

Deconvolution of TEOS/TEVS Xerogel by Single or Dual Organic Catalyst Addition

Anna Sumardi^{1,2}, Muthia Elma^{1,2*}, Aptar Eka Lestari^{1,2}, Zaini Lambri Assyaifi^{1,2},
Adi Darmawan³, Isna Syauqiah¹, Erdina Lulu Atika Rampun^{1,2}, Yanti
Mawaddah^{1,2}, Linda Suci Wati^{1,2}

¹Chemical Engineering Department, Universitas Lambung Mangkurat (ULM)
Jl. A. Yani KM 36, Banjarbaru, Kalimantan Selatan 70714, Indonesia

²Materials and membranes Research Group (M2ReG), Universitas Lambung Mangkurat
Jl. A. Yani KM 36, Banjarbaru, Kalimantan Selatan 70714, Indonesia

³Chemical Engineering Department, Universitas Diponegoro, Semarang 50275, Indonesia

*Corresponding author: melma@ulm.ac.id

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Abstract

Currently, xerogel has been applied as a filtration material, especially in membrane desalination. However, the xerogel matrix structure for desalination have to be designed properly in order to allow rejection of salt and obtain good hydro-stability, thus, silica precursor in the form of TEOS (tetraethyl orthosilicate)/TEVS (triethoxy vinyl silane) and organic acid catalyst are suitable material for fabrication. The aim of this study is therefore to fabricate and perform deconvolution of TEOS/TEVS xerogel by adding single or dual catalyst, using FTIR (Fourier-transform Infrared Spectroscopy) and Fityk software. The xerogel was fabricated by dried silica sol and calcined using RTP technique (rapid thermal processing) at 450 °C. Prior to this fabrication, the silica sol was synthesized by sol gel method, using a mixture of silica precursor TEOS/TEVS, ethanol solvent, and varied addition of single catalyst (citric acid) as well as dual catalyst (citric acid + ammonia) for 2 hours, at 50 °C. Subsequently, the xerogel was characterized by FTIR and the deconvolution was obtained through Gaussian approach, with Fityk software. All TEOS/TEVS xerogel samples indicated existence of silanol (Si-OH), siloxane (Si-O-Si) and silica-carbon (Si-C) functional groups. The xerogel deconvolution of TEOS/TEVS using single catalyst exhibit a peak area ratio of Si-OH/Si-O-Si, and this is similar to the dual catalyst counterpart of 0.24 (unit area) and 1.86 (unit area), for Si-C area ratio. This shows the addition of single catalyst was enough to produce deconvolution in TEOS/TEVS xerogel, dominated by siloxane functional group and carbon bonds with the ability to enhance membrane material hydro-stability's fabrication.

Keyword: Single catalyst, dual catalyst, TEOS/TEVS, xerogel, and membrane desalination.

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1. INTRODUCTION

Xerogel is a hydrogel with water content removable through a conventional process involving pressure or temperature increase (Ayu *et al.*, 2013; Czarnobaj, 2008). This hydrogel has been widely used as a catalyst, adsorbent, filtration and for other purposes. Generally, silica based xerogels are preferred for membrane filtration applications, due to the numerous advantages as a desalination membrane, including good strength, resistance to high temperatures, as well as high selectivity especially for separating salt and water molecules. Silica xerogel material are obtained from various precursors, including 1,2-bis

(triethoxysilyl) ethane (BTESE) (Gao *et al.*, 2017), tetramethylammonium hydroxide (TMAH) (Sakai *et al.*, 2018), TEOS (tetraethyl orthosilicate) (Lestari R. A. *et al.*, 2020; Wiyono, 2015) and TEVS (triethoxy vinyl silane) (Elma *et al.*, 2015a). However, the silica material in desalination membrane is limited by low hydro-stability due to the presence of hydrophilic silanol (Si-OH) groups (Elma *et al.*, 2020c; Elma *et al.*, 2020e; Maimunawaro *et al.*, 2020; Rahma *et al.*, 2020a).

The silanol group is reduced by inserting metal or carbon materials into the silica matrices (Pratiwi *et al.*, 2019). Previous studies

have used membranes with silica (TEOS) and cobalt (Elma and Saputro, 2020; Elma *et al.*, 2015b). However, cobalt and other similar metals are not recommended for producing potable water, thus carbon addition is more suitable. Other studies have also been conducted using TEOS as a silica precursor, where synthetic carbon P123 is inserted to form a triblock copolymer (Elma *et al.*, 2019; Rahma *et al.*, 2020b). In addition, pectin from apple peel is natural carbon and has also been studied as a material to increase the hydro-stability in silica membranes and produce relatively low silanol groups (Elma *et al.*, 2020a; Rahma *et al.*, 2019; Rampun *et al.*, 2019; Syauqiyah *et al.*, 2019).

Meanwhile, Rahman *et al.*, (2020b) conducted a study using carbon-containing silica precursors such as ES40, while Mawaddah *et al.*, (2020) and TEVS showed has the ability to increase silica xerogel gel stability. In addition to precursors, catalysts also play an important role in the formation of silanol and siloxane functional groups on silica xerogels.

Inorganic acid catalysts, including HNO_3 (Elma, 2018; Elma and Setyawan, 2018) and ammonia base catalysts (Elma *et al.*, 2018a), are often used in silica xerogel manufacture. The use of an acid catalyst in the hydrolysis reaction produces a silanol group with small pore size, while a basic catalyst produced a siloxane group with a relatively large pore size, in the condensation reaction (Elma *et al.*, 2020b; Elma *et al.*, 2020d). Thus, in the application of xerogel as a desalination membrane material, the pore size must not be too large or too small or mesoporous. Therefore, using dual catalysts helps to produce sufficiently balanced silanol and siloxane groups (Lestari *et al.*, 2020; Rahma *et al.*, 2020a). Furthermore, organic acid catalysts are suitable for fabricating silica xerogel due to the ability to act as a carbon source. Citric acid has the chemical formula $\text{C}_6\text{H}_8\text{O}_7$, and therefore has several carbon bonds, in addition to being organic in nature, thus able to increase the silica material's hydrophobicity (Amalia Enggar Pratiwi, 2019; Elma and Assyaifi, 2018).

The silanol and siloxane as well as other groups present are quantitatively measured using the deconvolution method, with the Fityk software. According to Saputra *et al.*, (2018) deconvolution is a method for measuring and

restoring FTIR (Fourier-transform Infrared Spectroscopy) spectra with the Gaussian approach. Thus, the siloxane/silanol peak area ratios are able to serve as a reference to determine the hydrophobic (stable to water) silica xerogel's structure. Therefore, this study aims to fabricate and reveal the deconvolution of TEOS/TEVS xerogels by adding single or dual catalysts, using FTIR and Fityk software.

2. MATERIALS AND METHODS

Materials

The materials used to fabricate xerogels include, TEOS and TEVS precursors, 0.1 N citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and ammonia base catalyst 0.0003 N (NH_3), while the final total molar ratio is TEOS : TEVS : EtOH : H_2O : (Acid: base) is 0.9 : 0.1 : 38 : 5 : X, where X represents a single and dual catalyst variation. Meanwhile, the molar ratio of single and dual catalyst were acid = 0.001, and acid: base = 0.0003: 0.00078, respectively.

Procedure

The first stage in this experiment was the synthesis of silica sol by mixing ethanol solvent and refluxed silica precursor TEOS: TEVS (9: 1) for 1 hour, at 0 °C. Subsequently, a variation of acid catalyst (citric acid) and acid-base catalyst (citric acid + ammonia) were added separately and the solutions obtained were refluxed for 2 hours at 50 °C. The silica sol obtained was then oven dried for 24 hours and crushed into a powder. This dry silica sol product was henceforth referred to as xerogel, then analyzed by FTIR (Fourier Transform Infra-Red xerogel is) and the xerogel deconvolution was determined using the Gaussian approach, with the Fityk software.

3. RESULTS AND DISCUSSION

In this study, Silica xerogel was successfully formulated from a mixture of TEOS and TEVS in a 9: 1 ratio using the sol-gel method, and calcined using the rapid thermal processing (RTP) method. TEVS is a silica precursor with the ability to act as a carbon source, due to the presence of double bonds undergoing hydrolysis and polymerization to form single C-C bonds sequentially, to fill more space in the porous structure (Kleitz, 2008; Muthia Elma, 2014), while TEOS is the main silica material source.

Figure 1 shows the FTIR spectrum of TEOS/TEVS xerogel functionalities with variations in single and dual catalysts contents. According to the image, there are three main functional groups found in all xerogel samples, namely silanol (Si-OH), siloxane (Si-O-Si) and silica-carbon (Si-C). Based on previous research (Rahman *et al.*, 2020a) the siloxane functional group is in the 1000-1200 cm^{-1} range, while silanol and silica-carbon are in the 940-970 cm^{-1} and $< 800 \text{ cm}^{-1}$, respectively (Riani Ayu Lestari, 2020).

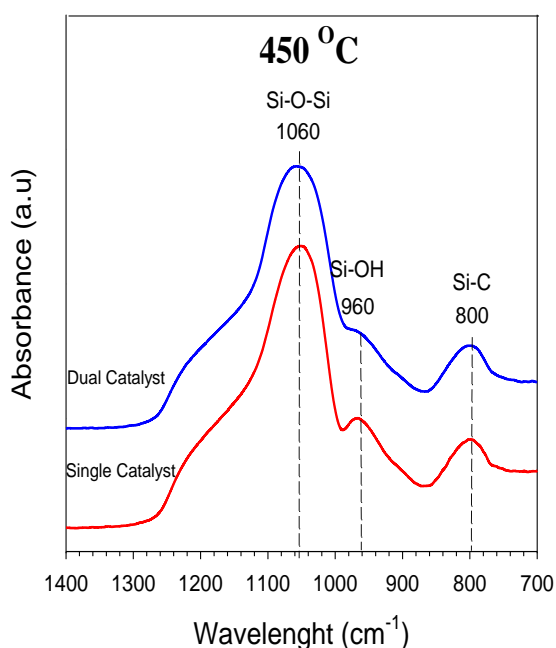


Figure 1. FTIR spectra (Fourier-transform Infrared Spectroscopy) TEOS/TEVS xerogel with variations in addition of single and dual catalysts.

The single catalyst (citric acid) showed siloxane, silanol and silica-carbon peaks at

1050 cm^{-1} , 964 cm^{-1} and 800 cm^{-1} , respectively. Meanwhile, the dual catalyst samples (citric acid and ammonia) exhibited siloxane, silanol and silica-carbon peaks at 1055 cm^{-1} , 961 cm^{-1} and 796 cm^{-1} . These results are similar to the previous results (Rahman *et al.*, 2020a; Rahman *et al.*, 2020b) which exhibited silanol, siloxane and silica-carbon peaks at 958 cm^{-1} , 1067 cm^{-1} and 796 cm^{-1} . Silanol is obtained from ammonia base catalyst, and is the result of the sol gel process occurring in the hydrolysis stage, where the precursor and reflux acid catalyst produce silanol (Elma and Assyaifi, 2018), while siloxane is obtained from citric acid catalyst, and is produced in condensation, the second stage, where the alkaline catalyst is added to convert silanol groups into siloxane.

FTIR analysis is also able to produce quantitative data from the resulting peaks area, and deconvolution data can be generated from functional group peaks, using a physical software application. This software utilizes the Gaussian line to form at least squares and peaks normalized to the baseline (Wojdyr, 2010). Table 1 shows the peak area produced by each functional group in the FTIR data. Each silanol, siloxane and Si-C group peak was fitted with the Fityk software through the Gaussian approach, thus, producing each group's output area values. According to Table 1, the silanol area in this study is higher, compared to other studies, however, the resulting siloxane area is also quite high. Meanwhile the results of previous studies using one per cursor, TEOS, were only able to produce peak Si-C areas of 0.41 (unit area) and 1.61 (unit area).

Table 1. Peak area results for the three Functional Groups (Siloxane, Silanol and Carbon Silica), using Fityk Software

Type of membrane	Siloxane (Si-O-Si) (unit area)	Silanol (Si-OH) (unit area)	Si-C	Type of membrane
TEOS Single Catalyst 250 °C	2.71	0.47	-	(Elma et al., 2018b)
TEOS + Citric Acid + NH ₃ 600 °C	11.70	1.03	-	(Elma et al., 2018b)
TEOS Single 250 °C	7.17	0.67	0.41	(Lestari, 2020)
TEOS Dual 250 °C	13.3	1.84	1.61	(Rahman et al., 2020a)
ES40 Hybrid P123	9.58	0.61	0.37	(Rahman et al., 2020a)
ES40 Templated P123	9.51×10^{-5}	1.0264×10^{-3}	0.37	(Rahman et al., 2020b)
Single Catalyst (citric acid)	12.42	3.02	1.86	This work
Dual Catalysts (citric acid and ammonia)	12.66	2.39	1.88	This work

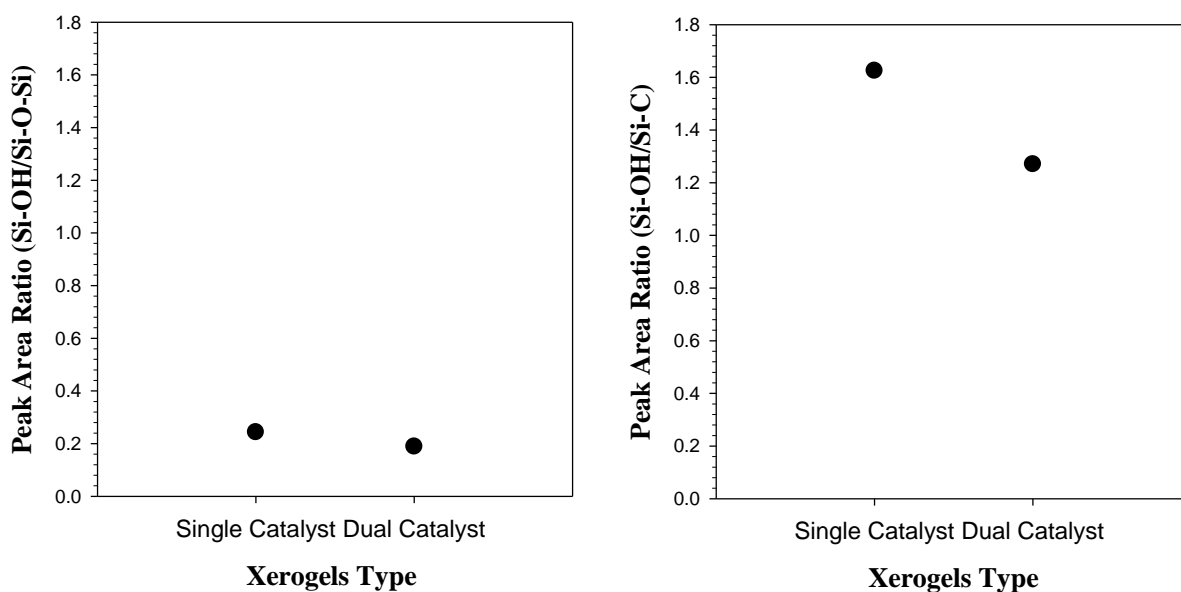


Figure 2. Deconvolution area for silanol/siloxane and silanol/silica-carbon, with a variety of single and dual catalyst addition.

The larger peak area was observed in the xerogel sample using 2 TEOS and TEVS precursors to produce 1.86 (unit area) in single and 1.88 (unit area), on the dual catalyst. This proves adding the TEVS precursor as a source of silica, as well as citric acid and ammonia based catalysts is able to increase the Si-C content (Muthia Elma, 2014; Yang *et al.*, 2017). An increase in carbon bonds formed reduced the amount of silanol, thus increasing the weak silica xerogel's hydrostability (Elma *et al.*, 2020c; Elma *et al.*, 2020f). Meanwhile, the desired silanol group is less, in contrast to siloxane. Table 1 shows the two xerogel samples in this study have desired area values, compared to other studies. However, the comparison between area peaks single and dual catalyst in this study did not differ much. Figure 2 shows the force deconvolution analysis performed using Fityk software, to determine the more dominant peak area's extent.

Figure 2 shows the peak area ratio of silanol/siloxane and silanol/silica-carbon, using single and dual catalysts. The optimum condition is indicated by the lowest ratio value (Darmawan *et al.*, 2018; Elma, 2013; Pratiwi *et al.*, 2019). This shows the siloxane concentration is greater, compared to silanol. Silanol has hydrophilic properties, consequently, the silica matrix bonds are broken in contact with water (Pratiwi *et al.*,

2019). However, inadequate silanol tends to make xerogel pores excessively small (Rahma *et al.*, 2019). The relatively lower siloxane/silanol ratio in this study was generated by dual catalysts of 0.2 (unit area), compared to single catalyst of 0.24 (unit area) (Figure 2). This shows siloxane is the dominant functional group, due to the replacement of silanol OH bond, in the presence of carbon bonds from the organic catalyst and TEVS. The results are also almost the same as the 0.114 unit area reported by Pratiwi *et al.*, (2019) on TEOS xerogels formulation with pectin carbon addition.

4. CONCLUSION

Silica xerogel formulated with the addition of a single catalyst (citric acid) exhibited siloxane, silanol, and silica-carbon peaks at 1050 cm^{-1} , 964 cm^{-1} , and 800 cm^{-1} , respectively. Meanwhile, the silica xerogel with dual catalysts (citric acid and ammonia) exhibited siloxane, silanol and silica-carbon peaks at 1055 cm^{-1} , 961 cm^{-1} and 796 cm^{-1} , respectively. The deconvolution of silanol/siloxane lowest unit ratio area of 0.19 (unit area) and Si-C largest unit area of 1.88 (unit area) was observed in the dual catalyst (citric acid- ammonia base). The low silanol/siloxane ratio area indicates siloxane is the more dominant functional group in the dual catalyst xerogel sample, and the OH group is

reduced to increase the silica xerogel's stability against water, during membrane desalination application.

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