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A Novel Method for the Growth of ZSM-5 Membranes on Stainless steel Supports by coating on Reactor Vessel with Surface-to-volume Ratio of Synthesis Governing Low Temperature Crystallization of ZSM-5

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Abstract

ZSM-5 membranes have been prepared using a novel seeding method. By sonicating ZSM-5 seed crystals in the presence of a stainless steel mesh of size followed by a controlled low temperature synthesis step it has been shown by XRD, FTIR, and SEM-EDX. The growth of ZSM-5 zeolite at stainless steel can be used to produce ZSM-5 zeolite membranes on reactor vessel with surface-to-volume ratio was the highest of the reactor vessel. Surface-to-volume ratio influences the heat-transfer during the synthesis, which further governs the crystallization of ZSM-5. It was found that the higher the surface-to-volume of the reactor, the more crystalline the resulting product. The result for the theoretical review paper were necessary to research the synthesis of ZSM-5 membrane based on the variation of type and size stainless steel and pretreatment of the stainless steel to use as a membrane suppport. The ratio of surface area to volume of the first reactor is the highest 1.44 influence more effective heat transfer process and the crystallinity of the zeolite ZSM-5 in the synthesis of ZSM-5 zeolite.

Keywords: ZSM-5 membrane, type and size of the stainless steel, pretreatment, vessel reactor.

1. Introduction

1.1 Backgrounds

ZSM-5 zeolite membrane is a precursor of zeolite ZSM-5 coated on a support such as gauze stainless steel and its synthesis could be done by coatings at low temperatures. The growth of ZSM-5 zeolite membranes requires some differences in synthetic techniques due to the porous (non-continuous) nature of the supports. A range of zeolite membranes have been successfully grown on the surface of porous stainless steel (SS) [1], porous alumina [2-6] and membranes have also been produced by incorporation of preformed zeolite crystals.

Factors such as cost, mechanical strength, thermal stability, resistance to chemical attack, thermal conductivity, and easy of fabrication, stainless steel is a particularly attractive support material for a microporous membrane. Recently, we have successfully realized the synthesis of ZSM-5 below 100 °C using a plastic bottle as reactor [1]. Decelerated crystallization as a consequence of lowering the temperature can be compensated using a dense gel system in which the concentration of each reactant is enhanced [7]. Lowering the temperature below 100 °C necessitates the substitution of the stainless-steel reactor by a low-cost plastic reactor, otherwise the high autogenous pressure cannot be created during synthesis. In this contribution, we provide an investigation on the effect of the surface-to-volume ratio of the plastic reactor used in low-temperature synthesis of ZSM-5. Our present result suggests that the crystallization of ZSM-5 at low temperature is sensitive to the surface-to-volume ratio of the reactor vessel, which is likely to be correlated with the occurring heat transfer.

1.2 Gauze *Stainless-steel* Types and Sizes

Composition of chemistry *stainless steel* grid 304 based on research Murniati *et al*. (2012) [8] and AISI 316 (Louis *et al*., 2001) [9] on the Table 1.

Table 1 *Stainless-steel of* Type Gauze 304 and AISI 316

Composition of chemistry (%)	AISI 316	304
C	≤ 0,080	≤ 0,60
Si	≤ 1,00	≤ 1,00
Mn	≤ 2,00	≤ 2,00
P	≤ 0,045	≤ 0,045
S	0,03	0,03
Cr	18 – 20	8 – 10
Ni	19 – 22	8 – 10
Mo	2,00 - 3,00	-

Gauze *stainless-steel* 304 sizes were -100 mesh, -200 mesh, -300 mesh, dan -400 mesh, and AISI 316 size was -180 mesh.

1.3 Pretreatment of support and ZSM-5 zeolite membrane synthesis

Before low temperature treatments, the SS supports were pretreated with the pretreatment process kind of the SS supports:

1.3.1 The SS supports were first soaked in 95% toluene for 12 h, then washed in an ultrasonic bath for 20 min and rinsed thoroughly with deionized water. After that, the SS supports were soaked in 5% hydrochloric acid for 6 h, and then washed thoroughly with deionized water in an ultrasonic bath. Finally, the SS supports were soaked in 0.1M tetra-propyl ammonium bromide for 12 h and dried in an oven at 80 °C and then stored in a drier [9,10].

1.3.2 The SS supports were first soaked in First, they were immersed in a HNO_3 solution (1 wt %) for 4 h at 60 °C; then they were cleaned with distilled water and dried at room temperature.Finally, the supports were cleaned in acetone in an ultrasonic bath for 1 h. The clean supports were stored at 100 °C [12].

1.3.3 The SS supports were first soaked in 15% NaOH solution during 20 min in order to remove organic and in a 15% hydrochloric acid solution during 20 min in order to remove inorganic contaminations and electroxidation with 20 % sulfuric acid solution during 20 min with voltase constant 3-5 V; dan current 0,01A and dried in oven at 383 K for 1 h [13].

1.4 The theoretical review papers

The theoretical review papers were necessary to research the synthesis of ZSM-5 membrane based on the variation of type and size stainless steel, some pretreatment of the stainless steel to use as a membrane suppports, and investigation on the effect of the surface-to-volume ratio of the plastic reactor used in low-temperature synthesis of ZSM-5.

2. Methods

2.1 Participants

The objectives of this study were to investigate ZSM-5 coatings grown on stainless steel grids. Stainless steel AISI 316, mesh size of -180, stainless steel grid 304 were mesh size of -100, -200, and -400 mesh was used as a starting material for the preparation of the structured catalytic bed with zeolite oatings. The chemicals used in this study were Ludox HS-40 (colloidal silica, Sigma Aldrich), sodium aluminate ($NaAlO_2$, Sigma Aldrich), tetrapropylammonium bromide (TPABr, Sigma Aldrich), sodium hydroxide 50 %wt (NaOH, Merck), hydrochloric acid, sulfuric acid, aceton (Merck), toluene. and demineralized water (H_2O), They were in reagent grade and used directly, without post-treatment.

2.2 Instruments

Becker-plastic, polypropilen reactors 50 ml,100 mL, 240 mL, desicator 3L, pothensiometer, Water bath, termometer, pH meter Checker Hanna, *ultrasonic cleaner* Bronso 3510, analytical electric of balance, Buchner bottles, *stirrer*, *waterbath*, thermometer, oven (OF-12), furnace (Thermoline 4800), *Scanning Microscope Electron* (SEM)–EDX JEOL JSM-6510LV, *X-Ray Difractometer* (XRD) Philips PW 1710 dan Bruker D8 Discover menggunakan radiasi Cu-Kα, Fourier Transform Infra Red (FTIR) Prestige-21 Shimadzu, Japan, dengan detektor MTG-21 dan Elmer 3100 spektrometer, *Scanning Electron Microscope* (SEM) JEOL JSM-6510 LA, and SEM-EDX.

2.3 Procedures

2.3.1 Pretreatment of support and ZSM-5 zeolite membrane synthesis

Before low temperature treatments, the SS supports were pretreated with the pretreatment process kind of the SS supports (sub title 1.3) with gauze *stainless-steel* types and sizes, Stainless steel grid (AISI 316, wire diameter of 250 mm and mesh size 800 mm), wire mesh size of 180 was used as starting material for the preparation of the structured catalytic bed with zeolite coatings. The structured support packing was arranged by 9 cm^2. Pretreatment of support below ZSM-5 zeolite membrane synthesis was to defects on the metal surface until crystallisation centres during the synthesis of the zeolite coating [13].

2.3.2 Synthesis of ZSM-5 using Reactor Vessels with Different Surface-to-volume Ratio

Surface-to-volume Ratio of Synthesis Reactor Vessel Governing Low Temperature Crystallization of ZSM-5 (7).

a. $NaAlO_2$ and NaOH solution were mixed together in four plastic (polypropilene) bottles reactors I, II, III and IV, with different surface-to-volume ratios serving as the synthesis reactor vessels, as illustrated in Figure 1. A stirred TPABr solution and Ludox HS-40 were then added to give a mixture with molar composition of 1 SiO_2: 0.005 Al_2O_3: 0.12 NaOH: 0.04 TPABr: 7.6 H_2O. The reactor vessel was sealed and vigorously stirred until a dense white gel was obtained.

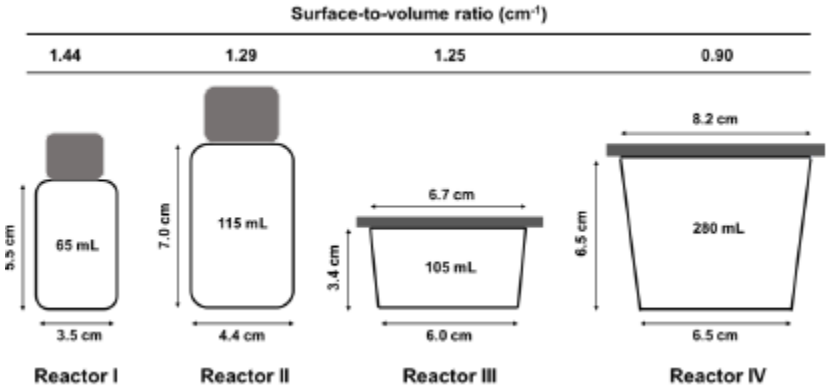

Figure 1 The reactor vessels with different surface-to-volume ratios used in the synthesis of ZSM-5 at low temperature.

b. The total weight of the synthesis mixture was fixed at 35 gram. The gel was afterwards poured in the polypropilene containing the vertically positioned catalytic support packing. The synthesis mixture was subsequently transferred to an oven and heated at a temperature of 90 °C for 4 days. After the reaction, ZSM-5 zeolite membranes were obtained and quenched to ambient temperature. These products were separated, washed with deionized water, dried at 100 °C and calcined at 550 °C for 6 hours. The coverage of a packing was determined as the mass of ZSM-5 zeolite coated referred to the geometrical surface of the support. The ratio between the amount of silicon incorporated in the zeolite matrix and the initial amount of silicon in the synthetic mixture gives the yield of the zeolite coating [7].

2.3.3 Synthesis of ZSM-5 Membranes on Stainless steel Supports by coating on Surface-to-volume Ratio of Synthesis Reactor Vessel Governing Low Temperature

The gel in procedures 2.3.2.(a) was afterwards poured in a polypropilene containing the vertically positioned catalytic support packing, the synthesis mixture was s1ubsequently transferred to an oven and heated at a temperature of 90 °C for 4 days. After the reaction, white solid products were obtained and quenched to ambient temperature. These products were separated, washed with deionized water, dried at 100 °C, and calcined at 550 °C for 6 hours. ZSM-5 zeolite membranes characterisized with XRD, FTIR, and SEM-EDX. This procedure is known to create defects on the metal surface, which become crystallisation centres during the synthesis of the zeolite coating in figure 2 [7].

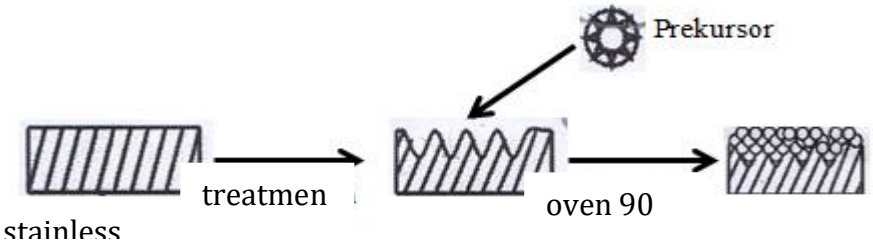

Figure 2 Synthesis of ZSM-5 using Reactor Vessels by coating method [7, 13].

3. Result

3.1 Synthesis of ZSM-5 using Reactor Vessels with Different Surface-to-volume Ratio

Based on research of Mukaromah *et al* (2016), crystallization of ZSM-5 at low temperature (90 ºC) was successfully achieved in 4 days. It should be noted that the TPABr used in this study was much lower than that of the typical syntheses with TPABr/Si ratio around 0.1-0.3. Figure 2(a) depicts the XRD patterns of the products from the different reactors. The products from reactors III and IV exhibited a bump around a 2θ angle of 15-35°, which is a characteristic feature of amorphous silica. Meanwhile, the products from reactors I and II displayed more intense reflections without observed amorphous bumps.

Figure 2(b) shows a plot of the surface-to-volume ratio of the reactors versus the crystallinity obtained from the XRD data. We found a proportional relationship between the crystallinity and the surface-to-volume ratio of the reactor, in which the higher the surface-to-volume ratio of the reactor, the higher the crystallinity of the obtained products.

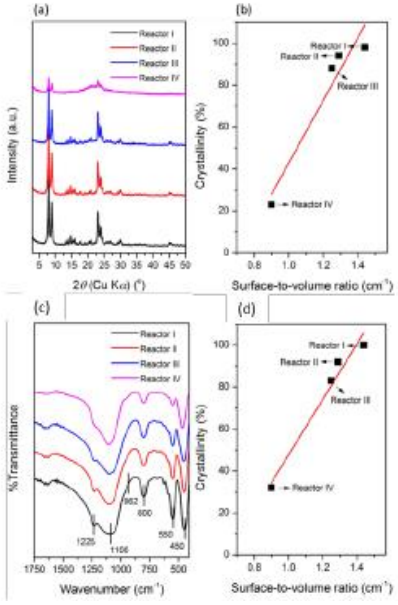

Figure 2 (a) XRD patterns
(b) plots of crystallinity derived from XRD pattern reactor I vs surface-to-volume ratio of the reactors
(c) FTIR spectra of the products and their plots of crystallinity versus surface-to-volume ratio of the reactors.

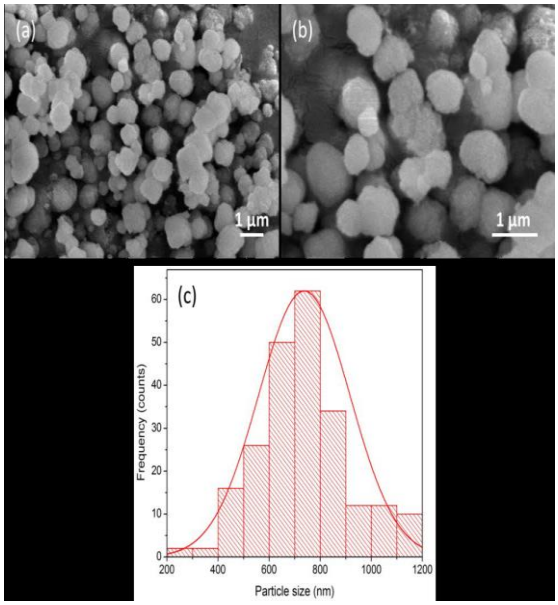

Figure 3 (a,b) SEM images of the products from (c) the corresponding histogram showing the particle size distribution of the ZSM-5 [7].

The results from the FTIR spectra support the insight that a reactor with a higher surface-to-volume ratio will result in higher crystalline products, as demonstrated by the XRD data. Reactors with a higher surface-to-volume ratio enhance the heat transfer. Presumably, a more effective heat transfer can induce nucleation more quickly since it is an energy-activated process, thus resulting in higher crystalline ZSM-5.

The information about the crystallinity of the products was estimated by the intensity ratio between the bands at 550 cm-1 and 450 cm-1 [14]. All of the band assignments were in accordance with the previous literatures [15, 16]. The order of the crystallinity showed a similarity compared to that of the XRD data, as shown in Figure 2(d). The results from the FTIR spectra support the insight that a reactor with a higher surface-to-volume ratio will result in higher crystalline products, as demonstrated by the XRD data. Reactors with a higher surface-to-volume ratio enhance the heat transfer. Presumably, a more effective heat transfer can induce nucleation more quickly since it is an energy-activated process, thus resulting in higher crystalline ZSM-5. It was clearly shown that the surface-to-volume ratio of the reactor governed the occurring crystallization of ZSM-5 below 100 °C.

It should be carefully noted that plastic material possesses lower thermal conductivity compared to that of stainless steel. Thus, the temperature increment rate that the inside part of a plastic reactor needs to reach the desired temperature is lower than that of a stainless-steel reactor. This merits further study to verify whether this temperature increment rate significantly influences the synthesis of ZSM-5 at low temperature. Nevertheless, it is interesting that not only high-temperature synthesis but also low-temperature synthesis of ZSM-5 is sensitive to the surface-to-volume ratio of the reactor. This provides a facile alternative way to control the crystallization of ZSM-5 at low temperature in addition to modifying the initial gel mixture or the synthesis conditions [7].

The products from reactor I were chosen to be further analyzed using SEM and an N2 adsorption-desorption method, since it possessed the highest crystallinity of the four samples. Figures 3(a) and (b) show an SEM image of the products from reactor I. The observed morphology was nearly spherical, with a size of around 700 nm as calculated by the histogram in Figure 3(c). The calculated crystallite size using the Scherrer equation, was 40 nm, suggesting that the observed particle was not a single particle but an aggregate composed of smaller ZSM-5 crystallites. Under low-temperature synthesis, a great number of nuclei may be formed resulting in nano-sized ZSM-5 crystallites. It has been previously reported that TPA^+ can act as a scaffolding agent to help assembling these nano-sized crystallites [1,17]. Furthermore, since the size of the

crystallites is smaller than 1 µm, van der Waals interaction can be particularly significant to keep the crystallites together in an aggregate [18]. This occurrence may enable the presence of mesopores through the voids between the smaller crystallites.

3.2. Pretreatment of support and ZSM-5 zeolite membrane synthesis

Based on research of Louis *et al.* (2001) [9], the objectives of this study were to investigate HZSM-5 coating grown on stainless steel grids for benzene oxidation by N_2O. Fig. 4 shows the yield of the zeolite coa ting and the support coverage in the three steps of synthesis. It is seen that during the first step only a 10% yield was obtained, while the second and the third steps gave an yield of 25%.

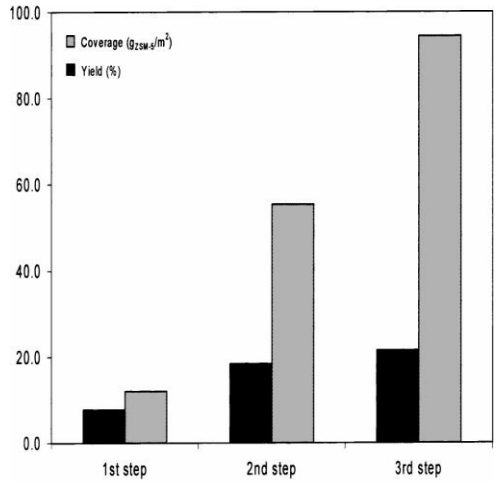

Fig. 4 Grid coverage and yields of the three steps synthesis of zeolite coatings.

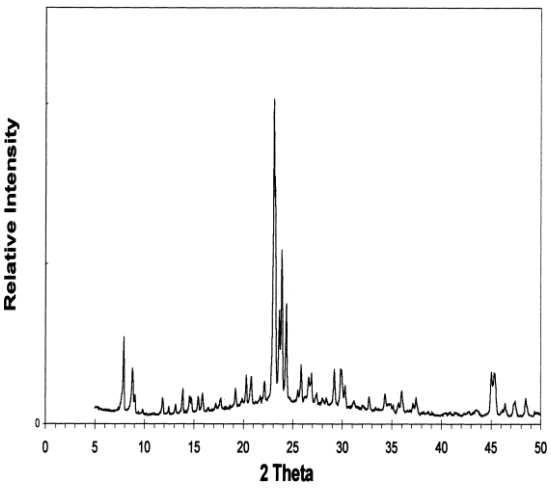

Fig. 5 X-ray powder diffraction pattern of zeolite ZSM-5 scratched from the stainless steel support.

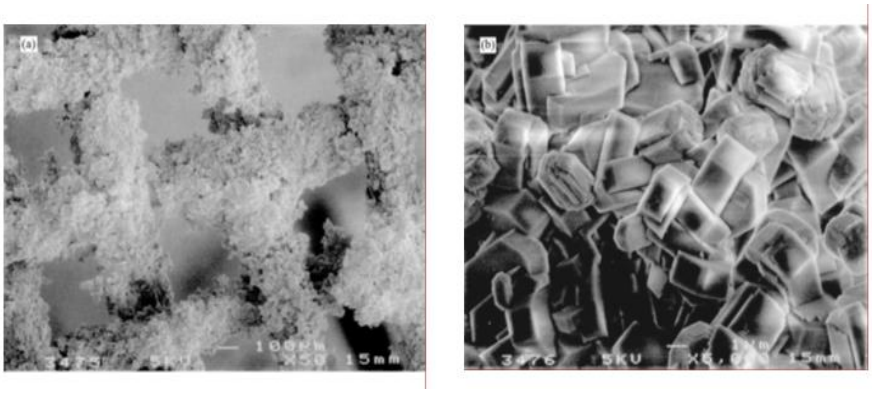

Fig.6. SEM photographs of zeolite coatings: (a) the surface of the grid; (b) morphology of the zeolite crystals.

Fig. 6a shows a SEM micrograph of the structured catalytic coating showing complete metal coverage. The thickness of the zeolite layer was estimated to be about 38mm. Fig. 6b shows the prismatic crystals orphology which is the character of ZSM-5. The elemental analysis of the zeolite layer studied by EDX analysis found a Si/Al ratio of 65. The XRD powder pattern of the crystals, which were scratched from the grid surface, confirmed the MFI structure (Fig. 5). The BET surface area was 302 m^2 g ZSM-5^{-1} with a total pore volume of 0.29 cm^3 gZSM-5^{-1} [9].

4. Discussion

` Crystallization of ZSM-5 at low temperature (90 °C) was successfully realized, even with a very low amount of TPABr. The course of crystallization is sensitive to the surface-to-volume ratio of the used plastic reactor due to the difference in heat transfer in each reactor. A more effective heat transfer may enhance the course of nucleation during the synthesis, which results in higher crystalline ZSM-5 products [7].

This pretreatment procedure on variation stainless steel types and sizes are known to create defects on the metal surface, which become crystallisation centres during the synthesis of the zeolite coating. The coverage of a packing was determined as the mass of zeolite coated referred to the geometrical surface of the support. The ratio between the amount of silicon incorporated in the zeolite matrix and the initial amount of silicon in the

synthetic mixture gives the yield of the zeolite coating [9].

5. Conclusions

In conclusion this result for study review papers are:

1. pretreatment of support below ZSM-5 zeolite membrane synthesis was to defects on the metal surface until crystallisation centres during the synthesis of the zeolite coating. It is therefore necessary to research the synthesis of ZSM-5 membrane based on the variation of type and size stainless steel and pretreatment of the stainless steel to use as a membrane suppport.
2. the ratio of surface area to volume of the first reactor is the highest 1.44 influence more e'ffective heat transfer process and the crystallinity of the zeolite ZSM-5 in the synthesis of ZSM-5 zeolite.

6. References

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