Effect of H$_2$O/SiO$_2$ molar ratio on direct synthesis of ZSM-5 from Bangka’s kaolin without pretreatment

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Graphical abstract

INTRODUCTION

Zeolite is aluminosilicate crystal that have pore and 3D framework. Based on their framework, International Zeolite Association (IZA) reported that zeolite have 218 framework (Kovo et al, 2009). Different type of zeolite framework has different application and properties.

Zeolite has many utilization on industrial area, it has many advantages compared with others mineral because it has a uniform and regularity pore, strength acid site, and some type of zeolite has good thermal stability (Sun et al, 2007). Many researchers use zeolite as adsorben, ion exchanger, molecular siever and catalyst. Zeolite also has ability to solve waste water problem like active sludge material (Soraya et al, 2012). Beside natural zeolite, zeolite synthetic also developed by many researcher.

Zeolite Socony Mobil-5 (ZSM-5) is a type of zeolite that have pore channel on it’s structure. Oil refinery and petrochemical industry use ZSM-5 as catalyst. In catalyst area, ZSM-5 called as heterogenous catalyst that have Brønsted and Lewis site. ZSM-5 use as catalyst for many reaction such as isomerisation, alkilation, catayltic cracking, epocpsidation, hydrolisis, etc (Kovo et al. 2011), utilization of tetrapropilamonium (TPA+) has many problem such as difficult to degradation, high cost, and need of higher temperature to release the template (Dey et al, 2013). The high temperature of calcined might able to destroyed zeolite structure and decreasing crystallinity of ZSM-5. So, another promising way to synthesis of ZSM-5 is direct synthesis. Kim et al reported to direct synthesis of ZSM-5 with two step, first is nucleation at 190°C and continuely by crystalization at 150-165°C (Kim et al, 2004). The advantages of direct synthesis is low calcined temperature, no treatment for source of silica and alumina (Kaolin). Synthesis of Zeolite use kaolin as source was reported by many researcher. Direct synthesis also use addition of ZSM-5 seed, after condensation and polymerisation reaction, percuor will form zeolite as well as their seed (Xue et al, 2012).

Direct synthesis of ZSM-5 without organic template was influenced by some factor like temperature, Si/Al molar ratio, and also H$_2$O/SiO$_2$ molar ratio. Generally, the higher temperature increase crystallinity, but every material has their limit. After optimum temperature, crystallinity of ZSM-5 would decrease, its caused higher temperature could broke zeolite structure (Dey et al, 2013 ;Hartanto et al, 2016). Another factor which influenced were H$_2$O/SiO$_2$ molar ratio. The amount of SiO$_2$ can controlled by addition of LUDOX as silica source and water play important thing in hydrothermal synthesis, its as place to crystal growth. But, if amount of water too much, process of synthesis would disturb by increasing amount of Na$^+$ and OH$^-$ on process reaction. Its would disturb crystal formation and the product would has low crystallinity. In this study focus to find optimum H$_2$O/SiO$_2$ molar ratio on ZSM-5 crystal formation.

EXPERIMENTAL

Materials

NaOH (Merck, 99%), LUDOX (Aldroich, 30 wt% of Si), Bangka Belitung’s Kaolin (45,86% of SiO$_2$ and 22% of Al$_2$O$_3$), ZSM-5 seed or Silicalite seed, and aquademineralization.
Synthesis of zeolite socony mobil-5 (ZSM-5)

In this research, ZSM-5 synthesized without organic template with different variation of H2O/SiO2 molar ratio : 15, 25, 30, and 35. The synthesis pathway follow a method was reported by Prasetyoko et al with 10Na2O:120SiO2:2Al2O3:1800H2O. 0.8 g of NaOH solute with water (Prasetyoko et al., 2012). Then, Kaolin added into NaOH solution under constant stirring until form white mixture. LUDOX was added into mixture and stirring during 8 hour (speed 400 rpm). The mixture left undisturbed condition during 12 hours at room temperature (aging). Next step, 0.085 (1 wt%) Silicalite seed added into the mixture and stirring for 30 minutes and then mixture moved into autoclave steel for hydrothermal process. Hydrothermal process under close condition at 175°C and the crystallization time is 24 hours. Solid product washed with aquadum and drying at 110°C during 12 hour.

Characterization of ZSM-5

The product of synthesis characterized by XRD JOEL JDX 3530 to determine crystal structure, Fourrrier Transform Infrared (FTIR) Shimadza Instrument Spectrum One 8400S to analyze function group on finger print area, and Scanning Electron Microscopy (SEM) FEI Inspect S25 and Energy Disspersive X-Ray (EDX) EDAX AMETEX to analyze morphology and compound of product, respectively.

Crystalinity of product also determine from diffractogram, which calculated using equation:

\[
\text{Crystallinity (\%) : Intensity of sample/Intensity of ZSM-5 Commercil x 100%}
\] (1)

RESULTS AND DISCUSSION

Direct synthesis of ZSM-5

Direct synthesis of ZSM-5 followed in this reaction (Xue et al., 2012):

\[
\text{Kaolin (s) + NaOH (aq) + H2O (l) + SiO2 (aq) } \rightarrow \text{ZSM-5(s)}
\] (2)

Reaction (Sun et al., 2007; Hartanto et al., 2016; Hartanto et al., 2016). Use water as solvent and the condition was closed. In this hydrothermal synthesis would form Al-O-Si or T-O-T (T = Al or Si) by condensation reaction, its continuously by polimerisation reaction and framework would follow ZSM-5 seed, the product will have same framework with ZSM-5 seed that followed Mordenite Framework Inverted (MFI) or researcher called product as ZSM-5.

Fig. 1 XRD Pattern of (a) Kaolin (b) ZSM-5 Seed (c) ZSM-5 Commercil, ZSM-5 with H2O/SiO2 molar ratio (d) 15 (e) 25 (f) 30 (g) 35

Diffractogram of ZSM-5

ZSM-5 characterized by XRD at 2θ between 5-40°. Diffractogram of Bangka Belitung’s kaolin (Fig. 1a) shown narrow peak at 2θ : 12.32, 19.87, 20.34, 24.85, 26.61, 34.95, 35.40, 35.91, 38.97, and 39.22°. This result match with kaolinit which has specific peak at 2θ on 20.5° and 35-38.5°. Based on XRD pattern, ZSM-5 have good stability, so kaolin can’t transform to ZSM-5 and the product has low crystalinity of ZSM-5 (Prasetyoko et al., 2012).

Infrared spectrum of ZSM-5

Synthesize product characterized by FTIR to analyze functional group at finger print area. Figure 2 exhibit infrared spectrum from Kaolin, ZSM-5 seed, and also the synthesis product. Infrared spectrum of kaolin on Fig 2a showed specific peak at 429, 468, 540, 697, 757, 789, 917, 1031, and 1108 cm⁻¹. Chandrasekar et al reported peak of kaolin, the wavenumber of 540 cm⁻¹ indicate vibration of Al-O, 789 and 914 cm⁻¹ represent vibration of Al-OH, 430, 693, 752, 974, 1035, 1096, and 1114 cm⁻¹ exhibit vibration of Si-O bonding on SiO₂(Treacy et al., 2001). The wavenumber of 1115 and 1008 cm⁻¹ obtained by stretching vibration from Si-O, the peak of 795 and 755 cm⁻¹ shown vibration of Si-O-Si, 755 and 697 cm⁻¹ is vibration of Al-O-H, 469 and 430 cm⁻¹ indicate vibration of Si-O (Treacy et al., 2001). Figure 2 represent peak of kaolin at 429, 468, 697, 757, 917, 1031, and 1108 cm⁻¹ did not appear on infrared spectrum of ZSM-5. Its indicate the bonding of kaolin have break and start to form new bond.

Infrared spectrum of ZSM-5 with different ratio shown in Fig 2(c-f). On spectrum appear peak at 453, 545, 792, 1092 and 1222 cm⁻¹. Based on previous research, ZSM-5 has 5 specific peak at 1221 and 1102 cm⁻¹ from stretching symmetric vibration of T-O-T, 796 cm⁻¹ obtained by stretching symmetric vibration of T-O-T, 546 cm⁻¹ showed framework vibration on pentacil ring and its characteristic of zeolite structure which has MFI type (Hartanto et al., 2016), and 450 cm⁻¹ exhibit bending vibration from T-O-T bondring, where T is Si or Al. Ali et al reported that peak of 1090 cm⁻¹ represent stretching asymmetric bending from SiO₄ tetrahedral, 545 cm⁻¹ showed external bonding from tetrahedral with framework and 455 cm⁻¹ represent bending vibration of Si-O bonding (Ali et al., 2003). Peak at 1224 cm⁻¹ exhibit a pore that have three dimention channel (Dong et al., 2003), its caused by external stretching asymmetric vibration of TO₄ (Ali et al., 2003; Hartanto et al., 2016). Based on data, it can concluded that the synthesize product is ZSM-5.

Based on Fig 2(c-f), peak of ZSM-5 at 543 cm⁻¹ from sampel with molar ratio 15 has lowest transmittance and molar ratio 30 has highest transmittance value.
Morphology of ZSM-5

The observation of morphology ZSM-5 using Scanning Electron Microscopy (SEM). Morphology of ZSM-5 with different molar ratio shown by fig 3 (a-c). ZSM-5 with H₂O/SiO₂ molar ratio 15 shown aggregation of crystal, and shape of crystal has irregularity. For ZSM-5 with molar ratio 25 and 30 exhibit uniformity of crystal shape. Based on figure, the shape of crystal is hexagonal prism.

Hexagonal prism of crystal confirm that product is ZSM-5. SEM micrograph result support XRD and FTIR result. The shape of crystal influenced by crystallinity of ZSM-5. The higher amount of crystallinity will produce good hexagonal prism on SEM micrograph. Beside that, uniformity of crystal shape also important to analyze. For more detail shape and size of crystal, its shown by fig 4 (a-c).

Crystal size determined by SEM and the result shown by fig 4. ZSM-5 with molar ratio 15 has lowest of crystal size with the value is 2.684 µm, crystal size of ZSM-5 with molar ratio 25 is 3.562 µm, and ZSM-5 with molar ratio 30 has highest of crystal size and its value is 3.795 µm. Increasing of crystal size equals with increasing of crystallinity of ZSM-5.

The increasing size of crystal at higher H₂O/SiO₂ molar ratio (15-30), its caused on this condition could break percusor crystal and hydrothermal synthesis was transformed percusor to ZSM-5. The higher amount of H₂O would increasing crystal size, H₂O is place to growth of crystal, increasing amount of water can increase crystal size. But, the amount of water has their limit and if its amount too much, its will decrease crystallinity.

Energy Disspersive X-Ray (EDX) result

EDX analysis has purpose to determine compound of ZSM-5 product, the result shown by Table 2. ZSM-5 contain Si, Al, Na, and O with different percentage. The high compound of ZSM-5 product is oxygen and its percentage reach 66.16% on ZSM-5 with molar ratio 25. Si/Al ratio of ZSM-5 product also determined on Table and the result
shown generally Si/Al for ZSM-5 product is 11.23, 11.70, and 11.41 for ZSM-5 with molar ratio 15, 25, and 30, respectively.

<table>
<thead>
<tr>
<th>H₂O/SiO₂</th>
<th>Percentage % Si Al Na O Si/Al</th>
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<tbody>
<tr>
<td>15</td>
<td>27.63 2.46 2.55 60.50 11.23</td>
</tr>
<tr>
<td>25</td>
<td>24.69 2.11 2.92 66.16 11.70</td>
</tr>
<tr>
<td>30</td>
<td>24.88 2.18 3.20 64.80 11.41</td>
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CONCLUSION

Bangka Belitung kaolin is promising natural resource as raw material to synthesis of ZSM-5. Where, its can use for direct synthesis and its product has different properties based on H₂O/SiO₂ molar ratio. The highest crystallinity is ZSM-5 with molar ratio 30 with the value 59.44%, its followed by molar ratio 25, 15, 35 and its value is 55.49; 24.88; 8.52%, respectively. The spectrum of infrared shows specific peak at 1221 and 1102 cm⁻¹ from stretching asymmetric vibration of T-O-T, 796 cm⁻¹ obtained by stretching symmetric vibration of T-O-T, 546 cm⁻¹ shown framework vibration on pentacil ring, and 450 cm⁻¹ exhibit bending vibration from T-O-T bonding, 545 cm⁻¹ shown external bonding from tetrahedral with framework and 455 cm⁻¹ shown bending vibration of Si-O bonding. Peak at 1224 cm⁻¹ represent a pore that have three dimention channel.

Observation of morphology from different H₂O/SiO₂ molar ratio represent different shape of crystal. ZSM-5 with H₂O/SiO₂ molar ratio 30 has shape like hexagonal prism and its also has highest crystal size with the value is 3.795 µm and followed by molar ratio 25 and 15 with value is 3.562 and 2.684 µm, respectively. EDX result shown Si/Al ratio for ZSM-5 with H₂O/SiO₂ molar ratio 15;25;30 is 11.23; 11.70; 11.41, respectively. From this work can concluded the optimum H₂O/SiO₂ molar ratio on direct synthesis of ZSM-5 is 30.

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REFERENCES