Synthesis of ZSM-5 Directly from Kaolin without Organic Template:
Part-1: Effect of Crystallization Time

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Zeolite socony mobile-5 (ZSM-5) have been successfully synthesized directly from kaolin without using organic templates. ZSM-5 were synthesized by hydrothermal method at 175 °C with variation on crystallization time of 12, 24, 48 and 72 h. The molar composition of the zeolite was 10Na2O:100SiO2:Al2O3:1800H2O. The analysis of both from X-ray diffraction and FT-IR spectra showed that the ZSM-5 started to be formed during the crystallization time of 12 h. ZSM-5 with crystallization time of 24 h exhibit the highest crystallinity, about 101.17 % based on the reference. The crystallinity decrease on the crystallization time of 48 and 72 h. In addition, the surface morphology of ZSM-5 investigated by SEM showed that the sample with Si/Al ratio of 5.74-9.49 with variation time of 24, 48 and 72 h formed aggregate with a hexagonal crystal shape without sharp angle. However, the samples with crystallization time of 12 h showed irregular shape.

Keywords: Kaolin, Kaolinite, ZSM-5, Zeolite, Hydrothermal, Synthesis.
Synthesis of ZSM-5: ZSM-5 were synthesized directly from kaolin without organic template. The crystallization times varied with variation of 12, 24, 48 and 72 h. The synthesis method was adopted from the method reported by Prasetyoko et al. [14]. The molar ratio composition of zeolites was 10Na2O:100SiO2:2Al2O3:1800H2O. Synthesis was started by weighing the demineralized water and dividing it into two parts. In the first half of demineralized water, 1 g of NaOH was dissolved. Then 1.15 g of kaolin was added under stirring. 22.83 g of LUDOX was then added and the stirring speed was increased. After the addition of silica sol (LUDOX), a homogeneous solution was formed. Meanwhile, the second half demineralized water was then added to the solution. The mixture was stirred at 550 rpm for 8 h. After stirring, the mixture was left for 12 h at room temperature. 0.09 g of silicalite was added as the seed of ZSM-5. After addition of silicalite, the hydrothermal process was carried out at 175 °C with variation time of 12, 24, 48 and 72 h, denoted as ZSM-5/12, ZSM-5/24, ZSM-5/48 and ZSM-5/72. The formed solid was washed with distilled water and dried in an oven at 110 °C for 12 h.

The crystal phase of the synthesized zeolite was identified using X-ray diffraction (XRD) with CuKα1 (λ = 1.5405 Å) radiation in 2θ from 5-40° with scanning step of 0.04°/sec. The crystallinity of synthesized zeolites were calculated using eqn. 1 with reflection at 2θ = 22.5-25°. Silicalite diffraction patterns is used as the reference reflection. The functional group contained in the zeolites was examined using FT-IR at wavenumber range from 4000-400 cm⁻¹. The zeolites morphologies were investigated using scanning electron microscope equipped with energy dispersive X-ray (SEM-EDX) to confirm the Si/Al ratio.

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\text{Crystallinity (%) = \frac{\text{Sample reflection intensity}}{\text{Reference intensity}}} \times 100 \ (1)
\]

RESULTS AND DISCUSSION

Synthesis of zeolite socony mobile-5 (ZSM-5): Synthesis was carried out with the molar composition of 10Na2O:100SiO2:2Al2O3:1800H2O. Silicalite seed was added in amount of 1 % of the mass of solids. Precursors including kaolin were used as a source of alumina and silica. Silica sol (LUDOX) is used as an additional source of silica, NaOH as a source of Na⁺ ions and as mineralization agent. The presence of NaOH has function to trigger the crystal formation. Silicalite seed crystals with MFI structure was added to help initiating the formation of ZSM-5 crystal and demineralized water was added as a source of H2O. The synthesis stages includes hydrolysis, gelation, aging and crystallization.

Synthesis was begun by dissolving NaOH in demineralized water. Then, the kaolin was added under stirring using magnetic stirrer. Silica sol (LUDOX) was added slowly to the mixture. The stirring was continued at the speed of 550 rpm for 8 h at room temperature to homogenize the mixture. In homogenous mixture, the composition of every part of the mixture were dispersed. In this process, hydrolysis and gelation stages occurred and produced a thick white gel. Furthermore, the aging process was carried out for 12 h. This aging process lead to the formation of bond and structural rearrangement of the solid and liquid phase [15]. After aging, the silicalite seed was added and stirred to disperse it. Once completed, the hydrothermal process was carried out at 175 °C with variation on crystallization time of 12, 24, 48 and 72 h. In general, reaction occurred in the synthesis is:

\[
\text{AlSiO} \_{12}(\text{OH})_8(s) + \text{H}_2\text{O}(l) + \text{NaOH}(aq) + \text{SiO}_3(aq) \rightarrow \\
\text{Na}_6[\text{Al}_n\text{Si}_{16-n}\text{O}_{42}] \cdot 16\text{H}_2\text{O} \text{Si(OH)}_4(aq) \ (2)
\]

Reactions in eqn. 1 occurs at high temperatures in a closed environment with water solvent. The system was closed so the composition of the reactants will not be changed or reduced. In the hydrothermal process, the condensation reaction allows for the formation of new bonds between atoms such as Si, Al-O-Si, Al (TOT) [13]. The resulted solid was washed using distilled water until it reaches neutral pH and then dried in an oven at 110 °C for 12 h to remove residual water from washing process.

Characterization of ZSM-5

X-ray diffraction (XRD): X-ray diffraction pattern of kaolin, silicalite and ZSM-5 with crystallization time of 12, 24, 48 and 72 h are shown in Fig. 1. The characteristic reflections of kaoline is identified by the presence of reflections at 2θ of 12.32; 19.87; 20.34; 24.85; 26.61; 28.51; 34.95; 35.40; 35.91; 38.37 and 39.22° (Fig. 1a). The XRD pattern of kaolin has a sharp reflections at 2θ of 12.3 and 24.8° and small broad reflections at 2θ 20.5 and 35-38.5°. These results are similar with previous report by Alkan et al. [16].

Fig. 1. XRD patterns of the samples (a) kaolin, (b) silicalite and ZSM-5 with a time of crystallization (c) 12, (d) 24 (e) 48 and (f) 72 h

The amorphous ZSM-5 is appeared on the crystallization time of 12 h by the presence of hump at 2θ 17-33°. Comparing
to the kaolin pattern which exhibits high intensity reflections, the hump indicates that the kaolin as zeolite precursor forms amorphous silica phase after hydrothermal process for 12 h. However, the presence of characteristic reflections of ZSM-5 with low intensity in ZSM-5/12 sample at 2θ 7.9, 8.7 and 23.13° indicates that the ZSM-5 crystal has begun to be formed. This result suggest that ZSM-5 with crystallization time of 12 h is still in the early stages of crystal nucleation process.

The characteristic reflections of ZSM-5 are appeared on ZSM-5/24, ZSM-5/48 and ZSM-5/72 samples as shown in Fig. 1d-f. These reflections appear at 2θ 7.85, 8.78, 22.99, 23.21, 23.61, 23.81 and 24.29°. Based on the these XRD patterns, the patterns seem to have the same characteristic reflections. This suggests that all three samples have the same phase. Analysis of the sample’s reflections based on XRD powder patterns for zeolites indicates that the pattern of reflections with 2θ of 7.94, 8.8, 8.9, 23.1 and 23.98° is in good accordance with the MFI (inverted mordenite framework) zeolite structure type, therefore, ZSM-5 samples with crystallization time of 24, 48 and 72 h have MFI structure [17].

In addition to the pattern reflections at the same 2θ, the XRD patterns of ZSM-5/24, ZSM-5/48 and ZSM-5/72 exhibit sharp reflections with high intensity. This result indicates that all of these samples are crystalline solids. Therefore, to determine the degree of crystallinity, the crystallinity was calculated using eqn. 1. The results of calculations are presented in Table-1.

| 2θ (°) | ZSM-5/12 | ZSM-5/12 | ZSM-5/12 | ZSM-5/12 |
|--------|----------|----------|----------|----------|
| 7.85-7.89 | 18.48 | 203.23 | 163.99 | 169.54 |
| 8.78-8.81 | 19.91 | 137.09 | 112.35 | 107.95 |
| 22.99-23.03 | 45.51 | 588.37 | 573.54 | 538.98 |
| 23.21-23.24 | - | 462.41 | 446.6 | 413.87 |
| 23.61-23.67 | - | 283.4 | 269.21 | 296.61 |
| 23.81-23.87 | - | 308.74 | 298.13 | 258.52 |
| 24.29-24.32 | - | 162.89 | 176.24 | 151.94 |

Crystallinity (%) (average): 2.55 101.17 98.81 93.00

ZSM-5/24 samples exhibits the highest crystallinity. It is about 101.17% relative to the reference. However, the crystallinity of the sample does not increase with the increasing of crystallization time (48 and 72 h). Prasetyoko and Ayunanda [14] reported that the solution of amorphous silica systems tends to form stable crystals at high temperature. Thus we predict that the formed ZSM-5 crystals were dissolved again to the solution forming more stable crystal within crystallization time of 48 and 72 h. In this study, the crystallization time was very influential on the formation of ZSM-5 crystals in which the optimum formation time of ZSM-5 is for 24 h at a temperature of 175 °C and the crystallinity of the solids is 101.17%.

**Infrared spectroscopy:** Analysis of infrared spectroscopy is used to determine functional group in synthesized solid. Kaolin sample exhibits bands at wavenumbers 429, 468, 540, 697, 757, 789, 917, 1031 and 1108 cm⁻¹ (Fig. 2a). According to Chandrasekhar [4], the bands in IR spectra of kaolin at wavenumber 540 cm⁻¹ indicates the Al-O bond vibrations in Al[O(OH)]₆; at 789 and 914 cm⁻¹ show the bond vibration of (Al-O-H) in Al[O(OH)]₆; at 430, 693, 752, 794, 1035, 1096 and 1114 cm⁻¹ show the vibration of Si-O bonding in SiO₂ group.

The kaolin bands at wavenumbers 429, 468, 697, 757, 917, 1031 and 1108 cm⁻¹ do not appear in the infrared spectra of samples of ZSM-5/12 (Fig. 2b). The disappearance of these bands indicate that the bonds in kaolin are disconnected to start forming new bonds. These data are supported by X-ray diffraction data on samples that high crystalline kaolin has turned into amorphous phase after hydrothermal process for 12 h as evidenced by the hump at 2θ 17-33°.

IR spectra of ZSM-5 is typically consist of five characteristic bands as shown in Fig. 2b. Band in 1221-1102 cm⁻¹ region is resulted from the asymmetric stretching vibration of T-O-T bond; 796 cm⁻¹ from the symmetric stretching vibration bond of T-O-T; 546 cm⁻¹ from the framework vibration at pentacyclic ring which is characteristic of the MFI-type zeolite structure and 450 cm⁻¹ resulted from vibration of the T-O-T bending bond, where T is Si or Al atoms [18].

Based on Fig. 2b-d, the bands of infrared spectra at wavenumbers around 543 cm⁻¹ from ZSM-5/12h has the lowest intensity while the ZSM-5/24 sample has the highest intensity. This intensity is steady to the sample with crystallization time of 48 and 72 h (ZSM-5/48 and ZSM-5/72). According to Mohammed [19] the bands at 450 and 542 cm⁻¹ are the characteristic of crystalline ZSM-5 which has the form of MFI structure [19]. The same result was reported by Somani et al. [20], who reported that the increasing band intensity at wavenumber of 550 cm⁻¹ shows the concentration of the higher MFI structure. These results are consistent with XRD result of the four samples.
[21] and Ali et al. [22], the band around 1229 cm\(^{-1}\) indicates the presence of three-dimensional shape of the channel pore. As described by Ali et al. [22] the bands at 1219 and 542 cm\(^{-1}\) are the characteristic bands of zeolite ZSM-5 which distinguish it with the others, due to the vibration of the MFI structure. Therefore, ZSM-5/12 samples has structure of ZSM-5 crystals, however the crystal are not perfect yet and is still in the early stages of nucleation.

**Scanning electron microscopy-energy dispersive X-ray (SEM-EDX):** Surface morphology of ZSM-5 samples are shown in Fig. 3. As seen in Fig. 3a, ZSM-5 sample with crystallization time 12 h has irregular morphology as fragments with diverse shapes. The particle sizes are around 0.57-2.57 µm. These results are consistent with X-ray diffraction data that the ZSM-5 samples with crystallization time 12 h has amorphous phase. However, the ZSM-5/24, ZSM-5/48 and ZSM-5/72 samples form the aggregate with a hexagonal crystal shape without sharp angle.

**Table 2**

| Sample (h) | Si  | Al  | O   | Na  | Si/Al | Particle size |
|------------|-----|-----|-----|-----|-------|---------------|
| 12         | 12.90 | 1.55 | 2.35 | 67.89 | 8.32  | Small         |
| 24         | 18.69 | 1.97 | 2.77 | 71.82 | 9.49  | Large         |
| 24         | 13.26 | 1.52 | 2.15 | 68.83 | 8.72  | Small         |
| 48         | 18.89 | 3.24 | 3.53 | 68.89 | 5.83  | Large         |
| 48         | 11.93 | 1.43 | 1.92 | 64.00 | 8.34  | Small         |
| 72         | 19.57 | 3.41 | 3.76 | 69.70 | 5.74  | Large         |
| 72         | 11.13 | 1.39 | 1.89 | 61.27 | 8.01  | Small         |

**Conclusion**

ZSM-5 has been synthesized directly from kaolin without organic template with crystallization time of 12, 24, 48 and 72 h. Synthesis was carried out with kaolin precursor as main source of alumina and silica; NaOH as an agent of mineralization and source of Na\(^+\) ions; silicalite as seed and LUDOX as a source of additional silica. The analysis using XRD and IR showed that the ZSM-5 began to be formed during the crystallization time of 12 h. ZSM-5 on the crystallization time of 24 h had the highest crystallinity and began to decrease at the crystallization time of 48 and 72 h. In addition, based on the SEM-EDX analysis of all samples shows the ratios of Si/Al between 5.74 to 9.49 with hexagonal shape, except for the sample at 12 h crystallization time which exhibited irregular shape.

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