed at 675 °C. The CH_4 permeance of the membrane pyrolyzed at 700 °C rarely varied with the modification time. In summary, the permeances of N_2, CO_2, and CH_4 decreased more significantly with increasing toluene vapor addition duration than the H_2 permeance. That is, the permeances of N_2, CO_2, and CH_4 were more sensitive to the pyrolysis temperature than the permeance of H_2.

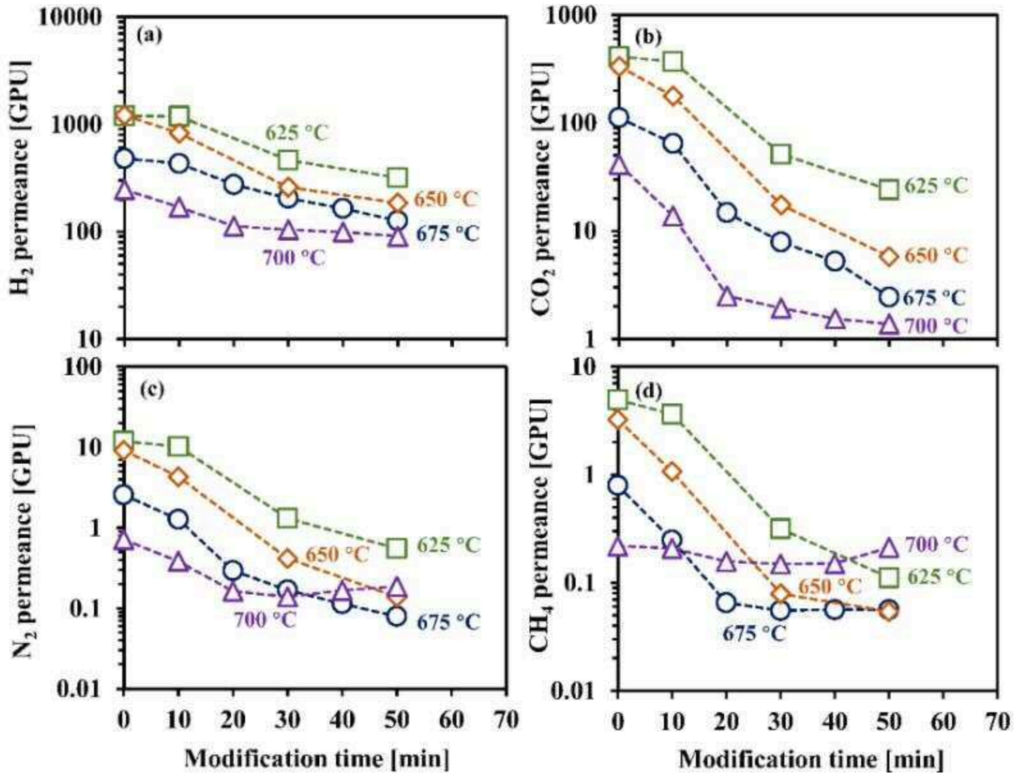

Figure 2-8. Permeances at 35 °C and 1 atm of CMS membranes pyrolyzed at different temperatures ranging from 625 to 700 °C as a function of toluene vapor modification time: (a) H_2, (b) CO_2, (c) N_2, and (d) CH_4 permeances.

2.3.3.3 Modification time on gas selectivity

Figure 2-9 plots the ideal selectivities as a function of the toluene vapor modification time. The H_2/CO_2 selectivities (Figure 2-9a) of all the CMS membranes pyrolyzed between 625 and 700 °C showed an increasing trend with the modification time. At a given modification time, a higher temperature was more conducive for achieving higher selectivity. In the case of H_2/CO_2 separation, membrane modification at a higher temperature (700 °C) with a shorter toluene treatment time of 30 min may be preferable for practical industrial applications. The modification of the CMS membrane with toluene for more than 30 min at 700 °C resulted in decreased H_2/N_2 selectivity (Figure

2-9b). Such a decline in H_2/N_2 selectivity was not observed in the cases of CMS membranes pyrolyzed at lower temperatures. Pyrolysis at 675 °C with a shorter toluene vapor modification time of 20 min is optimal for separating H_2/N_2. Figure 2-9c and d show that longer modification times are not suitable for achieving H_2/CH_4 and CO_2/CH_4 selectivities in the cases of the membranes pyrolyzed at 650 and 675 °C. Further, the H_2/CH_4 and CO_2/CH_4 selectivities of the membranes pyrolyzed at 700 °C decreased with the modification time, indicating that the H_2/CH_4 and CO_2/CH_4 separation performances of the CMS membranes cannot be improved via toluene vapor modification at higher pyrolysis temperatures. Although hydrogen selectivity seems to show regular changes based on the difference in diameter between the two molecules of a gas pair, the reasons for these trends are unclear at present.

Toluene vapor modification can significantly improve the H_2 selectivities of the CMS membranes; however, the mechanism remains unclear. Horikawa et al. [27] prepared CMS specimens from phenol–formaldehyde resin waste via the CVD of different hydrocarbons (benzene, toluene, *o*-, *m*-, and *p*-xylene) at 800 °C. They concluded that gas-phase hydrocarbons first adsorbed on the pore surface of the sample and then underwent pyrolysis, leaving carbon residues in the pore. A similar phenomenon may occur in our case.

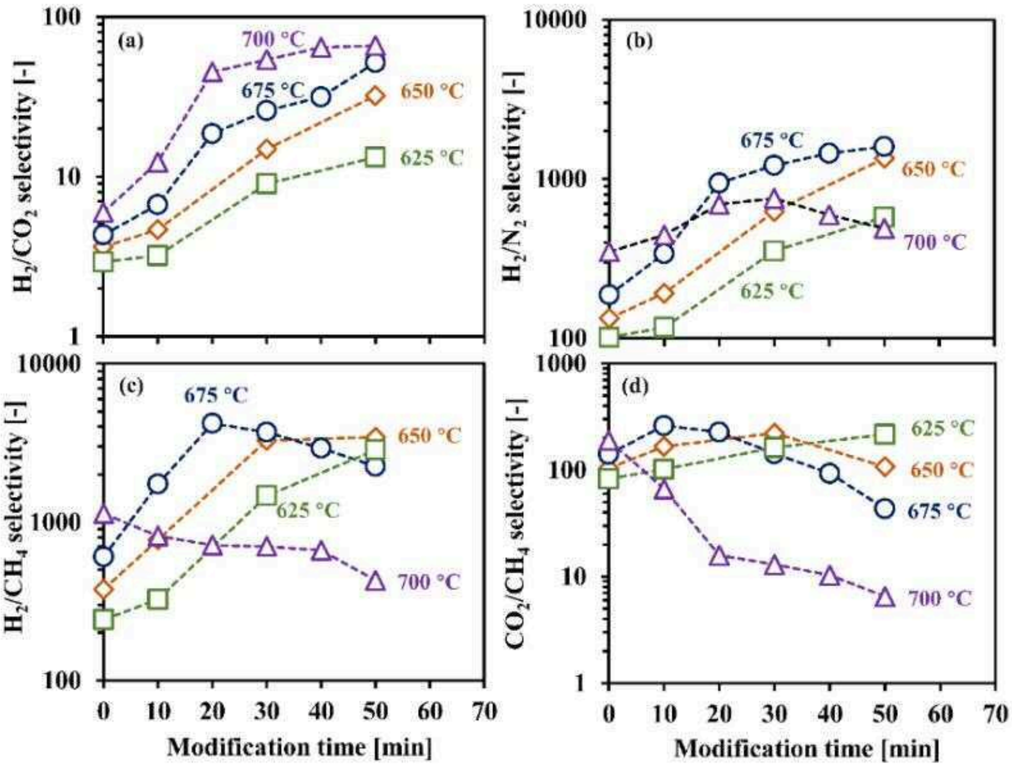

Figure 2-9. Ideal selectivities of CMS membranes pyrolyzed at different temperatures between 625 and 700 °C as a function of toluene vapor modification time: (a) H_2/CO_2, (b) H_2/N_2, (c) H_2/CH_4, and (d) CO_2/CH_4 selectivity. The selectivities were evaluated at 35 °C under 1 atm pressure.

2.3.3.4 Temperature dependence

Figure 2-10 shows the temperature dependences of permeance of the single-component gases on the C675 and C675tol10min membranes. Table 2-1 tabulates the apparent activation energies for C675 and C675tol10min membranes depending on the Arrhenius-type plots of the gas permeance data. The permeances for both modified and unmodified membranes increase with temperatures. This means the activation energy for diffusion using for H_2, CO_2, O_2, N_2, and CH_4 was higher than their heat of adsorption, i.e., the gas permeation behaviors are dominated by the activated diffusion mechanism.

The pore structure of CMS contains constrictions that approach the size of penetrating molecule. The gas molecule required the activation energies to permeate through the constrictions. The activation energy of gas molecule passing through modified membrane was higher than that passing through unmodified one, indicating that modified membrane possesses smaller pore size.

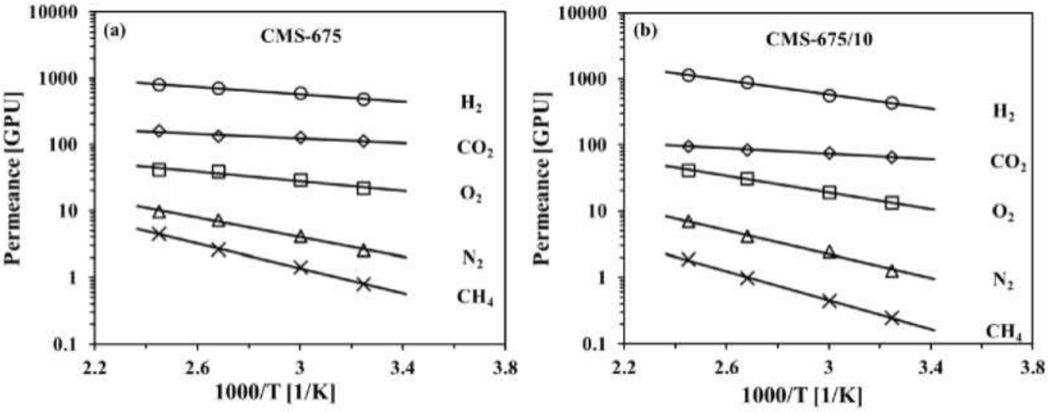

Figure 2-10. Temperature dependence of permeance for single-component gases on CMS-675 and CMS-675/10 membranes.

Table 2-1 Activation energies of permeation rates for pure gases

Membrane	Activation energy [kJ mol^{-1}]				
	H_2	CO_2	O_2	N_2	CH_4
CMS-675	5.2	3.3	7	14	18
CMS-675/10	10.2	3.9	12	17	21

2.3.3.5 Separation performance comparison

Figure 2-11 compares the gas separation performances of the carbon membranes developed in this work with those of some previously reported carbon membranes. In general, the permeation properties may vary significantly depending on the precursor material and preparation process. In this work, CMS membranes modified with toluene vapor under suitable conditions exhibited an increase in the ideal selectivity, but a decrease in the gas permeance. Figure 2-11a compares the H_2/CO_2 separation performance of the membranes prepared in this work with those of some of the previously developed membranes. The performances of the CMS membranes without toluene vapor modification in this work are lower than those of other carbon membranes derived from polydopamine [13], PI [32], polymer blend [33], cellulose acetate [34,35], and phenolic resin [36,37]. The membranes modified with toluene vapor at higher temperatures for longer durations exhibited comparable permeation properties. For example, CMS-700/50 membrane showed a H_2/CO_2 selectivity of 66 with a moderate H_2 permeance of 91 GPU. This is comparable to the H_2/CO_2 selectivity of a cellulose-based asymmetric carbon hollow fiber membrane [35].

Figure 2-11b and c compare the H_2/N_2 and H_2/CH_4 separation performances, respectively. Toluene vapor modification under suitable conditions to facilitate higher H_2/N_2 and H_2/CH_4 selectivities without the loss of H_2 permeance. For example, the CMS-675/20 and CMS-650/30 membranes with similar H_2 permeances showed higher selectivities than the CMS-700 membrane. Yoshimune et al. [19] prepared SPPO-based dense carbon hollow fiber membranes through the CVD of propylene. Propylene modification effectively enhanced the H_2 separation performance. Propylene modification for 20 min at the pyrolysis temperature of 700 °C decreased the H_2 permeance from 169 to 63 GPU, while the H_2/N_2 and H_2/CH_4 selectivities increased from 48 to 2213 and from 104 to 29940, respectively. Compared with the H_2/N_2 separation performance of the propylene-modified membrane, the CMS-675/50 membrane obtained in this study showed a higher H_2 permeance of 126 GPU with a moderate H_2/N_2 selectivity of 1600. Unfortunately, although the toluene-vapor-modified membranes prepared in this study showed competitive H_2 permeances, their H_2/CH_4 selectivity was considerably lower than that of the propylene-modified membrane. These post-treated CMS membranes performed better than most of the unmodified state-of-the-art carbon membranes reported previously. A similar post-treatment of these carbon membranes could result in a much higher H_2 separation performance.

Further, CMS membranes have been widely studied for natural gas upgrading. Figure 2-11d compares the CO_2/CH_4 separation performances of various membranes. Toluene vapor modification can effectively decrease the CO_2 permeance. It is therefore not a suitable method for improving the CO_2/CH_4 separation performance of the CMS membranes. However, toluene vapor modification for a shorter time is effective for enhancing the CO_2/CH_4 selectivity.

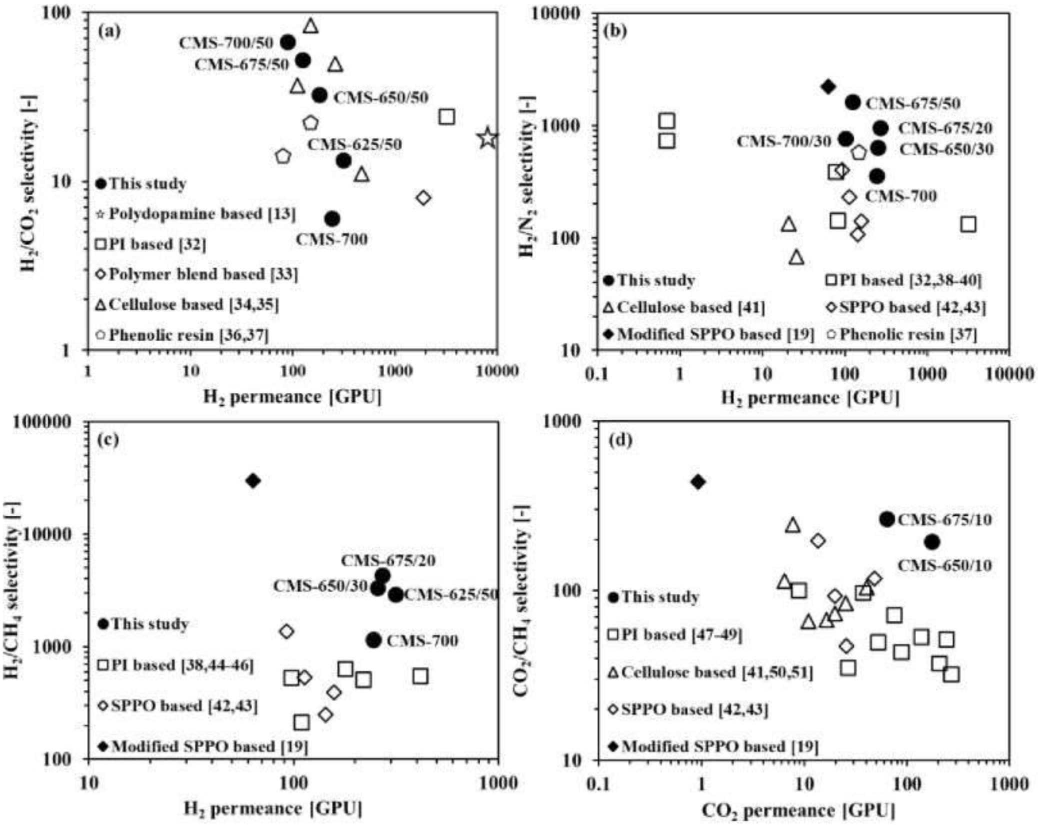

Figure 2-11. Comparison of the gas separation performances of CMS membranes pyrolyzed with and without using toluene vapor and some previously reported carbon membranes: (a) H_2/CO_2, (b) H_2/N_2, (c) H_2/CH_4, and (d) CO_2/CH_4 selectivities. Notations: PI = polyimide and SPPO = sulfonated poly(phenylene oxide).

2.3.3.6 Effect of physical aging

Figure 2-12 shows the change in the H_2 gas separation performance of the CMS membranes with and without toluene vapor after storage at room temperature and in an air atmosphere with an RH of 30–40% for 50 days. After 50 days of storage, H_2 permeances of all CMS membranes were decreased while the selectivities were increased. This result may be caused by the reduction in the pore volume and pore size because of an aging phenomenon. The aging phenomenon was related to the adsorption of oxygen, organic contaminants, and moisture onto CMS membranes [52] and rearrangements of the packing imperfections from graphene-like layers [53,54]. The change in the separation performance for both types of CMS membranes was similar, and the toluene-vapor-modified samples still maintained a higher selectivity for H_2. For example, the H_2 permeance of the CMS-650 membrane decreased from 1212 to 662 GPU, but its H_2/N_2 selectivity increased from 133 to 189. Furthermore, the CMS-650/10 membrane showed a similar degree of change in the H_2 permeance (827 to 485 GPU) and H_2/N_2 selectivity (192 to 309). The findings suggest that toluene vapor modification can’t be affected by physical aging.

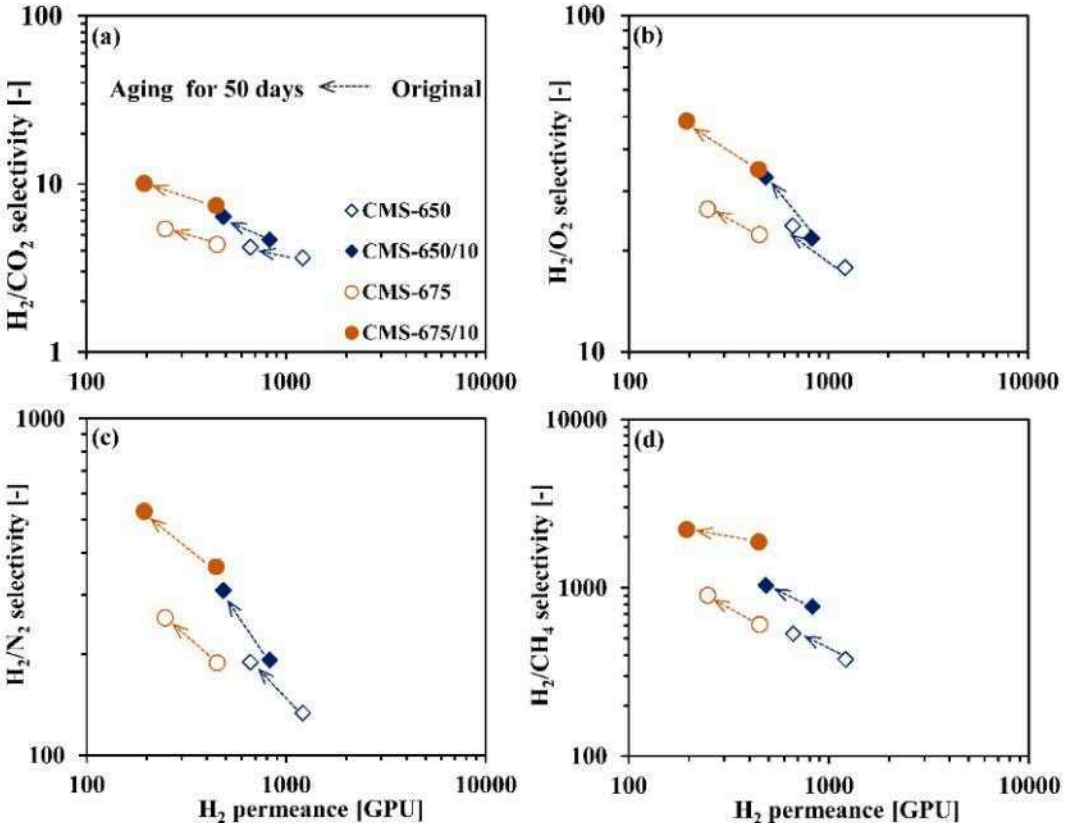

Figure 2-12. Separation performance of CMS membranes obtained with and without using toluene vapor modification after storage at room temperature and in an air atmosphere with an RH of 30–40% for 50 days.

2.3.3.7 Mechanical properties of CMS membrane

Figure 2-13 gives the photo of the CMS-700 and CMS-700/30 membranes. The CMS-700/30 membrane shows a more curved structure than the CMS-700 membrane. Both CMS membranes are not made into a ring because they are brittle, indicating that the CMS membranes without and with CVD modification from toluene have poor mechanical properties.

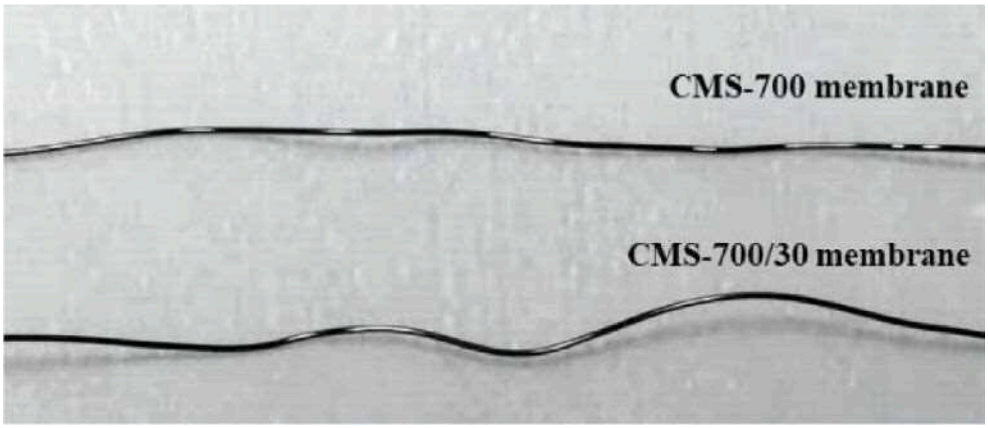

Figure 2-13. Photos of CMS-700 and CMS-700/30 membranes.

2.4. Conclusions

CMS membranes were prepared by pyrolyzing commercial PI hollow fiber membranes in a nitrogen stream. The addition of toluene vapor into the N_2 stream resulted in high H_2 selectivity, which could not be achieved by pyrolyzing the sample at a higher temperature. For example, the membrane pyrolyzed at 650 °C with 50 min of toluene vapor addition (CMS-650/50) showed H_2/CH_4 selectivity of 3000, while the membrane pyrolyzed at 700 °C without using toluene vapor (CMS-700) showed a lower H_2/CH_4 selectivity (1000). The former membrane showed H_2/N_2 selectivity of >1000, while the latter membrane showed H_2/N_2 selectivity of 300. Although the H_2 permeance of the former was slightly lower than that of the latter, toluene vapor modification led to the enhanced H_2 selectivity of the CMS membrane. The permeation properties of the membranes modified using toluene vapor rival those of the other state-of-the-art carbon membranes. Thus, this type of treatment can be effective for modifying CMS membranes derived from other precursors.

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Chapter 3 Characterization of Carbon Molecular Sieve Membranes Modified by Chemical Vapor Deposition Using Toluene Vapor

3.1 Introduction

Carbon molecular sieve (CMS) membranes are appealing materials for the investigation of gas separation, in terms of excellent performance, pore-size controllability, good thermal stability, and high chemical resistance [1,2]. They are typically inorganic porous membranes, consisting of rigid, slit-like pore structures characterized by a bimodal pore-size distribution, i.e. micropores of 0.7–2 nm and ultramicropores of <0.7 nm [3]. Such pore structures enable CMS membranes to have a superior molecular sieving function to effectively separate gas molecules with slightly different diameters.

CMS membranes can be fabricated by pyrolyzing polymeric precursor membranes under control parameters [4,5]. Varying the precursor, adjusting the pyrolysis parameters, and using the pre/post-treatments can tailor the pore size of CMS membranes [6]. Among these options, post-treatments are considered to be simple and effective methods of improving separation performance. More specifically, Koresh and Soffer [4] used a gaseous oxidant to open the pore system of CMS membranes derived from cellulose thereby improving the gas permeability. Furthermore, Suffer also applied a patent on using chemical vapor deposition (CVD) to improve selectivity of carbon membranes [7]. Recently, Qiu et al. [8] demonstrated that by hyperaging treatment on the fresh CMS membranes at a temperature beyond 90 °C but less than

250 °C, the H_2/C_2H_4 selectivity can exceed 250. Among them, the CVD is the preferred method for enhancing gas selectivity of CMS membranes because it can finely control the pore size. In previous work, we used toluene vapor as carbon source of CVD to modify the polyimide-derived CMS membrane and investigated the effect of pyrolysis temperature and duration of toluene vapor modification on separation performance [9]. Toluene vapor was introduced into the furnace through mixing with N_2 stream by a bubbling method during the peak temperatures of the pyrolysis process. For comparison, the CMS membranes without adding toluene vapor also prepared under the same pyrolysis conditions. The results indicated that toluene vapor modified membranes owned higher selectivities of H_2-related gas pairs compared to non-modified membrane pyrolyzed at higher temperature with similar H_2 permeance. Moreover, the pyrolysis temperature and duration of toluene vapor modification could adjust the modified membrane performance, and the optimum pyrolysis temperature and modification time were determined by desired separation gas pair. However, the mechanism of achieving high selectivity by toluene vapor modification is unclear.

Several authors have used CVD from propylene to modify CMS membrane and explained the modification mechanism. More Specifically, Hayashi et al. [10] carried out this modification at 650 °C for the fresh CMS membrane obtained at 700–800 °C. They indicated that carbonaceous matters were formed in the gas phase. Through dividing the pores of the CMS membrane into four sizes and constructing a model, they assumed carbonaceous matters firstly deposited on the mouth of wide pores, then might deposite narrow pores with small sizes at a relatively slow rate because it required densified or coked carbonaceous matters with small size. A patent [7] described that deposition of carbon might exist pore structure or might form a new layer on the outer surface of the membrane. Moremore, the modified carbon membranes might be an asymmetric structure because the CVD was carried out one side of the membrane. Yoshimune and Haraya [11] modified CMS membrane through adding nitrogen stream containing the propylene into electric furnace during soaking time of pyrolysis process. They measured the surface elemental composition by electron spectroscopy for chemical analysis (ESCA) and demonstrated that CVD from propylene resulted in carbon deposition on the surface of the modified membrane. Moreover, the size of the pores for separating gas molecules decreased with the CVD. Additionally, Haider et al. [12] treated CMS membranes derived from cellulose at 500 °C for a short time and indicated that the CVD treatment can form a new carbon layer on all accessible surface of CMS membrane.

On the other hand, benzene and toluene have been widely used to prepare the CMS in the adsorption and separation community. There have been several reports regarding carbon deposition mechanism using the benzene and toluene as carbon resource. Kawabuchi et al. [13] controlled the pore size of active carbon fiber (ACF) through CVD from benzene and explained the mechanism of reaching high sieving ability with CVD treatment. They indicated that carbon deposition depended on the deposition temperature. For the deposition temperature of 700–800 °C, the carbon deposition appeared on the pore wall thereby improving the molecular sieving ability. This was because benzene hardly decomposed at this temperature, it was firstly adsorbed on the pore wall in short time and was then formed carbon by catalytic action of the ACF surface. Whereas the carbon deposition primarily occurred on the outer surface of the ACF when the deposition temperatures was above 800 °C. Because benzene vapor was pyrolyzed at this temperature, generated highly reactive agglomerates that can not enter the pores. Horikawa et al. [14] prepared molecular sieving specimens derived from phenol-formaldehyde resin char through CVD process, where benzene, toluene, and *o*-, *m*-, and *p*-xylene were used as carbon source and were pyrolyzed at 800 °C. They demonstrated that the carbon sources, pyrolysis temperature, and CVD time had a significant effect on the control of the pore size. Moreover, they explained the mechanism of controlling the pore size as: hydrocarbon molecules were first adsorbed on the pore surface of the phenol-formaldehyde resin char and then underwent pyrolysis to form carbon.

This work is an extension of effect of CVD modification of toluene on gas separation performance of CMS membranes. To investigate the mechanism of improving the selectivity vis toluene vapor modification, sophisticated characterization techniques are used to characterize the CMS membranes with and without toluene vapor of 50 min.

3.2 Preparation and characterization of CMS membranes

3.2.1 Preparation of CMS membranes

Commercial polyimide hollow fiber (UMS-A2(V)series, Ube Industries Ltd.) is used as the precursor material. Two step producing process consisting with thermo-stabilization in atmospheric air (relative humidity (RH) of 30–40%) at 320 °C keeping

30 min followed by pyrolysis at 625-720 °C for 120 min under N_2 stream at 300 mL min^{-1} flow rate are performed to fabricate the CMS membrane without toluene vapor modification. In step 2, introducing N_2 stream containing toluene vapor into the electric furnace can prepare the CMS membrane with toluene vapor modification, where flow rate of N_2 stream is also 300 mL min^{-1}. The schematic of pyrolysis system and heating protocol have been provided in the previous report [9]. Here, we keep 10 to 50 min of toluene vapor modification.

3.2.2 Characterization

The elemental composition is analyzed by a Thermo K-Alpha X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA) under high vacuum of 1×10^{-7} and the pass energy for survey analysis of 150 eV and high resolution of 20 eV. The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the CMS membranes are collected by Fourier transform infrared spectrometer (FI-IR, JASCO 4600, Japan). The X-ray diffraction (XRD) patterns of CMS membranes are recorded by an Rigaku Ultima IV Protectus with CuKα radiation (Rigaku Corp., Japan) at room temperature with 40 kV and 30 mA and a scanning rating of 0.5° min^{-1} over the 2θ range of 3–70°. The pyrolysis of toluene is analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GCMS) that is composed of a pyrolyzer (Frontier, Py-2020iD) and a GCMS analyzer (Shimadzu, GCMS-QP2010Ultra). Silica gel is immersed in the toluene for one night. It is put into the pyrolyzer furnace at 700 °C. The product of toluene pyrolysis is analyzed by GCMS. CMS membrane without and with 50 min toluene vapor modification obtained at 700 °C are used for the samples to be measured. 700 °C and 50 min are the highest pyrolysis temperature and longest modification time in previous report, which is more significant effect on the CMS membrane.

3.3 Results and discussion

3.3.1 Chemical structure of CMS membranes

XPS analysis provides valuable information on the top < 10 nm depth of the surface region in materials. The carbon, oxygen, and nitrogen elements are detected in the CMS membranes without and with 50 min of toluene vapor modification. The CMS membranes easily adsorb water molecular in the air [15] thereby affecting the O At% measured by XPS. Thus, Table 3-1 tabulates the atomic percentage of carbon and nitrogen (composition renormalized excluding oxygen). For toluene vapor modification, the C At% slightly increases from 97.3% to 98.3% whereas the N At% decreases around 30%. These changes are attributed to carbon deposition from toluene vapor modification. A similar increase in the C At% was observed in carbon hollow fiber membrane modified by CVD of propylene [11]. Figure 3-1a and b show the high resolution C1s spectra of CMS membranes without and with toluene vapor modification. The C1s spectrum suggests the presence of the following functional groups: C–C (284.8eV), C–O/C–N (286.1eV), and C=O (288.1eV), as commonly reported for polyimide-based carbon materials [16].

Table 3-1. Surface atomic composition of CMS membranes.

Membrane	Element (atom%)		
	C1s	N1s	N/C Ratio
CMS-700	97.3	2.66	2.73
CMS-700/50	98.3	1.74	1.77

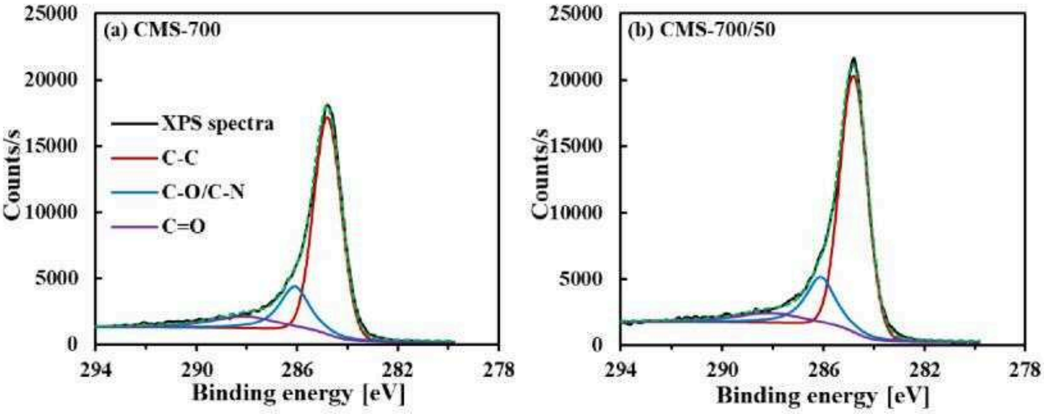

Figure 3-1. High-resolution of C1s XPS spectra of CMS membranes.

Figure 3-2a shows DRIFT spectrums of CMS membranes without and with toluene vapor modification. It can be seen that there is not significant difference in the spectrums between the two samples. This indicates toluene vapor modification does not change chemical properties of the membrane. Two strong peaks at ~3400 and 1230 cm^{-1} are observed, which are assigned to stretching vibration of O–H group and C–C group [17]. Moreover, several weak peaks also exist. Their spectra indicate the following: C–N (1390 cm^{-1}), aromatic rings (1610 cm^{-1}), C=N or –N=C=O (2300–2400 cm^{-1}), and C–H (2910, 2850 cm^{-1}), as reported in other carbon membranes [17,18]. To further investigate the effect of toluene vapor modification, we measure modified membrane using non-modified membrane as a reference. As shown in Figure 3-2b, several weak peaks are observed at ~ 1100, 1230, 2300–2400, 2900 cm^{-1}. These peaks also exist in Figure 3-2a. This means these peaks intensities for modified membrane are stronger compared with non-modified membrane. This may be due to toluene vapor modification decreasing the thermal decomposition of precursor because the modification behavior needs to consume heat.

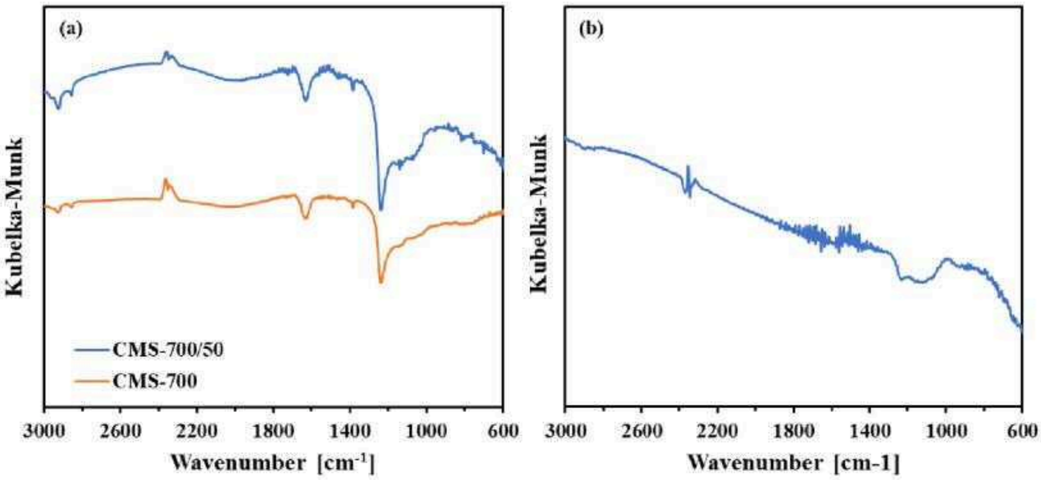

Figure 3-2. DRIFT spectrums: (a) CMS membranes without and with 50 min of toluene vapor modification, (b) CMS membrane with toluene modification using membrane without toluene modification as a reference.

Figure 3-3 shows X-ray diffraction of CMS membranes. Two broad peaks can be seen at around the 2θ value of ~24° and 43°, respectively, for both CMS membranes. The former corresponds to the diffraction of (002) plane in graphitic structure [19] and its interlayer spacing is 0.371 nm, calculated by Bragg's equation. The latter corresponds to the diffraction of (001) plane in graphitic structure [20]. Thus, the two membranes consist of graphite-like carbon structure. Additionally, no obvious changes in peak positions are observed for both CMS membranes, indicating that toluene vapor modification does not affect the crystalline structure of resulting materials.

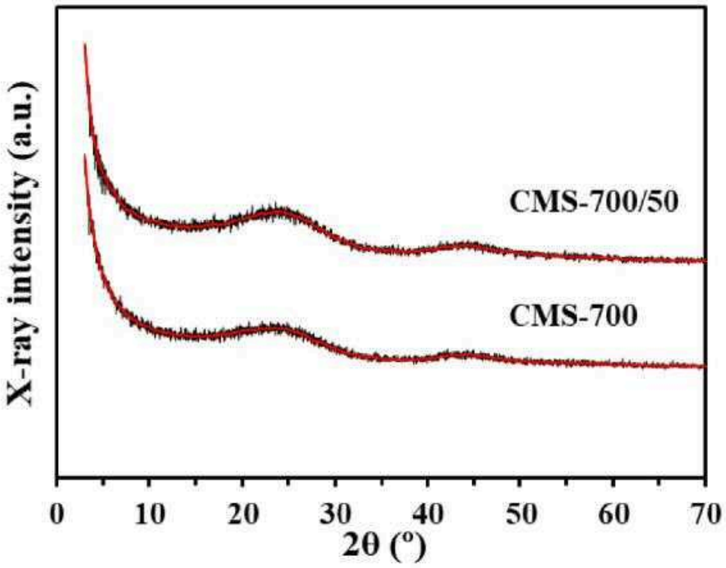

Figure 3-3. X-ray diffraction of CMS membranes without and with 50 min of toluene vapor modification.

3.3.2 Pyrolysis of toluene

We trap liquid from outlet through cooling system and analyze it by a gas chromatograph-thermal conductivity detector (GC-TCD), only one signal peak is detected in the chromatogram, whereas this peak has the same retention time as the peak of pure toluene. This may suggest that the main component of the trapped liquid is toluene. We also examine the pyrolysis of toluene at 700 °C by Py-GCMS. Figure 3-4 reveals the presence of toluene and a small amount of bibenzyl, indicating the cracking rate of toluene is very low at 700 °C. We predict that the trapped liquid may not contain other hydrocarbon species.

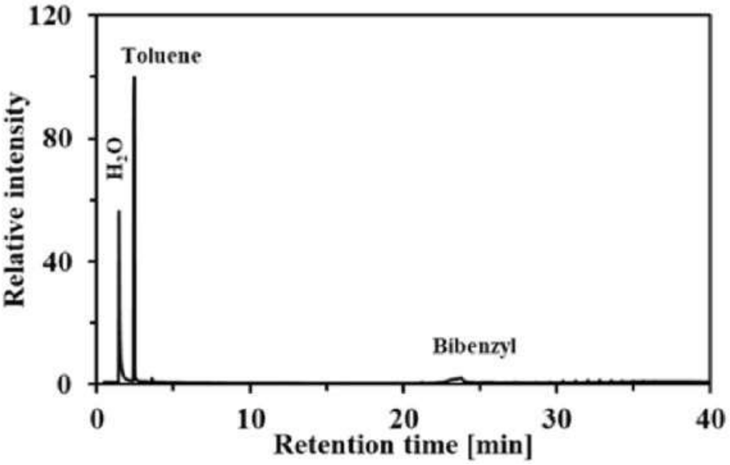

Figure 3-4. Py-GCMS chromatogram of pyrolysis of toluene at 700 °C.

3.3.3 Effect of toluene modification on separation performance

Figure 3-5 shows the gas separation performance of CMS-675 and CMS-675/50 membranes. The gas permeances of both CMS membranes decrease with increasing kinetic diameters of gas molecules, indicating molecular sieve properties. Toluene vapor modification decreases the gas permeance (Figure 3-5a) but significantly increases the selectivity of the H_2-related gas pairs (Figure 3-5b), compared with the CMS-675 membrane. H_2 permeance drops by more than one-half, from 450 GPU to 204 GPU, and selectivities of H_2/CO_2, H_2/O_2, H_2/N_2, and H_2/CH_4 increase from 4.3 to 50, 22 to 140, 190 to 1600, and 600 to 2250, respectively. A series of CMS membranes without and with toluene vapor modification are prepared at the pyrolysis temperature range of 625 to 725 °C, and the modification time is controlled between 10 and 50 min. In the pyrolysis temperature range of 625 to 650 °C, the gas permeances of CMS membranes with the toluene modification decrease over the modification time while the selectivities of H_2-related gas pairs increased relative to membrane without modification. The results are as expected because the CMS membranes obtained at low pyrolysis temperatures possess relatively large micropores.

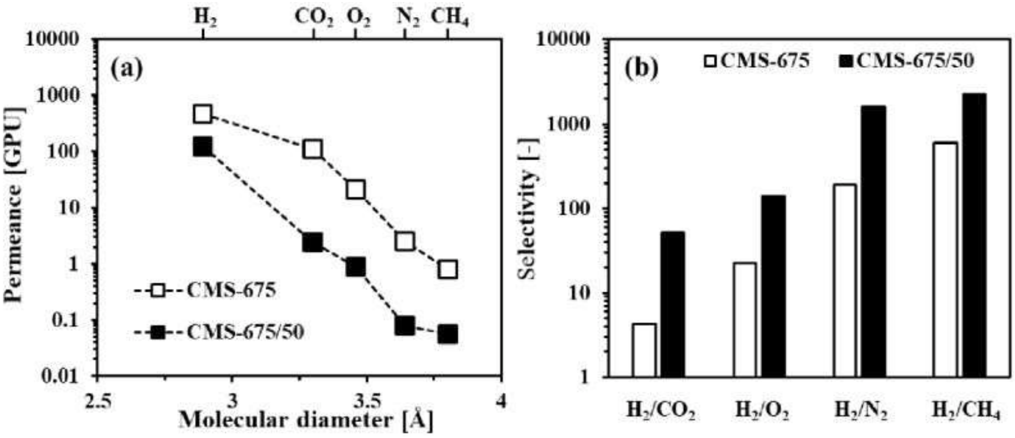

Figure 3-5. Gas separation properties of the CMS membranes without and with 50 min of toluene vapor modification obtained at 675 °C.

Figure 3-6 shows the gas separation performance of CMS membranes without and with toluene vapor modification obtained at 675, 700, and 725 °C. At all pyrolysis temperatures, H_2 permeance decrease over modification time while H_2/CO_2 selectivities increase monotonously with the highest value of 66 obtained at 700 °C with 50 min toluene modification. Whereas the improvement of H_2/N_2 selectivities only appears at lower pyrolysis temperature and shorter modification time. The H_2/N_2 selectivities of the CMS-700/40 and CMS-700/50 membranes are lower than those of CMS-700/y (y=10 to 30) membranes. The CMS-700/y (y=30 to 50) membranes have similar H_2 permeances, which may be attributed to toluene modification reaching saturation level. Similar decrease in H_2/N_2 selectivity is also observed in CMS-725/10 membrane.

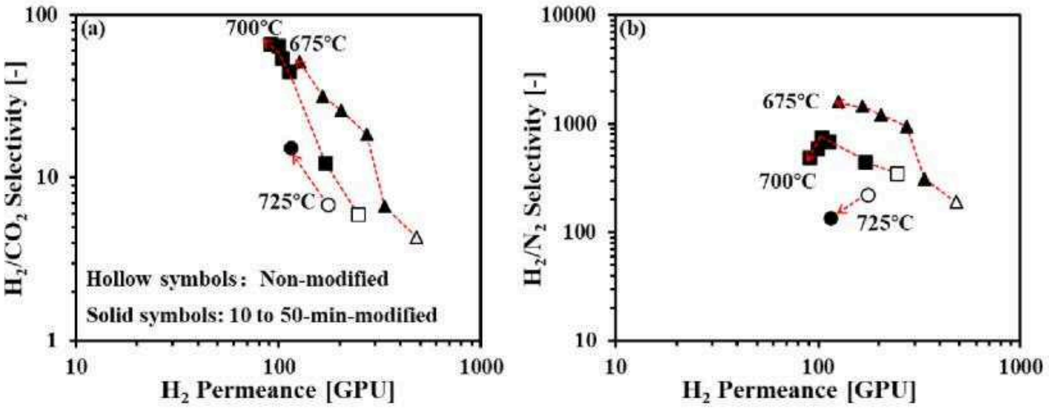

Figure 3-6. H_2/CO_2 and H_2/N_2 separation performance of CMS membranes without and with toluene vapor modification pyrolyzed at 675, 700, and 725 °C.

Figure 3-7 shows gas permeance of CMS membranes obtained at 700 °C as a function of kinetic diameters of gas molecules, which can explain the decrease in H_2/N_2 selectivities. After more than 30 min of toluene modification, the CH_4 permeance of modified membranes are higher their N_2 permeance, implying that some defects present in these membranes. That is, there are two permeation paths for gas species passing through these membranes, selective separation layer and defects. The permeance from selective separation layer varies depending on kinetic diameters of gas molecules while fluxes from defects are similar for all gas molecules. For smaller gas molecules, the permeances from selective separation layer are much higher than fluxes from defects. For larger gas molecules, the permeances from selective separation layer are similar with fluxes from defects. Thus, the increase in permeation due to the defects is more significant for larger gas molecules than for smaller gas molecules. This results in a decrease in selectivity between smaller gas and larger gas.

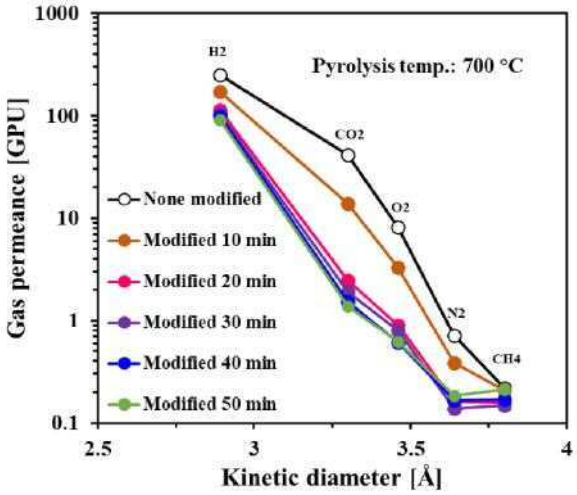

Figure 3-7. Gas permeance of CMS membranes pyrolyzed at 700 °C as a function of kinetic diameters.

3.3.4 Mechanism of toluene vapor modification

Figure 3-8 constructs preliminary insights regarding the mechanism of carbon deposition based on the above characterization. We speculate that toluene vapor is adsorbed onto the interior wall of wide pore located on the outside surface of CMS membrane and then formed the carbon coat owing to dehydrogenation for a long time in the high pyrolysis temperature (Figure 3-8i). Thus, the pore size of CMS membrane can be adjusted by controlling the amount of toluene molecule adsorbed. Another possibility is that toluene vapor is adsorbed on outside surface of the membrane, thereby forming a new carbon layer on the CMS membrane outside surface (Figure 3-8ii). Toluene vapor has good chemical stability at 700 °C because its cracking rate is very low at this temperature, which is agreed with report in literature [21]. Moreover, toluene molecules are not easily adsorbed on the outer surface of CMS membrane under the N_2 flow condition, and the short contact time may be not enough to form carbon deposition.

The carbon active surface was beneficial for the adsorption of hydrocarbon molecules [21]. Additionally, the toluene modification reduces the gas permeance and improves the selectivities of H_2-related gas pairs, suggesting that this treatment decreases the pore size. We conclude the former (i) to be more reasonable than the latter (ii), i.e. carbon deposition appearing on the interior wall of pore.

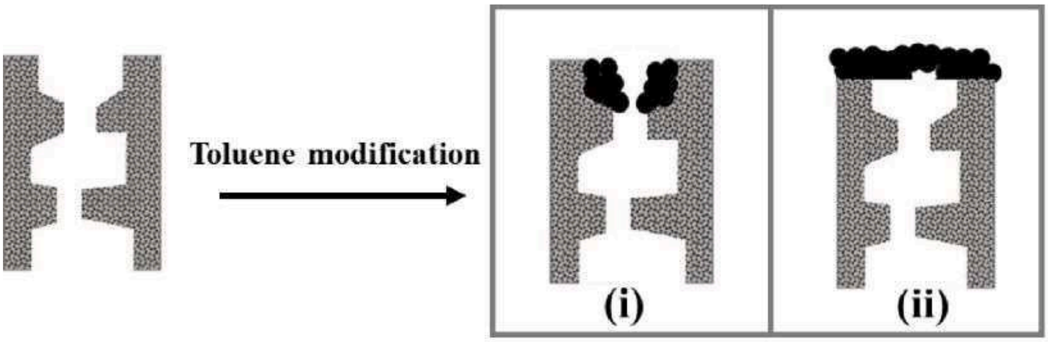

Figure 3-8. Possible carbon deposition mechanisms of the CMS membrane with toluene vapor modification.

3.4 Conclusions

The toluene vapor modification improved H_2-selectivities for CMS membrane derived from commercial polyimide hollow fiber. Moreover, this modification is promising preparation methods for CMS membranes with high selective and is suitable for CMS membranes derived from a variety of precursor materials. We use some sophisticated characterization techniques to characterize the effect of toluene vapor modification on the CMS membrane. The results indicates that toluene vapor modification form carbon deposition on outer surface of CMS membrane. Furthermore, toluene vapor modification does not change the chemical properties of CMS membrane. We also explain the mechanism of achieving high selectivity for the CMS membrane with toluene vapor modification, i.e. the toluene molecules are first adsorbed on the interior wall of wide pore on the outer surface of CMS membrane and then dehydrogenated to form carbon deposition owing to long time contacting at high temperature condition between toluene molecules and carbon surface, thereby decreasing the pore size.

3.5 References

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Chapter 4 Fabrication of Carbon Molecular Sieve Membranes Supported on a Novel Porous Carbon Fiber

4.1 Introduction

Carbon molecular sieve (CMS) membranes have received increasing attention in the field of membrane-based gas separation, as their separation properties for a variety of gas pairs exceed the upper bound curve of polymeric membranes. Their promising applications include hydrogen purification [1], olefin/paraffin separation [2], natural gas upgrading [3], and oxygen enrichment from air [4]. This exceptional separation performance originates from their unique pore structure. CMS membranes are generally obtained by the pyrolysis of polymeric precursors [5,6]. During this process, a rigid, slit-like pore structure is formed, which is composed of micropores (7–20 Å) and ultramicropores (<7 Å) that exhibit a strong size exclusion capability and good thermal and chemical stabilities.

Currently, the most promising membrane configurations for commercial applications are hollow-fiber-type membranes and tubular-supported membranes. Hollow-fiber-type CMS membranes possess a large surface-area-to-volume ratio, which is beneficial for assembling membrane modules with high separation performances, and they have also been investigated for use in large-scale gas-separation applications [7]. However, the production of hollow fiber membranes is complex, and only a few polymers are currently suitable for fabricating this configuration. Additionally, symmetric hollow fiber membranes have a relatively thick membrane layer, and so their permeance is usually low. Similarly, the permeance of asymmetric membranes is generally not as high as predicted based on their precursor structures because of the significantly thicker separation layer formed by the pyrolysis shrinkage of the partially supporting structure. Compared to hollow fiber membranes, tubular-supported membranes are easily prepared by means of a simple coating or deposition process, and various supported membranes can be obtained by varying the precursor material. In addition to the precursor materials, the use of a support is also essential, and the availability, cost, and structure of the support are of particular importance when considering the preparation of supported CMS membranes.

In this context, porous ceramic supports have been widely used for the preparation of supported membranes derived from different precursors, such as polyimides (PIs) [8], phenolic resins (PFs) [9], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [10], and poly(furfuryl alcohol) (PFA) [11]. More specifically, Hayashi et al. [8] prepared a CMS membrane layer on an α-alumina tubular support by means of repetitive coating and pyrolysis at 700 °C; the resulting membrane exhibited a C_3H_6/C_3H_8 mixture selectivity of 46 and a C_3H_6 permeance of 2 GPU at a permeation temperature of 35 °C. In addition, Ma et al. [12] employed γ-alumina to modify α-alumina tubular supports and prepared CMS membranes on macroporous α-alumina supports both with and without a mesoporous γ-alumina layer. They found that modification of the γ-alumina layer eliminated the effects of surface imperfections on the CMS membrane, resulting in the formation of a thinner defect-free membrane layer. For the single-gas permeation experiment, the γ-alumina-supported membrane exhibited an almost five times higher

C_3H_6/C_3H_8 selectivity than the α-alumina-supported membrane. Furthermore, stainless steel, coal-derived carbon, and resin have also been used as supports for the fabrication of CMS membranes. For example, Foley et al. [11] successfully employed a stainless steel support to prepare full-coverage and low-defect CMS membranes. They also studied the transport properties of gas molecules as functions of temperature and pressure [13], and found that the permeances were weakly related to the temperature, in contrast to the activated transport observed for similar carbon membranes [14]. Moreover, they indicated that two parallel routes existed for the transport of gas molecules, namely nanopores and larger defect pores. In addition, Song et al. [15] used coal-derived carbon tubes as a support to prepare PFA-derived CMS membranes, which showed excellent performances in the separation of H_2/N_2, CO_2/N_2, O_2/N_2, and CO_2/CH_4 gas pairs. This support exhibited good adherence to the membrane layer and had a low manufacturing cost, thereby providing an opportunity to realize large-scale production of CMS membranes [16]. Furthermore, Wei et al. [17] prepared a CMS membrane derived from a novolac phenol-formaldehyde resin on a porous resin support, and the resulting membrane possessed an asymmetric structure with a microporous membrane layer and a macroporous support. Interestingly, Toray Industries, Inc. recently developed a thin and light porous carbon fiber (PCF) with a nanosized continuous pore structure [18]. Although the developers successfully prepared a selective CMS membrane supported on PCF for C_3H_6/C_3H_8 separation [19], no specific details were reported. However, they did indicate that PCF could act as a support to prepare lightweight membranes, which is beneficial in the context of fabricating separation modules accommodating larger numbers of membranes, thereby increasing their gas separation performances.

Aromatic polymers, which are synthesized from petrochemical derivatives, are generally selected as precursors for CMS membranes. However, the overexploitation and overuse of fossil fuels have resulted in serious energy and environmental issues, and so the development of renewable resources as precursors has become important for the preparation of CMS membranes. In this context, wood is a widely available, natural, and renewable resource, which is viewed as an alternative to conventional non-renewable fossil fuels because of its similar components. For example, Koga and Kita [20,21] prepared CMS membranes through the pyrolysis of lignocresol, which is a lignin derivative extracted from wood via a phase-separation process. They found that the gas permeation properties of the resulting membranes were strongly dependent on the pyrolysis conditions, with the CMS membrane obtained at 600 °C giving the highest selectivities for CO_2/N_2, O_2/N_2, H_2/CH_4, and CO_2/CH_4 gas pairs (i.e., 50, 8, 290, and 87, respectively). In terms of an alternative material that can be obtained via the pyrolysis and gasification of wood, a liquid tar known as wood tar contains natural polyphenols and has a high carbon content [22]. Unfortunately, it is regarded as industrial waste because of its high viscosity and challenging separation and purification processes. Although Zhao et al. [23] successfully prepared carbon membranes using liquefied larch sawdust, the resulting membranes possessed mesoporous structures and exhibited a low CO_2/N_2 selectivity of 1.97. Moreover, although Kita reported that wood tar could be used as a precursor for CMS membranes

[24], this study was limited because of changes in the manufacturing strategy for porous ceramic supports.

Thus, we herein report the use of PCF to prepare wood-tar-derived CMS membranes. In addition, the effects of the coating solution concentration, the support, and the pyrolysis temperature on the gas separation performances of the obtained membranes are investigated.

4.2 Experimental

4.2.1 Porous tubular support

In this study, two different porous tubular supports were used to prepare the CMS membranes (as shown in Figure 4-1), namely, PCF developed by Toray Industries, Inc., Tokyo, Japan, and a commercially available ceramic tubular support (NA3) manufactured by Noritake Co., Ltd., Nagoya, Japan, for comparison purpose. PCF that can work on a smaller bending radius of 5–10 mm possesses good flexibility, with outer and inner diameters of ~300 and ~100 μm, respectively, and a porosity of ~40%. In contrast, tubular NA3 is a rigid support and has outer and inner diameters of 10 and 7 mm, respectively. The wall of the tube is 1.5 mm in thickness. The tube wall consists of two layers with a mean pore size of ~0.15 μm in the outer layer and ~1.3 μm in the inner layers. The porosities of both layers are ~40%. This information was obtained from the manufacturers.

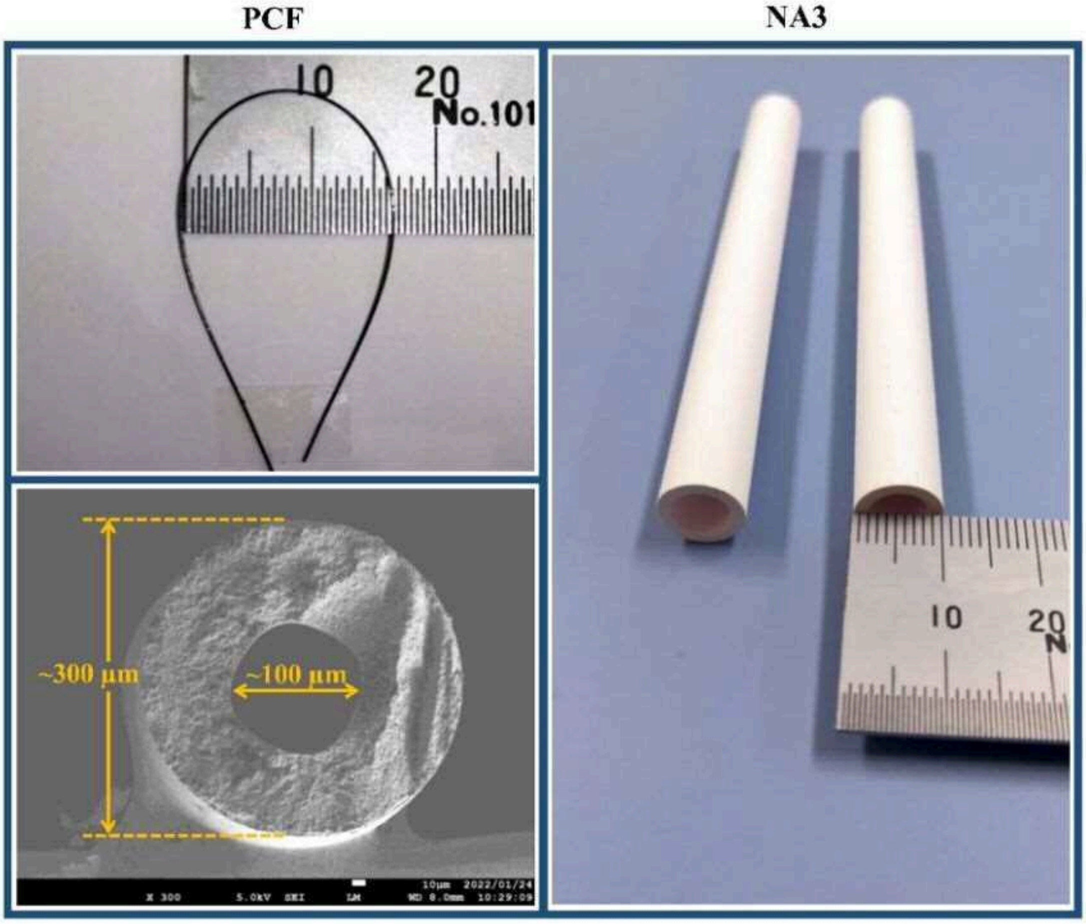

Figure 4-1. Porous tubular supports: PCF (left) and NA3 (right).

Figure 4-2 shows scanning electron microscopy (SEM) images of the outer surfaces and cross-sections of the two supports. The outer surface of PCF consisted of elongated carbon bundles—which were distributed in parallel—forming ellipsoid-shaped macropores and mesopores due to differences in thickness between the carbon bundles, as shown in Figure 4-2a. These surface pores of varying sizes were connected to the interior of the fiber. Figure 4-2c shows that the cross-section consisted of porous structures. The pores were interconnected (inset of Figure 4-2c) and had a bimodal pore size distribution, i.e. mesopores with a diameter of ~0.05 μm and macropores with a diameter of ~0.2 µm [25]. Overall, the entire fiber structure consisted of small carbon bundles that formed interconnected pores. The outer surface of ceramic tube was rough and loose as shown in Figure 4-2b. A large number of pores of varying shapes and sizes were observed on the surface, which were formed from the interstices between the particles. The wall is seen to consist of two layers; the outer layer, with a thickness of 30 µm, accounted for 2% of the total thickness of the wall (Figure 4-2d). The inset of Figure 4-2d shows the high magnification image of the outer layer, which was prepared from smaller particles than those in the inner layer and, therefore, contained smaller pores.

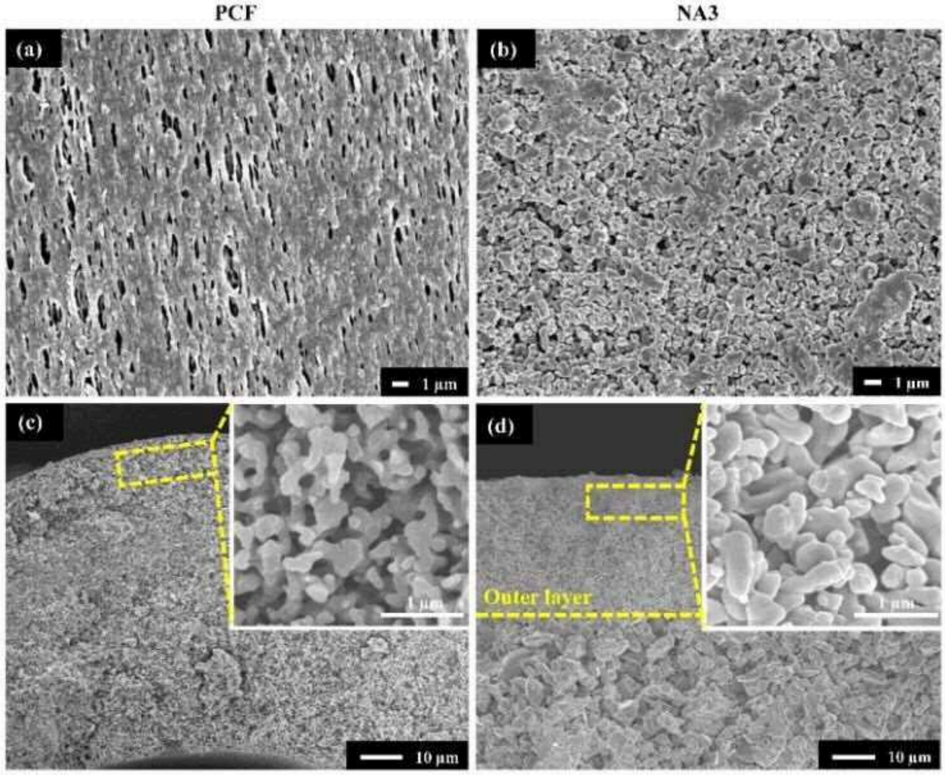

Figure 4-2. SEM images of the outer surfaces and cross-sections for the two supports: PCF (a, c) and NA3 (b, d). The inset presents magnified SEM image of the area near the outer surface.

4.2.2 Materials

Wood tar from *Alnus japonica* was obtained from the Kitami Institute of Technology. Tetrahydrofuran (THF) and cyclohexane were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). The silicone elastomer and silicone elastomer curing agent were purchased from Dow Corning Toray Co., Ltd (Tokyo, Japan).

4.2.3 Coating of the precursor membrane

The wood tar specimen (300 g) was dissolved in THF (1700 g) to prepare a 15 wt % diluted wood tar solution, which was stirred for 24 h at ~22 °C. After this time, the resulting solution was filtered through filter paper with a 2 μm pore size, and the majority of the solvent was removed by vacuum evaporation to give an 85 wt% solution of the wood tar extract in THF. To prepare coating solutions of different concentrations (40, 60, 70, and 80 wt %), this 85 wt % solution was diluted further with THF as required. The treating process was illustrated in Figure 4-3.

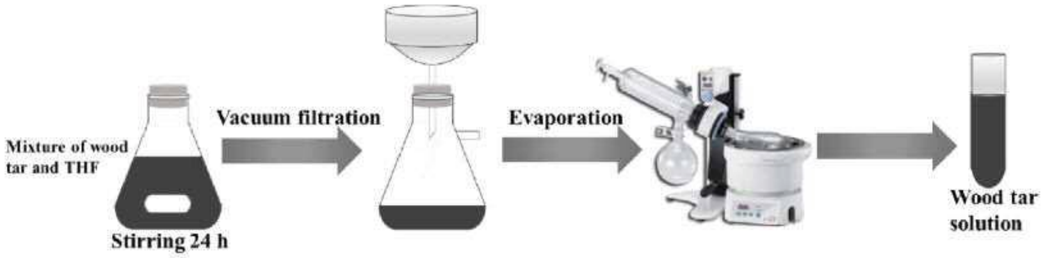

Figure 4-3. Treating process of the raw wood tar.

The above wood tar solution was coated on the surfaces of the porous supports by means of a dip-coating technique, as outlined in Figure 4-4. To prevent the coating solution from entering inside of the 10 cm tubular supports, the ends of the PCF and NA3 samples were closed using epoxy resin and a rubber stopper, respectively. Each porous support was then dipped into the desired coating solution for 1 min and then pulled out at a speed of 1 cm min^{-1}. The coating process was conducted under an air atmosphere with a relative humidity (RH) of 30–40%. Finally, the coated supports were dried for 20 h at 200 °C under air.

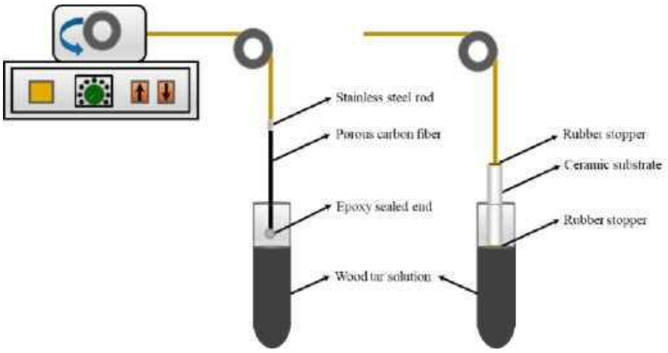

Figure 4-4. Schematic diagram showing the dip-coating of the PCF (left) and NA3 (right) supports in a wood tar solution.

4.2.4 Preparation of the CMS membrane

The dried precursor membrane was placed in the central region of a ceramic tube in an electric furnace (ARF-30KC, Asahi Rika Manufacturing Co., Ltd., Chiba, Japan), which was purged with nitrogen at a flow rate of 300 mL/min for 20 min. Subsequently, pyrolysis was carried out under a heating rate of 5 °C/min to reach the desired final temperature of 500–700 °C, which was maintained for a further 120 min. After this time, the temperature was reduced, and the nitrogen stream was maintained until the CMS membrane had cooled to a temperature ~100 °C. The heating protocol and schematic of pyrolysis setup of CMS membrane were shown in Figure 4-5. The resulting CMS membranes were designated as CMSx/y, where x is the concentration of the coating solution, and y is the support. For example, CMS70/PCF indicates a PCF-supported CMS membrane derived from a 70% solution.

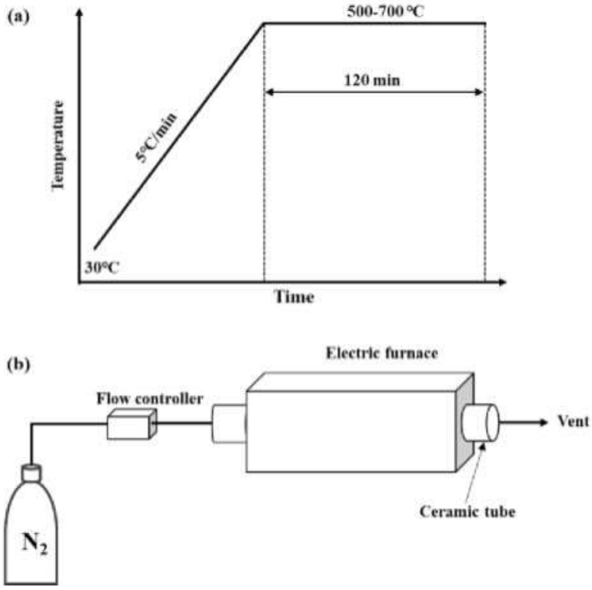

Figure 4-5. (a) Heating protocol and (b) schematic of pyrolysis setup for CMS membrane.

4.2.5 Silicone Rubber Treatment

Silicone rubber composed of a silicone elastomer and silicone elastomer curing agent were mixed in cyclohexane at a molar ratio of 10:1 and prepared as follow: the silicone elastomer was added to cyclohexene and stirred for 20 min, after which the silicone elastomer curing agent was added, followed by stirring for 1 h. A total of 10 and 20 wt% concentrations of silicone rubber were obtained upon the addition of the mixture (silicone elastomer and silicone elastomer curing agent), which accounted for total mass fractions of 10 and 20 wt% of the overall solution. Select measured CMS membranes were dipped into silicone rubber for 1 min and then pulled out at a rate of 1 cm/min.

The treated membranes were first dried at 80 °C for 2 h under vacuum conditions, and then heated to 135 °C for 1 h.

4.2.6 Characterization and gas transport properties

The chemical components of the wood tar solution were analyzed using gas chromatography-mass spectrometry (GC-MS; QP5050A, Shimadzu) with a Stabilwax capillary column (0.25 mm I.D. × 30 m length × 0.25 μm film thickness). The temperature of the injector was set to 250 °C, and helium gas was used as the carrier gas at a flow rate of 3 mL min^{-1}. The detected components were marked based on their characteristic mass spectra based on a comparison with the National Institute of Standards and Technology (NIST) spectral library. Thermal decomposition of the wood tar powder was carried out using a thermogravimetric analyzer (TG-8120, Rigaku Co., Tokyo, Japan) between room temperature and 1000 °C at a rate of 5 °C min^{-1} under a helium atmosphere. The viscosity of the wood tar solutions with different concentrations was measured using a rotational viscometer (TV-25, Toki Sangyo Co., Tokyo, Japan) at 25 °C. The microstructure of the supports and CMS membranes was analyzed though SEM (JSM-7600F, JEOL Ltd., Tokyo, Japan).

The gas separation performances of the CMS membranes were evaluated using a constant volume/variable pressure system with pure gases (H_2, O_2, N_2, CO_2, and CH_4) at 35 °C and 2 atm. The permeance (P) was calculated using the following equation:

$$P = 10^6 \cdot \frac{273}{760} \cdot \frac{V}{\Delta p \cdot A \cdot T} \cdot \left(\frac{dp}{dt}\right) \tag{1}$$

where V and T are the volume (cm^3) and temperature (K) of the downstream region of the chamber, respectively; *A* is the effective transport area of the CMS membrane (cm^2); *Δp* is the pressure difference between the upstream and downstream regions (cmHg); and *dp/dt* is the pressure rate in the steady state (Torr/s). The unit of *P* used here is GPU, which corresponds to 10^{-6} cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1} (i.e., 1 GPU = 3.35×10^{-10} mol m^{-2} s^{-1} Pa^{-1}). The ideal selectivity, $\alpha_{A/B}$ was calculated as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

where P_A and P_B are the permeances of gases A and B, respectively.

The binary gas permeation experiment of the PCF-supported CMS membrane was conducted with an equimolar mixture of CO_2/CH_4 at the total pressure of 400 kPa and 35 °C. The partial pressure of mixed-gas was equal to the pure gas feed pressure. The flow rate of the feed gas was 20 mL/min. Permeate compositions were analyzed with a gas chromatograph using a mass spectrometer with He as the carrier gas. The selectivity was calculated as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{y_A/y_B}{x_A/x_B} \tag{3}$$

where y_i and x_i were the mole fractions of component i on the permeate and feed sides, respectively.

4.3 Results and discussion

4.3.1 Gas permeation properties of the PCF and NA3 supports

Initially, the gas permeation properties of the PCF and NA3 supports were examined as a function of the inverse square root of the gas molecular mass. As shown in Figure 4-6, the permeances of both supports were proportional to the reciprocal of the square root of the molecular mass, indicating that gas permeation through these supports is dominated by the Knudsen mechanism [26]. In addition, the gas permeance of PCF was 4-fold higher than that of NA3, which confirms that PCF possessed a lower permeation resistance.

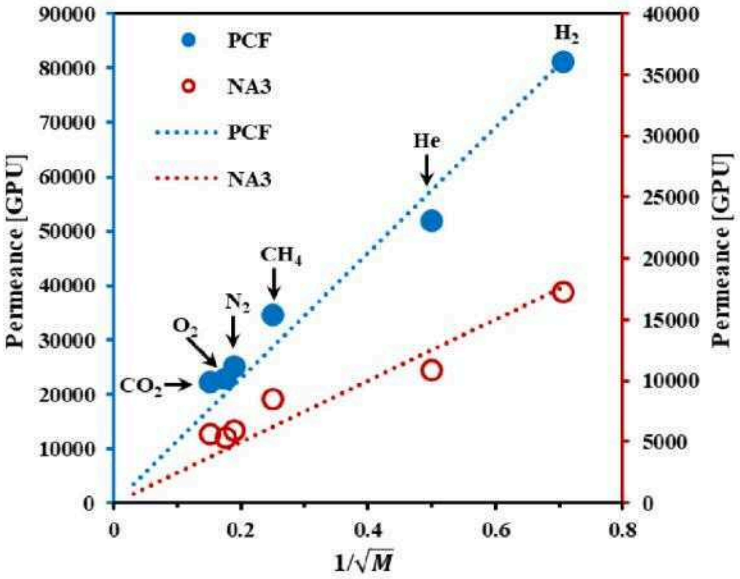

Figure 4-6. Gas permeation properties of the PCF and NA3 supports as a function of the inverse of the square root of the gas molecular mass.

4.3.2 Precursor characterization

It is known that *Alnus japonica* is a hardwood species and its lignin is mainly composed of guaiacyl and syringyl units. Thus, Figure 4-7 shows the GC-MS chromatogram of the wood tar sample, in addition to the chemical structures of its 12 main components, which include phenols, polycyclic aromatic hydrocarbons (PAHs), carboxylic acids, and ketones, as previously reported for wood biomass-derived tar [27]. Overall, phenols are the major constituents of wood tar. The guaiacol (3) and syringol (7) components originate from the pyrolysis of lignin, while various aldehydes, ketones, and alcohols are generated during the pyrolysis of cellulose [22]. Notably, the GC-MS results only showed the decomposed composition of wood tar by ion bombardment. The molecular weight of wood tar was much larger than the components detected by GC-MS measurement [28].

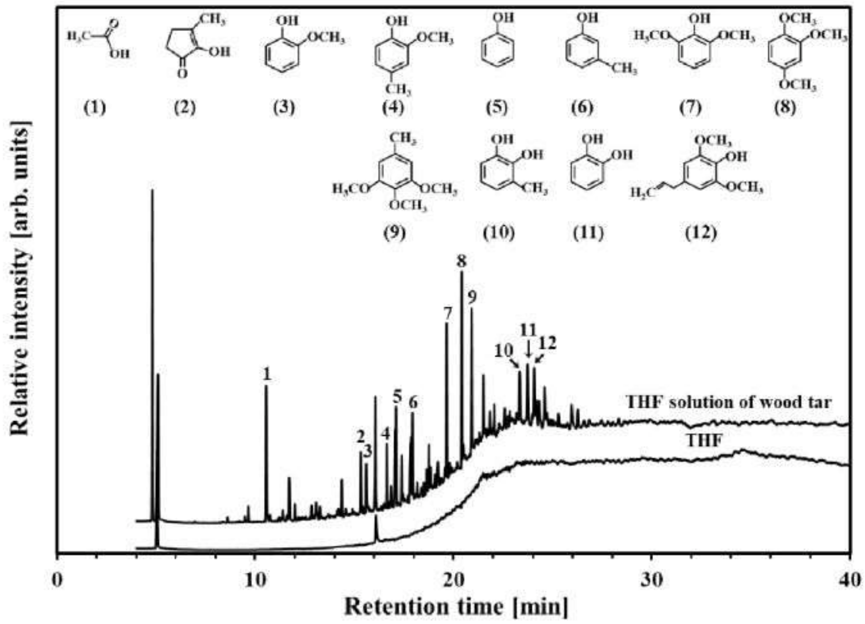

Figure 4-7. GC-MS chromatogram of the wood tar solution and the THF solvent, where the chemical structures and peak locations of the 12 major components of wood tar are given.

Viscosity is also a significant factor in the fabrication of the supported membranes. This is because a low-viscosity solution penetrates inside the support, resulting in a thin and discontinuous membrane layer. High-viscosity solution, in contrast, demonstrate limited flow, which affects the spread of solution on the surface of the support and results in a very thick membrane layer. Membrane thickness in turn is strongly correlated to gas permeability and as such it was necessary to measure the viscosity of the coating solutions. Figure 4-8 shows the results of the variation at a wood tar solution concentration at 25 °C and a shear rate of 10 s^{-1}. The viscous character of the sample increased as the proportionally to the solution concentration—for example, when the concentration increased from 60 to 70 wt%, viscosity increased linearly.

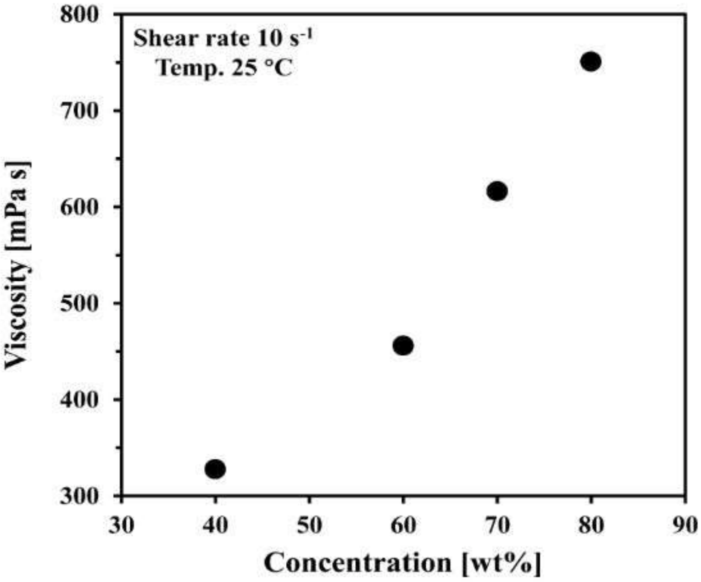

Figure 4-8. Viscosity of different concentrations of wood tar solutions measured at 25 °C and a shear rate of 10 s^{-1}.

Figure 4-9 shows the thermogravimetric analysis (TGA) curve recorded for the wood tar powder upon heating from room temperature to 1000 °C. As indicated, weight loss starts at ~200 °C, which is similar to the case of phenolic resin [29], but lower than that of the polyimide precursor [30]. In addition, the maximum weight loss rate was observed between 310 and 360 °C, at which point the weight reduced by ~13%. At 600 °C, a weight loss of 40% had been reached, although a further steady decline was observed upon heating further to 1000 °C. Below 500 °C, H_2O, CO, and CO_2 were evolved; in addition, p-cresol, xylenol, guaiacol, and methyl guaiacol were also produced within this pyrolysis temperature range [24].

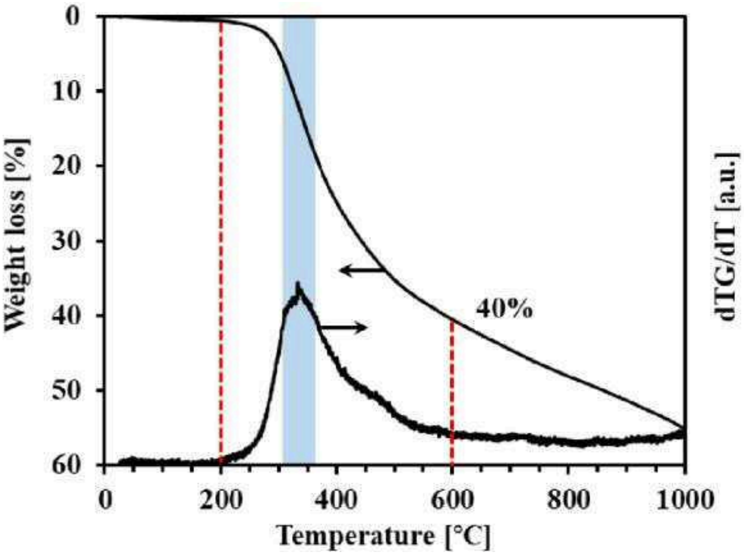

Figure 4-9. TGA curve for the wood tar powder.

4.3.3 Morphologies of the CMS membrane

Figure 4-10 shows cross-sectional SEM images captured close to the outer surfaces of the supported CMS membranes pyrolyzed at 600 °C following coating of the both supports using a range of solution concentrations. For both supported membranes, the surface of the support can be easily identified, and is indicated by the broken line in each image. In addition, a continuous dense layer was observed on the outer support surface. On the PCF support, this layer was extremely thin (< 1 μm) when the 40 wt% solution was employed for coating, although upon increasing the solution concentration from 60 to 80 wt%, the layer thickness increased from 1.5 to 7 μm. This was attributed to an increase in the viscosity of the coating solution. A similar observation was made for the NA3 support, wherein outer dense layer increased in thickness from 4 to 10 μm upon increasing the solution concentration from 40 to 80 wt%. It was also found that a thicker layer formed on the NA3 support than on the PCF support, and this was considered to be due to the different affinities for the two supports toward the solution. More specifically, carbon materials are hydrophobic, whereas ceramic materials are hydrophilic, and so the hydrophilic THF solution interacted more easily to the hydrophilic (i.e., the NA3) support.

A layer-like area was also observed for both membranes, wherein the carbon material appeared to have infiltrated into the support pores, as indicated by the yellow arrows in Figure 4-10. This layer was most dense close to the support surface, and gradually became more porous. In addition, the depth of this layer decreased from 7 to 1 μm in the PCF-supported CMS membranes when the solution concentration was increased from 40 to 80 wt%. This result confirms that this carbon layer originated from penetration of the coating solution during the coating process. It was also observed that a thicker penetration layer was formed inside the NA3 support compared to inside the PCF support, and again, this was attributed to the affinity between the solution and the support. However, due to the fact that this porous penetration layer should be as thin as possible to reduce the gas permeation resistance, the porous ceramic support appears unsuitable for use in the preparation of wood-tar-derived CMS membranes. Moreover, a crack was observed in the outer layer of the CMS80/NA3 membrane, as shown in Figure 4-10h, which might originate from an increase in outer layer thickness. Obviously, a thicker dense layer formed on the tubular support is more apt to crack during the drying and pyrolysis due to the thermal expansion between the thicker outer dense layer and the support. Since a thin penetration layer may function as an anchor for the carbon layer on the support surface, further investigations would be desirable out to adjust the parameters of the dip-coating process and produce a thinner dense outer layer on the PCF support, in addition to a thin penetration layer inside the support.

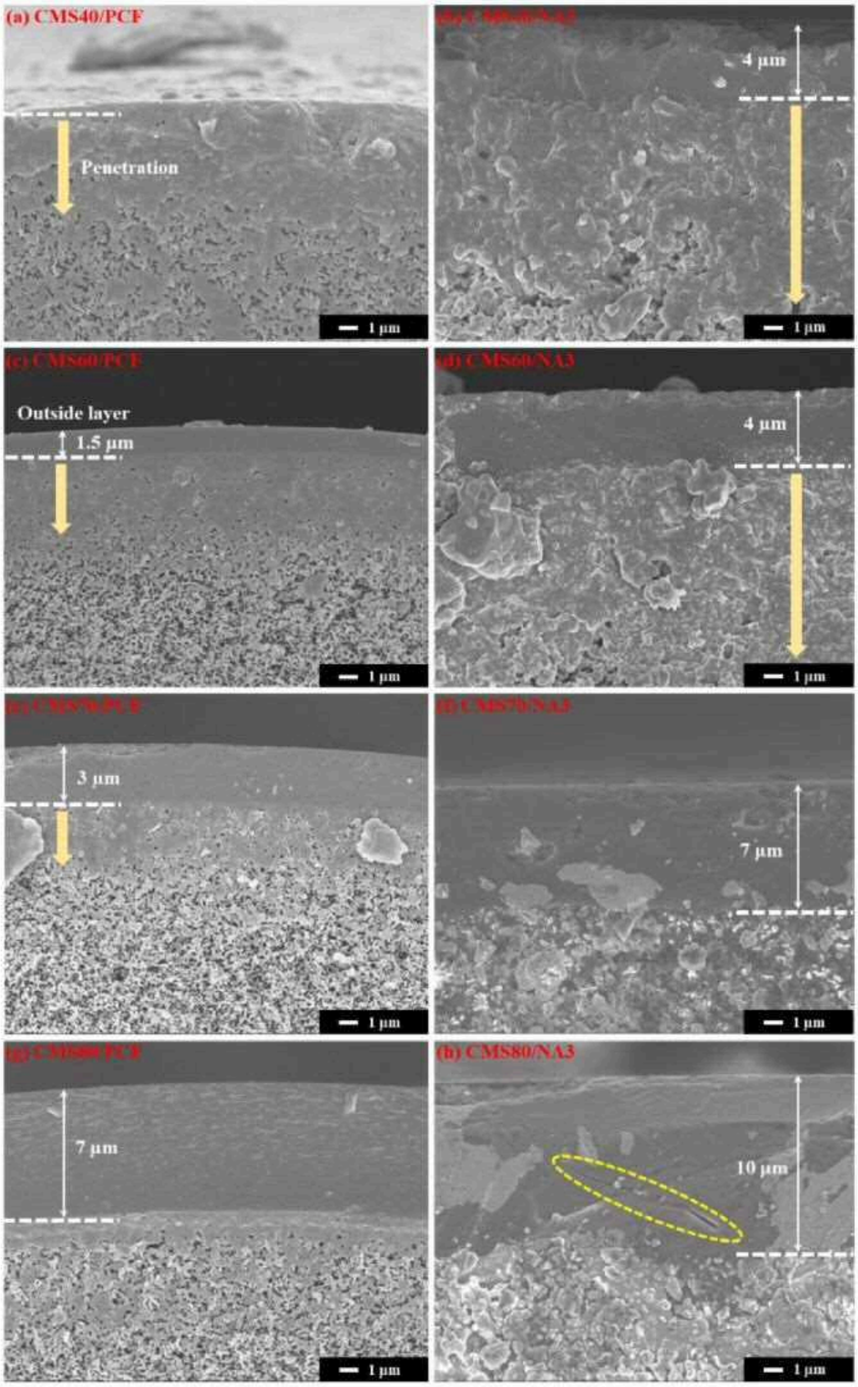

Figure 4-10. Cross-sectional SEM images of the PCF-supported and NA3-supported CMS membranes derived from the wood tar solutions of different concentrations (40,

60, 70, and 80 wt%): (a) CMS40/PCF, (b) CMS40/NA3, (c) CMS60/PCF, (d) CMS60/NA3, (e) CMS70/PCF, (f) CMS70/NA3, (g) CMS80/PCF, and (h) CMS80/NA3. Pyrolysis was carried out at 600 °C. The broken lines indicate the surfaces of the supports.

4.3.4 Effect of the solution concentration

Figure 4-11a shows the gas permeances of the PCF-supported CMS membranes derived from wood tar solutions of different concentrations as a function of the kinetic diameters of the gases. As indicated, from the figure, the gas permeances of the PCF-supported membranes decreased upon increasing the size of the gas molecules, which suggests that the separation mechanism was dominated by molecular sieving. However, for the CMS40/PCF system, the CH_4 permeance was found to be higher than that of N_2, thereby implying that some defects were present in the membrane. Furthermore, the permeances decreased upon increasing the concentration of the solution coating, and this was clearly attributed to the greater membrane thickness obtained at higher concentrations (Figure 4-10). These results therefore indicate that the thickness of the dense outer layer was mainly responsible for determining the gas permeance.

In addition, Figure 4-11b shows the permeances of the NA3-supported membranes prepared under the same conditions. More specifically, the permeances of the CMS60/NA3 and CMS70/NA3 membranes showed a similar trend to the PCF-supported membranes in terms of the molecular size, indicating again that molecular sieving was relatively dominant in these membranes. However, for the CMS40/NA3 and CMS80/NA3 membranes, the variation in permeance at different gas molecule sizes was less pronounced, and CH_4 was found to be more permeable than N_2. These results indicated that the CMS40/NA3 and CMS80/NA3 membranes contained a greater number of defects. Indeed, despite its thick outer layer, the CMS80/NA3 membrane generally exhibited gas permeances of the various ceramic membranes examined in this experiment; however, this was likely due to the cracks present in the membrane structure, as can be seen in Figure 4-10h.

It was also observed that for the CMS membranes derived from the 60 and 70 wt% coating solutions, the PCF-supported membranes exhibited higher permeances than the NA3-supported membranes. This can be explained in terms of their thinner outer layers. It should be noted here that due to the significantly higher gas permeances of both supports compared to the CMS membranes, the differences in gas permeances between the supports do not affect the results of this experiment.

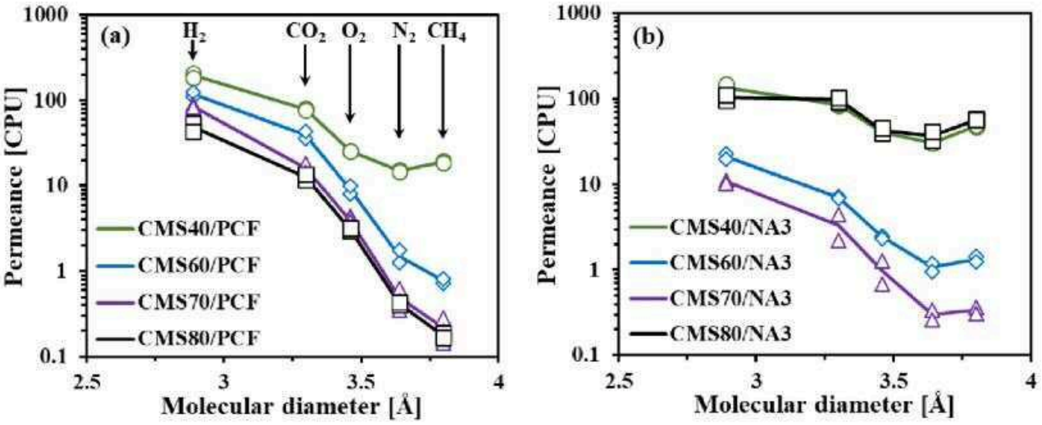

Figure 4-11. Gas permeances of the CMS membranes derived from wood tar solutions of different concentrations and pyrolyzed at 600 °C: (a) PCF-supported membranes and (b) NA3-supported membranes.

Figure 4-12a shows the selectivities of the PCF-supported CMS membranes derived from wood tar solutions of different concentrations. As indicated, the selectivity increased upon increasing the solution concentration from 40 to 70 wt%, and similar results were obtained for the CMS70/PCF and CMS80/PCF membranes. As mentioned previously, the lower selectivity of the CMS40/PCF membrane was attributed to the presence of defects caused by the increased penetration of the coating solution into the support. As shown in Figure 4-10a, the coating solution almost completely penetrated the support, with very little of the solution remaining on the support surface. Although a similar penetration was also observed in the CMS60/PCF membrane, a thin dense layer remained on the surface due to the higher viscosity of this solution. In contrast, as shown in Figure 4-12b, the selectivities of the NA3-supported membranes are lower than those of the PCF-supported membranes. It was therefore expected that due to the precursor and pyrolysis conditions employed, all of the prepared NA3-supported membranes may have contained defects.

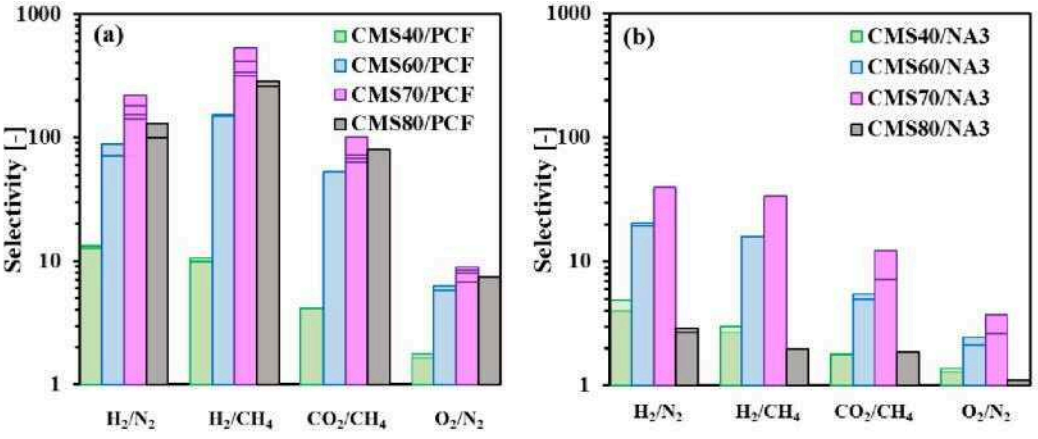

Figure 4-12. Selectivities of the CMS membranes derived from wood tar solutions of different concentrations and pyrolyzed at 600 °C: (a) PCF-supported membranes and (b) NA3-supported membranes.

According to reports in the literature, silicone rubber treatment reduces the effect of defects on the gas separation performance of membranes [31,32]. Therefore, this treatment step was implemented for the CMS membranes detailed above. As shown in Figure 4-13, after the 10 wt% silicone rubber treatment, the H_2 selectivity of PCF-supported CMS membranes derived from wood tar solutions of 60 and 70 wt% increased more than two times, whereas the gas permeance decreased. For example, H_2/N_2 and H_2/CH_4 selectivities for the CMS-70/PCF membrane increased from 155 to 333 and 340 to 704, respectively. These results suggest that the selective PCF-supported CMS membranes still contained a few defects. The 10 wt% silicone rubber treatment also improved the selectivities of the CMS-40/PCF and NA3-supported membranes; however, the gas permeation from defects still predominated, especially the CMS-80/NA3 membrane. The 20 wt% silicone rubber treatment was applied to these membranes; the gas permeation results of the NA3-supported CMS membranes before and after the silicone rubber treatment are shown in Figure 4-14. The results indicated that the 20 wt% silicone rubber treatment drastically reduced the defects in the CMS-60/NA3 and CMS-70/NA3 membranes, resulting in reduced gas permeances and improved selectivities. Moreover, the CMS-70/NA3 membrane after the treatment showed the highest separation performance. The 20 wt% silicone rubber treatment was more effective for CMS-40/NA3 membrane than CMS-80/NA3 membrane, which defects may be too large to be cured by the silicone rubber treatment.

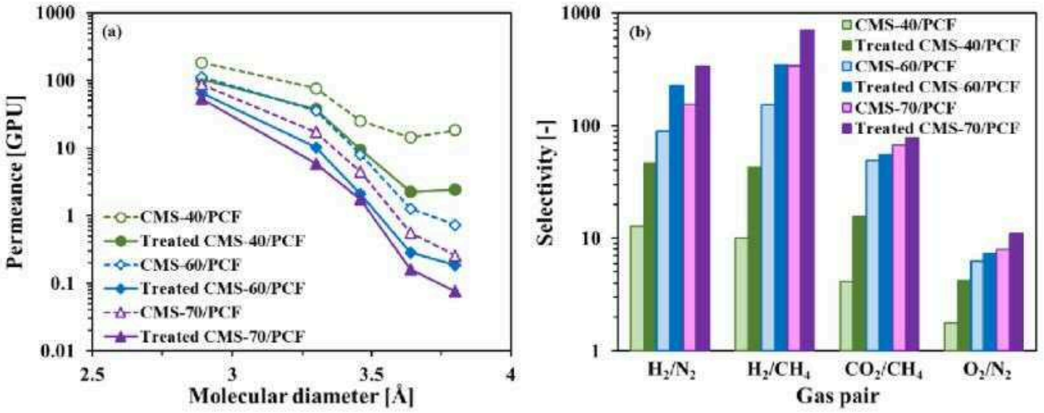

Figure 4-13. Effect of silicone rubber treatment on gas separation performance of the PCF-supported CMS membranes showing (a) gas permeance and (b) ideal selectivities of gas pairs. The CMS-60/PCF and CMS-70/PCF membranes were treated with 10 wt% silicone rubber, while the CMS-40/PCF membrane was first treated with 10 wt% silicone rubber, followed by 20 wt%.

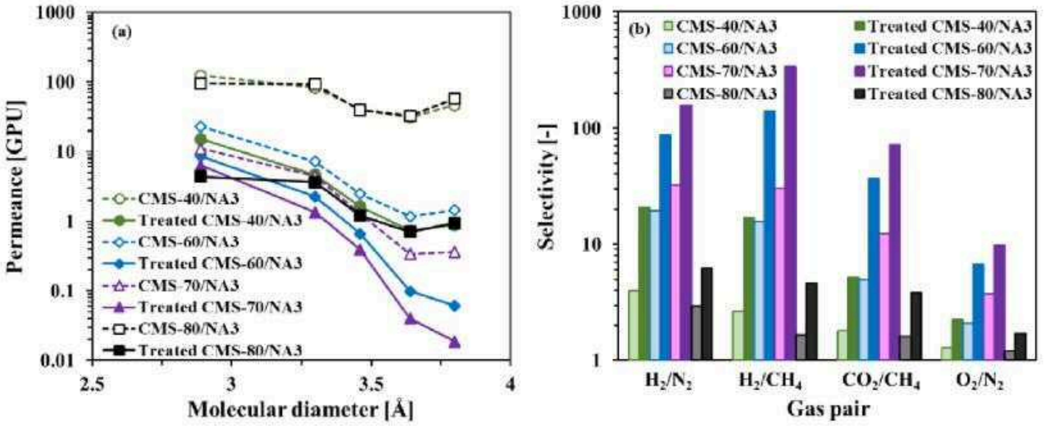

Figure 4-14. Effect of silicone rubber treatment on gas separation performance of the NA3-supported CMS membranes showing (a) gas permeance and (b) ideal selectivities of gas pairs. All NA3-supported CMS membranes were first treated with 10 wt% silicone rubber and then with 20 wt%.

4.3.5 Effect of the pyrolysis temperature

Figure 4-15 shows the effect of the pyrolysis temperature on the separation performances of the PCF-supported CMS membranes derived from a 70 wt% solution, which was determined to be the optimal solution concentration based on the results presented in Figures 4-10 to 4-12. More specifically, as the pyrolysis temperature increased from 500 to 700 °C, the permeances of the membranes decreased (Figure 4-15a), and this was attributed to the higher pyrolysis temperature resulting in micropore shrinkage, which in turn leads to a reduced gas permeance [33,34]. In addition, it was observed that the selectivities showed an increasing trend upon increasing the temperature range from 500 to 600 °C, prior to decreasing (Figure 4-15b). This change agrees with the previously reported results for lignin-derived carbon membranes [20]. However, it has been previously reported that the selectivity of the CMS membrane should increase upon increasing the pyrolysis temperature, as described for polyimide-derived CMS membranes [35], and so the results presented in Figure 4-15b therefore suggest that the CMS70/PCF membrane obtained at 700 °C may contain some defects. Specifically, a higher pyrolysis temperature typically results in further shrinkage of the micropores, while a continuous reduction in the mass of the wood tar sample at the higher temperature range was observed in Figure 4-9. Micropore shrinkage and defects may occur simultaneously in the CMS70/PCF membrane, and the former is dominant in gas permeation. Additionally, the defects had a more significant effect on the permeance of large-sized gas molecules than on that of small-sized gas molecules. Therefore, permeance and selectivity decreased for the CMS70/PCF membrane.

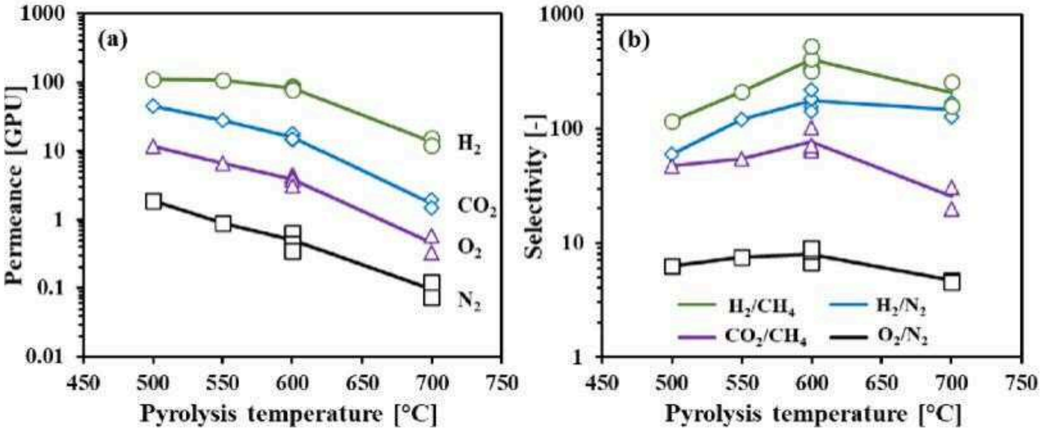

Figure 4-15. Effect of the pyrolysis temperature on gas separation performances of the PCF-supported CMS membranes derived from a 70 wt% coating solution: (a) The permeance, and (b) the ideal selectivity.

4.3.6 Comparison of the separation performance

Finally, we carried out a comparison between the H_2/N_2, H_2/CH_4, O_2/N_2, and CO_2/CH_4 separation performances of our CMS70/PCF membranes pyrolyzed at 500, 550, and 600 °C with those of other tubular-supported CMS membranes (Figure 4-16). For this purpose, the precursors are classified into two types, namely synthetic polymers (i.e., phenolic resins, aromatic polyimides, and polyphenylene oxides) and naturally-derived polymers (i.e., PFA, lignocresol, and wood tar). As shown in Figure 4-16, the logarithm of the ideal separation factor was plotted against the logarithm of the permeance to the higher permeable component for each CMS membrane, and it was observed that a trade-off appeared to exist between the selectivity and the gas permeance for each separation; the CMS membranes with higher gas permeances tended to display lower selectivities. For the H_2/N_2 and H_2/CH_4 gas separation experiments, both the selectivity and the H_2 permeance obtained for the wood-tar-derived CMS membranes were slightly lower than those obtained for the other CMS membranes, while for the O_2/N_2 and CO_2/CH_4 gas separation experiments, similar trade-off relationships were observed for all systems.

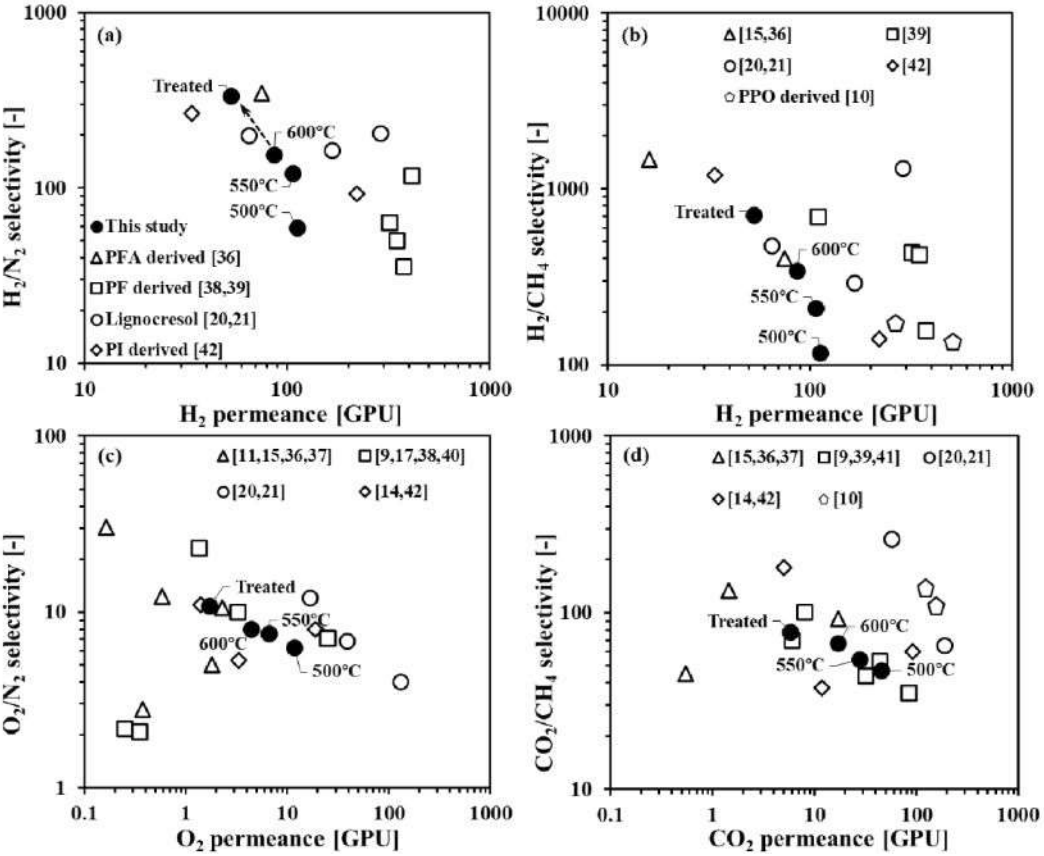

Figure 4-16. Comparison of previously reported tubular CMS membranes derived from different precursors with the PCF-supported CMS membranes prepared herein from the 70 wt% wood tar coating solution: (a) H_2/N_2, (b) H_2/CH_4, (c) O_2/N_2, and (d) CO_2/CH_4. Notations: PFA = Poly(furfuryl alcohol), PF = phenolic resin, PI = polyimide, PPO = polyphenylene oxide.

Overall, the obtained results indicated that the performances of the CMS membranes prepared from wood tar were moderate in the separation of O_2/N_2 and CO_2/CH_4. Although lignocresol is an attractive precursor because it is a renewable resource, and its CMS membranes display good selectivities, their usage is widespread. In contrast, there are currently few effective uses for wood tar, and a significant amount of wood tar is currently wasted, and so its use as a precursor for CMS membranes could be considered a potential effective usage of wood tar in the near future.

4.3.7 Binary Gas CO_2/CH_4 Permeation Properties

In order to see realistic separation performance of PCF-supported CMS membrane, the binary mixture 50%CO_2/50%CH_4 permeation experiment was conducted for the CMS-70/PCF membrane based on our measurement condition. The performance of CO_2/CH_4 is listed in Table 4-1. The CO_2 permeance for binary mixture was lower than single gas permeance. The separation factor for binary mixture was higher than the ideal selectivity of the single gas. This result is in good agreement with literature [3,43]. The reduction of CO_2 is because the competitive adsorption occurs in the pore. The adsorption was much more for CO_2 than CH_4 resulting in a higher selectivity.

Table 4-1. Performance of CO_2/CH_4 for PFC-supported CMS membrane derived from 70 wt% wood tar solution obtained at 600 °C.

Membrane	Feed	Permeance (GPU)		Selectivity
		CO_2	CH_4	CO_2/CH_4
CMS70/PCF	Pure gas	14	0.14	101
	Mixed-gas (50:50)	7.3	0.06	122

4.4 Conclusions

Wood-tar-derived carbon molecular sieve (CMS) membranes were fabricated on a novel porous carbon fiber (PCF) support by means of a facile dip-coating and pyrolysis protocol. The PCF employed herein consisted of interconnected pores, which provide additional paths and channels for gas transport. In contrast, the porous structure of the ceramic NA3 support consists of voids between the alumina particles. Following determination of the optimal wood tar coating solution concentration, the membrane prepared using the 70 wt% solution produced a continuous and dense layer on the outside of the PCF support, while a thin penetration area was observed inside the support. Under identical preparation conditions, the PCF-supported membranes exhibited superior separation performances than the NA3-supported membranes, and the highest selectivities were observed for both supports using a solution concentration of 70 wt%. Furthermore, upon increasing the pyrolysis temperature from 500 to 700 °C for the PCF-supported membranes derived from the 70 wt% coating solution, the gas permeances of the membranes were found to decrease gradually, while the selectivities initially increased prior to reaching a relatively constant value; the maximum selectivity was obtained at 600 °C. This membrane exhibited H_2/N_2 and H_2/CH_4 selectivities of 155 and 340, respectively, in addition to a H_2 permeance of 86 GPU. These results therefore suggest that PCF is a suitable support for the preparation of wood-tar-derived CMS membranes for gas separation. Indeed, this support is not only a promising support candidate, but it also has the potential to enhance the performances of composite gas separation membranes. We therefore expect that these results will lead to the development of superior CMS membranes for improved natural gas and biogas purification, and also for hydrogen production applications. Moreover, the use of wood tar as a precursor for CMS membranes could address some of the issues related to its disposal. Future work will focus on improving the CMS membrane performance. It is necessary to further adjust the parameters in dip-coating and pyrolysis processes to prepare a thinner carbon layer for improving the permeance. Further, post-treatments are also considered to enhance the selectivity.

4.5 References

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Chapter 5 Conclusions and Future Perspective

5.1 Conclusions

In Chapter 2&3, CMS membranes with high H_2 selectivity were successfully prepared using toluene as a CVD source. The separation performance of CMS membranes with toluene vapor modification can be adjusted by controlling the pyrolysis temperatures and toluene addition time. The optimal preparation conditions depended on the gas pairs to be separated. Additionally, although toluene addition increased the carbon concentration on the outer surface of CMS membrane，no additional carbon layer was formed on outer surface. This study demonstrated that the toluene modification may be a promising method for improving selectivity of the CMS membranes.

In Chapter 4, a porous carbon fiber was successfully used to prepare the supported CMS membrane. 70 wt% wood tar solution was optimal for CMS membrane preparation. Under the same condition, PCF-supported CMS membrane showed higher separation performance than commercial ceramic tube supported CMS membrane. The PCF-supported CMS membrane derived from the 70% wood tar solution and pyrolyzed at 600 °C exhibited the highest H_2 selectivity among the various membranes obtained over the pyrolysis temperature range of 500–700 °C.

5.2 Future perspective

Although the addition of toluene to the pyrolysis process can be used to improve selectivity of CMS membrane, the toluene is toxic compound and its mechanism of improving the selectivity of the CMS membrane is still unclear. Investigating the mechanism is beneficial for developing other organic carbon sources for preparation of highly selective CMS membranes. In the future, more advanced analytical techniques may be necessary to investigate its mechanism.

Additionally, although the porous carbon fiber (PCF) is considered a promising support due to its superior structural characteristics, it is currently used for preparing wood-tar-derived CMS membranes. Thus, it is valuable to prepare PCF-supported CMS membranes derived from other polymeric precursors and to investigate the gas separation performance.

List of publications

1. **Jing Nie**, Norimasa Yoshizawa, Kazuhiro Tanaka*, “Effect of chemical vapor deposition of toluene on gas separation performance of carbon molecular sieve membranes”, *Journal of Porous Materials* 2022, 29, 393–404.

   https://doi.org/10.1007/s10934-021-01188-9

2. **Jing Nie**, Fuuga Okada, Hidetoshi Kita, Kazuhiro Tanaka*, Takaaki Mihara, Dai Kondo, Yuuki Yamashita, Nahoko Yahagi, “Fabrication of carbon molecular sieve membranes supported on a novel porous carbon fiber”, *Energy & Fuels* 2022, 36, 7147–7157.

   https://doi.org/10.1021/acs.energyfuels.2c00907

Acknowledgements

Living and studying at Yamaguchi University has been a precious experience for me. There are many people who have made a significant impact on me during my studies at Yamaguchi University. I am sincerely grateful to my supervisor, Professor Kazuhiro TANAKA, for his guidance, support, and assistance in my research work. His wisdom, insights, and strong work ethic have been a great inspiration to me. He is a kind elder who cares about my life and is also a rigorous supervisor. He always took time out of his busy schedule to solve some trivial problems for me and guides me to be a researcher.

I am particularly grateful to Professor Hidetoshi KITA for giving me the opportunity to study at Yamaguchi University and for giving me a lot of helpful advice during my research. His energy and enthusiasm for academic research encouraged me to meet more research challenges. I would also like to express my sincere gratitude to Professor Xiangshu Chen, whose warm-hearted help and support made everything go well for me in Japan.

Sincere thanks to Mr. Nobuyuki HARADA and Mr. Tsuyoshi TONOSAKI for their kind and patient help in sample characterization. I was fortunate to have kind seniors Dr. Yongsheng Liu, Mr. Norimasa YOSHIZAWA, Mr. Takumi SHIMOMURA, and Mr. Tomoki TANAKA to help me in my experiments. I also had a wonderful time with Mr. Fuga OKADA and Mr. Yushi IMAMURA. Additionally, I would like to sincerely thank all the staff in the Dean's office for all the help they provided in my studies and daily life. Finally, I would like to thank my family, I love you all!

Nie jing

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