

Production and Characterization of Zeolite Membrane

Aprilina Purbasari^a, Titik Istirokhatun^b, Heny Kusumayanti^a, Ariestya Meta Devi^a, Lulluil Mahsunah^a, Heru Susanto^a

^a Chemical Engineering Department, Faculty of Engineering, Diponegoro University,
Jl. Prof Sudharto, SH-Tembalang, Semarang INDONESIA

^b Environmental Engineering Department, Faculty of Engineering, Diponegoro University,
Jl. Prof Sudharto, SH-Tembalang, Semarang INDONESIA
E-mail (for corresponding author): aprilinap@yahoo.com

Abstract :

The use of bioethanol as an alternative fuel with a purity of more than 99.5% wt has prompted research on bioethanol purification. One of the promising methods used for bioethanol purification is pervaporation membrane. This research is aimed to prepare and characterize zeolite membranes for pervaporation membrane. The membrane preparation consisted of two stages, namely support preparation and zeolite deposition on the support. In support preparation, α alumina and kaolin with specific composition (50:30; 40:40; 50:30) was mixed with additives and water. After pugging and aging process, the mixture became paste and extruded into tubular shape. The tube was then calcined at temperature of 1250 °C for 3 hours. After that, zeolite 4A is deposited on the tubes using clear solution made of 10 %wt zeolite and 90 %wt water and heated at temperature of 80 °C for 3 hours. Furthermore, the resulting zeolite membranes was washed with deionized water for 5 minutes and dried in oven at temperature of 100 °C for 24 hours. Characterization of zeolite membranes included mechanical strength test, XRD, and SEM. In the mechanical strength test, the membrane sample with alumina:kaolin = 50:30 (#membrane A#) has the highest mechanical strength of 46.65 N/mm². Result of XRD analysis for the membran A indicated that mullite and corundum phases were formed, which mullite phase was more dominant. Meanwhile the result of SEM analysis shows that zeolite crystals have been formed and covered the pores support, but the deposition of zeolite has not been optimal yet. The performance examination for bioethanol purification showed that the membrane could increase the purity of bioethanol from 95% to 98% wt.

Keywords: Alumina, Inorganic membrane, Kaoline, Zeolite

Introduction

Bioethanol can be used either as additive or as pure fuel (fuel grade). Moreover, bioethanol fueled vehicles produce lower carbon monoxide and carbon dioxide emissions, and the same or lower levels of hydrocarbon and oxides of nitrogen emissions. However, the purity of bioethanol is now the main issue of this realization. Most of the Indonesian bioethanol industries are only able to produce bioethanol with purity of less than 95%. To be used as fuel (not an additive), bioethanol should have a purity >99.5% based on SNI (Indonesia National Standard).

Problem of bioethanol purification is the formation of bioethanol-water azeotropic mixture at a concentration of ~ 95%. Distillation, separation technology based on boiling point difference, cannot be used any more to raise bioethanol concentration of >95%. Several methods have been proposed for the dehydration of bioethanol including molecular sieve adsorption system (Jeong et al., 2009; Carmo and Gubulin, 2002) and entrainer distillation (Al-Amer, 2000; Chianese and Zinamosca, 1990; Hunek et al., 2004). Both of these technologies in principle can increase the bioethanol purity, but the complexity and high operating costs hinder the industrial scale applications. More recently, pervaporation technology using a hydrophilic membrane has been offered as the dehydration of organic solvents. Examination results have shown that the hybrid process combining distillation and pervaporation technology resulted in better performance and more competitive compared to conventional processes. But there was swelling, process of wetting and swelling of the membrane pores by solvent (bioethanol), which decreases the performance of the process. The swelling process causes the loss of selectivity causing a decrease in the concentration of produced bioethanol. To solve this swelling problem, inorganic membranes have been proposed to replace the polymeric membrane (Wee et al., 2008; Baelen et al., 2005; Mohammadi and Kazemimoghadam, 2010).

Inorganic membranes, also referred to as ceramic membrane, are made of silica, alumina or zeolite possessing highly resistant to solvents, high temperature stability, and free from swelling. Therefore, these membranes can be used in applications with a wide range and at the same time these membranes have high selectivity and permeability.

Zeolite membrane has been studied for pervaporation process due to its unique characteristics such as pore size; the nature of adsorption; mechanical, chemical and biological stability. Zeolite membranes have so far shown good separation performance, but the permeate results are still low for practical applications. One of the challenges for making zeolite membranes is to make zeolite membranes with high permeance and high separation selectivity. In order to obtain a better separation performance, preferably zeolite membranes are made of pure zeolite crystals in small size and uniform particle. Several methods are reported for zeolite membranes synthesis. The structural stability of zeolite membrane is affected by its support. The most commonly supports used are generally from stainless steel and alumina in tubular or plated form. Alumina supports typically have pore diameter between 5 nm (γ -Al₂O₃) and 200 nm (Alpha-Al₂O₃) while stainless steel supports between 0.5 and 4.0 μ m. Two critical stage occurs during the formation of zeolite membranes support, namely the nucleation on the support followed by crystal growth to form a continuous zeolite layer and cover support. There are several methods of zeolite membranes synthesis, i.e. hydrothermal synthesis method, secondary growth method, continuous flow synthesis method, and microwave synthesis method.

This paper presents the first part of our research on preparation of pervaporation membrane from zeolite and fly ash. The purposes of this research are to determine the optimal composition of the support for zeolite membranes preparation, to study preparation of zeolite membrane, and to characterize zeolite membranes.

Materials and Methods

Materials used in this research are α -alumina (Merck), polyethylene glycol (Sigma), kaolin (CV. Indrasari), deionized water (Membrane Research Centre), sodium citrate (CV. Indrasari), carboxymethyl cellulose (CV. Indrasari), and MgSO₄ (CV. Indrasari), and zeolite 4A (Aldrich).

Production of zeolite membrane consists of two stages, namely support preparation and zeolite deposition on the support. In support preparation, α -alumina and kaolin with a specific composition, i.e. α -alumina:kaolin = 50 g : 30 g (sample A), α -alumina:kaolin = 40 g : 40 g (sample B); α alumina:kaolin = 30 g : 50 g (sample C), are mixed with additives (2 g carboxymethyl cellulose, 0.8 ml polyethylene glycol, 2 g sodium citrate, and 2 g MgSO₄) for 15 minutes. Then water is added to the mixture as much as 45% of the total weight of solids drop by drop. Pugging is done for 30 minutes to make paste mixture and followed by aging for 30 minutes. The paste is extruded into tube shape using extruder. Tubular support is dried at room temperature for 3 days and then calcined at temperature of 1250 °C for 3 hours.

Zeolite deposition is used method as practiced by Aguado et al (2009). Initially clear solution is made by dissolving 10 %wt zeolite and 90 %wt water followed by heating and stirring until the solution is saturated. Clear solution is heated to constant temperature of 80 °C and then tubular support is immersed into the clear solution with stirring rate of 0.25 ml/min for 3 hours. Deposited support or zeolite membrane is dried for 30 minutes and washed using deionized water for 5 minutes. Further zeolite membrane is dried at 100 °C using oven for 24 hours. The experiments are performed in triplicate. The zeolite membrane is characterized by mechanical strength test, XRD (X-Ray Diffraction), and SEM (Scanning Electron Microscopy). The resulting membrane was then tested for bioethanol purification using laboratory scale pervaporation unit.

Results and Discussion

1. Mechanical Strength

The mechanical strength characterization results are presented in Table 1. It is seen that sample A has the highest mechanical strength of 46.65 N/mm², while for samples B and C are 18.50 N/mm² and 12.40 N/mm², respectively. Support is a ceramics made through high temperature firing. Many processes occur at kaolin firing, such as: crystalline water comes out at temperatures of 450 - 700 °C; dehydration of aluminum hydrates at temperatures of 320 - 560 °C; oxidation of organic matter generally occurs at 200 - 700 °C, but oxidation of coarse carbon particles can occurs at 1000 °C. Besides those processes, particles in ceramics join together into an aggregate that has strength at sintering process (Reed, 1995). Sample A containing the highest α -alumina can give the highest mechanical strength so that sample A is the most appropriate support for zeolite membrane.

Table 1. Mechanical Strength of Support

Sample	Mechanical Strength (N/mm ²)
A	46.65
B	18.50
C	12.40

2. XRD Analysys

a. Identification of Formed Phase

XRD analysis was conducted by Hanawalt method using the Data Base of JCPDS (Joint Committee of Powder Diffraction Standard). The result shows corundum and mullite phases are formed in sample A and mullite phase is dominant as shown in Figure 1.

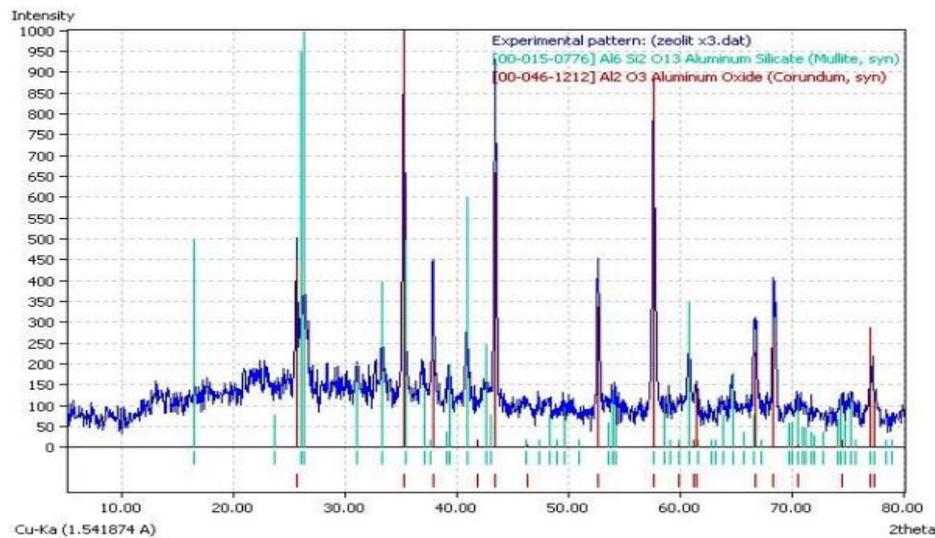


Figure 1. XRD analysis of sample A

In this composition formed corundum phase (Al_2O_3 , Aluminum Oxide) appears at the top with angle 2θ : 35.255; 37.873; 43.451; 53.97; 57.598; 64.675; 66.531; 68.227; 76.902. Meanwhile the formed mullite phase appears at the top with angle 2θ : 12.68; 25.679; 33.314; 35.255; 40.992; 61.424.

b. Crystal Size

Crystal size is calculated using Scherrer equation by FWHM (Full Width Half Maximum) analysis:

$$L_{ave} = \frac{k \lambda}{B_0 \cos \theta}$$

where L_{ave} is the crystal size, k is a constant, B_0 is the width at half-maximum (FWHM) of peak and θ is the diffraction angle. Crystal sizes in sample A are obtained from the XRD result are presented in Table 2. It can be seen at table 2 that the size of formed crystals on sample A is in a range of 3.398-12.246 nm for corundum phase and 3.16-7.25 nm for mullite phase.

Table 2. Crystal sizes in sample A

Corundum Phase (Al ₂ O ₃ , Aluminium oxide)			Mullite Phase (Al ₆ Si ₂ O ₁₃ , Aluminium silicate)		
2θ	FWHM	Crystal size (nm)	2θ	FWHM	Crystal size (nm)
35,255	0,5	3,398	12,68	0,45	3,16
37,873	0,45	3,906	25,679	0,45	3,42
43,451	0,5	3,823	33,314	0,6	2,76
53,973	0,4	5,897	35,255	0,5	3,39
57,598	0,5	5,179	40,992	0,5	3,67
64,67s	0,4	8,109	61,424	0,4	7,25
66,531	0,5	6,96			
68,227	0,45	8,31			
76,902	0,5	12,246			

3. SEM imaging

a. Comparison of support surface and zeolite membrane surface

The surface of support layer and zeolite membrane were visualized using SEM. The results are presented in Figure 2 and 3.

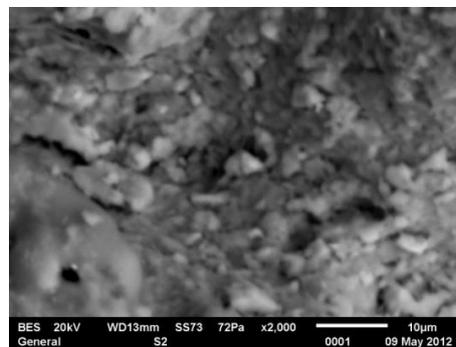


Figure 2. Top view of support with 2000 times magnification

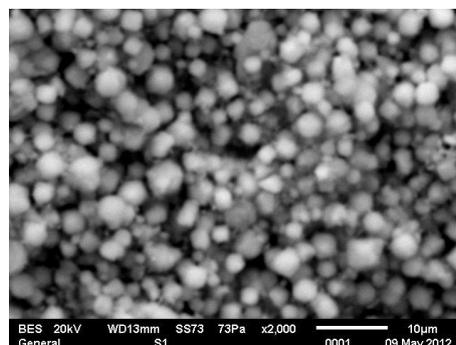


Figure 3. Top view of zeolite membran with 2000 times magnification

From Figure 2 it can be observed the support surface is covered by alumina bond derived from α -alumina and kaolin irregularly. The disorder bond causes pores forming on the support surface. Otherwise, figure 3 shows the support surface layer coated with zeolite 4A. Zeolite deposition on support makes membrane surface more homogeneous.

b. Comparison of zeolite membrane surface from conducted research to that from previous research

Figure 4 is the SEM of zeolite membranes by Wee et al in 2011 which bond of zeolite crystals is formed covering support. When compared with the result of zeolite deposition that has been carried out (Figure 3), zeolite 4A existing on the support surface has formed cubic zeolite crystal (Baerlocher et al, 2007). However, formation of zeolite crystals is not optimal yet because zeolite crystals spread unevenly on the entire surface of the membrane so that there are still cavities. This is due to the crystallization process of zeolite deposition has not reached its optimal state.

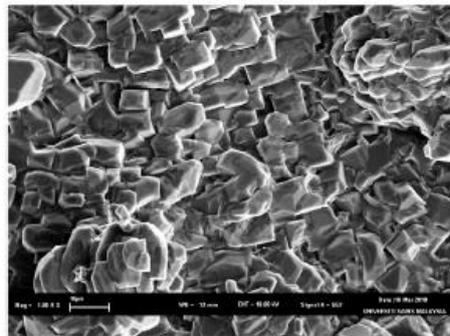


Figure 4. Top view of membrane zeolite from previous research (Wee et al, 2011)

4. Test results for bioethanol purification

In order to know the performance for bioethanol purification, the resulting the membrane A was examined using ethanol with the concentration of 95% at temperatur of 90 °C. The result showed that the concentration of ethanol could be increased to 98%. However, this concentration is still lower than the standard required for fuel grade bioethanol.

Conclusions

1. Sample A with composition of alumina:kaolin = 50:30 is optimal composition for support having mechanical strength of 46.65 N/mm².
2. Result of sample A characterization using XRD indicates corundum and mullite phases are formed which mullite phase is dominant. Crystal size of sample has an average size of 3.398 to 12.246 nm for corundum phase, while for mullite phase 3.16 to 7.25 nm
3. SEM characterization of sample A shows that zeolite crystals has deposited on the support surface, but the zeolite crystals formed on the support surface does not form bonds between the zeolite crystals so that there are cavities on the surface of membrane.
4. The performance examination for bioethanol purification showed that the concentration of ethanol could be increased but it is still lower than the standard required for fuel grade bioethanol.

Acknowledgements

The authors thank to Diponegoro University for the financial support of this research.

References

- [1] Aguado S, Gascón J, Jansen JC, Kapteijn F. 2009. Continuous Synthesis of NaA Zeolite Membranes. *Micropor. Mesopor. Mater.*, 120 : 170–176.

-
- [2] Al-Amer AM. 2000. Investigating polymeric entrainers for azeotropic distillation of the ethanol/water and mtbe/methanol systems. *Ind. Eng. Chem. Res.*, 39 : 3901–3906.
- [3] Baelen DV, Bruggen BV, Dungen KV, Degreve J, Vandecasteele C. 2005. Pre-vaporization of Water-alcohol mixture and acetic acid-water mixture. *Chemical Engineering Science*, 60 : 1583–1590.
- [4] Baerlocher C, McCusker LB, Olson DH. 2007. *Atlas of Zeolite Framework Types*. Elsevier Science, Switzerland.
- [5] Carmo MJ, Gubulin JC. 2002. Ethanol-Water Separation in the PSA Process. *Adsorption*, 8 : 235–248.
- [6] Chianese A, Zinamosca F. 1990. Ethanol dehydration by azeotropic distillation with a mixed-solvent entrainer. *Chem. Eng. J.*, 43 : 59–65.
- [7] Hunek J, Gal S, Posel E, Glavic P. 2004. Separation of an azeotropic mixture by reverse extractive distillation. *AIChE J.*, 35 : 1207–1210.
- [8] Jeong JS, Jang BU, Kim YR, Chung BW. 2009. Production of dehydrated fuel ethanol by pressure swing adsorption process in the pilot plant. *Korean J. Chem. Eng.*, 26(5), 1308–1312.
- [9] Mohammadi T, Kazemimoghadam M. 2010. The pilot-scale pervaporation plant using tubular-type module with nano pore zeolite membrane. *Desalination*, 255 : 196–200.
- [10] Reed JS. 1995. *Principles of Ceramics Processing*. John Wiley & Sons, New York.
- [11] Wee SL, Tye CT, Bhatia S. 2008. Membran Separation Process-Pre-vaporization Through Zeolite Membrane. *Separation and Purification Technology*, 63 : 500–516.
- [12] Wee SL, Tye CT, Bhatia S. 2011. Synthesis, characterization and pervaporation properties of microwave synthesized zeolite A membrane. *Desalination*, 277 : 383–389.