

Fabrication of silica ceramic membrane via sol-gel dip-coating method at different nitric acid amount

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Abstract. Fabrication of silica ceramics via the sol-gel method has offered more advantages over other methods in the fabrication of ceramic membrane, such as simple operation, high purity homogeneous, well defined-structure and complex shapes of end products. This work presents the fabrication of silica ceramic membrane via sol-gel dip-coating methods by varying nitric acid amount. The nitric acid plays an important role as catalyst in fabrication reaction which involved hydrolysis and condensation process. The tubular ceramic support, used as the substrate, was dipped into the sol of Tetraethylorthosilicate (TEOS), distilled water and ethanol with the addition of nitric acid. The fabricated silica membrane was then characterized by (Field Emission Scanning Electron Microscope) FESEM and (Fourier transform infrared spectroscopy) FTIR to determine structural and chemical properties at different amount of acids. From the XRD analysis, the fabricated silica ceramic membrane showed the existence of silicate hydrate in the final product. FESEM images indicated that the silica ceramic membrane has been deposited on the tubular ceramic support as a substrate and penetrate into the pore walls. The intensity peak of FTIR decreased with increasing of amount of acids. Hence, the 8 ml of acid has demonstrated the appropriate amount of catalyst in fabricating good physical and chemical characteristic of silica ceramic membrane.

1. Introduction

Sol-gel technique can be described as a process where the solution or sol experiences sol-gel transition, where at this transition, the solution turn into rigid non-fluid mass [1]. This method comprises forming of mineral phase starting from soluble molecular precursors, resulting an inorganic polymerization reaction. The reproduction of new porous nanomaterials with well-defined structures and complex shape has been manufactured by the sol - gel process [2]. Fabrication of ceramics and glasses by using sol-gel methods have been used for a long time [1]. Sol-gel techniques offer some advantages over other methods in the fabrication of ceramics, such as low temperature needed for synthesis to be carried out, high purity materials is produced, and xerogels porous texture such as pore size and structure can be modified [4]. Fabrication of silica by using the sol – gel technique is started by silicon alkoxides hydrolyzation through condensation, creating the silica nanoparticles. These silica particles then grow and form a sol, which are influenced by the reaction condition. Silica films can be formed



by depositing the sol onto a substrate. Parameters such as precursors, reactant molar ratio, pH, synthesis temperature, modifying agent, composition of the solvent, and aging and drying condition affected the textural and structural properties of the fabricated materials [2].

In sol-gel technique, the pH of the solution control the hydrolysis and condensation reaction, where it will affect the metal oxide microstructure. The pH of the solution can be modified by adding catalyst. Normally, silicon alkoxides reaction with water is slow. Hence, by adding the acid or base catalyst, the reaction of the process can be increased [5]. For example, after the addition of HCl into the solution of TEOS and ethanol, the gelation time was reduced to 92 hours from 1000 hours [6]. In the films fabricated by sol-gel methods, acid catalysts are normally used with a small amount of water ($R=4$) [7]. Previous work by Coltrain et al. [8] shows that under the acidic condition, the condensation of TEOS achieved maximum at $pH=7$ and minimum an $pH=2$, where the molar ration of the water, $R=4$. A study by Fardad [5] indicate that type of catalyst used while preparing precursor solution affected the thickness, shrinkage, porosity and optical quality of the film fabricated.

Catalyst concentration in silica sol is quite important as with only a small change in the concentration may affect the reaction greatly [9]. In acid-catalyzed reaction, hydrolysis is faster than condensation, where normally started after the completion of hydrolysis [10] [11] [12]. On the other hand, condensation step is faster than hydrolysis under base-catalyzed condition, which producing a highly condensed species that may agglomerate into fine particles [10]. Besides that, dense microporous (pore size $< 2nm$) networks is obtained, while mesoporous ($2nm < \text{pore size} < 50nm$) gels was produced under alkaline condition [13]. The pH also affected silica dissolution and precipitation [14]. More porous structures are produced at a high pH value as the solubility of the particulate in the sol may be high. However, at low pH condition, due to the low dissolution-reprecipitation rate, material with dense structure and fine pore network are obtained.

Previous work by Tuzun et al. [15], the silica sol was prepared by using the molar ratio of TEOS: water: ethanol is 1:4.7:3.8, with small amount of acid. However, the amount of the acid was not specified. In this paper, the effect of the amount of the nitric acid as a catalyst on the characteristics of the fabricated silica ceramic membrane via sol-gel dip-coating method is investigated.

2. Experimental procedures

2.1 Silica Sol Preparation.

Silica sols was prepared by mixing TEOS, water and ethanol together at 298 K with vigorous stirring. The molar ratio of TEOS: water: ethanol is fixed at 1:4.7:3.8 [15]. Then, the nitric acid was added to the solution as a catalyst. The amounts of nitric acid are varied at 8, 10, and 12 ml.

2.2 Membranes Fabrication.

The tubular ceramic support used was 10 inch Doulton OBE Ceramic with 32 mm, 48 mm internal and outer diameter while the support length of 200 mm. The ceramic support was dipped into the prepared silica solutions, and dried at room temperature for 24 hours. After that, the samples were calcined at 773 K with holding time of three hours. The dipping, drying and calcine process was repeated for three times.

2.3 Membranes Characterization

The morphology of the membrane surface and support were determined using the field emission scanning electron microscope (FESEM) (JSM 6700F, JEOL). X-ray diffraction (XRD), was used to determine the element of the fabricated membrane. The Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer System spectrum 100) was employed in determining the functional group of the membrane.

3. Results and Discussion

Figure 1 shows the FESEM image of the fabricated silica ceramic membrane for 8, 10 and 12 ml acid. From the FESEM images, morphology of the fabricated silica ceramic membrane was observed, where for FESEM image for 8 ml acid shows than the surface of the silica quite clear. However, with increasing on amount of acids, silica surface becomes rough as the agglomeration happens.

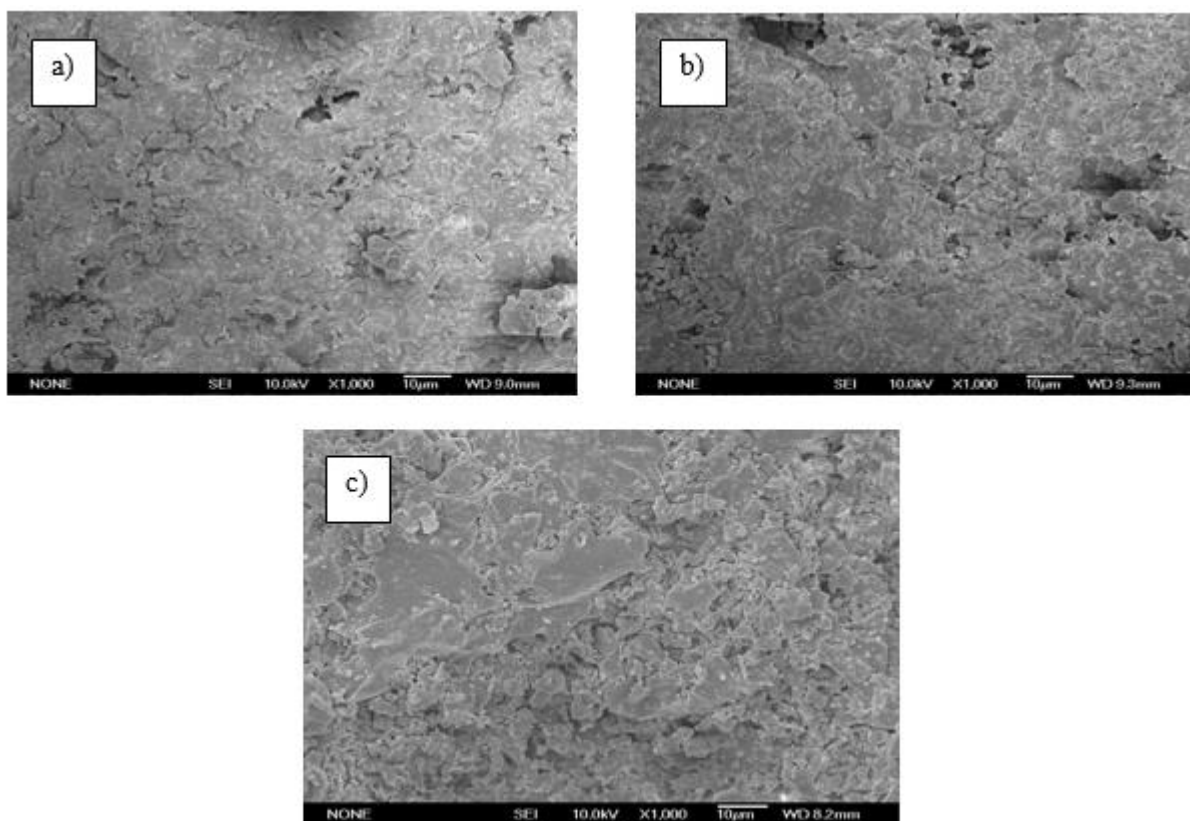


Figure 1. FESEM images of the fabricated silica ceramic membrane via sol-gel dip-coating at different acid amount; a) 8 ml, b) 10 ml and c) 12 ml.

Figure 2 shows XRD patterns fabricated silica ceramic membrane. The aim of this study is to fabricate silica ceramic membrane by using sol-gel dip-coating methods. From the XRD results, it is verified that silica was deposited on the substrate, as the detected reflections demonstrates the existence of silicate hydrates.

Figure 3 represents FTIR adsorption spectra of fabricated silica ceramic membrane by using different amount of nitric acid. It was discovered that the major peak in FTIR adsorption spectra of the silica, with different amount of acids as the catalyst, is around 1080 to 1090 cm^{-1} . The broad absorption band in the region is correlated to the Si-O-Si bond of silica, which then prove the presence of silica as the end results. However, different amount of acid used affect the intensity of the FTIR peak as shown, where increasing the amount of nitric acid used to reduce the peak intensity of FTIR.

Fabrication of the silica ceramics through sol-gel dip-coating technique is expected to be resulting in uniform pore size distribution. By varying the amount of nitric acid, the physical and chemical characteristic of the fabricated silica ceramic membranes is affected. The nitric acid amount are capable to control the hydrolysis and condensation process during fabrication. The 8 ml of nitric acid have shown the better physical and chemical characteristic of silica ceramic membrane compared to 10 ml and 12 ml of nitric acid.

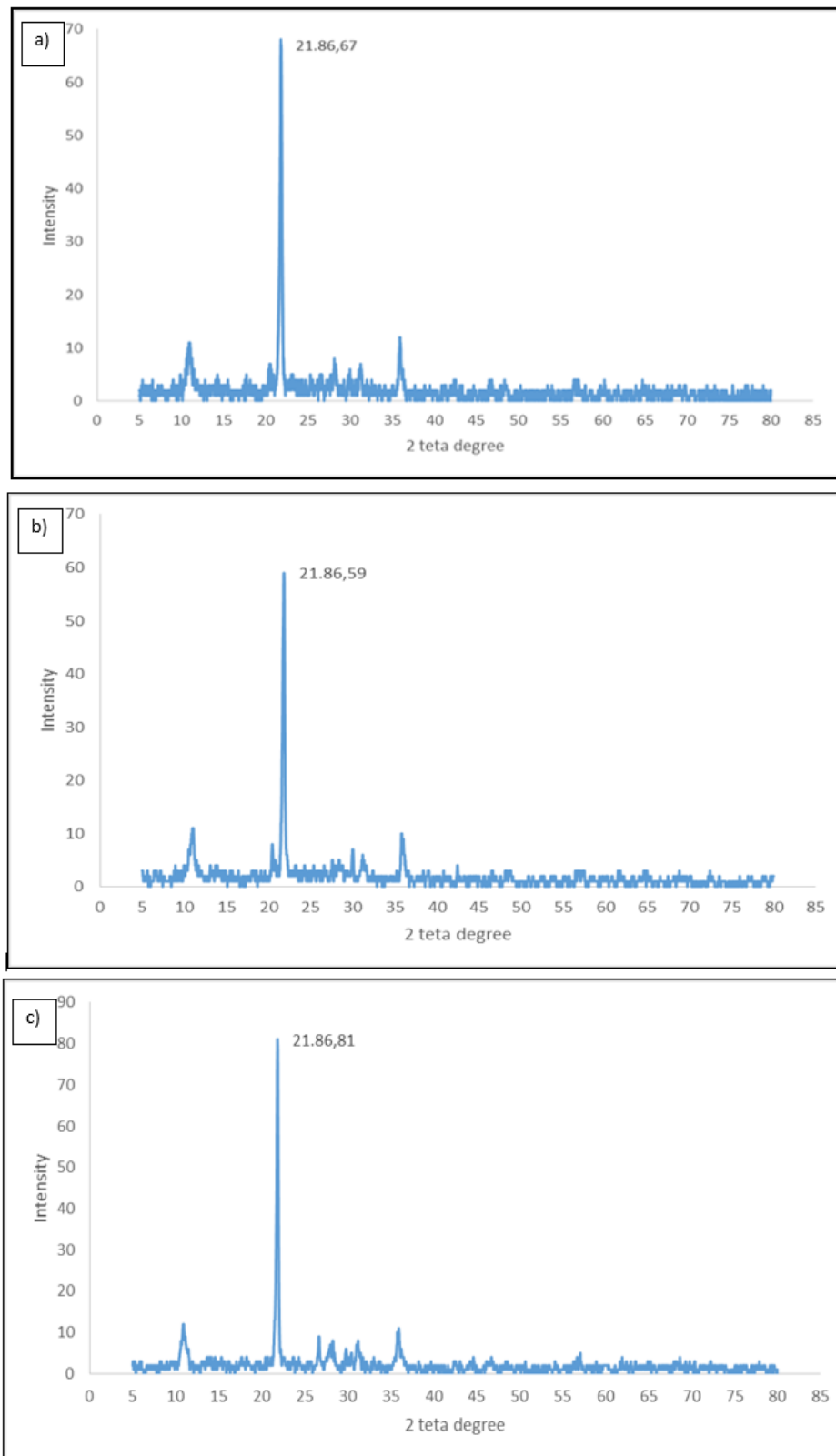


Figure 2. XRD pattern of the fabricated silica silica ceramic membrane via sol-gel dip-coating at different acid amount at; a) 8 ml , b)10 ml and c)12 ml.

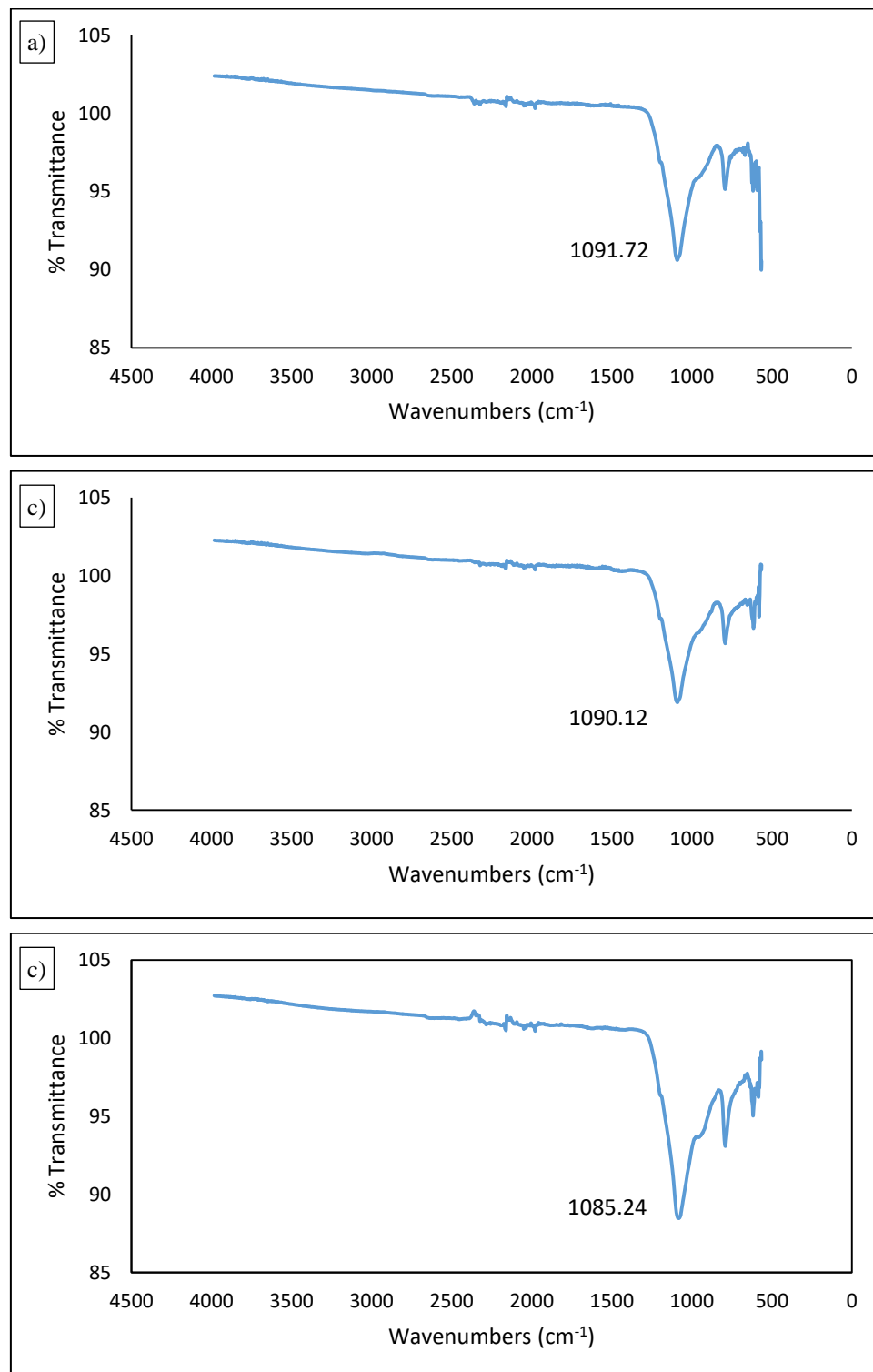


Figure 3. FTIR result of the fabricated silica ceramic membrane via sol-gel dip-coating at different acid amount for a) 8 ml, b)10 ml and c)12 ml.

4. Conclusion

In this study, silica ceramic membrane was fabricated by using the sol-gel dip-coating methods. The differences in characteristics of membranes were investigated as they were fabricated by using different amount of nitric acid. The differences in the amount of acid used as a catalyst, also control the concentration of the sol, which affect the properties of fabricated silica ceramic membrane. Increasing the amount of acid resulting in agglomeration on the silica surface. In FTIR analysis, the intensity decreased by increasing amount of acids. The fabrication of silica by sol-gel dip-coating method is considered as successful as the XRD pattern shows the existence of silicate hydrate in the end products. Therefore, the 8 ml of acid have presents the suitable amount of catalyst in producing good physical and chemical characteristic of silica ceramic membrane.

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