



## Conference Paper

# Natural Zeolits and Its Modifications with Protons and Copper As the Catalyst for Esterification of Ethanol with Acetic Acid

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## Abstract

Natural zeolite from Cikalong, West Java has been modified by attaching protons and copper (II) to the framework. These materials are characterized by X-Ray Fluourescence (XRF), X-Ray Diffraction (XRD) and Fourier Transform Infra Red (FTIR). The results of the analysis with these tools show that the framework of the natural zeolite sample did not change significantly after modification. The catalytic activity of natural zeolite samples and their modified forms were tested as heterogeneous catalysts in esterification of ethanol with acetic acid. The chemical process was carried out at 75 °C for 4 hours with the presence of 5% catalyst weight and with the mole ratio of ethanol and acetic acid at 2: 1. Ethyl acetate products formed were analyzed by Gas Chromatography (GC). In the catalytic test it was found that natural zeolites were more active than those modified with acid and copper, although the latter were also slightly better at reuse.

**Keywords:** Natural Zeolite, Catalyst, Esterification, Modification, Reuse

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## 1. Introduction

Indonesia is a country that is rich in natural minerals such as zeolite, clay, and bentonite which is one of the advantages of the area with volcanic soil [1]. For example zeolite, it has been stated by the Indonesian Ministry of Energy and Mineral Resources that this country has no less than 400 million tons of zeolite deposits [2]. Naturally, zeolite occurs through a process of change on earth [3, 4]. Most mordenite and clinoptilolite are natural zeolite types that are present in various content [5, 6].

It is well known that natural zeolite is commonly used as an adsorbent and catalyst. Many important organic reactions such as fat transesterification [7], bioethanol dehydration [8], and hydrocarbon cracking are processes that use zeolite as a catalyst [9]. Natural zeolite is generally used as a catalyst because of its good thermal, mechanical

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and chemical stability [10]. Then when compared with metal oxide catalysts, zeolite is more beneficial because of its abundance and requires low cost to use [11].

In recent years, many scientists have been interested in modifying natural zeolites to improve their performance as catalysts in organic reactions by treating zeolites with acids (mostly  $H_2SO_4$  and HCl) and transition metals such as Fe and Cu [12-15]. In the case of Cu-modified zeolites, it has been reported that copper-containing zeolites show better results compared to other zeolites with different metal transitions in oxidative dehydrogenation of methanol [16].

Ethyl acetate is one of the important chemical compounds used in many applications such as chemical reagents, coating agents, adhesives, perfumes and the pharmaceutical industry, solvents and plasticizers [17, 18]. Usually formed by esterification between ethanol and acetic acid with the help of a homogeneous catalyst. Sulfuric acid is the best homogeneous catalyst for the esterification process, because of its selectivity. However homogeneous catalysts have many disadvantages such as corrosive, environmental problems and difficult to separate [17]. This factor also has implications for many researchers to pay more attention to the development of heterogeneous catalysts that are environmentally friendly [19].

The synthesis of ethyl acetate catalyzed by zeolite is good to be studied further, because ethyl acetate is important in various applications, especially for organic reactions [20]. The use of natural zeolite as a heterogeneous catalyst for the fabrication of ethyl acetate is rarely reported. In this study, natural zeolite was modified using sulfuric acid and copper sulfate. Therefore, in this article we present a comparison of the catalytic capabilities between the original form and the modified form of natural zeolite obtained from the Cikalong area, West Java province, Indonesia.

## 2. Materials and Methods

### 2.1. Materials

Natural zeolite obtained from Cikalong West Java was purchased from Brataco co ltd while 97% sulfuric acid, 96% ethanol, and glacial acetic acid were purchased from Merck.

### 2.2. Instruments

The chemical composition was measured by PAN analytical Epsilon 3n X-Ray Fluorescence (XRF). X-Ray Diffraction Data (XRD) of zeolite powder was collected with Philip

X'pert Powder Type PW4030/60). The IR spectra were measured by a Thermo Scientific Fourier Transform Infra Red (FTIR) spectrometer. Esters products are measured with Gas Chromatography - Mass Spectrometry (GC-MS) of Chromeleon 7 Thermo Fischer Scientific 7.2.4.8179.

### 2.3. Catalyst preparation

A certain amount of zeolites are grounded using a mortar to increase the surface area, then suspended into distilled water for 24 hours. Zeolite suspension is filtered and dried using an oven below 150 °C for 3 hours. Dry zeolite (labeled NZC) was further analyzed using XRF, XRD and FTIR.

### 2.4. Acid treatment

0.5 M sulfuric acid was prepared by diluting 6.94 mL of 97% sulfuric acid to 250 mL with distilled water. Zeolite is stirred together with 0.5 M sulfuric acid for 24 hours with a ratio of zeolite to sulfuric acid is 1: 10. The suspension is then filtered and the catalyst solids obtained are washed with distilled water. Then the catalyst was dried in an oven at 100 °C for 3 hours. The catalysts were labeled as HZ and characterized using XRF, XRD and FTIR.

### 2.5. Copper treatment

0.5 M Copper solution obtained from dilution of 31.2 grams of  $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$  into 250 mL of distilled water at a ratio of 1: 10. Zeolite is stirred together with 0.5 M copper solution for 24 hours with a ratio of 1: 10. Suspension filtered and solids washed with distilled water. Here the catalyst is dried in an oven at a temperature of 100 °C for 3 hours. Catalysts were named CuZ and characterized by XRF, XRD, and FTIR.

### 2.6. Catalytic activity test

All prepared catalysts (NZC, HZ and CuZ) were tested on the synthesis of ethyl acetate. The ester derived from the esterification of ethanol by acetic acid with the molar ratio of alcohol to acid was 2: 1 and 5% by weight of the catalyst. The reaction is carried out in a simple reactor for 4 hours at 75 °C where the reactor is equipped with a round bottom flask, condenser, and batch of water. The result is cooled at room temperature, and the

solid catalyst is separated from the solution. The product predicted ester is distilled in a 250 mL round bottom flask and analyzed by gas chromatography. The catalyst was washed with distilled water and dried in an oven at 100 °C for 3 hours, so that it was weighed and reused for two more catalytic activities.

### 3. Results

#### 3.1. XRF analysis of the prepared catalysts

Natural zeolite from Cikalong West Java (NZC) used in this study has a greenish color where silica and alumina are the main compounds (Table 1). Potassium is the most metal element found in zeolite samples followed by calcium, magnesium, iron and copper. Because natural zeolite has a high Si/Al mole ratio, zeolite structure cannot be solved with a low pH [21] and with high ion exchange capacity [22]. Theoretically, zeolites with a high Si/Al mole ratio can act as catalysts [23]. We can also state that NZC is a type of mineral with a hydrophobic surface because the mole ratio of Si/Al is more than 4 which is good as a heterogeneous catalyst [21].

TABLE 1: XRF data of NZC, HZ and CuZ.

Catalysts	Metal oxide composition (%)							Ratio
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	CuO	
NZC	11.526	78.717	3.348	2.615	1.038	0.972	-	7.330
HZ	9.671	82.806	2.795	1.499	1.422	0.791	-	9.390

Increasing the mole ratio of Si/Al from the parent zeolite after being treated with acid (HZ) as read in Table 1 can cause an increase in its absorption power [24]. This result is consistent with the theory that the reaction with acid can cause dealumination of zeolite [25] as depicted in Fig. 1. Meanwhile the treatment of NZC with copper (II) actually decreases the Si/Al ratio.

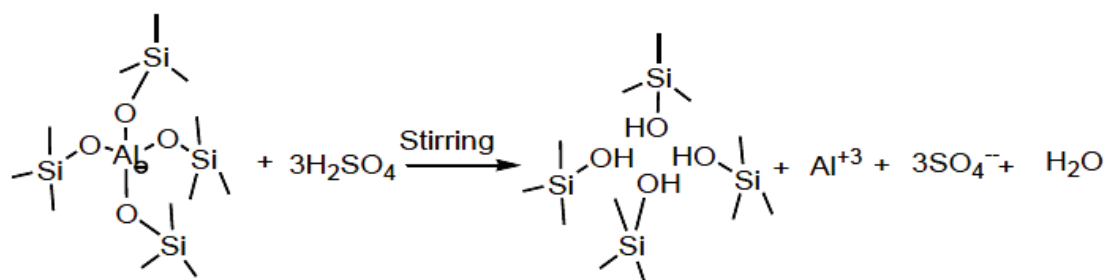
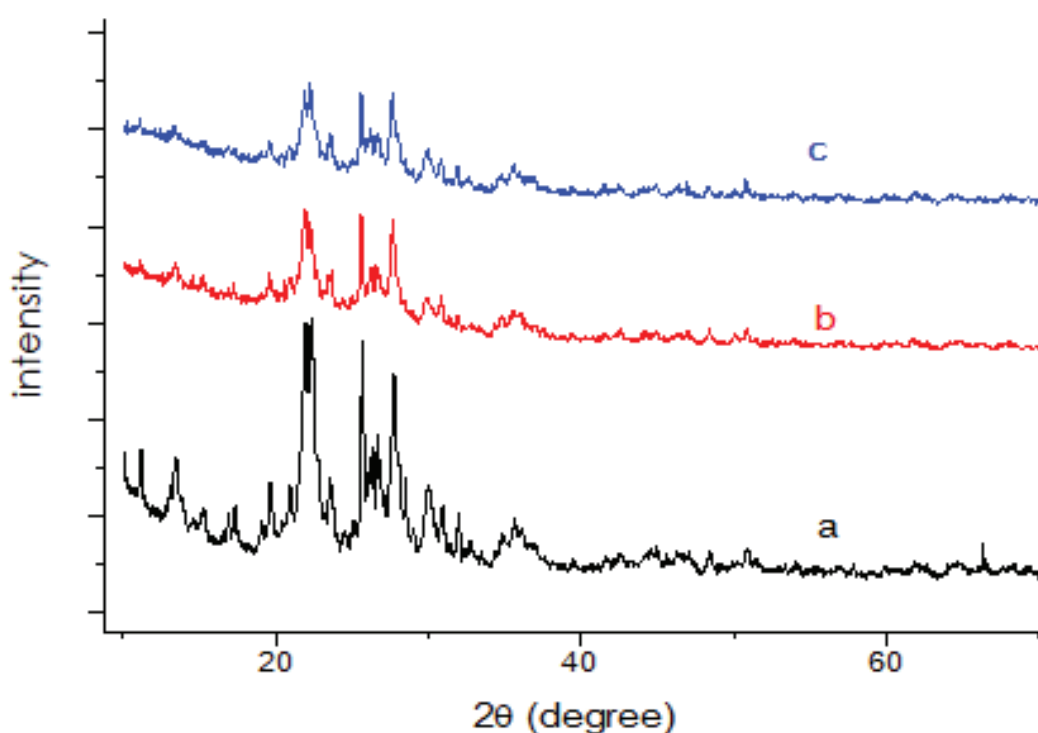


Figure 1: Schematic illustration of the dealumination process [12].

### 3.2. X-ray diffraction analysis of the prepared catalysts

Fig. 2 shows the XRD pattern of natural zeolite before and after modification with acid and copper (II). The parent Zeolite, NZC, contains mordenite with orthorhombic crystal structures ( $2\theta$  22.29°, 13.4°, and 27.67°) (ICDD 01-075-4223) as high minerals contained in natural zeolites. Other peaks at  $2\theta$  25.64° and 26.61° are called heulandites with monoclinic crystal structures (ICDD 01-078-4509).



**Figure 2:** XRD pattern of NZC (a), HZ (b) and CuZ (c).

Furthermore, there are other minerals contained in the NZC sample, namely orthoclase and cristobalite. Orthoclase is indicated by  $2\theta$  28.46° and 29.84°. Both orthoclase and cristobalite are impurities in natural zeolites. Cristobalite is a polymorph of  $\text{SiO}_2$  which is included as quartz with different crystalline structures while orthoclase is a typical feldspar group. Natural zeolite from Cikalong contains mordenite as its main mineral with feldspar as an impurity [26]. Another report stated that natural zeolite from Bandung consisted of mordenite [27]. The XRD peak intensity of natural zeolite after being attached by acid and copper ions is only slightly shifted which shows that the structure of the parent zeolite has not changed much and once again shows the chemical stability of this natural mineral.

### 3.3. Fourier transform infrared analysis of the prepared catalysts

Changes that might occur in zeolite structures were also analyzed using FTIR measurements. The main absorption peak can be observed at about  $300\text{-}1300\text{ cm}^{-1}$  for  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral as the basic framework in the overall zeolite structure. Meanwhile the absorption peak in the  $4000\text{-}1300\text{ cm}^{-1}$  region indicates a functional group consisting of zeolite. Fig. 3 shows the spectrum for each sample of NZC (a), HZ (b) and CuZ (c). We can see that absorption occurs at  $575, 790, 1028, 2018, 2201$ ; and  $3624\text{ cm}^{-1}$ .

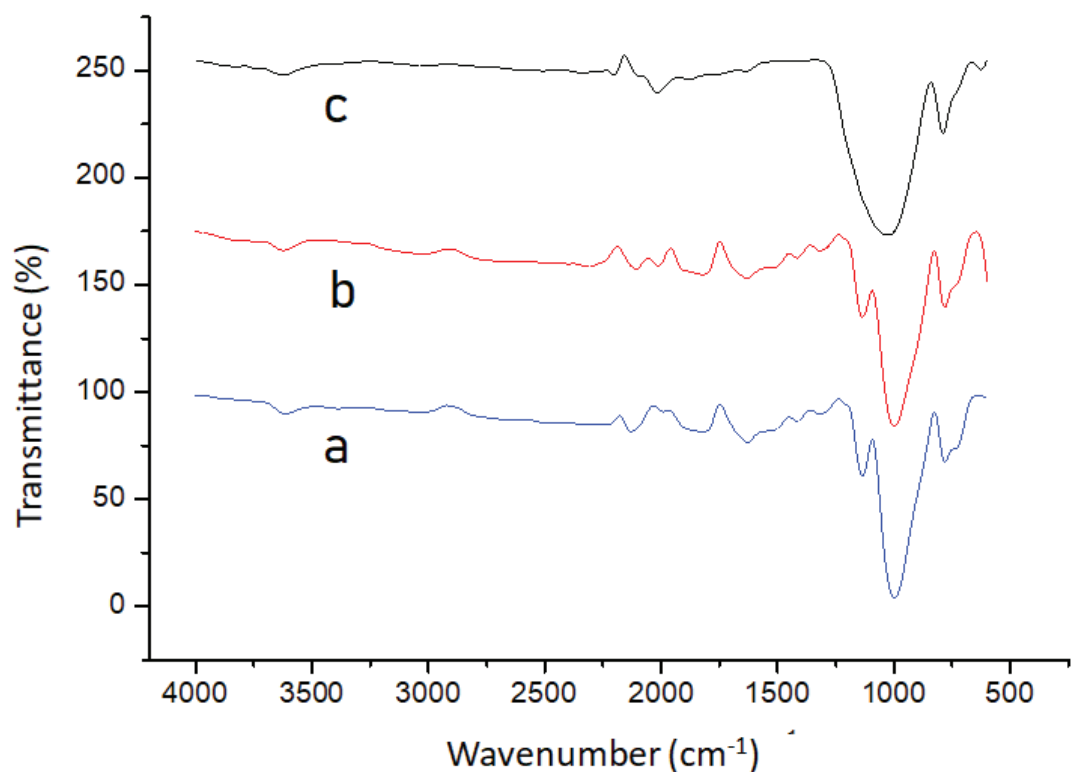


Figure 3: IR spectra of NZC (a) HZ (b) and CuZ (c).

The absorption peak at  $575\text{ cm}^{-1}$  shows existing deformation and a mixture of aluminum and silicon vibrations [27]. The absorption peak at  $790\text{ cm}^{-1}$ , shows the existence of an O-T-O vibration in the external relationship of zeolite, where T may be Si or Al, while the absorption peak at  $1028\text{ cm}^{-1}$  shows asymmetrical vibration stretching TOT (Si-O or Al-O) of the zeolite structure of TO4 [1, 37, 38 and 27]. Whereas the hydroxyl stretching vibration from the side of silanol can be observed in the absorption area of  $3540\text{-}3650\text{ cm}^{-1}$ . Table 2 shows the shift in peak of natural zeolite absorption. The shift shows the existence of zeolite external structural vibrations, which are caused by the loss of several Al atoms from the framework of zeolite structures after modification and possible changes in the bonding capacity and angle of Si-O-Si [1].

TABLE 2: The shifting of absorption peak of NZC, HZ and CuZ.

NZC	HZ	CuZ
790.21 $\text{cm}^{-1}$	782.22 $\text{cm}^{-1}$	780.63 $\text{cm}^{-1}$
1028.41 $\text{cm}^{-1}$	1135.23 $\text{cm}^{-1}$	1136.51 $\text{cm}^{-1}$
2201.32 $\text{cm}^{-1}$	2010.64 $\text{cm}^{-1}$	2131.20 $\text{cm}^{-1}$
3624.57 $\text{cm}^{-1}$	3624.06 $\text{cm}^{-1}$	3612.23 $\text{cm}^{-1}$

Due to the interaction between Cu and Al with OH silanol of zeolite, the modification process using  $\text{CuSO}_4$  tends to shift the vibration absorption peak into a higher amount of absorption [16]. We can assume that the presence of bivalent cations such as  $\text{Cu}^{2+}$  causes the zeolite external structure to vibrate. New absorption peaks (Table 3) appear at 1136 and 1137 respectively in HZ and CuZ which show  $\text{TO}_4$  vibrations and also in the region of  $1300\text{-}1650 \text{ cm}^{-1}$  which shows the vibration of H-O-H from  $\text{H}_2\text{O}$  absorbed.

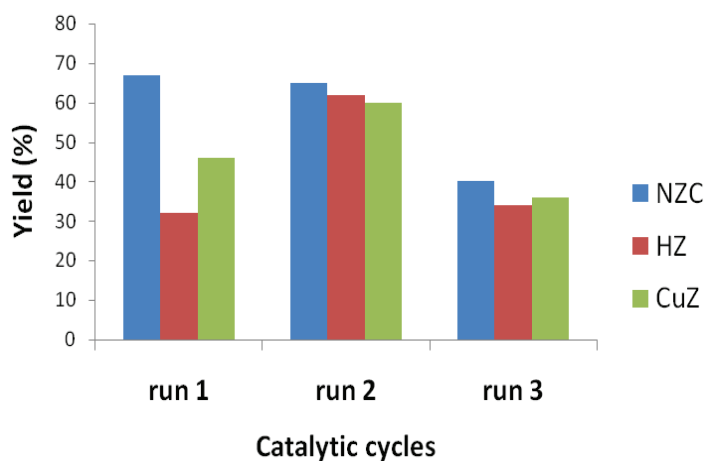
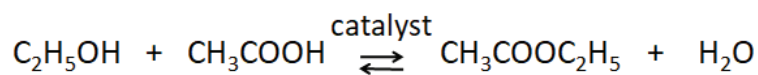
TABLE 3: The absorption peak of HZ and CuZ.

Modified Zeolites	Absorption Peak ( $\text{cm}^{-1}$ )							
	HZ	782.22	999.14	1135.23	1318.23	1631.64	1819.86	2109.17
CuZ	780.63	997.96	1136.51	1319.25	1629.66	1821.98	2131.20	3612.23

### 3.4. Catalytic activity

The catalytic activity of NZC, HZ and CuZ were tested on the esterification of ethanol with acetic acid (the molar ratio of ethanol to acetic acid was 2:1 and with the amount of catalyst 5% by weight of acetic acid). Ethyl acetate products are measured by GC-MS. The product shows a distinctive odor of ethyl acetate where the reaction equation is as follows:

As shown in Fig. 4, the first cycle clearly shows that NZC is better than HZ and CuZ. While for cycles two and three all catalysts show activities that are not too much different where the NZC remains slightly better. In the case of modification of zeolite with acid, as explained in the XRF characterization section, an increase in Si/Al ratio causes a decrease in its catalytic activity. When mixed with copper(II), the Si/Al ratio becomes lower which indicates that there are several silica frameworks that have been degraded, which also has an impact on the decrease in catalytic activity. Although not better than NZC, both HZ and CuZ showed catalytic activity that increased in the second cycle even though in the third one it returned which might be caused by the leaching of catalytic active centers to the solvent.



**Figure 4:** Catalytic test of NZC compared with both modification forms (HZ and CuZ) on esterification of ethanol with acetic acid for three reaction cycles.

## 4. Conclusion

From this work we can conclude that the Cikalong natural zeolite contains modernite and heulandite. Characterization with XRD shows that the structure of the natural zeolite crystal has not changed much after being modified with protons and copper(II). While measurements with XRF and FTIR indicated that there was a change in the Si/Al ratio which was opposite when natural zeolite was modified with acid compared with those modified with copper (II). The natural zeolite also shows catalytic activity which is generally better than the two modified forms of the mineral, but the latter is slightly better at reuse.

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