

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

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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 electrooxidated 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 electrooxidation 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 1. 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 2

Tavolaro in Shan et al. (2004)³ state that zeolite membrane preparation techniques include buffer pretreatment, in situ synthesis methods or layer by layer, hatchery methods, buffer impregnation, and elimination of minor defects. Several studies report that the physical structure and chemical composition of the buffer is very influential on the growth of the zeolite membrane.

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 solution⁴; (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 A⁵; (III) immersed in 95% 12 hours toluene, then in 5% s 6 hours HCl solution, and in 0.1 M TPABr solution for 12 hours⁴.

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 with 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

membrane coating synthesis at 90 °C to reduce CO gas concentration.

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 (Thermoline 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% toluent solution for 2h, in a 15% HCl solution for 20 minutes; immersed in 15% NaOH, 15% HCl, and electrooxidated 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.

Synthesiz 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 x3 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 550 °C in a muffle furnace for 6 hours. The ZSM-5 membrane synthesis process is shown in Figure 1.

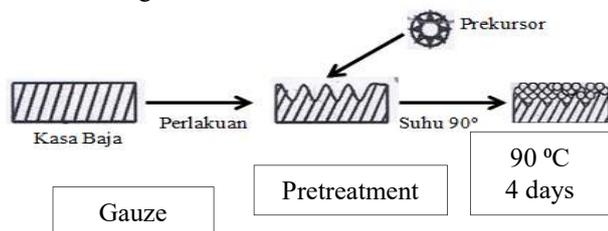


Fig. 1. ZSM-5 zeolite synthesis by coating (Gao et al., 2011).

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), λ is the wavelength of the X-ray (Å), d is the distance between the same plane plane (Å), and θ is the diffraction angle (°). The highest peak intensities at 2 θ 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 inferogram. The inferogram 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)

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 siza

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.

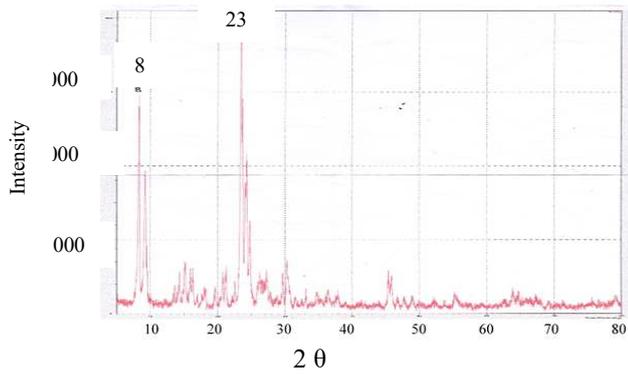


Figure 2 shows the ZSM-5 membrane X-ray diffraction pattern resulting that the highest intensities at $2\theta = 8$ and 23° are characteristic of the ZSM-5 standard (ICSD 91010).

Figure 2. ZSM-5 Membrane X-ray diffraction pattern (Diponegoro University Integrated Laboratory)

Pretreatment	SEM Gauze Magnification 300 x	SEM ZSM-5 Membrane Magnification 20.000 x
Initial		
I		
II		
III		

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 Pre-treatment % w / v	Composition PI %w/v	After PII % w/v	Pretreatment PIII % w/v
Awal	C	6.12	18.69	10.42	18.69
	SiO ₂	0.82	0.61	0.88	0.61
	Cr ₂ O ₃	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
	Na ₂ O		4.90	5.19	2.64
	Al ₂ O ₃		3.06	1.55	1.35
	SiO ₂		77.74	79.49	82.79
	SiO ₂ .		25.41	51.28	61.33
	Al ₂ O ₃				

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.

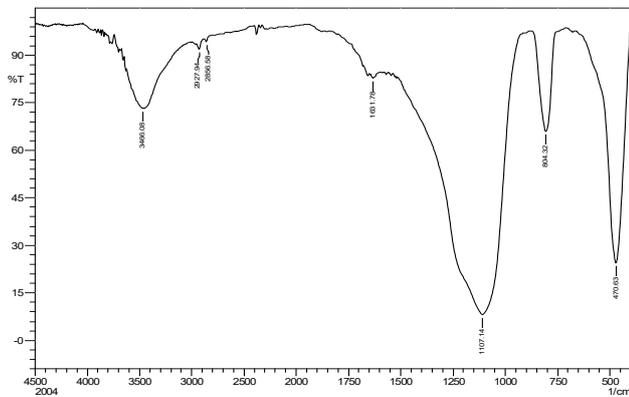


Fig 4. FTIR spectra of ZSM-5 membrane with a 304-200 supports that has been given pretreatment I soaked in 95% toluene for 12 hours, then in 15% HCl 15% solution for 20 minutes

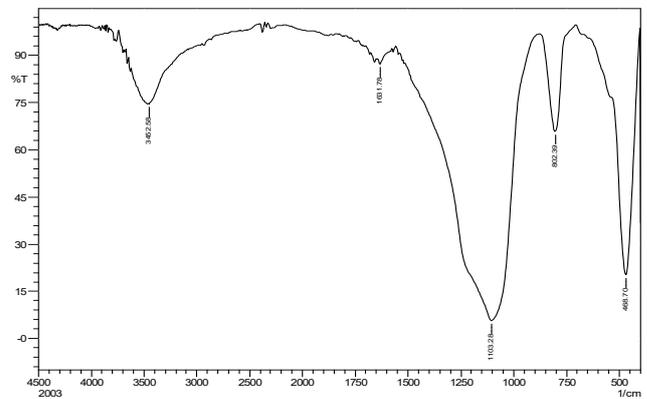


Fig 5. FTIR spectra of ZSM-5 membrane with a 304-200 supports that has been given pretreatment II (immersed in 15% NaOH, then immersed in 15% HCl solution, then electro-oxidized with 20% H₂SO₄ 20 minutes each with a constant voltage of 3-5 V and a strong current of 0.01 A)

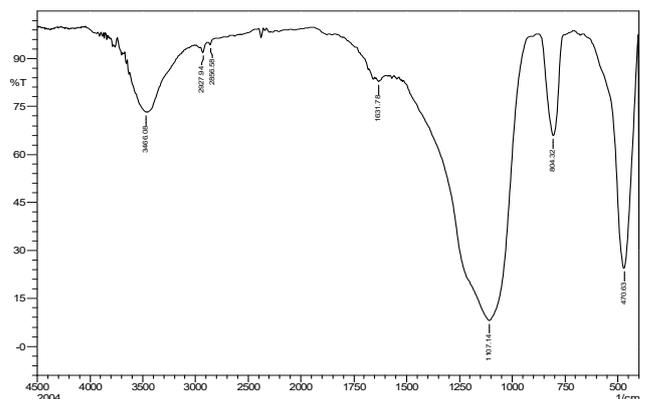


Figure 6. FTIR spectra of ZSM-5 membrane with a 304-200 supports that has been given pretreatment III (immersed in 95% toluene 12 hours, then in 15% HCl solution for 6 hours, and in 0.1 M TPABr solution for 12 hours).

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 research⁹.

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 0.1 M NaBrO₃ for 12 hours.

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