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Research article

Functionalization of hybrid organosilica based membranes for water desalination – Preparation using Ethyl Silicate 40 and P123 Materials Today: Proceedings, *In press, corrected proof,* Available online 31 January 2020 Sazila Karina Rahman, Maimunawaro, Aulia Rahma, Isna Syauqiah, Muthia Elma

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Deconvolution of carbon silica templated thin film using ES40 and P123 via rapid thermal processing method

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Abstract

This work aims to fabricate silica-P123 (Pluronic-123) xerogels and investigates the vibrational carbon groups of ES40-P123 xerogels using FTIR analysis and fityk software. In this work, ES40 (ethyl silicate 40) was used as the silica precursor, and P123 as the template agent. Meanwhile, HNO3 and NH3 take a role as acid and base catalyst. The combination of silica materials between of ES40 and P123 as an organic polymer was prepared via sol-gel process. The obtained of silica-P123 sol derived from ES40 was then dried at 33.15 K for 172,800 s which named xerogel. The molar ratio for ES40: ethanol: nitric acid: ammonia: aquadest: P123 were 1: 38: 0.0007: 0.003: 5: 0.0207, respectively. Rapid Thermal Processing (RTP) technique is favorable for calcination at 723 K for 3600 s. Then, FTIR analysis was applied to analyze the xerogel samples. The wavelength results were 800; 975; and 1080 (x10⁻² m⁻¹) for Si-C; Si-OH, and Si-O-Si, respectively. In addition, the area of pure ES40 for Si-O=9.21×10⁻⁵; Si-O-Si=1.0344×10⁻³; Si-C=8.28×10⁻⁵; and for ES40-P123 template were 9.51×10^{-5} ; 1.0264×10^{-3} ; 8.10×10^{-5} in m² unit. Hence, the peak area ratios of pure ES40 and ES40-P123 template were 0.089 and 0.093, respectively. It is clearly shown that the polymerisation by templating carbon groups into silica matrices was successfull and promising potential to apply in RTP technique as well as to then fabricate organosilica membrane for water desalination.

Keywords

ES40; Silica-P123 xerogels; Sol-gel process; RTP; Carbon-silica templated

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1. Introduction

The population growth and economic development cause the increasing demand of freshwater for over the past decades [1]. This condition become growing concern when in many countries lack access to have clean water, for examples; in the area in a great quantities of mining activities and salt intruding to the water source [2]. It should be handled so that the water scarcity could be solved.

Membrane technology become more popular and widely used in separation process, especially in water treatment. This technology has a faster process and there are no phase change during separation process. Silica materials especially combined with organic templates as well as surfactants have been reported as good hydrostability and molecular sieving membranes in desalination

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[3]. The other advantages, it does not need chemical addition, high selectivity and save more cost production [4]. Membrane material has many types which is widely used for desalination, such as organic by PSf (Polysulfone) [5,6], and inorganic membrane using zeolite [7] and silica [8–10].

However, the amorphous nature of the silica matrices consists of siloxanes (Si–O–Si) and silanols (Si–OH), of which the latter are hydrophilic and have been known to initiate the process of hydrolysis of siloxane groups via dissociative chemisorption of water molecules [11]. The matrices rapidly undergo severe densification and pore size widening as the consequence, which in turn changes flux and decreases selectivity within the first hour of membrane operation, especially at temperature above room conditions [12,13].

In this work, we report the effect of templating P123 into silica matrices ES40 using RTP method. The focus of work is to investigate the network representation during deconvolution process. Fityk software was used to understand the surface area of materi-

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als during vibration and stretching [14,15]. To get more detail, Infrared spectra had done to investigate functional group in silica matrices which is influenced by calcination. According to the previous work done by Elma, M [3,8], they improve the silica matrices with TEOS as the precursor and P123 as templating agent. They also need 86,400 s to obtain xerogel which is mean only a half drying duration of this work. Otherwise, as reported by Wang [16,17], they fabricated the pure ES40 but need a long time which is for over 172,800 s.

2. Methodology

A dual sol gel method was used to synthesized silica sol which is similar to the work done by Elma, M. [8,18]. But, the precursor of silica is different. This work use ES40 as precursor while the previous work used TEOS. Firstly, ES40 was added drop-wise to ethanol (EtOH, 99%) and then stirred for 300 s at 273.15 K condition. Subsequently, nitric acid solution (0.00078 N HNO3, Merck) was added, followed by stirring and refluxed for an hour at 323.15 K as shown at Fig. 1. After stirring, diluted ammonia (0.0003 N NH₃, Merck) was continuously added and stirred for another 7200 s. Next, P123 (Sigma Aldrich) was added into 5x10⁻⁵ m³ silica sols and stirred for 2700 s. The sols solution was cooled at room temperature, and was then dried at 333.15 K in the oven for 172800 s. The dried gel was grounded into powder and calcined at 723.15 K for 3600 s without applying ramping rate and dwelling time. The final molar ratio of this sols of ES40; ethanol; nitric acid; ammonia; aquadest; and P123 are 1: 38: 0.0007: 0.003: 5: 0.0207, respectively.

Silica xerogels were characterised by FTIR (Fourier transform infrared) spectroscopy to investigated the vibration bands and wavelengths of silanol (Si-OH), siloxane (Si-O-Si) and carbon group (Si-C). Wavelength range to generate spectra is 400–4000 $(\times 10^{-2} \text{ m}^{-1})$.

3. Results and discussion

The sol-gel method is one of the most simple and cost effective ways offering the flexibility to tailor the required porosity. Acid catalyst is added into sol gel procedure to hydrolyse ES40 to form silanol (Si-OH) groups, so that the reaction will help to form microporous structures in silica matrices [3,8,17]. It was then continued by adding base catalyst to continue condensation reaction and configurate siloxane (Si-O-Si) groups [8,16,17,19]. This NH₃ addition

literally manage that condensation reaction to form mesoporous structures. The both catalysts are taking a very important role in membrane fabrication and in desalination process. Silanol, siloxane and carbon groups are the chemical properties which were studied using FTIR. The existence of functional and bonding types in silica-P123 xerogel samples was investigated by FTIR. Meanwhile, to observe the peak deconvolution is using Fityk (curve-fitting) program based on Gaussian peaks.

Generally, ES40 as a silica precursor in sol gel reactions are related to hydrolysis reaction of alkoxides leading to the formation of silanol groups, otherwise, the condensation reactions leads to the formation of siloxane bridges [20–22]. Fig. 2 shows the representative FTIR spectra of xerogels of pure ES40 and P123 template which is calcined at 723.15 K. In the region of 1400–600 ($\times 10^{-2}$ m⁻¹), stretching modes are clearly showing that the bonds at 1080 ($\times 10^{-2}$ m⁻¹) and ~ 1218 ($\times 10^{-2}$ m⁻¹) are siloxane (Si-O-Si), whilst silanol (Si-OH) bonds appear near \sim 975 ($\times 10^{-2}$ m⁻¹). The stretching vibration of carbon is assigned at the peak near \sim 800 ($\times 10^{-2}$ m⁻¹). Although the peak is clearly shown for all xero-







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gel samples, the bending of ES40-P123 template was stronger than pure ES40. It is then called asymmetric stretching vibration and a bending of Si-O-Si (siloxane) group.

As depicted in Fig. 3, Fityk software is used to investigate the effect of carbon P123 addition to peak area. As presented by that figure, the peak area ratio of silanol groups versus siloxane groups (Si-OH/Si-O-Si) was analysed. The result shows the lower ratio for pure ES40 xerogel sample which has the same calcination temperature as ES40-P123 template xerogel sample (723.15 K). It was expected that in ES40-P123 template xerogel, the nitric acid as a carbon source was decompose at such temperature and remain silanol as well as siloxane in the silica matrices [8]. The highest area ratio of ES40-P123 template indicates the high surface area of silanol or seems that the bonding of Si-OH was higher than Si-O-Si. Otherwise, the lowest ratio of ES40 indicates the Si-OH bond was lower than Si-O-Si bond. The bonds are not only those Si-OH



Fig. 3. Peak area ratios between Si-OH /Si-O-Si and xerogel types.

Table 1

Peak area ratio Silanol vs Siloxane in several work.

No	Xerogels	Calcination temperatures (K)	Si-OH/Si-O- Si	Reference
1	Si-Pectin 0.1%	573.15	0.114	[23]
2	Si-Pectin 0.5%		0.095	
3	Si-Pectin 2.5%		0.068	
4	Si-Pectin 0.1%	673.15	0.116	
5	Si-Pectin 0.5%		0.072	
6	Si-Pectin 2.5%		0.107	
7	Pure ES40	723.15	0.089	This work
8	ES40-P123		0.093	
	35 wt%			

Table 2

Peak area using Fityk (curve-fitting) software calcined at 723.15 K.

and Si-O-Si, but there are also Si-C, $C\equiv C$, $C\equiv O$ or C-H bonds and usually not explained in briefly. However, the carbon chains' bonding in the silica-P123 materials were influenced by the temperature of calcination.

Table 1 shows the different optimum condition in each calcination temperatures. The higher calcination temperature, the quicker evaporation process. It then creates the matrices become dense. Meanwhile, at high calcination temperature might cause carbon decomposition easily [10,24]. This condition affects the formation of carbon become fewer up to null. Hence, the right/optimum calcination temperature is important to achieve the maximum results.

Table 2 shows the result of peak areas through deconvolution using Fityk software. The peak area ratio between Si-OH and Si-O-Si (Si-OH/Si-O-Si) for pure ES40 xerogel is also higher than ES40-P123 template xerogel, it is 0.089 and 0.093, respectively. The difference of calcination methods also contribute to the membrane thickness. RTP method duration is lesser than CTP (Conventional Thermal Processing). The duration is 3600 s/layer and 14400 s/layer for RTP and CTP, respectively. It makes the layer using RTP is thicker than using CTP due to the solvent might be trapped into silica matrices. The other benefit using RTP are time saving and efficiently where result is similar to CTP technique [10,17,25]. According to the work done previously by Wang [16], RTP technique creates water molecules being retained inside the xerogel pores at higher temperatures, thus favoring the condensation reactions and formation of siloxane bridges. Siloxane bridges and carbon chains in silica networks has been reported as it oppose the hydro-instability. According to FTIR analysis and curve-fitting peak area using Fityk, the concentration of nitric acid (HNO₃) used as catalyst has a tendency to crack if it continues to form thin film. It makes sense that the acid catalyst is usually added into sol gel procedure to hydrolyze ES40 to form silanol (Si-OH) groups. The addition of base catalyst (NH₃) continue condensation reaction and configure siloxane (Si-O-Si) groups, but it was not given the good area which measured through the Si-OH/Si-O-Si.

4. Conclusion

This work focuses on investigating the effect of P123 templated given into silica matrices of ES40 to fabricate material which applied for water desalination. The hydrophobicity properties of silica-P123 materials depend on the molar ratio of P123 concentration dissolved into silica mixtures and the homogenity of carbon templating agent dissolved in the silica mixtures. The wavelength results are 800; 975; and 1080 ($\times 10^{-2}~m^{-1})$ for Si-C; Si-OH, and Si-O-Si, respectively. For pure ES40 xerogel, the areas of Si-OH; Si-O-Si and Si-C are 9.21 \times $10^{-5};$ 1.0344 \times 10^{-3} and 8.28 \times $10^{-5},$ respectively and in m² unit. Those results are much higher than the areas of ES40-P123 template xerogel which have areas of 9.51×10^{-5} ; $1.0264 \times 10^{-3}; \, 8.10 \times 10^{-5}$ in m^2 unit for Si-OH; Si-O-Si and Si-C, respectively. Hence, it shows that the peak area ratio between Si-OH and Si-O-Si (Si-OH/Si-O-Si) for pure ES40 xerogel is also higher than ES40-P123 template xerogel, it is 0.089 and 0.093, respectively. P123 35 wt% is known as robust material due to the evaluation of functional groups. Despite of those result, the fabrication

Xerogel types	Area (m ²)	Area (m ²)			
	Si-OH	Si-O-Si	Si-OH/Si-O-Si	Si-C	
Pure ES40 ES40-P123 template	9.21×10^{5} 9.51×10^{-5}	$\begin{array}{c} 1.0344 \times 10^{-3} \\ 1.0264 \times 10^{-3} \end{array}$	0.089 0.093	8.28×10^{-5} 8.10×10^{-5}	

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of silica sols applying catalyst through sol gel process was successfull and promising potential application in desalination.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Membrane technology become more popular and widely used in separation process, especially in water treatment. This technology has a faster process and there are no phase change during separation process. Silica materials especially combined with organic templates as well as surfactants have been reported as good hydrostability and molecular sieving membranes in desalination

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water molecules [11]. The matrices rapidly undergo severe densification and pore size widening as the consequence, which in turn changes flux and decreases selectivity within the first hour of membrane operation, especially at temperature above room conditions [12,13].

In this work, we report the effect of templating P123 into silica matrices ES40 using RTP method. The focus of work is to investigate the network representation during deconvolution process. Fityk software was used to understand the surface area of materi-

[3]. The other advantages, it does not need chemical addition, high

selectivity and save more cost production [4]. Membrane material

has many types which is widely used for desalination, such as

organic by PSf (Polysulfone) [5,6], and inorganic membrane using

of siloxanes (Si-O-Si) and silanols (Si-OH), of which the latter

are hydrophilic and have been known to initiate the process of

hydrolysis of siloxane groups via dissociative chemisorption of

However, the amorphous nature of the silica matrices consists

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als during vibration and stretching [14,15]. To get more detail, Infrared spectra had done to investigate functional group in silica matrices which is influenced by calcination. According to the previous work done by Elma, M [3,8], they improve the silica matrices with TEOS as the precursor and P123 as templating agent. They also need 86,400 s to obtain xerogel which is mean only a half drying duration of this work. Otherwise, as reported by Wang [16,17], they fabricated the pure ES40 but need a long time which is for over 172,800 s whereas in this work we can produce xerogel within 172,800 s.

2. Methodology

A dual sol gel method was used to synthesized silica sol which is similar to the work done by Elma, M. [8,18]. But, the precursor of silica is different. This work use ES40 as precursor while the previous work used TEOS. Firstly, ES40 was added drop-wise to ethanol (EtOH, 99%) and then stirred for 300 s at 273.15 K condition. Subsequently, nitric acid solution (0.00078 N HNO₃, Merck) was added, followed by stirring and refluxed for an hour at 323.15 K as shown at Fig. 1. After stirring, diluted ammonia (0.0003 N NH₃, Merck) was continuously added and stirred for another 7200 s. Next, P123 (Sigma Aldrich) was added into 5x10⁻⁵ m³ silica sols and stirred for 2700 s. The sols solution was cooled at room temperature, and was then dried at 333.15 K in the oven for 172800 s. The dried gel was grounded into powder and calcined at 723.15 K for 3600 s without applying ramping rate and dwelling time. The final molar ratio of this sols of ES40; ethanol; nitric acid; ammonia; aquadest; and P123 are 1: 38: 0.0007: 0.003: 5: 0.0207, respectively.

Silica xerogels were characterised by FTIR (Fourier transform infrared) spectroscopy to investigated the vibration bands and wavelengths of silanol (Si-OH), siloxane (Si-O-Si) and carbon group (Si-C). Wavelength range to generate spectra is 400–4000 $(\times 10^{-2} \text{ m}^{-1})$.

3. Results and discussion

The sol-gel method is one of the most simple and cost effective ways offering the flexibility to tailor the required porosity. Acid catalyst is added into sol gel procedure to hydrolyse ES40 to form silanol (Si-OH) groups, so that the reaction will help to form microporous structures in silica matrices [3,8,17]. It was then continued by adding base catalyst to continue condensation reaction and configurate siloxane (Si-O-Si) groups [8,16,17,19]. This NH₃ addition

literally manage that condensation reaction to form mesoporous structures. The both catalysts are taking a very important role in membrane fabrication and in desalination process. Silanol, siloxane and carbon groups are the chemical properties which were studied using FTIR. The existence of functional and bonding types in silica-P123 xerogel samples was investigated by FTIR. Meanwhile, to observe the peak deconvolution is using Fityk (curve-fitting) program based on Gaussian peaks.

Generally, ES40 as a silica precursor in sol gel reactions are related to hydrolysis reaction of alkoxides leading to the formation of silanol groups, otherwise, the condensation reactions leads to the formation of siloxane bridges [20–22]. Fig. 2 shows the representative FTIR spectra of xerogels of pure ES40 and P123 template which is calcined at 723.15 K. In the region of 1400–600 (×10⁻² m⁻¹), stretching modes are clearly showing that the bonds at 1080 (×10⁻² m⁻¹) and ~1218 (×10⁻² m⁻¹) are siloxane (Si-O-Si), whilst silanol (Si-OH) bonds appear near ~975 (×10⁻² m⁻¹). The stretching vibration of carbon is assigned at the peak near ~800 (×10⁻² m⁻¹). Although the peak is clearly shown for all xero-



Fig. 2. FTIR spectra of the calcined silica xerogels.



Fig. 1. (a) Hydrolysis reaction; (b) condensation reaction.

gel samples, the bending of ES40-P123 template was stronger than pure ES40. It is then called asymmetric stretching vibration and a bending of Si-O-Si (siloxane) group.

As depicted in Fig. 3, Fityk software is used to investigate the effect of carbon P123 addition to peak area. As presented by that figure, the peak area ratio of silanol groups versus siloxane groups (Si-OH/Si-O-Si) was analysed. The result shows the lower ratio for pure ES40 xerogel sample which has the same calcination temperature as ES40-P123 template xerogel sample (723.15 K). It was expected that in ES40-P123 template xerogel, the nitric acid as a carbon source was decompose at such temperature and remain silanol as well as siloxane in the silica matrices [8]. The highest area ratio of ES40-P123 template indicates the high surface area of silanol or seems that the bonding of Si-OH was higher than Si-O-Si. Otherwise, the lowest ratio of ES40 indicates the Si-OH bond was lower than Si-O-Si bond. The bonds are not only those Si-OH



Fig. 3. Peak area ratios between Si-OH /Si-O-Si and xerogel types.

Table 1

Peak area ratio Silanol vs Siloxane in several work.

No	Xerogels	Calcination temperatures (K)	Si-OH/Si-O- Si	Reference
1	Si-Pectin 0.1%	573.15	0.114	[23]
2	Si-Pectin 0.5%		0.095	
3	Si-Pectin 2.5%		0.068	
4	Si-Pectin 0.1%	673.15	0.116	
5	Si-Pectin 0.5%		0.072	
6	Si-Pectin 2.5%		0.107	
7	Pure ES40	723.15	0.089	This work
8	ES40-P123		0.093	
	35 wt%			

Table 2

Peak area using Fityk (curve-fitting) software calcined at 723.15 K.

and Si-O-Si, but there are also Si-C, $C\equiv C$, $C\equiv O$ or C–H bonds and usually not explained in briefly. However, the carbon chains' bonding in the silica-P123 materials were influenced by the temperature of calcination.

Table 1 shows the different optimum condition in each calcination temperatures. The higher calcination temperature, the quicker evaporation process. It then creates the matrices become dense. Meanwhile, at high calcination temperature might cause carbon decomposition easily [10,24]. This condition affects the formation of carbon become fewer up to null. Hence, the right/optimum calcination temperature is important to achieve the maximum results.

Table 2 shows the result of peak areas through deconvolution using Fityk software. The peak area ratio between Si-OH and Si-O-Si (Si-OH/Si-O-Si) for pure ES40 xerogel is also higher than ES40-P123 template xerogel, it is 0.089 and 0.093, respectively. The difference of calcination methods also contribute to the membrane thickness. RTP method duration is lesser than CTP (Conventional Thermal Processing). The duration is 3600 s/layer and 14400 s/layer for RTP and CTP, respectively. It makes the layer using RTP is thicker than using CTP due to the solvent might be trapped into silica matrices. The other benefit using RTP are time saving and efficiently where result is similar to CTP technique [10,17,25]. According to the work done previously by Wang [16], RTP technique creates water molecules being retained inside the xerogel pores at higher temperatures, thus favoring the condensation reactions and formation of siloxane bridges. Siloxane bridges and carbon chains in silica networks has been reported as it oppose the hydro-instability. According to FTIR analysis and curve-fitting peak area using Fityk, the concentration of nitric acid (HNO₃) used as catalyst has a tendency to crack if it continues to form thin film. It makes sense that the acid catalyst is usually added into sol gel procedure to hydrolyze ES40 to form silanol (Si-OH) groups. The addition of base catalyst (NH₃) continue condensation reaction and configure siloxane (Si-O-Si) groups, but it was not given the good area which measured through the Si-OH/Si-O-Si.

4. Conclusion

This work focuses on investigating the effect of P123 templated given into silica matrices of ES40 to fabricate material which applied for water desalination. The hydrophobicity properties of silica-P123 materials depend on the molar ratio of P123 concentration dissolved into silica mixtures and the homogenity of carbon templating agent dissolved in the silica mixtures. The wavelength results are 800; 975; and 1080 ($\times 10^{-2}$ m⁻¹) for Si-C; Si-OH, and Si-O-Si, respectively. For pure ES40 xerogel, the areas of Si-OH; Si-O-Si and Si-C are 9.21×10^{-5} ; 1.0344×10^{-3} and 8.28×10^{-5} , respectively and in m² unit. Those results are much higher than the areas of ES40-P123 template xerogel which have areas of 9.51×10^{-5} ; 1.0264×10^{-3} ; 8.10×10^{-5} in m² unit for Si-OH; Si-O-Si and Si-C, respectively. Hence, it shows that the peak area ratio between Si-OH and Si-O-Si (Si-OH/Si-O-Si) for pure ES40 xerogel is also higher than ES40-P123 template xerogel, it is 0.089 and 0.093, respectively. P123 35 wt% is known as robust material due to the evaluation of functional groups. Despite of those result, the fabrication

Xerogel types	Area (m ²)			
	Si-OH	Si-O-Si	Si-OH/Si-O-Si	Si-C
Pure ES40 ES40-P123 template	$\begin{array}{l} 9.21\times 10^{5} \\ 9.51\times 10^{-5} \end{array}$	$\begin{array}{c} 1.0344 \times 10^{-3} \\ 1.0264 \times 10^{-3} \end{array}$	0.089 0.093	$\begin{array}{l} 8.28 \times 10^{-5} \\ 8.10 \times 10^{-5} \end{array}$

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of silica sols applying catalyst through sol gel process was successfull and promising potential application in desalination.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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