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PI/NCC- based carbon molecular sieve membranes for Hydrogen purification: Effect of aging times

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Abstract. In this study, the effect of stabilization temperature on the performance of tubular carbon Upgrade the gas separation performance of the resultant carbon molecular sieve (CMS) membrane, a synthesized nanocrystalline cellulose (NCC) utilizing tissue paper as an added substance was included into the simpleton arrangement at pyrolysis temperatures of 800°C. This paper shows the inference of CMSs from BTDA-TDI/MDI polyimide (PI) arranged by means of a dip-coating strategy on an inorganic cylindrical help surface, trailed by a heat treatment (adjustment and carbonization) under Ar gas stream. Extraordinary consideration was given to the physicochemical attributes of the subsequent PI/NCC-based CMS and its comparing gas permeation properties. Pure gas permeation tests were performed utilizing H₂, and N₂ at room temperature. The gas permeation information showed that the CMS displayed an amazing performance contrasted with the polymeric membrane. Upgrade in the two gas permeance and selectivity were watched arranged with fresh CMS membrane, with H₂/N₂ selectivity of 434.68±1.39, regarding the neat CMS. By controlling different aging times (fresh, 1 day, multi week, and 3 months), CMSs with various structures and properties were gotten.

Keywords: Carbon molecular sieve (CMS), Aging times, P84 co-polyimide, nanocrystalline cellulose (NCC), hydrogen purification.

1. Introduction

Considered as a perfect and productive energy bearer, hydrogen (H₂) can be truly conceivable to diminish the mounting worldwide energy and natural fiasco [1-3]. Hence, coming about H₂ got a regularly expanding interest. So as to satisfy the top-notch hydrogen item, creating productive hydrogen cleaning innovations is vital. This was no other because of the consumption of non-inexhaustible fossil assets, along these lines bringing the consideration up in green H₂ generation. Besides, the hydrogen burning does not discharge CO₂, as of those petroleum derivatives [3, 4]. Hence, H₂ as an elective fuel may guarantee in not so distant future. The gas offers the security in vitality supply and additionally lessening the creation of CO₂, in which is the primary giver toward environmental change. Be that as it may, H₂ does not exist normally the most. Roughly 80 % of H₂ is created from steam improving of flammable gas [5, 6]. To acquire high virtue H₂, the item from this procedure requires future sanitization. Since the contaminant of the item stream ordered as quick gas, an appropriate filtration treatment is important to answer this issue.

Since the membrane innovation is a generally new and quickly developing, it has basic advantages in three imperative regions, for example, energy proficient, monetarily powerful, and to wrap things up ecologically agreeable contrasted with the customary separation advances [7, 8]. Moreover, this innovation likewise can be combined with different procedures to improve the performance and productivity and financial aspects factor. To date, the membrane innovation was constrained in water separation just, as well as for vitality e.g. energy unit, and gas e.g. flammable gas improving, hydrogen recuperation from smelling salts cleanse gas, and air separation [9, 10] . As the interest of hydrogen continue developing thus the membrane innovation quickly developing that could reach to satisfy the



interest, membrane presently turn into an extremely encouraging innovation for hydrogen refinement. Taking preferences from positive advancement in materials science over ongoing years, some enhanced performance through auxiliary streamlining has officially experienced from ordinary membrane materials [11, 12]. Polymeric membrane is for the most part utilized membrane in mechanical process because of savvy and less energy concentrated. In any case, this membrane can't withstand unforgiving task condition, for example, high temperature, acidic condition that is looked amid hydrogen filtration from gaseous petrol steam transforming. Along these lines, it is fundamental to build up an elective membrane material to tackle the issue.

Inorganic membrane is a well-known technology for this issue, since the purification usually take place in a harsh condition in which the polymeric membrane cannot withstand [13]. The physical properties of inorganic membrane are tuneable as desired, which in this case the main factor is pore size. Light gas separation is generally suitable for microporous inorganic membranes with a pore diameter smaller than 2 nm and even less. The materials such zeolites, metal organic frameworks (MOF), and CMS membrane are widely studied molecular sieving materials that able to exceed the polymer performance limitation [14-16]. Among them, CMS membrane are the easiest membrane to fabricate. A CMS membrane can be described as polymeric membrane that received pyrolysis treatment at inert temperature to produce CMS. Among all studied polymeric precursor, polyimide and its derivatives are the most widely used precursors due to employ molecular sieving mechanism, high chemical and physical resistance [17, 18]. Moreover, the pore characteristic of this membrane is mainly controlled toward pyrolysis condition.

For optimum activity, particularly in mechanical use, the dependability of CMS membrane is imperative since it is identified with the membrane recovery and operational expense. Be that as it may, the work that concentrating on the security of CMS materials is moderately low [13, 18-20]. Incompletely because of the inflexible idea of CMS membranes and their upgraded concoction and heat obstruction contrasted with polymeric materials are fundamental properties that the solidness of a membrane was missing of consideration. So as to advance the utilization of CMS membrane in task, for example, Hydrogen filtration, it is really imperative to perceive the operational security of CMS membranes.

2. Experimental section

2.1 Materials

PI ($\rho = 1.31 \text{ g/cm}^3$, $T_g = 315 \text{ }^\circ\text{C}$) was supplied by Sigma Aldrich. N-methyl-2-pyrrolidone (NMP) was obtained from Merck Millipore. In this study, NCC was synthesized from recycled paper. The experimental work involved in the synthesis of NCC was briefly explain by previous study [21] whereas a porous tubular ceramic (TiO_2) support (length = 8 cm, thickness = 3 mm, pore size = $0.2 \text{ } \mu\text{m}$, porosity = 40-50%) was procured from Shanghai Gongtao Ceramic Co., Ltd as tabulated in Figure 1. All the tubular alumina ceramic supported were polished utilizing SiC paper and cleaned with distilled water in a sonication bath for 30 min and then dried in air to remove any dust and unnecessary particles that can influence the final results.



Figure 1: Ceramic tube supports

2.2 Dope Preparation

15 wt.% of PI was dissolved in NMP under constant stirring at 80°C , followed by a gradual addition of 7 wt.% of NCC. The solution was used to form a uniform membrane of polymeric precursor over the

external surface of the tubular support as reported in our previous study [22]. The dope solution was stirred for 24 hours and followed by sonication for degassing purposes.

2.3 Formation of tubular polymeric precursor membranes

The supported polymeric membranes were prepared via dip-coating of the tubular support into PI/NCC dope solution for 45 minutes, followed by drying at 80 °C for 24 hours in an oven. Subsequently, the membranes were equilibrated in methanol for 2 hours before finally being dried at 100 °C for 24 hours.

2.4 Formation of CMSs

The porous tubular ceramic alumina was coated via the dip-coating method using PI/NCC dope solution. The tubular then dried in an oven overnight at 80 °C before it was heat treated in Carbolite's horizontal tubular furnace. Before carbonization, the polymeric membranes were stabilized at 300 °C for 30 min under 200 ml/min Ar gas flow at a constant heating rate of 3 °C/min. The purpose of the stabilization stage is to avoid the melting of the membrane when it undergoes the carbonization stage. Later, the stabilized membranes were carbonized at 800 °C for 30 min with the sweeping of 200 ml/min flowing Ar at a heating rate of 3 °C/min. After cooling, four samples at different aging stages were prepared by manipulating aging time ranges (fresh, three days, one month, and three months), respectively.

2.5 Pure gas permeation test

As described in our previous study [23], the performance test of CMS membranes was conducted by using gas permeation system. In this system, 8cm of CMS membrane had been placed in 14cm stainless steel tubular module. The leakage of the tubular membranes during housing within the module can be prevented by using rubber O-rings. Pure gas H₂ (0.289 nm) and N₂ (0.364 nm) were fed individually into the module at 8 bars (trans membrane pressure). The permeance, *P/l* (GPU) and selectivity, α of the membranes were computed by employing the equations below:

Permeance, *P*:

$$(P/l)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{\eta \pi D l \Delta P} \quad (1)$$

Selectivity, α :

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

where *P/l* is the membrane permeance, *Q_i* the gas *i*'s volumetric flow rate of at standard temperature and pressure (cm³ (STP/s), *p* the difference in pressure between the feed the permeation side of the membrane (cmHg), *A* the area of membrane surface (cm²), *n* the fiber quantity in module, *D* the membrane's outer diameter (cm), and *l* the membrane's effective length (cm). The selectivity is defined as the permeation ratio of fast gas permeation to slow gas permeation.

3. Results and discussion

3.1 Gas Permeation Measurements

In gas separation, the performance of a membrane on how well it performs is dictated by these two principle parameters, penetrability and selectivity. In a perfect world, an ideal CMS membrane is to have high porousness and selectivity. In this examination, it is seen that expanding aging time bringing about diminishing the penetrability and selectivity. Moreover, the term of perfect selectivity is closely resembling diffusivity selectivity. It is as of now clarified in the arrangement dissemination show that perfect selectivity is the result of solvency selectivity and diffusivity selectivity [1, 27, 28]. Subsequently, we can presume that the adjustment in diffusivity selectivity control the selectivity of polymeric membrane because of physical aging. **Table 1** displays the gas separation characteristics of both polymeric and PI/NCC-based CMSs. PI/NCC CM that was freshly prepared showed high H₂/N₂

selectivity (434.68) thus revealing high N₂ (3.22) and H₂ (1399.66) fluxes. Similar to conventional glassy polymers, physical aging also happens to CMS, especially the ones made up of precursors with high free volume. The findings proved that the transport properties of CMS can be significantly influenced by factors like the glass composition, the membrane preparation conditions, the membrane dimension and the operating parameters used to investigate its properties [29-31]. Physical aging is not just subjected to tubular membranes but also occurs in flat sheet membranes. Symmetric morphology of the membrane offers simplicity as it can show physical aging phenomenon in CMS better than the more complex asymmetric structures.

Table 1: Gas permeation performance of PI/NCC Polymeric and PI/NCC CMS membranes produced from different aging times

Sample	CMS membrane		
	Permeance		Selectivity
	N ₂	H ₂	H ₂ /N ₂
PI/NCC Polymeric membrane	0.70 ±1.54	50.77±3.4.51	72.53±2.13
PI/NCC CMS fresh	3.22±3.21	1399.66±5.22	434.68±1.39
PI/NCC CMS 1 day	2.61±2.86	755.96±2.19	289.64±1.25
PI/NCC CMS 1 month	1.94±3.27	487.46±3.22	251.29±2.76
PI/NCC CMS 3 months	1.79±1.74	299.31±2.63	167.21±2.73

A fast decrease of porousness in the span of roughly 30 days is utilized to portray and record the underlying stage, which can be later used to assess overabundance non-balance free volume. At the accompanying stage (some time ago known as "aging knee"), a continuous porousness decrease occurs at slower rate as the aftereffect of the change of "characteristic" miniaturized scale porosity [31, 32]. In conclusive stage, the porousness turns out to be slower as the versatility of CMS chains is progressively limited contrasted with in their shiny states. Already, analysts recommended that aging in various forerunner determined CMS membranes was expected to either oxygen, water or natural adsorption. Along these lines, oxygen chemisorption could be the reason of permeance decrease in barometrical capacity, as detailed in present work, however it isn't following the fundamental conduct of the membrane put away in vacuum. As opposed to in air condition, a wide range of adsorption would be unimportant in vacuum condition. In this way, the membrane would not experience aging, thus saving its common state. It is estimated that physical aging happens in CMS membranes equivalent to in polymeric membranes [29, 30].

Wonder of aging can cause the decline of gas permeability. Likewise, it might likewise generally lessen the selectivity of quicker gas contrasted with slower gas. In 3 months' time, CMS membranes manufactured in comparable conditions demonstrated a decreased performance notwithstanding having conflicting starting separation performance. The adsorbed water responded with the dynamic destinations of PI/NCC CM membrane to frame oxygen useful gatherings which later limit the pore estimate [24, 33]. To guarantee this kind of membrane is obvious from the adsorbed gases, a persistent clearing is required before gas permeation test. Regularly, it is urgent to utilize a similar testing convention and truly balance out the membranes earlier testing to get astounding gas permeation. Other approach to accomplish a relentless rate of permeation without enough departure process is by checking the expanding rate of downstream weight. To do that, data, for example, the time slack must be known, else it would be exceptionally hard to foresee the length required for the procedure. The span required could likewise be resolved to look at between the tests for blended gas and pure gas. Before each pure gas test, a sufficient departure process is required as the membrane encounters aging. On account of unstabilized membrane, the permeation tests for pure gas are directed independently on various membrane tests to guarantee information precision. It turns out to be progressively hard to think about the permeation consequences of pure gas and blended gas. This is a direct result of the pretended by the aging procedure between pure gas tests and rivalry impact. All things considered, permeation test utilizing blended gas is by a wide margin progressively dependable as it mirrors the genuine use conditions with right estimation of the membrane transport properties [34, 35].

Other than physical aging, different elements adding to CMS membranes aging are water vapor

adsorption, natural adsorption, oxygen chemisorption [36]. In vacuum condition, the diminish of porousness can't be respected to water or oxygen adsorption as they were missing in the framework. There was an inclination for the vacuum pump oil vapor to diffuse into the membrane regardless of being secured with alumina foreline trap. The contention is aging was not caused by natural adsorption but rather the synthetic concoctions from vacuum pump oil, with wasteful recovery technique. To affirm the legitimacy, another test was directed under surrounding conditions without the utilization of vacuum pump. There was a huge decrease of CMS membrane selectivity after a long capacity span under idle gas condition. In their early state, CMS membranes are firmly reliant upon outside factor i.e. temperature, environmental conditions [26, 37]. Whenever misused, unwanted attributes of membrane would be acquired with conflicting outcomes. Process like adjustment can unquestionably impact the membrane division performance. Without considering the history reliance highlight of CMS membranes, they are known for their high unbending nature and strength with time. To dispose of the conceivably adsorbed substances, the feed and penetrate sides of the membrane are right to firstly emptied [38,39]. This procedure may guarantee the membrane to accomplish relentless state properties. This could legitimize the distinction of qualities estimated by different testing conventions.

4. Conclusion

The effects of differing aging times on PI/NCC CMS membrane have been considered. It was discovered that the membrane pores ended up littler at longer aging time as they will in general shrink after some time to end up thermodynamically stable condition. Furthermore, CMS membrane with the most limited aging time displayed high H₂/N₂ selectivity (434.68) with high N₂ (3.22) and H₂ (1399.66) motions.

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