Characterization of ZSM-5 Zeolite Membrane Synthesis Results with 304-200 Gauze Supports with Pretreatment variations

Abstract—Characterization of the ZSM-5 zeolite membrane synthesized with 304-200 gauze buffer was carried out. The purpose of this study is to first synthesize ZSM-5 membranes with 304-200 gauze buffer in various pretreatments. The second objective is to characterize the synthesized ZSM-5 membrane with X-Ray Diffraction (XRD), Scanning Electron Microscope Energy dispersive X-Ray Spectroscopy (SEM-EDS) and The fourier-transform infrared (FTIR). ZSM-5 membrane was synthesized through the first step, namely the pretreatment variation of 304-200 stainless steel gauze soaked in toluene 95% for 2 hours, in a 15% HCl solution for 20 minutes; immersed in 15% NaOH, 15% HCl, and electro-oxidated with 20% H2SO4 for 20 minutes each; immersed in toluene 12 hours, in a solution of HCl 15% 6 hours and in TPABr solution 0.1 M 12 hours. The next step is the manufacture of ZSM-5 precursors, and the coating process on the gauze buffer at 90 °C for 4 days. The resulting ZSM-5 membrane was characterized using XRD, SEM-EDX and FTIR. Based on XRD, SEM-EDX, and FTIR characterization of the synthesized product, it was concluded that pre-treatment of 304-200 gauze that can produce a good ZSM-5 membrane is pretreatment immersed in 15% NaOH, 15% HCl, and 20% H2SO4 electro-oxidation respectively - each for 20 minutes; and soaked in toluene 12 hours, HCl 15% 20 minutes, and TPABr 0.1 M 12 hours. The resulting membrane is the ZSM-5 membrane.

Keywords: pretreatment, ZSM-5 membrane, XRD, SEM-EDX, FTIR

I. INTRODUCTION

ZSM-5 zeolite is a medium sized zeolite (5.1-5.6 Å) with a three-dimensional pore structure. The acidic properties of ZSM-5 cause this zeolite to be often used as a catalyst for gas conversion in the field of petroleum and petrochemicals. ZSM-5 zeolites have a large surface area and have channels that can filter ions or molecules. Zeolite can be used as a molecular filter, ion exchange, filter material, and catalyst.

The problem is the difference in surface shape between the gauze material and ZSM-5 zeolite, making it difficult for the membrane to grow very well on the surface of the screen, so some treatment is needed before it is used as a buffer for the zeolite membrane. The purpose of this study was to characterize ZSM-5 membranes with 304-200 gauze buffer based on variations of pretreatment using XRD, SEM-EDX and FTIR. The treatment of variations in the type and size of the gauze before being used as a buffer are (I) soaked in toluene 95% 12 hours, then in a 15% 20 minute HCl solution; (II) immersed in 15% NaOH, then immersed in 15% HCl solution, then electro-oxidized with 20% H2SO4 20 minutes each with a constant voltage of 3-5 V and a strong current of 0.01 A; (III) immersed in 95% 12 hours toluene, then in 5% 6 hours HCl solution, and in 0.1 M TPABr solution for 12 hours.

The results of research by Saputri MJ et al6 that the highest percentage of reduction in CO gas levels was AISI 316 180 gauze in treatment was immersed in 15% NaOH, 15% HCl and 20% H2SO4 was 15.07 ± 1.05%. The highest adsorption capacity was found in the variation of treatment which was soaked in 15% NaOH, 15% HCl and 20% H2SO4 of 81047.46 ± 3809.98 mg/g. There is an effect of variations in stainless steel treatment AISI 316 180 with ZSM-5 zeolite...
II. METHODS

This type of research is an experimental study. The research materials are stainless steel gauze types 304-200, toluene, HCl, H2SO4, TPABr, Ludox HS 40% w/w, Al2O3, NaOH 50% w/v all made from Merck. The tools used are chemical beaker, dropper, stirring rod, volume pipette, measuring cup, polypropylene container, waterbath, thermometer, Bronso 3510 ultrasonic cleaner, analytical balance, stirrer, oven (OF-12), muffle furnace (Thermolaine 4800), XRD, SEM EDX and FTIR.

Pre-treatment of the gauze before it is used as a supports.

First 304 stainless steel 200 mesh size with a diameter of 3 cm x 3 cm are soaked in a 95% toluene solution for 2h, in a 15% HCl solution for 20 minutes; immersed in 15% NaOH, 15% HCl, and electrooxidized with 20% H2SO4 for 20 minutes each; immersed in 95% toluene for 12 hours, in a solution of 15% HCl for 6 hours and in 0.1 M TPABr solution for 12 hours.

Syntheziz of ZSM-5 Zeolite Membranes at coating low temperature.

Making of ZSM-5 Zeolite Precursor

0.1360 g of NaAlO2 and 1.3900 g of NaOH 50% w/v were weighed and placed in a polypropylene container. 1.5490 g of TPABr was dissolved with 7.3788 g of water and put in a polypropylene container, stirred with a magnetic stirrer for 5 minutes. After that 24,490 g of ludox HS-40% was added, semi gel occurred and stirred at 900 rpm for 6 hours.

Synthesis of ZSM-5 membrane at low temperature for 4 days by coating

Gauze 304-200 with a size of 3m x 3 cm that has been given pre-treatment is immersed in a ZSM-5 precursor, then put into a polypropylene container with a surface area ratio of 1.447 and heated at 90 °C for 4 days. Furthermore, the resulting ZSM-5 membrane was washed with distilled water, dried at 60 °C overnight and then heated at 350 °C in a muffle furnace for 6 hours. The ZSM-5 membrane synthesis process is shown in Figure 1.

ZSM-5 membrane characterization with XRD, SEM-EDX, and FTIR

The principle of XRD is that X-ray diffraction is fired at a crystalline solid and will hit electrons in the atom, so that the electron will vibrate and diffraction X-rays which interfere to form a specific characteristic pattern that is different for each crystalline form. The diffracted rays produced follow Bragg's law in the following equation:

\[ n \lambda = 2 d \sin \theta \]

where “n” is the path of the X-ray (integer), \( \lambda \) is the wavelength of the X-ray (Å), \( d \) is the distance between the same plane plane (Å), and \( \theta \) is the diffraction angle (°). The highest peak intensities at 2θ are 8 and 23 ° are characteristic of ZSM-58.

The fourier-transform infrared (FTIR)

Infrared spectrometry (IR) is one of the instruments that can analyze chemical compounds by providing an overview of the structure of these compounds/ molecules. IR spectrometry is the interaction between light radiation and matter in the infrared region (light spectra at wave numbers 12,900 to 10 cm-1). The absorbed or transmitted infrared ray will be captured by the detector which converts the received signals into an interferogram. The interferogram is then processed by a computer into spectrum data at a specific wave number giving clues about the bonds contained in the compound. FTIR was carried out to identify bond vibrations in the zeolite framework at 4000 cm-1 to 400 cm-1 wave numbers with KBr pellet technique ie 1 mg of sample was crushed with 100 mg of dry KBr so that it became transparent solid. FTIR spectra of ZSM-5 membranes showed the presence of Si-O bonds at wavelengths from 1400 cm-1 to 400 cm-1 example absorption at wave numbers 1100 cm-1 showed the transversal asymmetric strain of Si-O-Si bonds, absorption at 800 cm-1 explains the asymmetrical strain vibrations of Si-O-Si bonds and buckling vibrations appear at 468 cm-1 which is a characteristic of ZSM-59.

SEM (Spectro Electromagnetic Microscope)

ZSM-5 zeolite membrane synthesis begins with pretreatment of various types and size

The surface morphology of small solids SEM is used with SEM-EDX to determine the composition of metals or metal oxides on gauze, ZSM-5 membranes, and to observe the morphology of micro-sized particles. The principle of SEM is the firing of an electron beam into a sample, resulting in the reflection of electrons with lower energy. The reflected electron beam will provide information about the surface image or morphology of a sample. In general, the material analyzed by SEM is conductor, while for insulating material such as zeolite must be coated with a conductor such as gold or platinum using a sputtering tool. To produce the results of a qualitative analysis of the elements in the sample, it is connected with an EDX (Energy dispersive X-Ray Spectroscopy) tool10.

III. RESULTS AND DISCUSSION

ZSM-5 zeolite membrane synthesis begins with pre-treatment of various types and size

ZSM-5 zeolite membrane synthesis begins with pre-treatment of various types and sizes of gauze. Furthermore, the gauze before and after pre-treatment was characterized by XRD shown in Figure 2 and the EDX SEM is presented in Figure 3 and Table 1.
Figure 2 shows the ZSM-5 membrane X-ray diffraction pattern resulting that the highest intensities at $2\theta = 8$ and $23^\circ$ are characteristic of the ZSM-5 standard (ICSD 91010).

| Pretreatment | SEM Gauze Magnification 300 x | SEM ZSM-5 Membrane Magnification 20,000 x |
|--------------|--------------------------------|-----------------------------------------|
| Initial      | ![SEM Initial](image)         | ![SEM ZSM-5 Initial](image)             |
| I            | ![SEM I](image)               | ![SEM ZSM-5 I](image)                  |
| II           | ![SEM II](image)              | ![SEM ZSM-5 II](image)                 |
| III          | ![SEM III](image)             | ![SEM ZSM-5 III](image)                |

Fig 3. SEM of gauze 304-200 with various pre-treatment (Diponegoro University Integrated Laboratory)

Information:
(I) soaked in toluent 95% 12 hours, then in HCl 15% solution for 20 minutes

(II) immersed in 15% NaOH, then immersed in 15% HCl solution, then electro-oxidized with 20% H2SO4 20 minutes each with a constant voltage of 3-5 V and a strong current of 0.01 A
(III) immersed in 95% toluene 12 hours, then in 15% HCl solution for 6 hours, and in 0.1 M TPABr solution for 12 hours.

TABLE 1. EDX GAUZE 304-200 WITH PRETREATMENT VARIATIONS INFORMATION PI, PII, PIII AS SHOWN IN FIGURE 3

| Pretreatment | Component | Composition Before Pretreatment % w/v | Composition PI % w/v | Composition PII % w/v | Composition PIII % w/v |
|--------------|-----------|--------------------------------------|----------------------|-----------------------|------------------------|
| Awal         | C         | 6.12                                 | 18.69                | 10.42                 | 18.69                  |
|              | SiO₂      | 0.82                                 | 0.61                 | 0.88                  | 0.61                   |
|              | Cr₂O₃     | 20.67                                | 17.77                | 19.12                 | 20.26                  |
|              | FeO       | 63.25                                | 51.61                | 59.10                 | 61.94                  |
|              | NiO       | 6.30                                 | 4.85                 | 6.33                  | 6.42                   |
| Membrane     | C         | 11.25                                | 12.82                | 10.45                 |                        |
|              | Na₂O      | 4.90                                 | 5.19                 | 2.64                  |                        |
|              | Al₂O₃     | 3.06                                 | 1.55                 | 1.35                  |                        |
|              | SiO₂      | 77.74                                | 79.49                | 82.79                 |                        |
|              | Al₂O₃     | 25.41                                | 51.28                | 61.33                 |                        |

Figure 3 shows SEM images with pre-treatment before and after pretreatment I, II, and III, the surface is rough, this is possible due to the reduction in components C, SiO2, Cr2O3, FeO and NiO on the screen 304-200 (Table 1), while the SEM image membrane after pretreatment that forms the morphology of coffin is pretreatment II and III the ratio of SiO2: Al2O3 is high pretreatment II, and III (Table 1). The FTIR characterization of ZSM-5 membranes with 304-200 gauze supports and after pretreatment is presented in Figure 4.

Fig 4. FTIR spectra of ZSM-5 membrane with a 304-200 supports that has been given pretreatment I soaked in 95% toluene for 12 hours, then in 15% HCl solution for 20 minutes

Fig 5. FTIR spectra of ZSM-5 membrane with a 304-200 supports that has been given pretreatment II soaked in 15% NaOH, then immersed in 15% HCl solution, then electro-oxidized with 20% H2SO4 20 minutes each with a constant voltage of 3-5 V and a strong current of 0.01 A)

Fig 6. FTIR spectra of ZSM-5 membrane with a 304-200 supports that has been given pretreatment III (immersed in 95% toluene 12 hours, then in 15% HCl solution for 6 hours, and in 0.1 M TPABr solution for 12 hours).

Figures 4, 5 and 6 inform the FTIR spectra of the three pretreatment ZSM-5 membranes showing the presence of Si-O bonds at wavelengths of 1400 cm⁻¹ to 400 cm⁻¹ ie absorption at 1100 cm⁻¹ wave numbers showing the existence of transverse asymmetric strain bonds Si-O-Si,
uptake at 800 cm⁻¹ explains the asymmetrical strain vibrations of Si-O-Si bonds and buckling vibrations appear at 468 cm⁻¹ which is a characteristic of ZSM-5. This is consistent with the results of his research 9.

IV. CONCLUSION

Based on XRD, SEM-EDX, and FTIR characterization of the synthesized membrane with 304-200 gauze buffer, it was concluded that pre-treatment of 304-200 gauze that can produce a good ZSM-5 membrane is pretreatment immersed in 15% NaOH, 15% HCl, and 20% H₂SO₄ electrooxidation for 20 minutes each, or soaked in toluene 12 hours, 15% HCl for 20 minutes, and 0TPABr 0.1 M 12 hours.

REFERENCES

[1] Cejka J, Bekkum HV 2005 Zeolite and Ordered Mesoporous Materials: Progress and Prospect (Czech republic: The 1st FEZA School on Zeolites, Pague Studies in Surface Science and Catalysis) 157 p 311-325

[2] Mukaromah A H 2017 Synthesis of ZSM-5 Zeolite Membranes by Both Electrodeposition and Coating at Low Temperature to Reduce Carbon Monoxide Gas Concentration Doctoral Dissertation Institut Teknologi Bandung

[3] Shan W, Zhang Y, Yang W, Ke C, Gao Z, Ye Y, dan Tang, Y 2004 Electrophoretic deposition of nanosizes in non-aqueous medium and its Application in fabricating thin zeolites membranes J Microporous and Mesoporous Materials, 69, 35-42.

[4] Kong C, Lu J, Yang J, Wang J 2006 Preparation of silicate-1 membranes on stainless steel supports by a two-stage varying-temperature in situ synthesis, J Membrane Science 285 p 258–264.

[5] Gao Y, Chen M, Zhang T, dan Zhen g X 2011 A novel method for the growth of ZSM-5 zeolite membrane on the surface stainless steel J Material Letter 65 p 2789-2792

[6] Saputri MJ, Mukaromah, A H, dan Yusrin 2017 Synthesis ZSM-5 Membrane with coating in 90°C with Treatment Variety Steel Gauzee AISI 316 180 Mesh to decrease Carbon Monoxide (CO) gases National Seminary Proceeding University of Muhammadiyah Semarang Sept 2017 p 687-692

[7] Mukaromah A H, Kadja G T M, Mukti R R, Pratama I R, Zulfikar M A, dan Buchari (2016): Surface to volume ratio of synthesis reactor vessel governing low temperature crystallization of ZSM-5. J Mathematical and Fundamental Science 48(3) p 241-251. ITB Journal Publisher ISSN: 2337-5760 DOI 10.5614

[8] Thommes M, Kaneko K, Neimark A V, Olivier J P, Rodriguez-Reinoso F, Rouquerol J, Sing K S W 2015 Physisorption of gases with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) J Pure Applied Chemistry 87 p 1051-1069

[9] Al-Oweini R, El-Rassy H 2009 Synthesis and characterization by FTIR spectroscopy of silica aerogels prepared using several Si(OR)₄ and R’Si(OR)₃ precursors J Molecular Structure 919 140-145

[10] Mukaromah A H, Azizah I H, Artiaydi T, Miibukhaddim M 2018 Characterization of ZSM-5 Membrane based in size and type gauzee variety with Pre-treatment soaked in NaOH, HCl and Electrooxidation with H₂SO₄, National Seminary Proceeding University of Muhammadiyah Semarang, 30 September 2018 194-205