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Research Article

Direct Synthesis of Highly Crystalline ZSM-5 from Indonesian Kaolin

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Abstract

Direct synthesis of ZSM-5 from Indonesian kaolin without calcination for the formation of metakaolin was done through the addition of an alkaline solution (sodium fluoride and sodium hydroxide) and the fusion using sodium hydroxide. Crystallization was conducted through hydrothermal method at 80 °C for four days. XRD diffractogram and FTIR spectra showed that the addition of sodium fluoride solution in the ratio Si/Al = 100 could produce highly crystalline ZSM-5, whereas the use of a sodium hydroxide solution and fusion process did not produce the crystalline ZSM-5.

Keywords: Kaolin; Sodium fluoride; Synthesis of ZSM-5; crystalline ZSM-5

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1. Introduction

ZSM-5 are widely applied as a catalysts in a variety of industrial processes and environmental protection [1,2]. Generally, the ZSM-5 are synthesized with mole ratio of Si/Al over 5 and using TPA^+ cation as structure directing agent (SDA) [3]. Zhu *et al.* [4] have synthesized ZSM-5 by adding tetraethylorthosilicate (TEOS) as silica source and aluminum isopropoxide as an alumina source. Some researches use natural material as silica and alumina sources for examples rectorite [5,6], rice husk ash [7,8], kaolin [9,10], and diatomaceous earth [11]. The use of natural materials as silica and alumina source in synthesis of zeolite is more advantageous than the commercial chemical because it is more economical.

Kaolin has been used as silica and alumina sources in synthesis of ZSM-5 through calcination of kaolin to be metakaolin in an attempt to activate of kaolin [9,10,12]. Liu *et al.* [12] synthesized ZSM-5 from metakaolin by adding silica and alumina, Pan *et al.* [9] used dealuminated metakaolin, and Hartati *et al.* [10] used metakaolin by addition of silica. In this research, a novel method of ZSM-5 synthesis was proposed directly without pretreatment such as calcination or the formation of metakaolin. Silica of TEOS was added to complete the mole ratio of Si/Al in the formation of ZSM-5.

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2. Materials and Methods

2.1. Materials

Kaolin was obtained from Blitar, East Java, Indonesia; sodium hydroxide (Merck, ≥ 99 %); sodium fluoride (Merck, ≥ 99 %), tetraetilorthosilicate (TEOS) (Merck, ≥ 99 %), tetrapropylammonium hydroxide (TPAOH) (Merck, ~40 %), and aquadest.

2.2. Synthesis of ZSM-5

In this research, we compared the method of ZSM-5 synthesis: direct synthesis of ZSM-5 from kaolin and synthesis of ZSM-5 by preparation of kaolin through alkaline fusion with sodium hydroxide and preparation kaolin by adding sodium hydroxide solution without fusion process. Preparation of kaolin through fusion process was conducted by mixing 2.5 g kaolin and 3 g sodium hydroxide in a porcelain-Teflon crucible. The mixture was calcined at 600 °C for 1 h. The fusion was crushed in the agate mortar, and was added by 62 mL aquadest and stirred by magnetic stirrer. Amount of sodium hydroxide added can be adjusted with the molar ratio of expected Si/Al [13].

Preparation of kaolin without fusion was performed by mixing 2.5 g kaolin with 10 mL of 3.2 M sodium hydroxide. The mixture was stirred using a magnetic stirrer for 1 hour [13]. In addition, preparation of kaolin was also performed by mixing 0.8 g of kaolin with 18 mL of 0.33 M sodium fluoride accordance with the procedures in the preparation of kaolin with sodium hydroxide solution.

Three kinds of resulted samples were then used as a material for the synthesis of ZSM-5 using methods of Eimer *et al.* [14] with some modifications. Some TEOS added to the prepared kaolin, and then stirred for 30 minutes at room temperature. A 10 mL TPAOH was added to the mixture, and then stirred for 15 hours, so that the mixture had a mole ratio as $1SiO_2$: xAl_2O_3: 0,2TPAOH: $38H_2O$ (1/2x is the mole ratio Si/Al) [15]. The hydrothermal process was done at 80 °C for 4 days. The solid were then washed using a centrifuge until neutral, dried at 60 °C, and calcined at 550 °C for 7 h in the air, with the rate of temperature 2 °/min. Table 1 show the detailed information of synthesis condition in this research.

2.3. Characterization

The chemical compositions of the kaolin samples were determined by X-ray fluorescence (XRF) technique conducted on a PAN analytical spectrometer Minipal 4. The FTIR spectra were obtained on a Shimadzu spectrograph 8400S with infrared optical, in the range of wavenumber from 400 cm^{-1} to 4000 cm^{-1}, a spectral resolution of 4 cm^{-1}, 45 scans, at 20 °C. X-ray Diffraction (XRD) patterns were used to identify the phase and determine the crystallinity of the powder samples. XRD patterns were recorded using an Philips X'pert diffractometer with Cu Kα radiation with a step scan of 0.02° and counting time of 10 s. Data were recorded in the 2θ ranges of 5-50°.

3. Results and Discussion

The chemical composition of obtained kaolin based on data from XRF is shown in Table 2. The results showed that the percentage of Si in kaolin is only about three times the percentage of Al, so as to obtain a mole ratio Si/Al to be

Table 1. Method of kaolin preparation, hydrothermal condition, and mole ratio Si/Al in the synthesis of ZSM-5

No.	Sample Name	Method of preparation	Hydrothermal condition	Mole Ratio of Si/Al
1.	C-20	Alkaline-treatment	80°C, 4 days	20
2.	C-40	Alkaline-treatment	80°C, 4 days	40
3.	F-20	Alkaline-Fusion	80°C, 4 days	20
4.	F-40	Alkaline-Fusion	80°C, 4 days	40
5.	F-100	Alkaline-Fusion	80°C, 4 days	100
6.	N-100	NaF-treatment	80°C, 4 days	100
7.	N-170	NaF-treatment	170°C, 1 days	100

Table 2. Chemical composition of kaolin

Element	Al	Si	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Eu	Re
%	20.2	65.8	4.36	2.46	2.02	0.069	0.04	0.27	4.21	0.15	0.10	0.11	0.06	0.1

used in the synthesis of ZSM-5 should be added silica.

Kaolin Blitar has highly content of quartz, as seen in X-ray diffraction in Figure 1. Preparation of kaolin was done in three different ways. The first is the conventional preparation, the addition of alkali on kaolin directly before hydrothermal process [13]. The alkali is able to break bonds and the release of Si and Al in the kaolin [16]. The second way is the preparation of kaolin with alkali fusion method [13]. Figure 1 also shows the diffractogram of Blitar kaolin before and after fusion with sodium hydroxide. Characteristic peaks of kaolin appear at 2θ around 12.31° and 26.61°. The peaks do not appear in the diffractogram of fused kaolin. In addition, the peak at 2θ 20.84° which is the typical peak gypsite and shows that alkaline fusion of kaolin reduction of gypsite. This is consistent with those reported by Ríos *et al.* [13] that the the kaolin crystal can react with alkaline at high temperatures.

The results of the synthesis of ZSM-5 with three treatment kaolin and variation mole ratio of Si/Al is shown in Figure 2. Alkaline-treatment on the mixture with a mole ratio of Si/Al = 20, followed by hydrothermally at a 80 °C results the transformation of kaolin into amorphous solid (C-20), while the mole ratio of 40 (C-40) did not alter the structure of kaolin, which is shown with typical peak kaolin at 12.31° and 26.61°. The treatment of alkaline-fusion on kaolin before hydrothermal led to the an amorphous solid on the mole ratio of Si/Al = 40 and 100 (F-40 and F-100). In the mole ratio of Si/Al = 20 (F-20), it results various minerals like kaolin, mordenite, natrolite, and unknown compounds. XRD patterns showed that treatment of kaolin in alkaline and alkaline-fusion at 80 °C for 4 days did not produce ZSM-5, because the absence of peaks at 2θ around 7.9; 8.8; 23.1; 24.0; and 24.4 which correspond to the characteristic peak of ZSM-5.

The third way is the treatment using a solution of sodium fluoride with a mole ratio of 100 at 80 °C for 4 days (N-100) generates high intensity peaks at 2θ around 7.9, 8.8, 23.1,

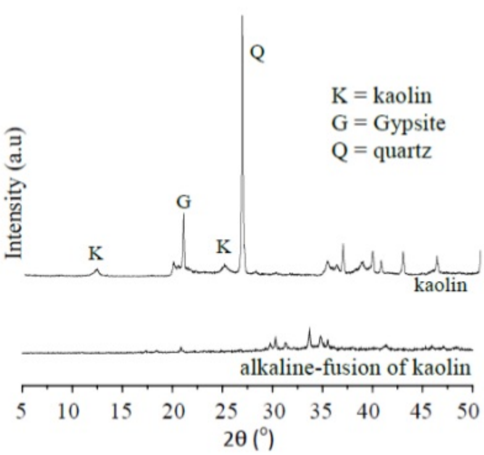

Figure 1. XRD patterns of kaolin and alkaline-fusion of kaolin

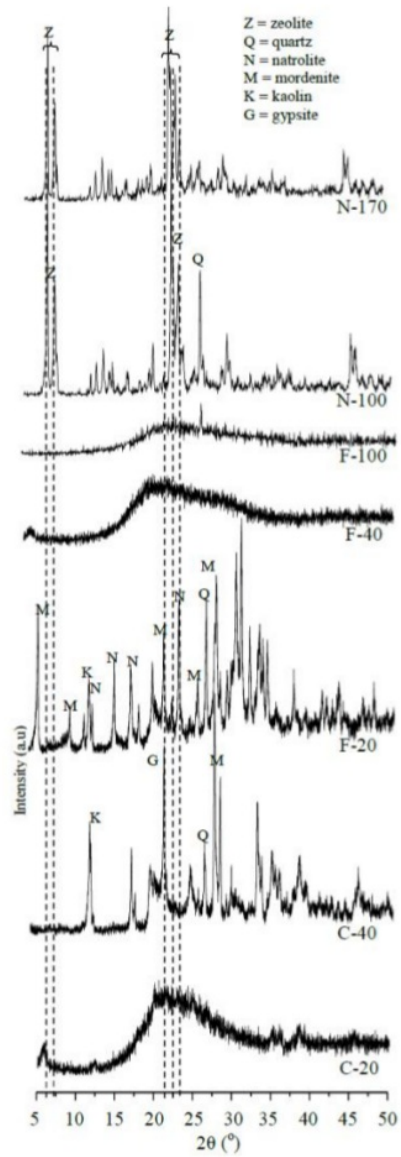

Figure 2. XRD patterns of products

24.0, and 24.4° that indicates the typical structure of ZSM-5 with a high crystallinity [17]. This method results quartz as a by-product, proved by peaks at 2θ at around 26.59°. Quartz is not found when the hydrothermal temperature increased to 170 °C for 1 day (N-170). Diffractogram of sample N-100 and N-170 show high crystallinity, which can be seen from the typical sharp peak. For this phenomenon, it can be stated that in high mole ratio of Si/Al, ZSM-5 can be synthesized in lower pH than the pH of alkaline media method as reported Corma *et al.* [18]. The pH of mixture using sodium fluoride is only 12, while when using alkaline-treatment, the pH of the mixture is 14.

FTIR spectra of C-20 in Figure 3 shows the absorption band at about 1200, 550, and 450 cm^{-1}, while the C-40 shows absorption band at around 1080, 550, and 450 cm^{-1}. The band at around 550 cm^{-1} is attributed to a structure-sensitive vibration caused by the double five-member rings of the external linkages, while the absorption band at around 550 and 450 cm^{-1} is a typical band of the crystal structure of ZSM-5 [14]. Samples F-20, F-40, and F-100 do not show the typical bands of ZSM-5, mainly because there is no absorption band at around 550, 790, 1080, and 1200 cm^{-1}. The FTIR spectra of sample N-100 and N-170 contain absorption band at around 1200, 1080, 790, 550, and 450 cm^{-1}. This suggests that the samples have ZSM-5 structure. The bands around 790, 1080, and 1200 cm^{-1} are characteristics of TO_4 (T = Si, Al) tetrahedron units. The band near 790 cm^{-1} is assigned to the symmetric stretching of external linkages.

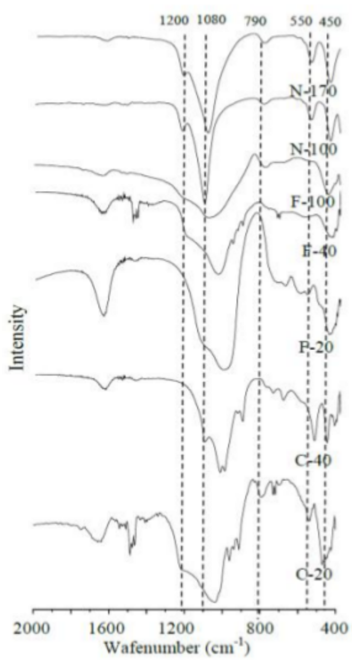

Figure 3. FTIR spectra of products

4. Conclusions

ZSM-5 with high crystallinity can be synthesized from kaolin Indonesia with quartz as impurities through treatment with the addition of sodium fluoride prior to hydrothermal process at 80 °C for 4 days or at 170 °C for 1 day with a mole ratio of Si/Al = 100. Synthesis of ZSM-5 directly from kaolin by conventional treatment using sodium hydroxide solution and through alkaline fusion can not be done, because the results obtained are amorphous or other crystalline material.

Acknowledgments

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