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To cite this article: Norazlianie Sazali *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **788** 012036

IOP Conf. Series: Materials Science and Engineering **788** (2020) 012036 doi:10.1088/1757-899X/788/1/012036

Fabrication of Carbon Molecular Sieve (CMS)-based membranes: A review

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Abstract. Carbon molecular sieve (CMS) is a type of carbon-based membranes with amorphous microporous structures that is the most conventional and has been studied for more than half a century. High permeability and high selectivity can be acquired concurrently by several structural characteristics. Intensive investigations done by various studies demonstrate that the properties of polymeric precursor, pyrolysis conditions (soak time, pyrolysis temperature, and pyrolysis atmosphere), pre-treatment and post-treatment mainly affect the micropore structures formation as well as the properties of gas transportation and finally identified the gas separation performances for the CMS membranes synthesized.

Keywords. Carbon molecular sieve (CMS); carbonization process; pyrolysis conditions; separation process.

1. Carbon-based membranes

In general, fabrication of CMS membranes is done under vacuum or inert atmosphere through pyrolysis or carbonization of numerous polymeric precursors for example polyimide [1-3], polyacrylonitrile [4-6], poly(furfuryl alcohol) [7, 8], phenolic resins [9-11] as well as their derivatives. Between them, the most familiar carbon precursors is the polyimide as well as its derivatives having the structural variability through the mixture of various dianhydrides and diamines types [12, 13]. Summary of carbonization behaviours of an aromatic polyimides series, relationship between structure as well as the synthesized carbon materials property can be found in the literature. Creation of CMS membranes pore system is caused by polymers degradation comprises of huge gaps with comparatively small constrictions [12, 14, 15]. Bigger pores (0.6–2.0 nm) are accountable for adsorption capacity, whereas smaller pores (<0.6 nm) are accountable for molecular sieving properties [16, 17]. There are two categories of CMS membranes can be identified which is the supported membranes with good mechanical strength and comparatively high gas permeance and the unsupported membranes for example the carbon hollow fiber membranes. Support properties for example pore structures and surface roughness play an important role for supported CMS membranes in forming defect-free thin CMS layer [18, 19].

In order to avoid the defects, a few coating–pyrolysis cycles is needed resulting to gas permeance reduction. Thus, a mesoporous intermediate layer is usually required between microporous CMS layer and macroporous supports in guaranteeing the development of thin coating without pinhole [10, 20, 21]. Furthermore, the plasma-enhanced chemical vapor deposition technique was utilized in forming ultrathin defect-free coating as an alternative to conventional spin-coating process which is advantageous in improving its reproducibility [22, 23]. Carbon hollow fiber membranes is a typical instance of unsupported CMS membranes which have gained various attention in the current years due to its high packing density. Superior gas separation performance is shown by some newly-developed CMS hollow fiber membranes with successful fabrication of the corresponding modules [14, 15]. Nevertheless, gas permeance through CMS hollow fiber membranes is expected to be lower than anticipated during the translation of dense flat film to hollow fiber. This is mainly caused by the microporous structure morphology densification. Restriction of morphology collapse is suggested by certain treatments [14, 24, 25].

2. CMS membranes for implementation

Extensive studies can be found on CMS membranes for implementation in natural gas purification (CO_2/CH_4 and N_2/CH_4) [26], air separation (O_2/N_2) [27, 28], hydrogen recovery (H_2/N_2 and H_2/CH_4)[29] and CO_2 capture (CO_2/N_2)[30, 31]. Meanwhile, H_2/CO_2 separation is a focus of a few studies. Based on the data of pure gas of various reported CMS membranes, the H_2/CO_2 ideal selectivity of most CMS membranes is lesser than 20 with expectation for the H_2/CO_2 gas combination selectivity to be lesser [10, 32, 33]. Furthermore, brittleness is one of their major disadvantage which restricts practical implementation of CMS membranes, although it could be limited to some level through technological parameters and precursor structures optimization for pyrolysis process. Hence, under high pressure, the mechanical strength of CMS membrane need to be refined to fulfil the practical implementation demand.

In the current years, a recent type of carbon-based membrane known as the graphene-based membrane was developed as an addition to the traditional carbon-based membranes. Materials made from graphene for example graphene oxide and graphene attract various attentions over the past five years in the area of separation science especially in ion-selective transport, gas separation and water desalinization [34, 35]. A complete review of graphene-based membranes as well as their consequences in molecular separation was published recently [36]. In theory, materials of graphene-based are excellent candidates in the fabrication of separation membranes due to their inherent features such as great mechanical strength, single-atom thickness as well as good chemical stability [4, 37]. Conversely, it was proven by the study that perfect graphene is resistant to all liquids and gases [38, 39]. Hence, it is required for pores with appropriate shape and size to be drilled in order to reach selective gas permeation.

Various chemical and physical techniques were implemented in generating pores on graphene sheets over the previous years for example helium ion bombardment, laser irradiation, steam etching and electron beam irradiation [40]. In general, modifying the dose of electron or ion could tune the pore size of porous graphene prepared via physical techniques whereas porous graphene prepared through chemical techniques have a comparatively small distribution of size [37]. In recent events, development of a scalable and general fabrication technique for porous graphene was done through carbonization reaction of graphene oxide imprinted by metal oxide particles produced from polyoxometalates (POMs) and oxometalates (OMs) [41]. The pore size could be altered within the range of 1-50 nm in this technique by controlling the metal oxide particles' size. Likewise, preparation of nitrogen-doped porous graphene can also be done utilizing ammonium group-containing POMs and OMs. Additionally, Wang and co-workers have developed high porosity large-scale porous graphene membranes with small distribution of pore size [42]. These characteristics indicate porous graphene-based membranes as having the ability to display a conclusive resistant feature of gas and liquid. However, the pore size produced according to these two scale-up techniques might be too huge for application on the separation of small gas. According to the high selectivity for H_2/CO_2 separation, accurate control of the pore size need to be done according to the angstrom scale.

3. Molecular-sieving transportation

Unlike many membranes where flaws could lead to major separation performances deterioration, inhernet structural flaws within graphene oxide flakes could act as molecular-sieving transportation means. Development of thin graphene oxide membranes was done on anodic aluminium oxide supports through the vacuum filtration technique by Lee et al. (2006) and the thickness of the membrane can be altered by modifying the dispersion solutions concentration of graphene oxide [43]. This work proposed for the H_2 predominant transport route to be discerning towards structural imperfections within graphene oxide flakes where CO_2 will not be able to permeate across with negligible gas transportation in interlayer area between the graphene oxide flakes. Nevertheless, Kim et al. speculated a contrasting conclusion stating that the permeated gas not only causes imperfections but also causes spacing between graphene interlayers [44]. Major advancement in gas separation for membranes of graphene-based was accomplished over the previous years. Conversely, mechanism of gas transport via porous membranes of graphene-based continues to be elusive. Numerous researchers ventured to investigate the mechanism of gas transport utilizing various simulation techniques [39, 45].

Regular gas separation membranes mechanisms of gas transport might not be appropriate for porous graphene membranes having a thickness of a single-atom, whereas the commonly received perspective is gas molecules permeation via porous graphene membranes is nearly associated to transportation rate to the surface as well as molecular adsorption on the graphene sheet surface including size and pores functionalization [46, 47]. Up till now, perfect theory in explaining transportation properties of gas in membranes of graphene-based is still in non-existent, which may lead to guideline deficiency in designing high-performance membranes of graphene-based. In overall, a very good quality porous graphene fabrication, highly selective flaws generation, and gas transport mechanism study in graphene-based membranes are the main concerns in the membranes of graphene-based development for gas separation.

4. Conclusion

The separation and purification of gas mixtures by separation is an important unit operation in the chemical and petrochemical industries. The demand of products with high purity has increased and, therefore, attention has focused on separation processes. These CMS have some advantages over molecular sieve zeolites, including shape, selectivity for planar molecules, higher hydrophobicity, and higher resistance to both alkaline and acid media and thermal stability at high temperatures. CMS are prepared from a wide variety of carbonaceous raw materials, using a range of different procedures, although commercial CMS are mainly manufactured from activated carbons following deposition of pyrolytic carbon at the mouth of the pores, to “fine-tune” entrance dimensions.

Acknowledgement

Authors would like to extend their gratitude to Ministry of Higher Education Malaysia and Universiti Malaysia Pahang (UMP) with grant number RDU180317.

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