Kaolin as a Source of Silica and Alumina For Synthesis of Zeolite Y and Amorphous Silica Alumina

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Abstract. Kaolin is the clay mineral which containing silica (SiO_2) and alumina (Al_2O_3) in a high percentage, that can be used as a nutrient in the synthesis of zeolites and amorphous silica alumina (ASA). The objective of this research is to convert the Belitung kaolin into silica and alumina as nutrients for the synthesis of zeolites and amorphous silica alumina, which are required in the preparation of the catalysts. Silica and alumina contained in the kaolin were separated by leaching the active kaolin called as metakaolin, using HCL solution, giving a solid phase rich silica and a liquid phase rich alumina. The solid phase rich silica was synthesized to zeolite Y by adding seed of the Y Lynde type, through the hydrothermal process with an alkaline condition. While, the liquid phase rich alumina was converted into an amorphous silica alumina through a co precipitation method. Characterization of zeolite and ASA were done using XRD, surface area and pore analyzer and SEM. The higher of alumina in liquid phase as a result of the rising molar of HCL in the leaching process was observed, but it didn't work for its rising time. Products of ASA and zeolite Y were obtained by using liquid phase rich alumina and solid phase rich silica, respectively, which resulted through leaching metakaolin in 2.5 M HCl at temperature of 100°C for 2 hours.

1 Introduction

Kaolin is the clay mineral which containing silica (SiO_2) and alumina (Al_2O_3) which are inert and inactive, which can be activated through the process of calcination. When the calcination of the kaolin is taken place, the regular crystal structure of kaolinite with inactive Si-O and Al-O bonds is converted to metakaolin with an irregular amorphous aluminosilicate structure, with active Si-O and Al-O bonds.

Zeolite and Amorphous Silica Alumina (ASA) are built by atoms of Al, Si and O, therefore these materials can be synthesized with raw materials containing silica and alumina compounds. Accordingly, kaolin is a cheap natural material that containing silica and alumina in a high percentage. However, kaolin is inert and inactive, so it requires activation to form the active kaolin, that can be done through the process of calcination. Metakaolin is a relatively inexpensive active kaolin, in which the silica and alumina content can be separated through leaching by acid, that will produce silica-rich solids and alumina-rich liquids. The Silica-rich solids with a certain silica/alumina molar ratio are required in the synthesis of zeolites [1]. Both of the process conditions of calcinating kaolin and leaching metakaolin will affect the results of the separation of silica and alumina. When metakaolin is leached, the Al sheet would be dissolved, that causes the different environment of the Si atoms to form microporous silica [2].

There are few papers reporting on leaching metakaolin for using silica-rich solid as a nutrient in the synthesis of zeolites. Process of leaching metakaolin using H_2SO_4 5.2N at temperature of 90°C within 2 hours, resulting in silica-rich solids having a

surface area of $400\text{ m}^2/\text{g}$ and a pore size of 0.7 nm, as a source of silica for the synthesis of zeolite Y [3]. Ajayi (2010) reported that leaching metakaolin using $\text{H}_2\text{SO}_4 > 50\%\text{-w}$ in the starting material will result in ratio of Si/Al $> 5\text{ w/w}$ [4]. Mamani (2014) has successfully separated silica and alumina in metakaolin using HCl 3M at temperature of 115°C during 2.5 hours, which produces a silica-rich solid with molar ratio of silica/alumina between 20-40 mol/mol, that is suitable for nutrient of the synthesize ZSM5 [5]. Leaching of metakaolin by using H_2SO_4 has also been done by Adeoye (2017), which produces silica-rich solids with a molar ratio between 3-8 mol/mol [6].

The main purpose of this paper is to improve efficiency of the synthesis process of zeolite Y from kaolin that has been done previously [7-8], by substituting the supply of porous silica through the process of leaching metakaolin rather than calcinating of kaolin at high exothermic temperature. Furthermore, alumina-rich liquids were be used as nutrients for synthesis of ASA.

2. Experimental

2.1 Materials and methods

The material for the synthesis of Zeolite Y comprises of the silica-rich solids resulting in leaching metakaolin, Sodium hydroxide, demineral water and crystal seed of Lynde Type Y wherein contain Merck sodium silicate, Aldrich sodium aluminate, technical sodium hydroxide and demineral water. The material for ASA synthesis comprises of mother liquor resulted of leaching metakaolin, and ammonia or sodium hydroxide.

2.1.1 Metakaolin

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Metakaolin is an active kaolin of Belitung kaolin which is required to provide Si-O and Al-O actives, which are the source of silica and alumina for the synthesis of zeolite Y and ASA. Metakoline was prepared by calcinating of kaolin in Nabertherm GmbH furnace at 700°C for 2 hours, where the kaolin dehydroxylation process takes place to form metakaolin completely, through endothermic reaction.

This temperature is determined by kaolin thermal characterization, using a DSC / TGA.

2.1.2 Silica and Alumina

Preparation of the active silica and alumina was done by leaching process using HCl between 2-3 M at temperature 100°C, with the weight ratio of HCl/metakaolin solution was 10: 1 w / w, for 2-4 hours. The leaching product of metakaolin is filtered to obtain silica-rich solids, and alumina-rich solutions.

The silica-rich solids are rinsed to neutral pH, dried in an oven at temperature of 110°C for 8 hours, and characterized by AAS. The alumina-rich solution was analyzed by gravimetric method. The condition of the leaching process is adjusted to obtain a silica-rich solids having silica / alumina molar ratio in between 7-10 mol / mol.

2.2. Synthesis Zeolite NaY

Stages of the process in the synthesis of zeolite Y include: preparation and aging of crystal seed Lynde Type Y, preparation and aging starting materials, and hydrothermal synthesis.

2.2.1 Seed

Crystalline seed was prepared by adopting Lynde Type Y of Ginter et al (1992), by stirring the starting material consisting of: 2.72 grams of Na_2SiO_3 solution, 2.09 grams of NaAlO_2 , 4.07 grams of NaOH and 19.95 grams of H_2O at moderate speeds for 1 hour, and continued by aging at room temperature for 24 hours [9]

2.2.2 Starting Material

The starting material for the synthesis of Zeolite Y from kaolin was prepared by adopting of Rahayu et.al. (2014) with modify by using micropore silica resulted in leaching metakaolin.

The molar ratio of silica / alumina in starting materials is adjusted for having to about 10 mol / mol, whereas the amount of silica is a combination of silica from silica-rich solids and from seed, as well as for the amount of alumina.

The content of silica-rich solids in a starting material solution is set in between 5-10% -w. Furthermore, the starting material was aged at room temperature for 11 hours and pH 13 to produce gel form, before being processed hydrothermally.

2.2.3 Synthesis of NaY Zeolite

The Gel of starting material was synthesized hydrothermally in a stirred reactor made of teflon, which is equipped with reflux, at temperature between 91-93°C by using oil bath, to form zeolite Y. Sampling of synthesis product was started at 12nd hours and filtered and rinsed to pH 8.

The synthesis product is dried in an oven with a temperature of 110°C for 8 hours, prior to characterize of mineralalogi by XRD Rigaku Smartlab tool, morphology with SEM JEOL tool, and pore structure with NovaWin Quantachrome.

2.3 Synthesis of ASA

The synthesis of ASA was carried out by using a co-precipitation method with stages of a neutralization of alumina acid solution with an ammonia or sodium hydroxide solution, which it fed into reactor with flow in parallel for 1 hour at a temperature of $\pm 65^\circ\text{C}$ to form the sol, followed by stabilization for 30 minutes before injection of sodium solution silicates, then done aging for 1-5 hours with pH 8-9 to form a gel that grows to form an amorphous phase.

The product was filtered and rinsed to a neutral pH, dried in an oven with a temperature of 110°C for 8 hours, and analyzed by a NovaWin Quantachrome for pore structure, mineralogy analysis with XRD Rigaku Smartlab tool, and morphology analysis with SEM JEOL tool

3. Results and Discussion

3.1 Thermal Analysis

Figure 1 show the result of thermal analysis of the kaolin Belitung. The DSC curve forms a downward peak at temperatures between 480°C – 600°C, where indicating the area of an endothermic reaction in which the kaolin is converted to metakoline.

FIG 1 DSC/TGA Curves of Kaolin Belitung

Kaolin is converted to metakaolin through dehydroxylation process mechanism, which accompanied of release of water as in the equation of the reaction 3.1, and as shown in the TGA curve, Furthermore, a temperature of 700°C is set as calcining

temperature of the kaolin Belitung to maximize releasing of bonded water in kaolin.

3.2 Dealumination Metakaolin By Leaching

Table 1 shows that is important to determine the process conditions of leaching accurately, to obtain silica-rich solids having an appropriate $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio for using as a raw material for the synthesis of zeolite NaY.

Table 1. Influence of leaching condition to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in silica-rich solid

Concentration of HCl (M)	Time of Leaching (Hours)	Ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mol/mol)
1	2	3,0
	3	2,9
	4	3,1
2	2	5,8
	3	6,0
	4	6,2
2.5	2	10,5
	4	9,9
3	2	23,6
	3	24,5
	4	24,7

When leaching of metakaolin was carried out using HCl 2.5 M at temperature of 100°C during 2 hours, a good results were obtained. That resulting in silica-rich solids having a suitable $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio for NaY formation, ie between 7-10 mol / mol [1].

The concentration of HCl solution greatly influenced the molar ratio of silica / alumina in solid product, while the processing time did not have much effect. The alumina concentration in the solution of leaching product in between 25-28 g / L was obtained by using HCl 2.5 M at temperature of 100C, which is used as an alumina source in ASA synthesis.

3.3 Synthesis of NaY Zeolite from Kaolin

3.3.1 Diffractogram of Results of Synthesis NaY Zeolite From Kaolin

Synthesis of NaY Zeolite were performed in a teflon stirred reactor equipped with a reflux, using a heating oil bath to achieve a reaction temperature in between 91-93°C, pH $\pm$ 13, and starting material with a varied of NaOH, $\text{SiO}_2/\text{Al}_2\text{O}_3$ and H_2O , where these materials were provided as a combined of rich-silica solids with seed. Table 2 and FIG. 2 - 5 show the results of NaY zeolite synthesis, using variations of the starting material formulations.

Table 2. Effect of Synthesis Process Conditions on Zeolite NaY Product

Synthesis Process		Zeolite NaY	
Starting Material (mol/mol)	Time of Synthesis (hour)	Ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mol.mol)	Other Zeolite
1,5Na ₂ O:Al ₂ O ₃ :10,4SiO ₂ :774 H ₂ O	15	3,61	v
2,6Na ₂ O:Al ₂ O ₃ :10,4SiO ₂ :694H ₂ O	12	3,43	v
	15	3,46	v
	18	3,70	v
	21	3,58	v
1,5Na ₂ O:Al ₂ O ₃ :9,9SiO ₂ :375H ₂ O	15	3,08	v
2,5Na ₂ O:Al ₂ O ₃ :9,9SiO ₂ :350H ₂ O	15	3,02	-

Table 2 shows that the synthesis of zeolite Y from kaolin requires a high mineralizer solution with a molar ratio of $\text{Na}_2\text{O}/\text{H}_2\text{O}$ is not more than 140 mol/mol, and the starting material concentration has a molar ratio of 2.5 Na₂O: Al₂O₃:9,9 SiO₂:350 H₂O suitable to produce zeolite NaY. This starting material has the molar ratio of $\text{SiO}_2 / \text{Al}_2\text{O}_3$ as recommended by Murat 1992 of about 10 mol / mol, with high SiO₂ and Al₂O₃ concentrations that will increase reaction velocity, also increase the greater Si-O and Al-O collision to build skeleton towards NaY zeolite formation. Synthesis time of 15 hours can prevent the occurrence of further reaction to form zeolite P.

FIG. 2 is a diffractogram of the NaY synthesis produced by starting material with the formulation of Starting Material 1.5: Na₂O Al₂O₃: 10.41 SiO₂: 774 H₂O, containing silica with $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio of about 10 mol / mol, from leaching process in HCl 2.5 M solution during 2 hours called silica-rich solids, and seeds.

FIG. 2. Product of Zeolite NaY, 15 Hours, 1.5Na₂O:Al₂O₃:10.41SiO₂:774H₂O

How much silica-rich solids can be dissolved by the mineralizer under the conditions of the synthesis process, can be expected to be identical to how high

purity zeolite NaY is in the crystals formed in the synthesis product.

The Diffractogram in FIG. 2 shows that the synthesis using a starting material formulation of $1.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10.41\text{SiO}_2:774\text{H}_2\text{O}$ produces a side reaction which forms zeolite P and another zeolite, which are probably. The results of parallel reaction. Increasing the quantity of Na_2O and decreasing H_2O , as well as the extension of reaction time will be studied its effect on the ability of silica-rich solids mineralization in the reaction system by increasing Na_2O in the starting material formulation $2.6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10.41\text{SiO}_2:694\text{H}_2\text{O}$, and the extension of reaction time. This formulation produces synthesis products with diffractograms as shown in FIG. 3.

FIG. 3. Product of Zeolite NaY, 15 Hours, $2.6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10.41\text{SiO}_2:694\text{H}_2\text{O}$

The result of synthesis Zeolite NaY using the starting material formulation of $2.6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10.41\text{SiO}_2:694\text{H}_2\text{O}$ is presented in FIG. 3, and showing a slightly higher the relative intensity in NaY zeolite. The addition of molar Na_2O to the starting material, which does not increase the molar ratio of $\text{Na}_2\text{O}/\text{H}_2\text{O}$ significantly, so that it does not significantly affect the quality of the synthesis product significantly was observed. Accordingly, the concept of the collision frequency required to increase the reaction rate was involved in the design of this study, by increasing the SiO_2 and Al_2O_3 concentrations, and the starting material formulation being $1.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:9.9\text{SiO}_2:375\text{H}_2\text{O}$ with higher of SiO_2 and Al_2O_3 concentrations, but lower of Na_2O , and $2.6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:9.9\text{SiO}_2:350\text{H}_2\text{O}$ with higher of SiO_2 and Al_2O_3 concentrations, also higher of Na_2O , and giving diffractogram on FIG. 4 and FIG. 5 respectively.

Diffractogram of these synthesis result shown in FIG. 5 has a much higher NaY purity than in FIG. 4. This result proves that high concentrations in a reaction greatly affect the reaction rate, but there is a diffractogram of the synthesis shown in FIG. 5 having a much higher NaY purity than in Figure 4. These results prove that high concentrations in a reaction

system are highly advantageous in terms of quantity and product quality, if the mineralizer is still capable of dissolving high solids.

FIG. 4. Product of Zeolite NaY, 15 Hours, $1.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:9.9\text{SiO}_2:375\text{H}_2\text{O}$

FIG. 5. Product of Zeolite NaY, 15 Hours, $2.6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:9.9\text{SiO}_2:350\text{H}_2\text{O}$

Diffractogram of the synthesis result shown in FIG. 5 has a much higher NaY purity than in FIG. 4. This result proves that high concentrations in a reaction greatly affect the reaction rate, but there is a diffractogram of the synthesis shown in FIG. 5 having a much higher NaY purity than in FIG. 4. These results prove that high concentrations in a reaction system are highly advantageous in terms of quantity and product quality, if the mineralizer is still capable of dissolving high solids.

This study was conducted by using the ratio of seed Lynde Type Y/silica rich solids = 0.5 - 1.0 w/w. For comparison, the ratio of seed / active kaolin in Rahayu

(2014) = 4.4 w / w, while the ratio in Brown is 2.4 b / w and pH = 14, and yields 20% -b NaY [7]; [10].

3.3.2 Micrograph of Results of Synthesis NaY Zeolite From Kaolin

The zeolite NaY with highest purity in the product was analyzed using SEM, JEOL JSM-6510A Analytical Scanning Electron Microscope, shown in FIG. 6 (a) and FIG. 6 (b) with successive magnification of 5000 and 10,000 times.

(a)

(b)

FIG. 6. Micrograph of Zeolit NaY, 15 Hours, $2.6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:9.9\text{SiO}_2:350\text{H}_2\text{O}$

(a) Mikrograph of NaY zeolite with magnification 5000 times

(b) Mikrograf of NaY zeolite with magnification 10,000 times

The micrograph shown in FIG 6 shows the mixture of the zeolite crystalline phase Y and the amorphous phase in the synthesis product. The white / gray crystal plates are zeolite Y crystals, while dark-colored clumps are amorphous.

In comparison to similar processes, the synthesis of zeolite Y from kaolin that Rahayu has done (2014) with a reaction time of 15 hours and the same process conditions, but using a mixture of 3 types of active kaolin: K700C, K1013C, K1050C, the composition is

arranged to form a starting material formulation $6.4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10.4\text{SiO}_2:932\text{H}_2\text{O}$, the Zeolite NaY with molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 4.8 mol/mol and the purity of zeolite Y 86% in crystals was obtained. While the crystallinity of product was 46% [7]

3.4 Synthesis of ASA from Kaolin

The synthesis of ASA using alumina from alumina-rich solution of leaching metakaolin was done by co-precipitation method, with process conditions at temperature of 60-65°C and pH in between 7-8 at neutralizing stage to form sol and temperature of 50-55°C and pH 8-9 at aging stage process to form gel. A 10% ammonia and 2 M NaOH are solution used for neutralizing acid in neutralization stage. The ASA synthesis results were analyzed their pore structure with the NovaWin Quantachrome tool, shown in Table 3, diffractogram with XRD Rigaku Smartlab, shown in FIG.7, and the morphology with SEM, JEOL JSM-6510A, shown in FIG 8.

Table 3. Effect of Process Conditions on Pore Structures

Synthesis Process			Pore Structure of ASA		
Neutralizer	Rasio Si/Al, (w/w)	Aging Time (Hours)	Average Pore Diameter (Å)	Specific Surface Area (m ² /g)	Pore Volume (mL/g)
NH ₄ OH	0,11	1	57,7	437	1,26
		3	59,3	428	1,27
		5	58,5	432	1.26
	0,22	1	62,5	439	1,37
	0,33	1	62,4	430	1.34
NaOH	0,11	1	52,6	372	0,98

The results of the ASA synthesis shown in Table 3, appear to have a good pore structure, especially on high surface area and total pore volume, which will be used as a hydrocracking catalyst or matrix. But, average pore diameter slightly lower than desired (70 Å).

Surprisingly, the addition of silica or an increase in Si/Al ratio does not have a significant effect on the pore structure. As it is known that silica is required to provide acidic properties to ASA, via a silanol form attached to Al such as: [(H) O-Si-O-Al]. However, the addition of Si to the formation of ASA may destroy the pore structure, thus affecting mainly the pore specific surface area. In addition, the replacement of the Al atomic site by the Si atom can excessively remove the Bronsted acid-forming group (Si-OH-Al), which will decrease the Bronsted acid concentration (Chizallet, 2000).

Rahayu (2014) has also done the synthesis of ASA from kaolin by various procedures, but still has not achieved ASA with a high specific surface area and sufficient pore diameter. Furthermore, ASA was synthesized by using synthetic materials of aluminum sulphate [$\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$] and Sodium Aluminate (NaAlO_2). The best ASA with a specific surface area of

383.5 m²/g, average pore diameter = 80.7 Å, and total pore volume = 0.78 ml / g was obtained.

The success of study of the ASA synthesis is also supported by ASA diffraction result, that similar to the commercial ASA as shown in Figure 7, and the ASA micrograph in Figure 8.

FIG.7. Diffractogram of ASA

FIG. 8. Micrograph of ASA with magnification 10,000 times

4. Conclusion

Research on the synthesis of NaY and ASA zeolites from kaolin, using silica and alumina from the results of leaching metakaolin has been successfully performed, with high purity NaY zeolite, and ASA having high surface area, which is suitable for use as hydrocracking catalyst component. The silica and alumina were obtained by leaching in a solution HCl

2.5 M, at temperature of 100°C for 2 hour.. Overall, the process undertaken is more efficient and cheaper compared to what has been done before (Rahayu, 2014)

5. Reference

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