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Fabrication of Interlayer-free P123 Caronised Template Silica Membranes for Water Desalination: Conventional Versus Rapid Thermal Processing (CTP vs RTP) Techniques

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Abstract. This work demonstrates the comparison techniques between conventional and rapid thermal processing (CTP Vs RTP). It is to fabricate the interlayer-free P123 carbonised template silica membranes. The aim of this work is to understand the performance of fabricated membranes for water desalination. The silica sols pH 6 were prepared from a two acid-base catalyzed sol gel method by applying tetraethyl orthosilicate (TEOS) as the precursor. Triblock copolymer of Pluronic P123 was used as the templating agent and mixed homogenously with silica sols. The mixtures were calcined in two method called CTP and RTP. CTP is a slow calcination and takes 4 hours with 1 $^{\circ}$C min-1 for dwelling time. On the other hand, RTP is rapid technique calcined in air (1 h without dwelling time). CTP confirms higher surface area (50 % higher), porosity (34 % higher) and thinner (60 %) than RTP. RTP technique is supposed to save time, energy and cost during membranes fabrication.

1. Introduction

Main problems which mostly facing in developed country especially is water scarcity. Portable water would be hard to get due to high population of citizen. Membrane technology can be alternative option to desalination application. It have some advantages such as does not need chemical addition, high selectivity and save more cost production [1].There many types of membrane material widely used for desalination, such as organic by PSf (Polysulfone) [2, 3], and inorganic membrane using zeolite [4] and silica [5-7].

Lately, most common material which often get attracted in many studies is silica. The silica membranes give a good performance [8, 9], thermal stability [10] and good molecular sieving properties that contribute to obtained high performances in desalination. However there is drawback of silica because the hydrophilic reacts with water and can resulting poor performance [11].

Some studies have been reported to improve silica ability material for water treatment including carbon template [11, 12], hybrid organic-inorganic [7] and metal oxide embedded [13].

Recently, for the first time Elma, Wang [5] are prepared TEOS-P123 templated (Tetraethyl orthosilicate-Triblock Copolymer of Pluronic) without interlayer. Whereas other works introduce smooth support with required interlayer coupled with many thin films at the top layer. Indeed, interlayer-free can reduce membrane thickness and offered higher water flux. But these process spend

long of time production as known conventional thermal processing (CTP) with slow calcination and 1 ^{o}C min^{-1} for dwelling time [11]. Hence, rapid thermal processing (RTP) could be an option in terms of saving time because during calcination, there is no need dwelling time [14]. In this work we demonstrate the comparison between CTP and RTP method to produce interlayer-free P123 carbonised template silica membrane.

2. Methods

2.1. Materials, Xerogel Preparation and Characterisation

The synthesized of silica sols by a dual acid-base sol gel method have been done as to previous research of Elma, Wang [5], Elma, Wang [15]. Tetraethyl orthosilicate (TEOS, 99.0 %, Sigma-Aldrich) as precursor of silica was added drop wise ethanol (EtOH, 99 %) and stirred for 5 min in cold condition at 0 ^{o}C to avoid hydrolysis reaction followed by addition of (0.00078 N HNO$_3$, Merck) and refluxed for 1 h at 50 ^{o}C. Diluted of (0.0003 N NH$_3$, Merck) was added drop wise into the silica sols and stirred for 2 h at the same condition. The pH sol was adjusted to pH 6 ± 0.1 by dual catalyst. After that, the templating agent that used is P123 (triblock copolymer Pluronic, Sigma-Aldrich) was added into silica sol. The silica-P123 sol was conducted with the final molar ratios is the TEOS:EtOH:H$_2$O:NH$_3$:HNO$_3$:P123 sol were calculated to be 1:38:5:0.00008:0.0003:x, where x was varied of pectin concentration such as reported in [5]. In this research we choose the optimum molar ratio of P123 from our previous research [5] of P123-35 (35 %) for calcined at 350 ℃ in vacuum with CTP technique. Then, for the RTP technique with the same concentration that calcined in air at the same temperature. The final molar ratio is the TEOS:EtOH: HNO$_3$:H$_2$O:NH$_3$:P123-35 sol were calculated to be 1:38:0.0008:5:0.0003:0.00024.

The silica-P123 sol was dried into oven at 60 ℃ for 24 h to obtain the dried gel then grounded into powder and calcined in air condition at 450 ℃ for 4 h (CTP technique) with 1 ℃ min^{-1} of ramping and cooling rates in a furnace and 1 h at 350 ℃ (RTP Technique) with no ramping rates. The vibrational bands and peak wave of silanol, siloxane and carbon was measured by FTIR at wavelength range 400-4000 cm^{-1}, to performing of FTIR spectra deconvolution by using the Fityk computer program with Gaussian peak fitting as the preferred curve. The specific surface area also measured and was determined from Brunauer, Emmett and Teller (BET) method.

2.2. Membrane Fabrication and Characterisation

Silica-P123 thin film were coated four times directly onto macroporous alumina substrates (α-Al2O3 tubular support (Ceramic Oxide Fabricators, Australia)) via dip-coating process with dwelling time of 2 min and dipping and withdrawl rate of 10 and 5 cm min^{-1}, respectively. Then the membrane layer was dried into an oven then calcined in a furnace for 4h per layer (for CTP) and 1 h per layer (for RTP) at 350 ℃. the total layers of membrane is 4 layers. The membrane morphology and thickness were characterized by SEM (Scanning Electron Microscopy), FESEM JOEL 7001.
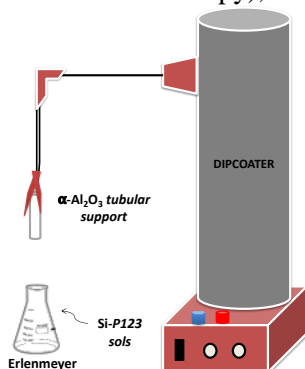

Figure 1. Dip-coating set up in membrane fabrication

3. Results and Discussion

3.1. Xerogel Characterisation

As shown at Figure 2 (a) shows that silica-P123 calcined by RTP technique was higher vibrational bands at wavelength 600-1400 cm^{-1} than with CTP technique. The peak of siloxane bridges (Si-O-Si) was assigned at 1070 cm^{-1}, silanol groups at 960 cm^{-1} and then Si-C at 800 cm^{-1}. The copolymer P123 here has a function as carbon templated that changes the Si-O-H bonds to Si-C. A carbon that contains in P123 is replacing a hydrogen that bonds with silica. As can be seen at Figure 2 (b) the peak area ratio between Si-OH against Si-O-Si shows the lowest one is P123 with RTP techniques. The highest ratio of Si-OH against Si-O-Si indicate the silanol contain in network was higher than siloxane and vice versa. The lowest peak area ratio could be explained that the Si-OH was replaced as Si-O-Si bridges or new bonding of Si-C [16]. So, it suggested that the silica-P123 using RTP technique is more hydrophobic rather than silica-P123 via CTP. The similar results were reported by Yang, Elma [7] that fabricated silica-carbon membrane from TEOS-TEVS-P123, then Saputra, Astuti [16] that synthesized silica thin film from inorganic-organic materials of TEOS and DMDMS. Both of that research obtain the hydrophobic materials.

Meanwhile, if we compare both of membranes that calcined via RTP and CTP, the membrane with RTP technique is higher although the concentration of P123 was same. That happened because the different condition of calcination included of calcine temperature and method of carbonisation. P123-CTP was calcined in vacuum condition at 450 °C of calcine temperature, whereas the P123-RTP was calcined in air at 350 °C. These condition was affected to the bonding in silica-P123 matrices and of course on the membrane surface. Ibrahim, Nagasawa [17] reported that calcination under air could improve the hydrophilicity. However, from different literature reported the peak ratio of Si-H groups was lower when membrane calcined under air atmosphere. Especially at lower temperature that caused the oxygenation of Si-H groups were started coincide with the forming of Si-OH groups [18]. That's why the membrane calcined under air condition via RTP contains more Si-O-Si bridges and Si-C bonds.
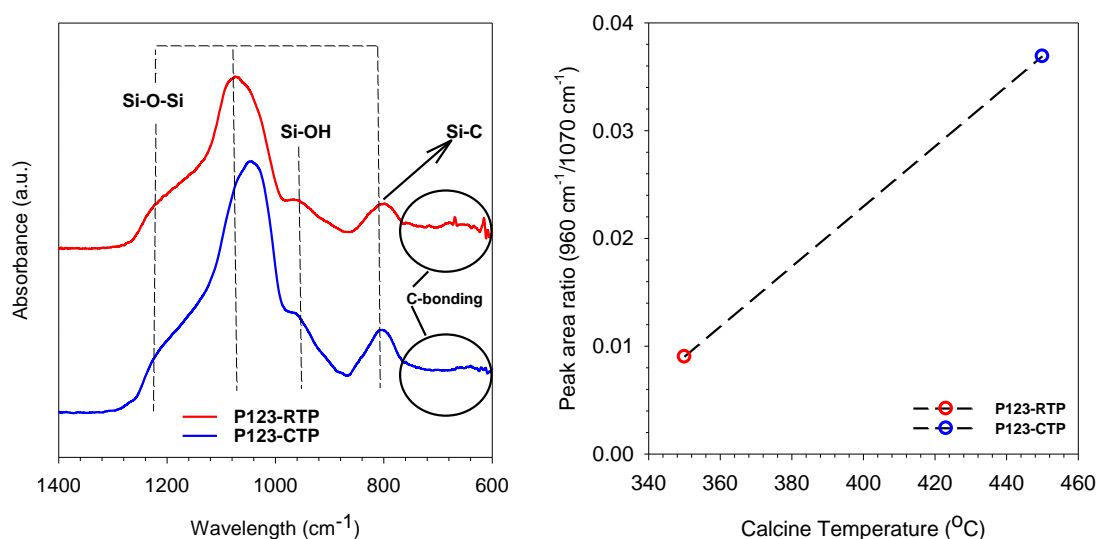

Figure 2. (a) FTIR spectra of xerogels calcined in air by CTP and RTP technique (b) peak area rations between silanol (960 cm^{-1}) and siloxane (1070 cm^{-1})

Furthermore, the surface area and pore properties were analyzed by N2 sorption as can be seen at Figure 3 that shows the differences hysteresis of both silica-P123 membrane. The P123-CTP sample started hysteresis at 0.40 p/p°. While the P123-RTP the hysteresis occurred at relative pressure

approximately 0.45 p/p°. The results categorized all membrane as mesoporous structures as synchronized to pore size as shown at Table 1. If compare of both xerogels, the sample that prepared via CTP techniques has a higher surface area, although the pore volume and pore size for pure silica were similar [19]. This could be explained due to the CTP techniques can lead to forming the close till dense network in silica matrices as the function of time of calcination. The samples were calcined under vacuum for 4 h per layer then via RTP techniques is faster only spend 1 h per layer. A long time of calcination influence the carbonization of carbon chains and the evaporation will done well and avoid to thermal stress. However, this work contrary to Wang, Wang [14], Wang, Wang [20] that reported the higher surface area can achieved via RTP. This could be happened due to the different of water molar ratio used in this work and different material of silica precursor that they used ES40. However, the dual catalyst using in this work makes the mesoporous structure that able to membrane fabricated for desalination.
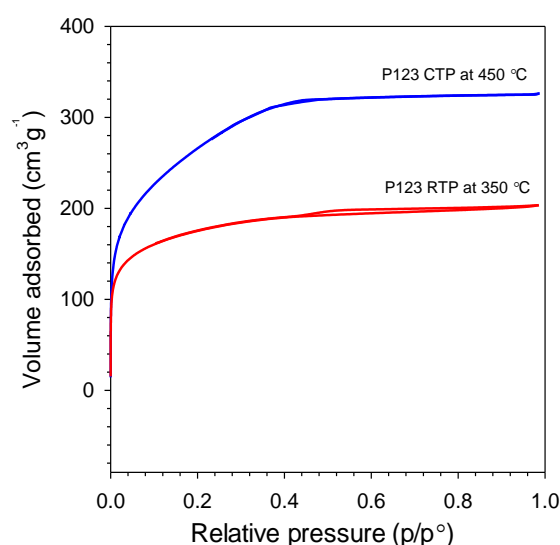

Figure 3. N_2 sorption of xerogels in air condition by CTP and RTP techniques

Table 1. Surface properties of bulk xerogels calcined in air

Membrane type	BET surface area ($m^2.h^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Average pore size (nm)	Thickness (nm)	References
Silica-P123 calcined in air at 350 °C by RTP	572	0.31	2.21	~1000	This work
Silica-P123 calcined under vacuum at 450 °C by CTP	965	0.50	2.31	~400	[5]

3.2. Membrane Morphology

The effect of different condition of vacuum and air calcination must be concerned. The xerogel sample calcined under vacuum condition that led to slight densification of silica structures. Elma, Wang [5] prove that the highest decomposed of carbon was obtained in calcination under air than under vacuum or N_2 atmosphere particularly at high temperature. The carbon templated of P123 is retained in the networks by calcine under N_2 and vacuum calcination. The materials calcined under vacuum condition were more hydrophobic due to the higher carbon retained in the carbon–silica matrices [7], opposite to calcination under air. As shown at Figure 4 the surface and cross section of membrane calcined via CTP and under vacuum condition there is no defect films formation on the top of the substrate that suggested the sol-gel infiltrated into porous substrate. The vacuum pressure opposed the capillary stresses during the calcination process that caused to dense pore of film matrices. On the other hand,

RTP SEM image in air condition led to wide spread of cracks on top film like shown on Figure 4. It is because RTP technique calcined in air without dwelling and cooling rate time, so it suggested cause of thermal stressing.
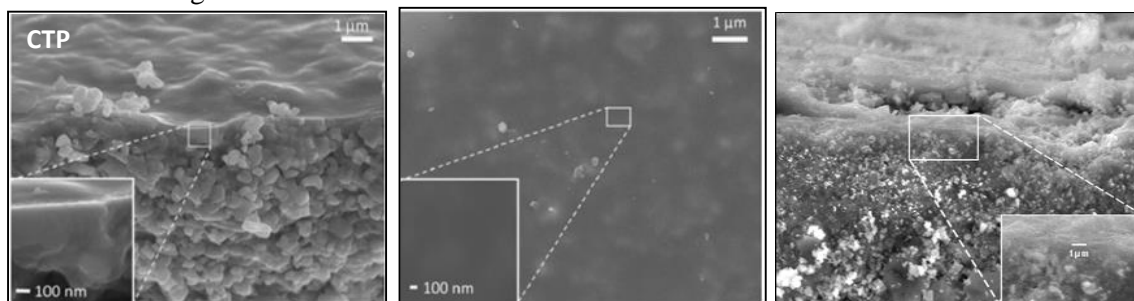

Figure 4. P123 CTP technique at 450 °C (vacuum) and P123 RTP technique at 350 °C (air) SEM image respective

Li, Chen [21] was reported the calcination under air in high temperature can enhanced the shrinkage. The decomposition some materials such as carbon can be happened with the significant effect if calcine in air (with the oxygen presence). Ibrahim, Nagasawa [17] also reported in BTESE membrane that calcine under N_2 gas atmosphere showed low weight loss compared calcine in air that explained the calcine method with N_2 was slow decomposition of the organic bonds and makes the structure more rigid. **Figure 5** shows the illustration of carbon chains bonding in silica matrices. There's different carbon chains consist in multiple techniques (CTP and RTP). The membrane that calcined via CTP has more carbon chains rather than RTP techniques. The higher carbon chains in silica network could improve mechanical properties that makes these material more strengthen [5]. So that gained best desalination performance of membrane.
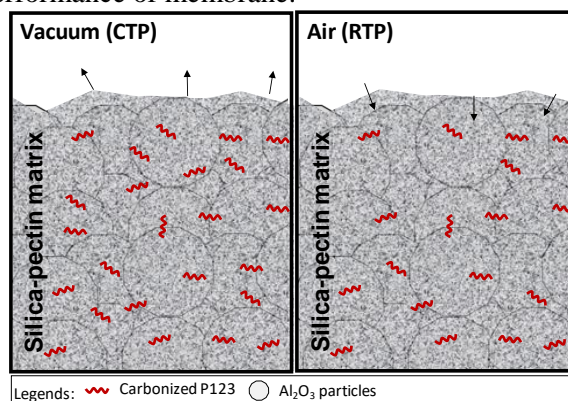

Figure 5. Illustration of carbon chains connected to Al_2O_3 particles of mesoporous alumina support for silica-P123 membrane calcined via CTP and RTP

4. Conclusion

The different of membrane fabrication technique have crucial affect toward of membrane characterisation obtained. Comparison technique between conventional and rapid thermal processing (CTP Vs RTP) for fabricate the interlayer-free P123 carbonised template silica membranes was conducted in this work. RTP results in great reducing time fabrication less than 1 day over CTP technique. Whereas CTP is a slow calcination and takes 4 hours with 1 °C min^{-1} for dwelling time. In other hand, CTP confirms higher surface area (50 % higher), porosity (34 % higher) and thinner (60 %) than RTP. RTP technique is supposed to save time, energy and cost during membranes fabrication.

Acknowledgement

References

[1]   Ahmad SA. Hybrid Process (Pervaporation- Distillation): A Review 2012.

[2]   Ba-Abbad MM, Mohammad AW, Takriff MS, Rohani R, Mahmoudi E, Faneer KA, et al. Synthesis of Iron Oxide Nanoparticles to Enhance Polysulfone Ultrafiltration Membrane performance for Salt Rejection. *Chem. Eng. Trans.* 2017;**56**:1699-704.

[3]   Ahmad A, Yunos MZ, Harun Z, Hassan MF, Adzila S, Arifin AMT, et al. Effect of Polyaniline on Surface Properties of Polysulfone Membrane. *Chem. Eng. Trans.* 2017;**56**:691-6.

[4]   Drobek M, Yacou C, Motuzas J, Julbe A, Ding L, Diniz da Costa JC. Long term pervaporation desalination of tubular MFI zeolite membranes. *J. of Mem. Sci.* 2012;**415-416**:816-23.

[5]   Elma M, Wang DK, Yacou C, Costa JCDd. Interlayer-Free P123 Carbonised Template Silica Membranes for Desalination with Reduced Salt Concentration Polarisation. *J. of Mem. Sci..* 2015;**475**:376-83.

[6]   Elma M, Hairullah, Assyaifi ZL. Desalination Process via Pervaporation of Wetland Saline Water. *IOP Conf. Ser.: Earth and Environmental Science*. 2018;**175**(1):012009.

[7]   Yang H, Elma M, Wang DK, Motuzas J, Diniz da Costa JC. Interlayer-free hybrid carbon-silica membranes for processing brackish to brine salt solutions by pervaporation. *J. of Mem. Sci..* 2017;**523**:197-204.

[8]   Duke MC, Mee S, da Costa JCD. Performance of porous inorganic membranes in non-osmotic desalination. *Wat. Res*. 2007;**41**(17):3998-4004.

[9]   Elma M, Yacou C, Wang DK, Smart S, Diniz da Costa JC. Microporous Silica Based Membranes for Desalination. *Water*. 2012;**4**(3).

[10]   El-Feky HH, Briceño K, Jardim EdO, Silvestre-Albero J, Gumí T. Novel silica membrane material for molecular sieve applications. *Microporous and Mesoporous Materials*. 2013;**179**:22-9.

[11]   Wijaya S, Duke MC, Diniz da Costa JC. Carbonised template silica membranes for desalination. *Desal*. 2009;**236**(1):291-8.

[12]   Elma M, Wang DK, Yacou C, Diniz da Costa JC. Interlayer-free P123 carbonised template silica membranes for desalination with reduced salt concentration polarisation. *J. of Mem. Sci..* 2015;**475**(Supplement C):376-83.

[13]   Elma M, Wang DK, Yacou C, Motuzas J, Diniz da Costa JC. High performance interlayer-free mesoporous cobalt oxide silica membranes for desalination applications. *Desal*. 2015;**365**:308-15.

[14]   Wang S, Wang DK, Smart S, Diniz da Costa JC. Improved stability of ethyl silicate interlayer-free membranes by the rapid thermal processing (RTP) for desalination. *Desal*. 2017;**402**:25-32.

[15]   Elma M, Wang DK, Yacou C, Motuzas J, Costa JCDd. High performance interlayer-free mesoporous cobalt oxide silica membranes for desalination applications. *Desal*. 2015(365):308-15.

[16]   Saputra RE, Astuti Y, Darmawan A. Hydrophobicity of silica thin films: The deconvolution and interpretation by Fourier-transform infrared spectroscopy. *Spectr. Acta Part A: Mol. and Biomol.r Spect*. 2018;**199**:12-20.

[17]   Ibrahim SM, Nagasawa H, Kanezashi M, Tsuru T. Organosilica bis(triethoxysilyl)ethane (BTESE) membranes for gas permeation (GS) and reverse osmosis (RO): The effect of

preparation conditions on structure, and the correlation between gas and liquid permeation properties. *J. of Mem. Sci*. 2017;**526**:242-51.

[18] Kanezashi M, Sazaki H, Nagasawa H, Yoshioka T, Tsuru T. Preparation and gas permeation properties of thermally stable organosilica membranes derived by hydrosilylation. *J. of Mat. Chem. A*. 2014;**2**(3):672-80.

[19] Elma M, Yacou C, Costa CJDd, Wang DK. Performance and Long Term Stability of Mesoporous Silica Membranes for Desalination. *Membranes*. 2013;**3**(3).

[20] Wang S, Wang DK, Motuzas J, Smart S, Diniz da Costa JC. Rapid thermal treatment of interlayer-free ethyl silicate 40 derived membranes for desalination. *J. of Mem. Sci*. 2016;**516**:94-103.

[21] Li L, Chen M, Dong Y, Dong X, Cerneaux S, Hampshire S, et al. A low-cost alumina-mullite composite hollow fiber ceramic membrane fabricated via phase-inversion and sintering method. *J. of the Euro. Cer. Soc*. 2016;**36**(8):2057-66.