On The Synthesis of ZSM-5 Directly from Kaolin Bangka with Aging Time

D Hartanto1,*, A B Pambudi1, D N Cahyanti1, and W P Utomo1
1Department of Chemistry, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia.

*Corresponding author: djokohar@chem.its.ac.id

Abstract. ZSM-5 has been synthesized in this study using hydrothermal method with addition of ZSM-5 seed. Synthesis of ZSM-5 in this study using kaolin bangka as alumina source with aging time of 0, 12, 24 and 36 hours and the effect of aging time was also investigated. Samples were characterized by XRD, FT-IR, SEM and SEM EDX. ZSM-5 samples with aging 24 hours has the highest intensity at 2θ = 23.03° with crystallinity of 69.60%. The vibration at wavenumbers 540 and 1220 cm⁻¹ was shown in the sample with 24 hours aging, it was indicated that a large number of pentasil rings have been formed. These results are consistent with XRD data which shows that samples with aging 24 hours have the highest crystallinity. The size of ZSM-5 sample with an aging time 24 hours was about 4.5 μm. EDX results obtained Si / Al ratio in samples with aging time 0, 12 hours and 24 hours is 10.77; 11.23 and 8.34. All samples showed a Si / Al ratio above 5 which showed that the ZSM-5 had been formed. But morphologically, samples with aging 24 hours have a more uniform crystal shape.

1. Introduction
ZSM-5 is one of the microporous crystalline aluminosilicate zeolites with MFI structure which has a channel opening size of 5.2-5.6 Å [1,2]. Among zeolites family, ZSM-5 has an excellent heterogeneous acidity, great thermal and mechanical stability, well shape selectivity and interconnected two-dimensional micropore system which contribute to usage as catalyst in petroleum and petrochemical industry [3]. ZSM-5 are commonly synthetized by the hydrothermal method of the mother liquor containing precursor of silica, alumina and organic template as SDA [4,5]. However, the usage of Structure-directing agent (SDA), which is Tetrapropyl ammonium hydroxide (TPAOH) or tetrapropyl ammonium bromide (TPABr), in the synthesis of ZSM-5 cause many adverse problem such as coke deposition due incomplete combustion, harmful gas production from thermal decomposition, water contamination and high production cost [6,7]. Therefore, to overcome those adverse problem, many research has been conducted to synthesis ZSM-5 in the absence of organic template.

Bangka Belitung kaolin is promising natural resource as raw material to synthesis of ZSM-5. The element deposits can be estimated using geostatistics and geotechnical methods [8,9]. According to Hartanto et al. (2016) the use of sources of alumina and silica from natural materials such as kaolin, ash and rice flies can reduce the cost of basic ingredients for the synthesis processes. Kaolinite [Al₂Si₂O₅(OH)₄] is a two-layered aluminosilicate clay mineral, consisting of one alumina octahedron sheet and one silica tetrahedron sheet in a 1:1 stoichiometric ratio. Because its alumina content, kaolinite has been frequently used as the starting material for synthesis of zeolite such as SAPOs,
LTA, FAU and MOR \[10,11,12\]. Synthesis of ZSM-5 requires high Si/Al ratio, which means it necessary to further processing of the kaolinite. Some efforts have been devoted to synthesizing ZSM-5 zeolites from kaolinite via dealumination of the metakaolin or addition an alternative silica source \[13,14\].

Here, we report direct synthesis of ZSM-5 using kaolin bangka as the Si and Al sources without prior pre-treatment with seeding method. ZSM-5 seed was employed in this procedure as structure-directing agent (SDA) to obtain MFI-type framework, while LUDOX used as additional silica to control Si/Al ratio. The transformation of kaolin into zeolite was monitored by the change of functional group, phase and crystallinity at various aging condition.

## 2. Experimental

### 2.1. Materials

All materials used in this work were analytical grade. NaOH (Merck, Germany). LUDOX® HS-40 colloidal silica (30 % Si in water) was purchased from Aldrich, Germany. Kaolin (containing 57 % SiO$_2$ and 22 % Al$_2$O$_3$) was taken from Bangka Belitung, Indonesia without further purification. The self-synthesized ZSM-5 were used as the seed. Aqua DI was taken from a Millipore Milli-Q system and used within 1 week.

### 2.2. Methods

Synthesis of ZSM-5 without organic templates was used hydrothermal method and addition of ZSM-5 seed. ZSM-5 which was synthesized has a molar ratio : 10Na$_2$O : 120SiO$_2$ : 2Al$_2$O$_3$ : 1800H$_2$O. The Synthesis was started by weighing an aquademiner which according to its molten composition of 16.5927 grams. Aquademiner was divided into two parts. In the first half, 0.8 grams of NaOH were added and stirred until dissolved. After dissolved completely, 0.9266 grams kaolin bangka were added while stirring with a magnetic stirrer. Then, 22.5817 grams LUDOX was added slowly and the stirring rate was increased to 400 rpm. After the zeolite solution, half the second part of the aquademiner was added to the mixture. The stirring rate was increased to 550 rpm and stirred for 8 hours. After stirring was completed, aging has been done at room temperature with variations of 0, 12, 24 and 36 hours. The results of aging was added ZSM-5 seed by 3% by weight, which is 0.255 grams while stirring with magnetic stirrer for 30 minutes. Then the results of the mixture were put in a stainless steel autoclave for hydrothermal processes at a temperature of 175°C for 24 hours. The slurry of hydrothermal was neutralized with aquademiner until the pH of the solid neutral. After that, the samples was dried in oven at 110°C for 12 hours.

### 2.3. Characterization

Characterization of resulted product was measured by powder X-ray diffraction (XRD) patterns on PANalytical X'pert diffractometer with Cu Kα (λ=1.5418 Å) radiation generated at 40 kV, 40 mA. The crystallinity of synthesized product was calculated using reflection at 2θ = 23.01°. The functional group identification of product was carried out using Fourier Transform Infrared (FTIR) Shimadzu Instrument Spectrum One 8400S to analyse function group on finger print area. The morphology of the synthesized particles was examined by SEM (Model: Zeiss, EVO MA 10, Germany) operating with an accelerating voltage of 10 kV.

## 3. Result and Discussion

### 3.1. XRD Analysis

The XRD patterns from Bangka kaolin, ZSM-5 seed, ZSM-5 samples with aging time 0, 12, 24 and 36 hours are shown in Fig. 1. The XRD patterns from Bangka kaolin in Fig. 1a. shows the peaks at 2θ = 12.32; 19.87; 20.34; 24.85; 26.61; 34.95; 35.40; 35.91; 38.37 and 39.22°. The characteristic diffraction peaks of kaolin can be observed at 2θ = 12.3; 24.8; and 38.3° \[15\]. Fig 1c, 1d, 1e and 1f shown peaks at 2θ = 7.9; 8.8; 8.9; 23.0 and 23.1°. These peaks correspond to the characteristic peaks of the ZSM-5 with MFI structures \[16\]. The characteristic diffraction peaks of kaolin at 2θ = 12.3; 24.8; and 38.3°
did not appear on the diffractogram of ZSM-5 with aging variation. This indicates that kaolin has dissolved and formed ZSM-5 crystals.

The XRD pattern from ZSM-5 samples with aging 0 hours (Fig. 1c) shows sharp peaks at $2\theta = 7.91; 8.85$ and $23.02^\circ$. These sharp peaks indicated that the ZSM-5 crystal has been formed and allows the crystalline nucleus to have formed although aging time 0 hours. However, the crystallinity of ZSM-5 with aging time of 0 hours was still low due to crystal growth was not optimal.

XRD patterns from ZSM-5 samples with aging 12 and 24 hours are shown in Fig 1d and 1e. The results of the diffractogram from these samples have a pattern that is not different from the ZSM-5 sample with aging 0 hours. The highest peaks in aging samples 12 and 24 hours were at $2\theta = 8.82; 8.85; 7.91; 7.94$ and $23.03^\circ$. Fig. 1e show the peak at $2\theta = 23.03^\circ$, it was higher than the three other aging variation samples. The peak height indicated that the ZSM-5 sample with aging 24 hours has the highest intensity which means it also has the highest crystallinity.

![Graph showing diffractogram pattern](image)

Figure 1. Diffractogram pattern of (a) Kaolin Bangka, (b) ZSM-5 seed, ZSM-5 sample with aging (c) 0 hours, (d) 12 hours, (e) 24 hours and (f) 36 hours.

ZSM-5 samples with an aging time of 36 hours had peaks that were identical to other aging time variation samples at $2\theta = 8.01; 8.93$ and $23.17^\circ$. In the ZSM-5 sample with 36 hours aging variation,
it have a decrease in crystallinity but not significant. In the ZSM-5 sample with aging 12 and 24 hours, crystal growth occurred, this was evidenced by the increase in crystallinity with increasing aging as shown in Table 1.

Aging time has a role in the crystallinity of the ZSM-5 samples formed. Table 1 shown that ZSM-5 samples with aging 0 hours have the lowest crystallinity. Crystallinity during aging 12 and 24 hours increased in a row but when aging 36 hours decreased crystallinity. The longer the aging time during synthesis, the percentage of crystallinity of ZSM-5 produced was greater but with prolonged aging time, the crystallinity of the ZSM-5 sample were reduced. The nucleation and growth of crystals from zeolite was occured during the aging process [17]. Therefore, each sample of ZSM-5 has a different amount of crystals. Increasing amount of crystal facet of the ZSM-5 sample, then the x-ray was reflected are increasing so that their intensities higher. Therefore, in this study aging time was very influential on the formation of ZSM-5 crystals where the optimum formation of ZSM-5 was aging 24 hours with crystallinity of 69.60%

Table 1. The intensity and crystallinity of ZSM-5 samples with aging time variation.

| Sample            | 2θ (°) | Intensity (cps) | Crystallinity (%) |
|-------------------|--------|----------------|-------------------|
| ZSM-5 seed        | 23,14  | 1813           | 100               |
| Aging 0 hours     | 23,14  | 904            | 49,86             |
| Aging 12 hours    | 23,02  | 971            | 53,55             |
| Aging 24 hours    | 23,03  | 1262           | 69,60             |
| Aging 36 hours    | 23,12  | 1088           | 60,01             |

3.2. FT-IR Spectra

The infrared spectra of kaolin samples, ZSM-5 seeds, ZSM-5 samples with aging time 0 hours, 12 hours, 24 hours and 36 hours are shown in Fig. 2. The infrared spectra of kaolin (fig. 2.a) show peaks at wave numbers 430, 470, 538, 700, 754, 788, 912, 1008, 1029 and 1110 cm\(^{-1}\). This result was supported by Panda et al. (2010) reports that specific peaks of kaolin are in the 912 cm\(^{-1}\) region indicating the bending vibration of the Al-Al-OH bond [18]. In the wave number regions 1032, 1100 and 1114 cm\(^{-1}\), there is a Si-O bending bond. The wave number area of 755 cm\(^{-1}\) indicates the Si-O-Al bond. In the wave number area 693 and 541 cm\(^{-1}\) both show the vibration of the Si-O and Si-O-Al bending bonds.

The spectra of ZSM-5 seed (fig. 2b) show specific peaks at wave numbers 453, 563, 798, 1103, and 1226 cm\(^{-1}\). Flanigen et al. (1971) reported that the peaks in the wave number are peaks that result from internal bond vibrations of SiO\(_4\) or AlO\(_4\) tetrahedral [19]. The peak at wave number 453 cm\(^{-1}\) shows the internal bond vibration of the Si-O-Si bond, the peak at 550 cm\(^{-1}\) shows the vibration of the pentasil ring frame which shows the formation of MFI structures [20]; the peak at 798 cm\(^{-1}\) shows the symmetrical stretching vibration of the Si-O-Si bond; and peaks at 1103 cm\(^{-1}\) and 1226 cm\(^{-1}\) show asymmetric stretch vibrations of Si-O-Si bonds. Similar results have also been reported by Prasetyoko (2006) [21].

The infrared spectra of the ZSM-5 sample in Fig. 2(c),(d),(e) and (f) show the five wave number peaks of about 452, 545, 792, 1090 and 1222 cm\(^{-1}\). While the peaks in the regions of 430, 470, 700, 754, 912, 1110 cm\(^{-1}\) which are typical of kaolin have been lost, this indicates that the kaolin bonds are broken and begin to form new bonds. This is in accordance with the report of Mohammed et al. (2005) that the absorption band that appears around 1200-1000 cm\(^{-1}\) shows the internal bond of the tetrahedral asymmetric stretch vibration of the Si-O-T where T is Si or Al [22]. Vibration of external asymmetry
stretching is indicated by the absorption band at 1200 cm\(^{-1}\) while the internal vibration of asymmetry is indicated by the absorption band of 1100 cm\(^{-1}\). Absorption band around 788 cm\(^{-1}\) shows internal stretch vibration. Goncalves et al (2008) reported that the fifth ring in the ZSM-5 pentasil zeolite structure can be shown from the absorption band around 546 cm\(^{-1}\) [23]. The band around 455 cm\(^{-1}\) shows the tetrahedral bending vibration of TO\(_4\). The existence of the ZSM-5 can be determined by the appearance of peaks in these areas. Wave numbers that appear around 1225 and 545 cm\(^{-1}\) are sensitive peaks of the MFI structure [24].

![Figure 2. IR spectra of (a) Bangka Kaolin, (b) ZSM-5 seeds, ZSM-5 samples with aging (c) 0 hours, (d) 12 hours, (e) 24 hours and (f) 36 hours](image)

The areas in wave numbers around 1220 and 540 cm\(^{-1}\) did not have a sharp peak in the ZSM-5 sample without aging. This shows that there are still few MFI structures formed in the sample without
aging. These results support the results of the XRD pattern of ZSM-5 samples without aging which indicates that the sample without aging still has low crystallinity. Meanwhile, samples with an aging time of 12 hours showed a fairly sharp peak at wave numbers 540 and 1220 cm\(^{-1}\), but not too significant when compared with aging samples 0 hours. The peak is also found in other aging variations. These results indicate that the structure of ZSM-5 has been well formed in the sample with variations in aging time 12, 24 and 36 hours. The sharp peak intensity in wave numbers 540 and 1220 cm\(^{-1}\) is show in the sample with 24 hours aging indicating that a large number of pentasil rings have been formed. These results are consistent with XRD data which shows that samples with aging 24 hours have the highest crystallinity. However, it appears that the peak intensity in the sample with aging 36 hours in the wave number area 540 and 1220 cm\(^{-1}\) decreases. This indicates that the number of pentasil rings that mark the ZSM-5 structure has been reduced. This result is also consistent with the results obtained from XRD data which showed that the crystallinity of the sample decreased at 36 hours of aging. The peaks from the results of infrared spectroscopy characterization on samples with aging times 0, 12, 24 and 36 hours are shown in Table 2.

Table 2. The wavenumbers of infrared spectra from ZSM-5 samples with variations in aging time.

| Sample  | Stretching vibration asymmetry (cm\(^{-1}\)) | Stretching vibration symmetry (cm\(^{-1}\)) | Pentacle structure (cm\(^{-1}\)) | Bending vibration T-O (cm\(^{-1}\)) |
|---------|---------------------------------------------|---------------------------------------------|----------------------------------|-----------------------------------|
| 0 hours | 1222                                        | 1091                                        | 792                             | 545                               |
| 12 hours| 1222                                        | 1091                                        | 792                             | 545                               |
| 24 hours| 1222                                        | 1089                                        | 792                             | 545                               |
| 36 hours| 1222                                        | 1089                                        | 792                             | 545                               |

3.3. SEM images and SEM EDX
Morphology and size of crystals from solids were observed using Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray to determine the abundance of the elements present in the sample. Fig. 3, Fig. 4 and Fig. 5 are the morphology of ZSM-5 samples with aging times 0, 12 and 24 hours. The crystal formed is like a rectangle (hexagonal) with a sloping elbow.
The Crystal Morphology from ZSM-5 samples with aging 0 hours in Fig.3. looks uniform. This crystal uniformity shows that ZSM-5 crystals have formed even without aging. This is consistent with the XRD results of aging 0-hours ZSM-5 samples that appear typical of ZSM-5 peaks. The size of formed ZSM-5 in aging 0 hours samples was around 1.7 μm. In the ZSM-5 sample with an aging time 12-hours, ZSM-5 crystal hexagonal formed with a sloping elbow but clustered. The size of the ZSM-5 formed is about 2.6 μm. Morphology from the ZSM-5 sample with aging 24 hours was not different from the aging sample 12 hours but more uniform, not clustered and the size of the sample was larger which was about 4.5 μm. Crystal sample uniformity with 24-hours aging was supported by XRD results with the highest crystallinity of 69.60%

From the results of the SEM analysis above shows that the bulk size increases as the aging time increases. At the time of aging the crystal growth process occurs, the longer the aging process is given, the more time for the crystal growth process so that the size of the crystal formed increases. The elements contained in the ZSM-5 sample synthesized with aging variations 0, 12 and 24 hours can be seen from the EDX results. Table 3. shows the EDX results from each sample having the same content, namely Si, Al, Na, and O. The distribution of these elements is quite evenly distributed from the three samples and has almost the same percentage levels. Based on EDX results obtained Si / Al ratio in samples with aging time 0, 12 hours and 24 hours is 10.77; 11.23 and 8.34. All samples showed a Si / Al ratio above 5 which showed that the ZSM-5 had been formed. But morphologically, samples with aging 24 hours (Fig. 5) have a more uniform crystal shape.
Table 3. EDX results of ZSM-5 sample with aging time variation

| Sample   | Atom percent (%) |       |       |       |       |
|----------|------------------|-------|-------|-------|-------|
|          | Si    | Al    | Na    | O     | Si/Al |
| 0 hours  | 24.57 | 2.28  | 2.36  | 66.07 | 10.77 |
| 12 hours | 27.63 | 2.46  | 2.55  | 60.50 | 11.23 |
| 24 hours | 25.23 | 3.06  | 2.67  | 63.58 | 8.34  |

Figure 6. EDX results of ZSM-5 samples with an aging time of 24 hours

4. Conclusion

ZSM-5 has been synthesized using hydrothermal method with addition of ZSM-5 seed and kaolin bangka as alumina source. Synthesis ZSM-5 was used variations aging time of 0, 12, 24 and 36 hours to determine which ZSM-5 sample has a good crystallinity. ZSM-5 sample with 24-hours aging has the highest crystallinity of 69.60% was supported by XRD results with the larger particle size was about 4.5 μm. In XRD analysis, the ZSM-5 sample with aging 12 and 24 hours, crystal growth occurred, this was evidenced by the increase in crystallinity with increasing aging but with aging 36 hours it have a decrease in crystallinity but not significant. In FT-IR analysis, the areas in wave numbers around 1220 and 540 cm\(^{-1}\) did not have a sharp peak in the ZSM-5 sample without aging. Meanwhile, samples with an aging time of 12, 24 and 36 hours showed a fairly sharp peak at wave numbers 540 and 1220 cm\(^{-1}\). These results indicate that the structure of ZSM-5 has been well formed.

From the results of the SEM analysis shows that the bulk size increases as the aging time increases. At the time of aging the crystal growth process occurs, the longer the aging process is given, the more time for the crystal growth process so that the size of the crystal formed increases.

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