2016

Can kaolin function as source of alumina in the synthesis of ZSM-5 without an organic template using a seeding technique?

Djoko Hartanto, *Institut Teknologi Sepuluh Nopember*
Lai Sin Yuan, *University Technology Malaysia*
Sestriana Mutia Sari, *Institut Teknologi Sepuluh Nopember*
Djarot Sugiarso, *Institut Teknologi Sepuluh Nopember*
Irmina Kris Murwani, *Institut Teknologi Sepuluh Nopember*, et al.

MJFAS MALAYSIAN JOURNAL OF FUNDAMENTAL AND APPLIED SCIENCES
PRINT ISSN: 2289-5981 | ONLINE ISSN: 2289-599X

RESEARCH ARTICLE

Can kaolin function as source of alumina in the synthesis of ZSM-5 without an organic template using a seeding technique?

Djoko Hartanto [a], Lai Sin Yuan [b], Sestriana Mutia Sari [a], Djarot Sugiarso [a], Irmina Kris Murwani [a], Taslim Ersam [a], Didik Prasetyoko [a,*], Hadi Nur [b,*]

[a] *Department of Chemistry, Institut Teknologi Sepuluh Nopember, Jl. Arief Rahman Hakim, 60111 Surabaya, Indonesia*
[b] *Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*

* *Corresponding authors: hadi@kimia.fs.utm.my (H. Nur) and didikp@chem.its.ac.id (D. Prasetyoko)*

Article history
Received 10 March 2016
Received in revised form 15 June 2016
Accepted 29 June 2016

Abstract

ZSM-5 has been successfully synthesized by hydrothermal method using Indonesian Bangka kaolin as the aluminium source without an organic template and preactivation by calcination utilizing silicalite and ZSM-5 seedings. There are three parameters that made kaolin a very suitable aluminium source in the synthesis of ZSM-5 by using this method. The first parameter was the presence of types of seeds (silicalite and ZSM-5). Secondly, the molar ratio of Si/Al was in the range of 40–60. Thirdly, the concentrations of NaOH were varied from 6 to 12 mol with 1800 mol water. Interestingly, the use of silicalite seed produced pure ZSM-5 zeolite, whereas analcime and mordenite appeared as side products when ZSM-5 was used as the seed. The above effects can be illustrated by the following mechanism. Kaolin was fully dissolved in the basic mixture solution containing concentrated NaOH and silica sols, and followed by the crystallization in the presence of seeds (silicalite and ZSM-5). The mechanism was postulated on the basis of XRF, XRD, ^{29}Si and ^{27}Al MAS NMR analyses.

Keywords: Kaolin, silicalite seed, ZSM-5 seed, without organic template, hydrothermal, crystallinity

INTRODUCTION

The environments have been bestowed or conferred with abundant of resources that are very useful and beneficial in the manufacture of catalysts. Some minerals and synthetic chemicals can be adopted to synthesize the desired zeolites in this research, i.e. ZSM-5. ZSM-5, first made by Argauer and Landolt in 1972 [1], is a medium pore (~6 Å) zeolite with three-dimensional channels defined by 10-membered rings. Due to its unique channel structure, thermal stability, acidity, shape-selective property, ZSM-5 has been used as sorbents and catalysts, and applied to the petrochemical processing, fine chemical production, liquid and gas separation [2, 3]. ZSM-5 is also effective for hydrocarbon conversions [3, 4]. Moreover, its acidity can replace many hazardous acidic catalysts such as HF, HCl and H_2SO_4 [5], and hence, promoting the green technology or green chemistry. Since the ZSM-5 zeolite has been intensively studied, some natural and synthetic materials have been included in the synthesis processes are as such; (i) natural materials: smectite-type clay material [6], serpentine mineral [7], lignite fly ash and rice husk ash [8], kaolin or kite [9, 10]; (ii) synthetic materials: aluminium isopropoxide and tetraethylorthosilicate [11], sodium aluminate and silica sols [12], sodium silicate and aluminium sulfate [13], and other potential aluminium and silica sources.

In this research, we focus on kaolin or kaolinite which plays an exceptional role as an aluminium source to form ZSM-5 zeolite. Kaolinite, with the chemical formula $Al_2[Si_2O_5](OH)_4$, is a naturally occurring inorganic polymer with a layer structure consisting of siloxane and gibbsite-like layers. The siloxane layer is composed of SiO_4 tetrahedra linked in a hexagonal array [14, 15]. Kaolinite is formed by silicon tetrahedral sheets and aluminum octahedral sheets. Adjacent layers are linked by van der Waals forces and hydrogen bonds. The most reactive functional groups in kaolinite are hydroxyl groups, which are capable of taking part in many chemical reactions as well as ion exchange processes [16]. Kaolinite, an important industrial raw material, has a wide variety of applications in industry, particularly as a paper filler and coating pigment [17]. It is used as an extender in aqueous based paints [18] and a functional additive in polymers [19]. Kaolinite has also been used in polymer-based functional composites, plastic and rubber industry [9].

To date, natural kaolinite still has not yet been fully explored in the route of zeolites synthesis despite many researchers have dedicated in this field. It is reported that nano zeolite NaX formed from pre-heated Vietnamese kaolin was good for cumene adsorption, its crystallinity increased with alkaline and silica contents while the optimum crystallization temperature and aging time were 80 °C and 96 h, respectively [20]. Other research group used pre-heated Chinese Kaolin that was undergone hydrothermal method, the addition of NaOH and sodium silicate, to form alkali-modified pyrokaolin microspheres (AMKM) using ZSM-5 as seeds and without any templates. To compare to pyrokaolin microspheres (PKM) that synthesized by calcination only, the former one achieved better characteristics in terms of total surface area, micropore area, total pore volume, and micropore volume. Khatamian and Irani [10] adopted kaolin from Iran to produce ZSM-5 that pre-heated at 600 °C using tetrapropylammonium hydroxide (TPOH) as the template. They have found that the nanosized ZSM-5 crystallize at 168 h, 180 ºC and 0.02

Table 1 Composition of precursors, parameters of synthesis and physical properties of ZSM-5 zeolite.

Sample	Composition of precursors / wt%				Concentration of NaOH / mol	Aging time / h	Concentration of water / mol	Si/Al of precursor[b]	Structure of product[c]	Si/Al of product[d]	Relative crystallinity of ZSM-5 / %
	Kaolin	Seeds[a]		Silica sols							
		Silicalite	ZSM-5								
ZSM5(1)	7.5	0.6	-	92.0	10	24	1800	30	ZSM-5, amorphous	-[e]	3.6
ZSM5(2)	5.2	0.4	-	94.4	10	24	1800	40	ZSM-5	12.9	77.1
ZSM5(3)	4.0	0.3	-	95.7	10	24	1800	50	ZSM-5	13.1	100
ZSM5(4)	3.3	0.3	-	96.7	10	24	1800	60	ZSM-5	26.3	91.0
ZSM5(5)	4.0	-	0.31	95.7	10	24	1800	50	ZSM-5, analcime, mordenite	-[e]	100
ZSM5(6)	4.0	-	-	96.0	10	24	1800	50	amorphous	-[e]	-

[a] Two types of seeds, i.e. silicalite and ZSM-5, were used as precursors, respectively. There are two reaction systems in the synthesis of ZSM-5 zeolite; (i) Silicalite seed, kaolin, silica sols and NaOH; (ii) ZSM-5 seed; kaolin, silica sols and NaOH.
[b] The variation of initial molar ratios Si/Al in the synthesis of ZSM-5 zeolite calculated based on the concentration of kaolin and silica sols.
[c] The structure of products were determined by XRD.
[d] Molar ratios of Si/Al in ZSM-5 zeolite were determined by ^{29}Si MAS NMR (equation 2).
[e] Application of equation 1 to determine the Si/Al ratio by ^{29}Si MAS NMR is only possible if all signals can be assigned exclusively to crystalline ZSM-5.

Kaolin/silicic acid (%wt) achieved the highest crystallinity, meanwhile by increasing the Si/Al ratio in the zeolite, the crystal size of ZSM-5 became smaller. There is another kaolin from Nigeria, named as Nigerian Akoho Kaolin, being used by Kovo and co-workers [21] to form Zeolite Y and ZSM-5 [21]. Initially, quartz was removed from the kaolin. The next step is to heat the kaolin to metakite (activated phase) at short time (6 min) and low temperature (600 °C). Organic template, TPAOH was also adopted as a directing agent to form structures of ZSM-5 zeolites. There is other types of Kaolin, i.e. Jordanian kaolinite was used to study the relationship between the acid concentration and the SiO_2/Al_2O_3 ratio in the ZSM-5 final product [22]. The synthesis method for Jordanian kaolinite was quite similar with other kaolinite, in which it was calcined at 600 °C for 6 h to form metakaolinite. The metakaolinite was then dealuminated by sulphuric acid. Lastly, TPABr as the organic template was used to assist the formation of the ZSM-5 zeolitic framework.

Herein, Indonesian Bangka Kaolin, the natural kaolin is first time used for the synthesis of ZSM-5 zeolite. Therefore, many factors that influenced the formation of ZSM-5 from this kaolinite without using organic templates, which involving types of seeds, aging time, crystallization time, molar ratios of Si/Al, concentration of NaOH and water, were studied. According to some researchers [21, 23], kaolin has to be preactivated to form metakaolin by thermal treatment (900–1000 °C). Here, it has been demonstrated there is no preactivation is required when Indonesian Bangka Kaolin was used as the alumina source.

EXPERIMENTAL

Materials

All materials used in this work were analytical grade. NaOH (99 %) was purchased from Merck, Germany. LUDOX® HS-40 colloidal silica (30 % Si in water) was purchased from Aldrich, Germany. Kaolin (containing 57 % SiO_2 and 22 % Al_2O_3) was taken from Bangka Belitung, Indonesia. The self-synthesized silicalite and ZSM-5 were used as the seed.

Methods

ZSM-5 was synthesized directly from kaolin without the organic template. The synthesis method was adopted from the previous procedure reported previously [14]. The crystallization time was 72 h. The composition of precursors and parameters to synthesize ZSM-5 was tabulated in Table 1. The synthesis was started by weighing the demineralized and deionized water and dividing it into two parts. NaOH was dissolved in the first half of demineralized and deionized water. Then, kaolin was added under stirring. LUDOX® was then added and the stirring speed was increased. After the addition of LUDOX®, a homogeneous solution was formed. Meanwhile, the second half of water was then added to the solution. The mixture was stirred at 550 rpm for 8 h. After stirring, the mixture was aged at room temperature. 0.09 g of silicalite or ZSM-5 seeds was added as the seed of ZSM-5. After addition of silicalite or ZSM-5 seed, the hydrothermal process was carried out at 175 °C for 72 h. The effects of the composition of precursors, concentration of NaOH and concentration of water were studied with the variations of the amount of NaOH (2, 4, 6, 8, 10 and 12 mol), the amount of water (1500, 1800, 2000 and 2500 mol) and seed variation (ZSM-5 and silicalite). The obtained solid was washed with distilled water and dried in an oven at 110 °C for 12 h.

Characterizations

The crystal phase of the synthesized zeolite was identified using X-ray diffraction (XRD) with CuK_α (λ = 1.5405 Å) radiation in 2θ from 5–40° with scanning step of 0.04°/s. The relative crystallinity of synthesized zeolites was calculated using equation 1 using reflection at 2θ = 22.5-25°. The sum of the integrated areas from the XRD pattern of all the obtained samples were then compared with the sum of the integrated areas from the XRD pattern of the ZSM-5 with the highest crystallinity (equation 1).

$$\%\ \text{Crystallinity} = \left[\frac{\text{Area (sample)}}{\text{Area (reference)}}\right] \text{x } 100\% \qquad \text{(equation 1)}$$

Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on an Agilent DD2 500 MHz. The ^{29}Si spectra were recorded at resonance frequencies of 99.32 MHz with spinning rate of 9 kHz, a pulse width of 1.0 s and a recycle delay of 5 s. The NMR spectra were deconvoluted by using a Gauss-Lorentz peak shape (Gauss/Lorentz ratio = 1:1). The integrated areas of the deconvoluted peak were used to quantify the Si/Al framework ratio using the following formula.

$$\left(\frac{\text{Si}}{\text{Al}}\right) = \sum_{n=0}^{4} \text{I}_{\text{Si(nAl)}} \,/\, \sum_{\text{n=0}}^{4} \frac{\text{n}}{4}\left[\text{I}_{\text{Si(nAl)}}\right] \qquad \text{(equation 2)}$$

where $\text{I}_{\text{Si(nAl)}}$ = the total area of Si(nAl).

RESULTS

Composition of kaolin

Table 2 shows the composition of Indonesian Bangka Kaolin as analysed by X-ray Fluorescence (XRF). Alumina and silica are the major components in the kaolin, whereas the weight percentages of the other components, such as P_2O_5, K_2O, CaO, TiO_2 or Fe_3O_4 are less than 10%.

Table 2 The composition of Indonesian Bangka Kaolin.

Components	wt %
Al_2O_3	22.0
SiO_2	57.0
P_2O_5	3.9
K_2O	4.3
CaO	1.8
TiO_2	2.2
Fe_3O_4	8.9

Effects of different parameters towards formation of ZSM-5 zeolites

Table 1 shows the effects of the composition of precursors, concentration of NaOH, concentration of water, aging time on the structure and crystallinity of ZSM-5 zeolite product synthesized by using silicalite or ZSM-5 seeds with kaolin and LUDOX® as sources of alumina and silica, respectively. It is revealed that the types of seeds, the molar ratio of Si/Al, and the concentration of NaOH affect the structure of the product, the molar ratio of Si/Al (which is determined by ^{29}Si MAS NMR), and crystallinity of ZSM-5.

The relationship between the variation of NaOH concentration and relative crystallinity of ZSM-5 zeolite is studied, and the results are shown in Fig. 1. It is showed that the relative crystallinity or intensity of the diffraction peak in XRD patterns increased only after 4 mol NaOH. It is also revealed that the amount of water is one of the parameters that cannot be neglected. It is observed that low concentration water in the range of 1500–1800 mol possessed higher relative crystallinity compared to the high concentration of water (2000–2500 mol) (Fig. 2).

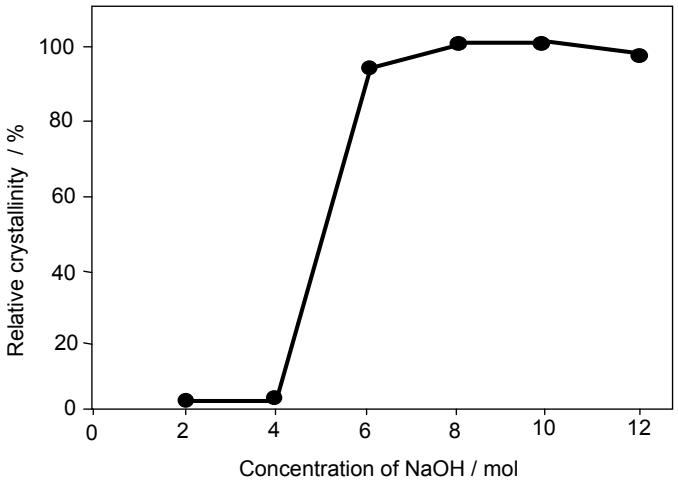

Fig. 1 Effect of concentration of NaOH (mol) towards crystallinity intensity (%). ZSM-5 zeolite was synthesized with molar ratio Si/Al 50, aging time 24 h, crystallization time 72 h, 1800 mol water and the presence of silicalite seed.

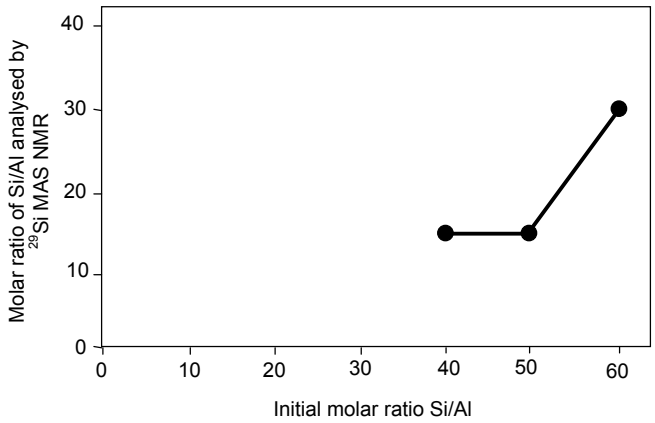

Fig. 2 Molar ratio of Si/Al determined by 29Si MAS NMR after formation of ZSM-5 zeolite. ZSM-5 zeolite was synthesized with 10 mol NaOH, aging time 24 h, crystallization time 72 h, 1800 mol water and the presence of silicalite seed.

According to Fig. 3, it can be observed that the series of the initial amount of SiO_2 added into the solution were not corresponded to the amount of SiO_2 as analysed by ^{29}Si MAS NMR. There is less amount of SiO_2 involved in the formation of ZSM-5 zeolite compared to the initial molar ratio of Si/Al were 40 to 60. Despite this, the trend of the SiO_2 amount determined by ^{29}Si MAS NMR was increasing in response to the initial molar ratio Si/Al up to 60.

XRD patterns analysis

Fig. 4 illustrates that the XRD patterns of kaolin and zeolite products synthesized with composition described in Table 1. It can be clearly seen that zeolitic products based on XRD diffractive peaks from seeds of ZSM-5 and silicalite are distinctive from kaolin. In light of this, it can be deduced that kaolin has fully dissolved in concentrated NaOH and lost its original structure in the process of synthesis. It is also found that only silicalite seeds can form ZSM-5 zeolite, but not for ZSM-5 seeds, as analcime and mordenite side products, were also produced from ZSM-5 seeds (see also Table 1).

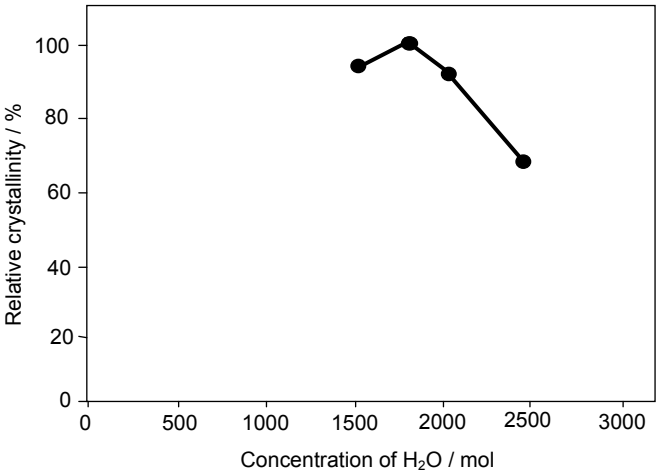

Fig. 3 Effect of addition of water (mol) towards crystallinity intensity (%). ZSM-5 zeolite was synthesized ZSM-5 zeolite with molar ratio Si/Al 50, 10 mol NaOH, aging time 24 h, crystallization time 72 h and the presence of silicalite seed.

^{27}Al MAS NMR analysis

^{27}Al MAS NMR spectroscopy was used to determine the coordination number for aluminium in ZSM-5 and indentify if there is extraframework of aluminium oxide species. Fig. 6 shows that

broadening sign al with larger peak area for molar ratio Si/Al 30 while sharpening with lower peak area at molar ratio Si/Al 40 to 60. This elucidates aluminium atoms have coordinated neatly in ZSM-5 framework after molar ratio Si/Al 30. ^{27}Al NMR spectra also elucidates that the absence of aluminium oxide species in extraframework at approximately 25 and 13 to –17 ppm. Furthermore, aluminium chemical shifts appear at approximately 50 ppm, indicating the aluminium atoms are tetrahedrally coordinated to their neighbouring species.

^{29}Si MAS NMR analysis

The results of ^{29}Si solid state MAS NMR is shown in Fig. 5. It is seen that ZSM-5 zeolite consists of two main peaks, which are denoted as Q^3=$HOSi(OSi)_3$ (−97 ppm) and Q^4=$Si(OSi)_4$ (−107 ppm). Typically, the Q^4=$Si(OSi)_4$ and $HOSi(OSi)_3$ are located at chemical shift of −110 and −100 ppm. As shown in Fig. 2, the Q^3 and Q^4 peaks are not well resolve (Fig. 2a) when molar ratio of Si/Al with 30 was added into the mixture solution containing kaolin, NaOH, water, and silicalite seed.

DISCUSSION

Effects of molar ratios Si/Al, aging time, concentration NaOH and water towards crystallinity

There are three main precursors for the synthesis of ZSM-5: Kaolin was adopted as a source of aluminium; silicalite and ZSM-5 were chosen as the seeds; silica sols were treated as silica source in controlling the molar ratio of Si/Al. NaOH was added into the reaction mixture to destruct and dissolve kaolin's layered structure.

Silicalite and ZSM-5 were alternatively utilized as the seeds in the synthesis process. Based on the observation, it is intriguing to note that the silicalite is the appropriate choice that could form ZSM-5 crystalline structure, however, the products obtained using ZSM-5 seed contained analcime and mordenite as the major components as shown in the XRD pattern (Fig. 4). It is probably due to ZSM-5 seed is not stable and underwent partial dissolution in the strong basic environment and disturb the formation of ZSM-5.

Stability of the silicalite seeds can be proven by the addition of NaOH into the mixture solution. It can be seen that silicate seeds cannot or very slow to be dissolved by NaOH regardless increasing of NaOH concentration at room temperature, on the other hand, ZSM-5 seeds containing Al can be easily dissolved into NaOH. These findings are in agreement with the thermal stability of silicalite presented by previous literature [24, 25].

Other than the above factors, the findings showed that molar ratio of Si/Al can also influence the crystallinity of ZSM-5. ZSM-5 cannot be synthesized with the molar ratio of Si/Al was 30. This is owing to alumina gives very strong repulsion effect in the highly negative environment. Therefore, by adding more amount of silica, from Si/Al molar ratios of 40 to 50, could definitely increase the crystallinity of ZSM-5 zeolite. In this case, the concentration of alumina is the critical factor to form ZSM-5 since, in this experiment, the minimum amount of the molar ratio of Si/Al was 40. This phenomenon can be explained by the fraction of Al atoms in the next nearest neighbours (NNN) T sites, in which the molar ratio Si/Al=24 is the minimum ratio for the formation of ZSM-5 based on proximity statistics analysis [26].

Structure of ZSM-5

There is another significant factor that plays the role in the formation of ZSM-5 structure, i.e. crystallization time, reported in our previous article [27]. It is displayed that highly ordered; the crystalline structure can be produced with longer crystallization time. Nonetheless, its optimum crystallization time was 24 h and the crystalline structure reduced after 36 h.

To further improve the crystallinity of ZSM-5, there was an approach used, i.e. the addition of water with the variation of concentration. It is found that fewer amount of the water, the better the crystallinity was observed. It is because the seeds were well-dispersed in the solution and meanwhile, they are located far from each other in the dilute environment. With such surrounding, the seeds could grow steadily under hydrolysis and condensation process of silica sols, silicalite, kand water, to produce highly ordered, crystalline ZSM-5 structure. Moreover, water present during synthesis occupies the internal voids of the structure. The water sorbed phase and organic non-framework cations can be removed by thermal treatment in the process, making the intracrystalline space available [28]. This ensures that the pore openings are uniform throughout the zeolites.

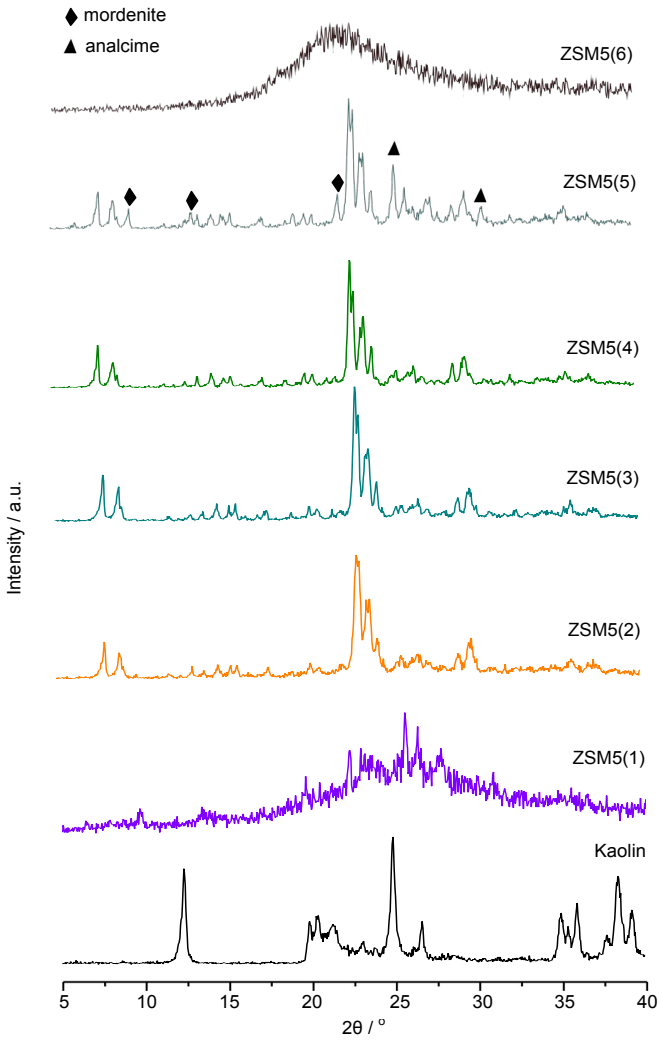

Fig. 4 XRD patterns of kaolin and ZSM-5 zeolites synthesized by using kaolin as alumina source.

The XRD patterns, ^{31}Si and ^{27}Al MAS NMR spectra of kaolin and ZSM-5 synthesized with a variation of Si/Al molar ratios are very significant in proving that the local coordination of silicon and aluminium are in a pure and crystalline ZSM-5 structure. As shown in Fig. 4, XRD pattern of kaolin is included as a comparison to show the structure of kaolin was disappeared to form ZSM-5 after some treatments, and also the increase of molar ratios Si/Al have no more contained the kaolin phase. It is clearly seen that the XRD pattern of molar ratio Si/Al 30 is broad without any apparent sharp peak, indicating it is in bulk, unorganized arrangement or amorphous structure. It is in agreement with ^{27}Al MAS NMR results (Fig. 6), which are broad peaks and their resonances at slightly higher chemical shifts. Conversely, Fig. 1 and Table 2 show the increasing in relative peak intensities with higher molar ratios of Si/Al (40–50), signifying the crystallinity of ZSM-5 have increased gradually. This is

corresponding to the sharp peaks of ^{27}Al NMR spectra (Fig. 6), which showing the neat coordinative bonding or arrangements (high crystallinity) as in XDR patterns.

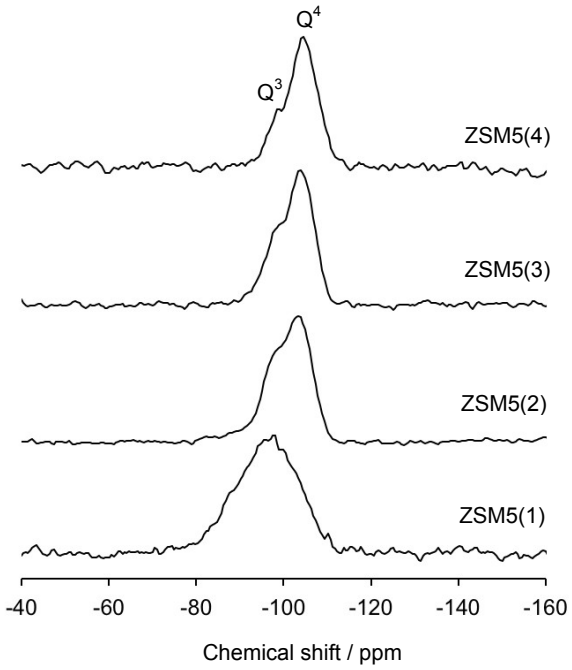

Fig. 5 The 29Si solid state MAS NMR spectra of ZSM-5 zeolite synthesized by using kaolin as alumina source.

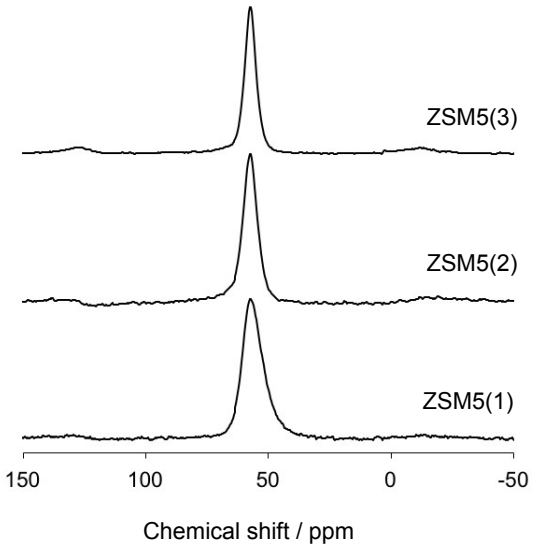

Fig. 6 The ^{27}Al MAS NMR spectra of ZSM-5 zeolite synthesized by using kaolin as alumina source.

As shown in Fig. 5, the Q^3 and Q^4 peaks in the ^{29}Si MAS NMR spectrum of ZSM5(1) are not well-resolve when molar ratio of Si/Al with 30 was added into the mixture solution containing kaolin, NaOH, water, and silicalite seed. It is due to the presence of aluminium amount is nearly equal to silicon concentration, whereby aluminium and silicon concentrations are proportional to the intensities of all the resonances, represented by these environments $Si(OSi)_{4-x}(OAl)_x$. There is another worth noting information in ^{29}Si MAS NMR spectrum of ZSM5(1), in which the spectrum is broader compared to ^{29}Si MAS NMR spectrum of ZSM5(2), ZSM5(3) and ZSM5(4) because involvement larger amount of aluminium from kaolin but lower silicon concentration from silicalite, has caused local disorder in the lattice of ZSM-5 framework substitution. Since the ZSM5(1) sample is amorphous (Table 1 and Fig. 4), application of equation 2 to determine the Si/Al ratio by ^{29}Si MAS NMR is not possible due to this equation can be applied only exclusively to crystalline ZSM-5.

As shown in Fig. 5, it is observed that Q^3 and Q^4 peaks are well-resolve with increase the amount of SiO_2 (molar ratios of Si/Al from 40 to 60). This evidence shows that the silicon coordinates in ordered way with its neighbouring –OSi or –OAl groups. In contrast, the Q^3 peak intensities decrease (^{29}Si MAS NMR spectra of ZSM5(2), ZSM5(3) and ZSM5(4) in Fig. 5) with higher amount of SiO_2 added, which indicating that the concentration of Q^3=HO–Si(OSi)$_3$ and AlO–Si(OSi)$_3$are reduced and more Q^4=Si(OSi)$_4$ signals are formed with gradual chemical shift to lower ppm.

Mechanism from seed to ZSM-5 zeolite

Fig. 7 illustrates the route synthesis of ZSM-5 products from different types of seeds: (i) silicalite; and (ii) ZSM-5. It is expected that both of the crystal seeds could be able to form ZSM-5 zeolitic framework as both of them are comprised of the product composition building units. Interestingly, only silicalite seeds can give out the desired zeolitic framework, whereas ZSM-5 seeds produced other types of the framework rather than ZSM-5 products, including mordenite and analcime structures.

Now, explanation of the route of syntheses and product formation explanation are as follows: Firstly, kaolin, as the source of alumina, was fully dissolved in the mixture solution containing concentrated NaOH and silica sols, followed by 24 h of aging time. Then, silicalite and ZSM-5 seeds were added into the basic solution, respectively. Here, it can be seen that silicalite seeds are very stable while ZSM-5 seeds partially dissolved in the strongly basic environment. Alumina source from kaolin, which was well-dispersed in the solution, can deposit onto the surface of silicalite seeds to form composite building units with terminal OH of the external sites; thereby, silica sols from the environment will be attracted to attach to the terminal OH of the seeds due to the hydrogen bonding. The composite units are continuously piling up and forming building blocks to produce the zeolitic framework of ZSM-5. The pure framework is successfully obtained from primary nucleation.

On the contrary, since ZSM-5 seeds were partially dissolved in the basic solution, then the only limited amount of alumina compositions can deposit onto the surface of ZSM-5 seeds to form ZSM-5 zeolite. At the meantime, the dissolved disappearance of these crystal seeds is owing to their transformation into mordenite and analcime frameworks as demonstrated in XRD results (see Fig. 4). The building blocks will pile up based on the mordenite and analcime in latter structure development. The existence of foreign crystal seeds in the solution has induced secondary nucleation.

CONCLUSION

In this research, it has been proven that Indonesian Bangka can be used as the aluminium source in the synthesis of ZSM-5 without an organic template using silicalite or ZSM-5 as seeds. It has been demonstrated that types of seed and the molar ratio of Si/Al are the determining factors for the success of the formation of highly crystalline ZSM-5. The concentration of NaOH also plays an important key factor in the synthesis of ZSM-5 since it can destruct and dissolve kaolin to deposit onto silicalite seed to form ZSM-5 zeolite. Lastly, we conclude that, based on the results, kaolin is a promising aluminium source in the synthesis of ZSM-5 without an organic template and preactivation by calcination, up to some extent.

ACKNOWLEDGEMENTS

The authors acknowledge to Directorate of Higher Education, Ministry of Education and Culture, Republic of Indonesia for financial support and Laboratory of Energy Studies ITS for technical support.

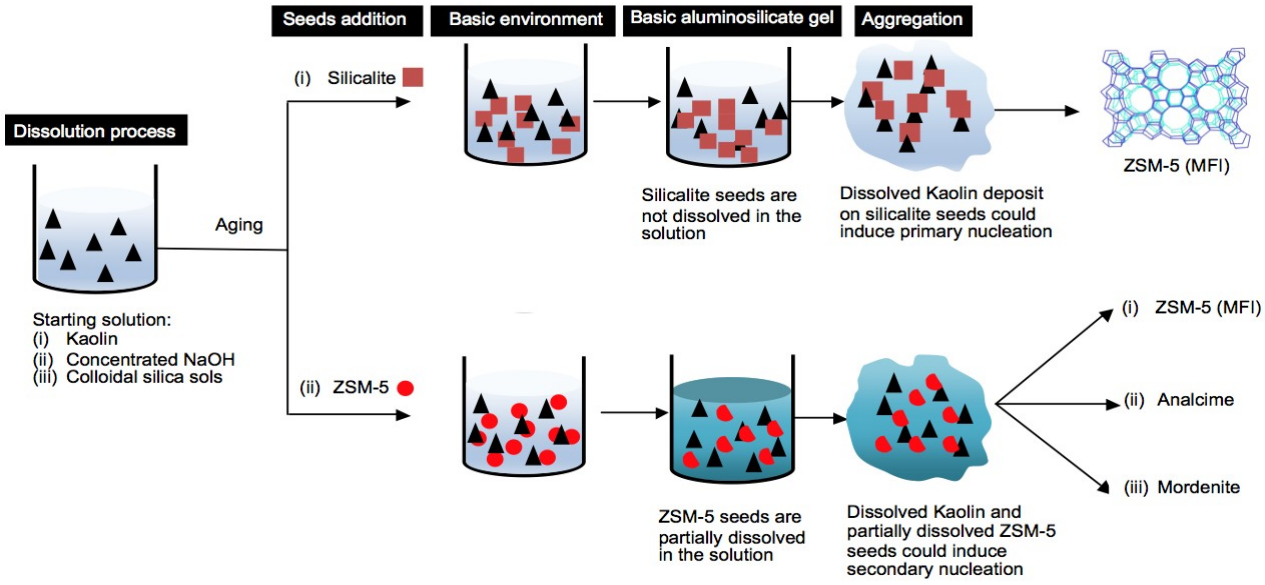

Fig. 7 Plausible mechanisms of ZSM-5 product formation from (i) silicalite and (ii) ZSM-5 as the seeds.

REFERENCES

[1] R.J. Argauer, G. R. Landolt, Crystalline zeolite ZSM-5 and method of preparing the same, in US Patent. 1972.

[2] C. Falamaki, M. Edrissi, M. Sohrabi, Studies on the crystallization kinetics of zeolite ZSM-5 with 1, 6-hexanediol as a structure-directing agent. Zeolites. 19 (1997) 2-5.

[3] N. Kumar, V. Nieminen, K. Demirkan, T. Salmi, D. Yu, Murzin, E. Laine, Effect of synthesis time and mode of stirring on physico-chemical and catalytic properties of ZSM-5 zeolite catalysts. Appl. Catal. A, 235 (2002) 113-123.

[4] T. Danuthai, S. Jongpatiwut, T. Rirksomboon, S. Osuwan, D.E. Resasco, Conversion of methylesters to hydrocarbons over an H-ZSM5 zeolite catalyst. Appl. Catal. A, 361 (2009) 99-105.

[5] S.E. Lehman and S.C. Larsen, Zeolite and mesoporous silica nanomaterials: greener syntheses, environmental applications and biological toxicity. Environ. Sci. Nano. 1 (2014) 200-213.

[6] K. Abdmeziem, B. Siffert, Synthesis of large crystals of ZSM-5 zeolite from a smectite-type clay material. App. Clay Sci. 8 (1994) 437-447.

[7] D.J. Kim, H.S. Chung, Synthesis and characterization of ZSM-5 zeolite from serpentine. App. Clay Sci. 24 (2003) 69-77.

[8] M. Chareonpanich, T. Namto, P. Kongkachuichay, J. Limtrakul, Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash. Fuel Process. Technol. 85 (2004) 1623-1634.

[9] H. Cheng, Q. Liu, J. Yang, S. Ma, R. L. Frost, The thermal behavior of kaolinite intercalation complexes - A review. Thermochim. Acta. 545 (2012) 1-13.

[10] M. Khatamian, M. Irani, Preparation and characterization of nanosized ZSM-5 zeolite using Kaolin and investigation of Kaolin content, crystallization time and temperature changes on the size and crystallinity of products. J. Iranian Chem. Soc. 6 (2009) 187-194.

[11] T. Armaroli, L.J. Simon, M. Digne, T. Montanari, M. Bevilacqua, V. Valtchev, J. Patarin, G. Busca, Effects of crystal size and Si/Al ratio on the surface properties of H-ZSM-5 zeolites. App. Catal. A 306 (2006) 78-84.

[12] Y. Cheng, R.H. Liao, J.S. Li, X.Y. Sun, L.J. Wang, Synthesis research of nanosized ZSM-5 zeolites in the absence of organic template. J. Mater. Process. Technol. 206 (2008) 445-452.

[13] N. Y. Kang, B. S. Song, C. W. Lee, W. C. Choi, K. B. Yoon, Y. Park, The effect of Na_2SO_4 salt on the synthesis of ZSM-5 by template free crystallization method. Micropor. Mesopor. Mater. 118 (2009) 361-372.

[14] R.L. Frost, J. Kristof, L. Rintoul, J.T. Kloprogge, Raman spectroscopy of urea and urea-intercalated kaolinites at 77 K. Spectrochim. Acta A. 56 (2000) 1681-1691.

[15] P.M. Costanzo, J.R.F. Giese, Dehydration of synthetic hydrated kaolinites: a model for the dehydration of halloysite (10Å). Clay Clay Miner. 33 (1985) 415-423.

[16] H. Ming, Modification of kaolinite by controlled hydrothermal deuteration-a DRIFT spectroscopic study. Clay Miner. 39 (2004) 349-362.

[17] W.N. Martens, R. L. Frost, J. Kristof, E. Horvath, Modification of kaolinite surfaces through intercalation with deuterated dimethylsulfoxide. J. Phys. Chem. B. 106 (2002) 4162-4171.

[18] F.M. Alabi, M. O. Omojola, Potentials of Nigerian calcined kaolin as paint pigment. Afr. J. Pure Appl. Chem. 7(12) (2013) 410-417.

[19] I.M. Alwaan, A study on the adhesion of styrene-butadiene rubber with red kaolinite on aluminum surface. ISRN Chem. Eng. 2014 (2014) 1-7.

[20] D.T. Ngoc, T.H. Pham, K.D.H. Nguyen, Synthesis, characterization and application of nanozeolite NaX from Vietnamese kaolin. Adv. Nat. Sci.: Nanosci. Nanotechnol. 4 (2013) 1-12.

[21] A.S. Kovo, O. Hernandez, S.M. Holmes, Synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique. J. Mater. Chem. 19 (2009) 6207-6212.

[22] A.A.F. Lafi, S.K. Matam, H.A. Hodali, New synthesis of ZSM-5 from high-silica Kaolinite and its use in vapor-phase conversion of 1-phenylethanol to styrene. Ind. Eng. Chem. Res. 54 (2015) 3754-3760.

[23] S.-H. Sun, J.-T. Ma, X.-H. Gao, Synthesis of ZSM-5 on kaolin microspheres in the absence of an organic amine template. Clay Miner. 42 (2007) 203-211.

[24] S.P. Zhdanov, N. N. Feoktistova, N. I. Kozlova, M. M. Piryutko, Silicalites and their thermal stability. Inorg. Chem. 34(12) (1985) 2467-2472.

[25] V.R. Choudhary, S.G. Pataskar, Thermal decomposition of TPA-ZSM-5 zeolites: effect of gas atmosphere and Si/Al ratio. Thermochim Acta 97 (1986) 1-10.

[26] M.J. Rice, A.K. Chakraborty, A.T. Bell, Al next nearest neighbor, ring occupation, and proximity statistics in ZSM-5. J. Catal. 186 (1999) 222-227.

[27] D. Hartanto, O. Saputro, W.P. Utomo, A. Rosidah, D. Sugiarso, T. Ersam, H. Nur, D. Prasetyoko, Synthesis of ZSM-5 directly from kaolin without organic template: Part-1: Effect of crystallization time. Asian J. Chem. 27(12) (2015) 1-5.

[28] P. Payra, P.K. Dutta, Handbook of zeolite science and technology. Zeolites: A Primer, ed. S.M. Auerbach, K.A. Carrado, and P.K. Dutta. 2003, New York, Basel: Marceld Ekkeirnc, Inc.