Synthesis of NaY Zeolite Using Mixed Calcined Kaolins

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Abstract. Kaolin is one of several types of clay minerals. The most common crystalline phase constituting kaolin minerals is kaolinite, with the chemical composition $Al_2Si_2O_5(OH)_4$. Kaolin is mostly used for manufacturing traditional ceramics and also to synthesize zeolites or molecular sieves. The Si-O and Al-O structures in kaolin are inactive and inert, so activation by calcination is required. This work studies the conversion of kaolin originating from Bangka island in Indonesia into calcined kaolin phase as precursor in NaY zeolite synthesis. In the calcination process, the kaolinite undergoes phase transformations from metakaolin to mullite. The Bangka kaolin is 74.3% crystalline, predominantly composed of kaolinite, and 25.7% amorphous, with an SiO_2/Al_2O_3 mass ratio of 1.64. Thermal characterization using simultaneous DSC/TGA identified an endothermic peak at 527 °C and an exothermic peak at 1013 °C. Thus, three calcination temperatures (700, 1013, and 1050 °C) were selected to produce calcined kaolins with different phase distributions. The best product, with 87.8% NaY zeolite in the 54.7% crystalline product and an SiO_2/Al_2O_3 molar ratio of 5.35, was obtained through hydrothermal synthesis using mixed calcined kaolins with a composition of $K_{700C} : K_{1013C} : K_{1050C} = 10 : 85 : 5$ in %-mass, with seed addition, at a temperature of 93 °C and a reaction time of 15 hours.

Keywords*: calcined kaolin phases; hydrothermal synthesis; kaolin; NaY zeolite.*

1 Introduction

Kaolin consists mainly of the kaolinite phase with the chemical composition of $Al_2Si_2O_5(OH)_4$ and relatively inert Si-O and Al-O structures. Breck [1] stated that among clay minerals kaolin is the most commonly used in manufacturing traditional ceramics and is also used to synthesize zeolites or molecular sieves because of the reactivity of calcined kaolin to alkali solutions. Many researches have been carried out using treated kaolin to produce NaY zeolite. Brown [2] reacted calcined clay and aqueous alkali to produce a mixture of crystalline zeolitic aluminosilicate and a porous amorphous silica-alumina. Htay [3] obtained zeolite Y with an SiO_2/Al_2O_3 molar ratio of 3.53 by activation of kaolin and treatment using sodium hydroxide and hydrothermal crystallization. Zheng [4] observed that, due to the inert nature of kaolin, in the process of

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kaolin in-situ crystallization to form NaY zeolite, the kaolin must be calcined to form active SiO_2 and Al_2O_3.

This work studies the conversion of kaolin originating from Bangka island in Indonesia into calcined kaolin phase as precursor in NaY zeolite synthesis.

2 Materials and Methods

Starting materials for synthesis of NaY zeolite in this study were calcined kaolin phases originating from Bangka island in Indonesia after pretreatment by beneficiation and spray drying. The Bangka kaolin is the largest deposit of clay found in Indonesia, contributing 224 milion ton to a total of 732.8 million ton in the Indonesian kaolin reserve [5].

2.1 Chemical and Mineral Analysis of Kaolin

The oxide composition of the Bangka kaolin was analyzed using a wet chemical method to estimate its feasibility as precursor in NaY zeolite synthesis. Phase analysis using XRD was performed on a Philips analytical X-ray diffractometer utilizing Ni-filtered CuKα radiation to identify the structure and mineral composition of the kaolin.

2.2 Thermal Analysis

Simultaneous differential scanning calorimetry/thermal gravimetry analyses (DSC/TGA) were performed on a Dupont 2000 thermal analyzer to investigate the phase transformations through identification of the endothermic and exothermic temperature of the kaolin and to investigate the mass changes from kaolin to mullite during heating based on the DSC/TGA curves.

2.3 Surface Analysis

The physical characteristics of the sample were determined by BET (Brunauer-Emmett-Teller) nitrogen adsorption measurement on a Quantachrome Nova 1000 to investigate the textural properties of the calcined kaolin phases through the observed values of pore diameter size, specific surface area and pore volume. The pore diameter size could be incorporated with the presence of the amorphous phase, which is more easily dissolved in alkali.

2.4 Synthesis of NaY-Zeolite

The calcined kaolin phases were synthesized to form NaY zeolite through hydrothermal treatment with aqueous NaOH and with seed addition. Calcined kaolins K_{700C}, K_{1013C}, K_{1050C} were prepared by heating the kaolin at 700, 1013

and 1050°C for 2 hours in a Thermolyne furnace. This work used varying amounts of calcined kaolin phase, i.e. 10-30%-mass for K_{700C}, 60-90%-mass for K_{1013C} and 5-10%-mass for K_{1050C} as precursor in NaY zeolite synthesis at a temperature of ± 93°C for 7-21 hours. The seed was prepared by adopting the procedure for Linde type Y zeolite [6].

3 Result and Discussion

3.1 Mineral and Chemical Analysis of Bangka Kaolin

Table 1 shows the results of the oxide and mineral phase composition of the raw Bangka kaolin as analyzed using a wet chemical method and X-ray diffraction, respectively. A high kaolinite content of 63.6%-mass was indicated. The oxide analysis identified SiO_2 and Al_2O_3 as the predominant oxides. With a SiO_2/Al_2O_3 %-mass ratio of 1.64, additional silica is needed for the NaY zeolite synthesis. Furthermore, the low Fe content is beneficial for the NaY zeolite synthesis, as Basaldella has reported [7].

Table 1 Chemical and Mineral Composition of Kaolin

Kaolin Bangka			
Chemical Composition	**%-mass**	**Mineral Composition**	**%-mass**
SiO_2	49.86	Kaolinite	63.6
Al_2O_3	30.51	Gibsit	2.65
Fe_2O_3	0.69	Quartz	1.6
TiO_2	0.29	Muscovite	8.3
CaO	1.49		
MgO	1.07		
Na_2O	0.45		
K_2O	0.59		
LOI	15.05		

3.2 Thermal and Surface Analysis

Phase transformations and mass changes of kaolin to mullite occured during heating. An endothermic peak at 527°C can be seen in the DSC/TGA curves (Figure 1). Here, dehydroxylation of the crystalline kaolinite structure took place, resulting in the formation of calcined metakaolin phase. The weight loss of the Bangka kaolin upon heating at 450-700°C was observed to be about 14%, mostly due to the loss of combined water in the structure of the kaolinite.

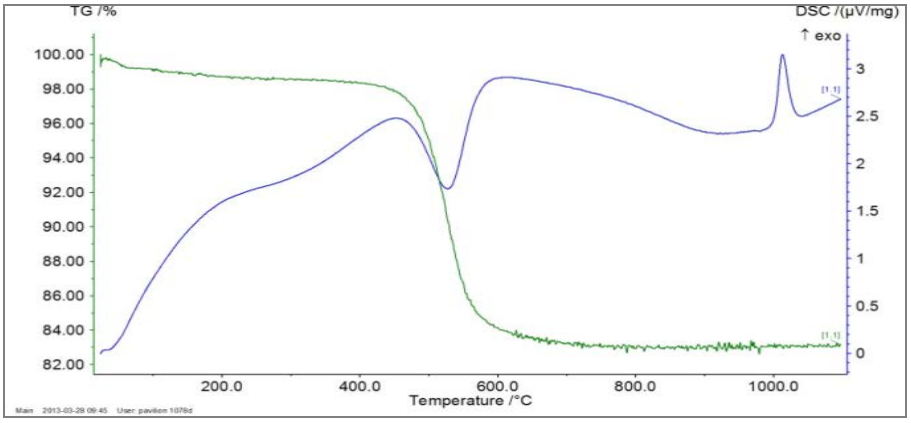

Figure 1 Thermal analysis of Bangka kaolin by DSC/TGA.

An exothermic peak was observed at 1013 °C, which indicates that the metakaolin structure was changed to calcined kaolin spinel and amorphous silica phases. The formation of mullite phase was observed at temperatures above the exothermic peak. Furthermore, these thermal analysis temperature data were used for producing the desired calcined kaolin phases. Based on the results of the thermal analysis carried out by DSC/TGA, the following transformations are proposed:

1. formation of metakaolin at 450-700°C
2. formation of spinel & amorphous silica at 995-1040°C
3. formation of mullite & cristobalite at > 1050°C.

The XRD patterns of the calcined kaolins are shown in Figure 2. The absence of kaolinite peaks in K_{700C} indicates that the conversion to metakaolin was complete. At a higher temperature metakaolin remains up to near the exotherm temperature. At 1013°C exotherm temperature, spinel and amorphous silica would have been produced, but the spinel content was too low and poorly crystalline to be detected by XRD. When kaolin is heated at 1100°C mullite becomes the dominant crystalline phase. Mullite diffraction peaks can be seen at 2θ =16.5, 26, 35.5, 41, 44 and 60.8. These peaks started to occur in K_{1013C} and were more pronounced as the temperature was increased to 1100°C.

Table 2 shows the surface characteristics determined by the BET method and semiquantitative evaluation of amorphous and crystalline phase contents. The pore diameter increased with the temperature up to 1050°C and then decreased. Similar to the observation by Zheng [4], the amount of active SiO_2 increased with increasing temperature and decreased with further temperature increase. It is known that a larger pore size is associated with a higher degree of

amorphosity and higher reactivity in an alkaline environment, such as in the synthesis of Y zeolite.

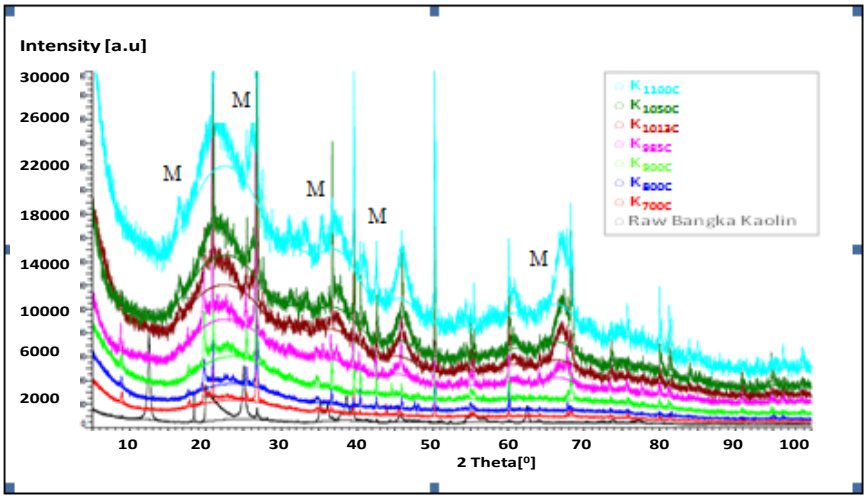

Figure 2 Diffractogram pattern of raw Bangka kaolin and calcined Bangka kaolin.

Table 2 Properties of Calcined Kaolin.

Calcination		BET Analysis			XRD Analysis	
Temperature (°C)	t (hour)	Avg Pore Diameter (A^0)	SSA (m^2/gr)	Tot Pore Vol (ml/gr)	Amorphous (%)	Crystaline (%)
700	2	295	12.92	0.095	59.9	40.1
700	4	287	14.31	0.103	61.5	38.5
800	2	312	14.22	0.111	61.7	38.3
945	2	328	11.00	0.090	64.4	35.6
985	2	378	8.11	0.077	65.2	34.8
985	4	314	11.24	0.088	59.8	40.2
1013	2	338	10.11	0.085	63.5	36.5
1050	2	404	7.95	0.080	63.4	36.6
1100	2	234	10.62	0.062	61.4	38.6

3.3 NaY Zeolite Synthesis

A mixture of kaolins calcined at several temperatures were used as precursor in NaY zeolite synthesis, designated as K_{700C}, K_{1013C}, K_{1050C}. These were prepared by heating the raw Bangka kaolin in an electric furnace at 700, 1013 and 1050°C, respectively, for 2 hours. The contents of each calcined kaolin in the mixed kaolins were 10-30%-mass for K_{700C}, 60-90%-mass for K_{1013C} and 5-10 %-mass for K_{1050C}. The synthesis of NaY zeolite was carried out under a hydrothermal condition, at a temperature of 93°C, for 7-21 hours. Zeolite crystal seed, necessary to initiate the formation of the NaY zeolite phase, was

prepared by adopting the procedure for Linde type Y zeolite. The SiO_2/Al_2O_3 ratio in the starting material influences the type of zeolite product. Brown has suggested the use of small quantities of metakaolin phase in the synthesis zeolite for smoothing out the process of zeolite synthesis [2]. NaY zeolite was obtained by providing a high SiO_2 content in the starting material. This could be facilitated by calcining the kaolin at a high temperature or by adding another SiO_2 source, such as sodium silicate. A seed is needed in NaY zeolite synthesis to accelerate the crystallization of the NaY zeolite. Accordingly, the NaY zeolite synthesis carried out by using a calcined kaolin mixture with a composition of K_{700C} : K_{1013C} : K_{1050C} = 10 : 85 : 5 in %-mass and with seed addition obtained the best NaY-Zeolite, with 87.8% NaY zeolite totally in crystalline form and with an SiO_2/Al_2O_3 molar ratio of 5.35. In this process, using Bangka kaolin as raw material with an SiO_2/Al_2O_3 %-mass ratio of 1.64, the calcined kaolin K_{1013C} was enriched with SiO_2 in order to obtain a high molar ratio of SiO_2/Al_2O_3 in the NaY zeolite product. This is a method that differs from the zeolite synthesis by Kovo, *et al*. [8], who used Ahoko kaolin as raw material with an SiO_2/Al_2O_3 %-mass ratio of 3.82.

4 Conclusion

With an SiO_2/Al_2O_3 %-mass ratio of 1.64 of kaolin, additional silica is needed for NaY zeolite synthesis. Except for using mixed calcined kaolins, the silica was mainly provided by K_{1013}. The NaY zeolite synthesis with a mixed calcined kaolin composition of K_{700C} : K_{1013C} : K_{1050C} = 10 : 85 : 5 in%-mass and with seed addition produced the best NaY zeolite, with 87.8% NaY zeolite totally in crystalline form and with an SiO_2/Al_2O_3 molar ratio of 5.35. K_{700C} was used to provide metakaolin because the conversion of kaolinite to metakaolin is complete at 700 °C and K_{1013C} was used to provide amorphous silica because at 1013°C an amorphous silica with low mullite would be produced. A small amount of mullite could strengthen the zeolite but an excess of it would retard the NaY synthesis.

Acknowledgements

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