

Metal supported on natural zeolite as catalysts for conversion of ethanol to gasoline

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Abstract. A various of metal supported into natural zeolite was prepared via wet impregnation method. The transition metals impregnated are nickel, cobalt, copper and zinc. The catalytic properties both of physical and chemical properties were characterized by X-ray Diffraction (XRD), Thermo Gravimetri Analysis (TGA)-Differential Scanning Calorimetry (DSC), Surface Area Analyzer-Porositymeter and also gravimetry method for acidity measurement following by the adsorption of organic bases. The results showed that different metals impregnated into natural zeolite affected physical and chemical properties, i.e. crystalinity, surface area, pore size, pore volume and acidity. Their catalytic activity was tested for conversion ethanol to gasoline and showed high conversion up to 80-90% with the aromatics as major product.

1 Introduction

Catalysis is one of the important steps in chemical processes[1,2]. Bifunctional catalysts involved two active sides, both of metal and acid sites. The metal sites usually come from a supported transition metal, such as Ni, Mo, W, Co, or their combinations, oxide, or sulfide of group VIII and/or group VI B[3]. While, the acid sites come from alumina-silica [4-6], various zeolites such as ZSM-5 [7], Y [8,9] and beta [10], MCM-41, and amorphous silica-alumina.

Zeolite is known to have great potential as catalysts or catalyst supports because of their properties, such as high surface area, high porosity, high adsorption capacity, and easy to separate from reactant and products. The catalytic reactions depend on catalyst's structure, acidity and reaction condition. [11,12].

Indonesia has abundant natural zeolite. One of the natural zeolite deposits in Indonesia, which has a large silica content of approximately 60% is in Gunung Kidul, Yogyakarta with the deposit of 55,000,000 m³. These minerals are often found in the hills area of Baturagung, Gedangsari and Ngawen [13].

Bioethanol from biomass can be blended into gasoline in small percentage as oxygenate component to improve the fuel quality with low emissions of CO, CO₂ and hydrocarbon [14]. Ethanol has vapor pressure limitations where 10 % volume ethanol is blended into gasoline will give evaporative emissions and increase aldehyde emissions [15,16] and also its addition in large percentage requires the modification of the engine system. It needs for conversion of ethanol into gasoline components such as aromatics and iso-paraffins which have high octane number.

The conversion of ethanol into gasoline involved

several reactions as shown generally in Figure 1. First is dehydration ethanol to ethylene. Ethylene possible will have several reactions, which are oligomerization, isomerization, cracking or aromatization to produce various kinds of hydrocarbons, both paraffin (ethene, propene, butene, etc.) and aromatics (benzene, toluene, C₈-10, gasoline).

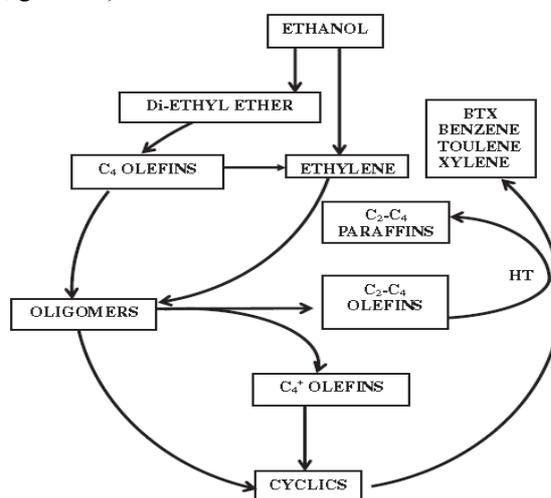


Fig.1. Reaction Pathways of Ethanol to Gasoline [16].

A recent review on the catalytic conversion of bioethanol to hydrocarbon fuels reported by Tretyakov et.al [17]. The addition of Ni into ZSM-5 improves the catalyst stability against coking [18]. Freeman et.al. [19] also investigated this reaction over Ga₂O₃/HZSM and Ga₂O₃-WO₃/alumina catalysts at 400°C and found that the addition of Ga₂O₃ to HZSM increases the selectivity to aromatics at the expense of C₂-C₄ hydrocarbons. Cr/Bentonite compared to HZSM-5 was also reported as

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promising catalysts for ethanol conversion to gasoline range (C4-C12) [20].

Sudiyarmanto et al. [21] reported the conversion of ethanol into aromatics by using various transition metals, which are Cu, Co and Zn supported into commercial zeolite catalyst. The addition of transition metals resulted the yield aromatics more than 90%.

In this research, we prepared metal/natural zeolite catalysts through impregnation method and characterized their physical and chemical properties. The effects of variation of transition metals loading were studied. Their catalytic activities were tested for conversion of ethanol to gasoline.

2 Methodology

2.1. Materials

The metal precursors consist of cobalt (II) nitrate hexahydrate, copper (II) nitrate hexahydrate, nickel (II) nitrate hexahydrate, and zinc (II) nitrate hexahydrate in pure grade (Merck), while the other materials used are natural zeolite (NZ) from Gunung Kidul-Indonesia.

2.2. Catalyst preparation

The natural zeolite (NZ) from Gunung Kidul-Indonesia was activated before by using HCl [22]. A various of the transition metals (M=Ni, Cu, Co and Zn) was impregnated into natural zeolite. The procedure was conducted as follow: Aqueous mixture of 10 g of natural zeolite and 20 % of metal loading was refluxed and stirred constantly at temperature of 80 °C for 24 h. Then, catalyst samples were separated, dried overnight at 100 °C and calcined for 2 h at 500 °C as illustrated in Figure 2.

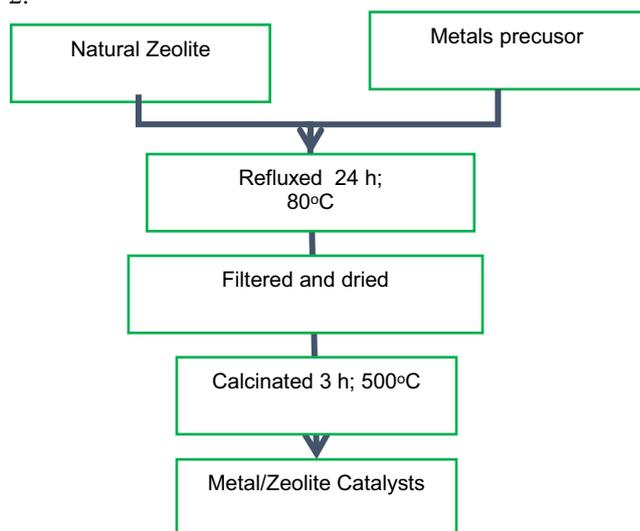


Fig.2. Diagram of preparation method.

2.3. Characterization of catalyst

For crystallographic phase identification, X-Ray Diffraction (XRD) analysis used a Rigaku diffractometer, with Cu K α radiation at 40 kV and 30 mA, and a secondary graphite monochromator.

The calcinations temperature was determined by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) instrumentation by Linseis under heating up to 1000 °C.

The specific surface area was measured by the Brunauer-Emmet-Teller (BET) while the pore volume and pore size of the particles were measured by Barret-Joyner-Halenda (BJH) method. Both of the methods used N₂ adsorption/desorption at 77.3 K (Tristar II 3020 Micromeritics Instrument).

The total and surface acidity of samples were determined by the irreversible adsorption of organic base, which are pyridine and ammonia. While, the nature and types of groups and acid site was observed by using Fourier Transform – Infra Red (FT-IR) spectroscopy in KBr phase using Shimadzu, Prestige-21 with ATR 4000 attached to an automatic data acquisition center.

2.4. Catalytic activity test

Catalytic activity tests were tested by introducing 1% of catalyst loading in a fixed bed reactor electrically heated with adjustable temperature control. A total of 100 ml of ethanol feed was pumped into the reactor. The reaction was conducted at 350 °C for 2.5 h as described in Figure 3.

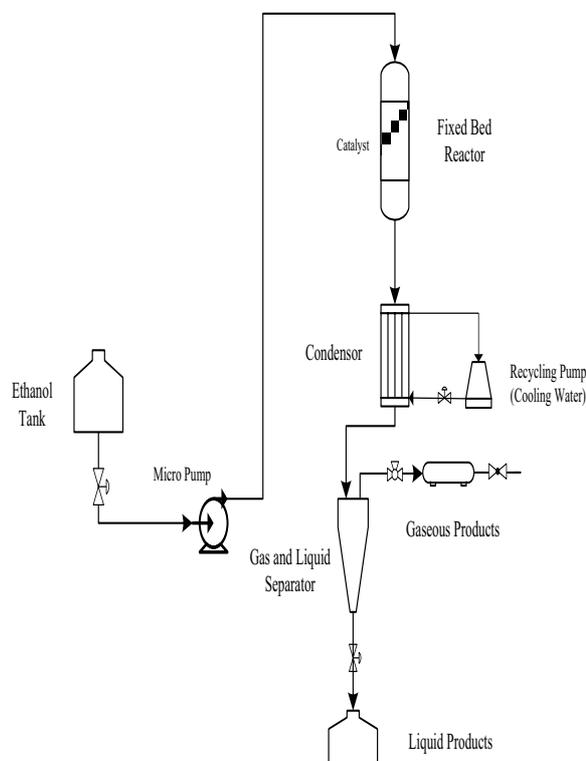


Fig.3. Schematic diagram of the reactor.

2.5. Product Analysis

The liquid product was analyzed by using Gas Chromatography Mass Spectrometry (GC-MS) Agilent 19091S-436, equipped by HP-5MS, 0.25mm x 60m x 0.25um column.

3 Result and discussion

3.1. X-Ray diffraction (XRD) analysis

X-ray diffraction pattern for the metal/natural zeolite samples are shown in Figure 4. In the natural zeolite (NZ) sample, there are five main peaks exhibited in the 2θ region 9.828° , 22.392° , 26.440° , 26.640° , and 28.016° . These peaks are the characteristic of mordenite according to JCPDS data. The loading transition metals into natural zeolite decreased the crystallinity as indicated by a decrease in the intensity of some characteristic peaks.

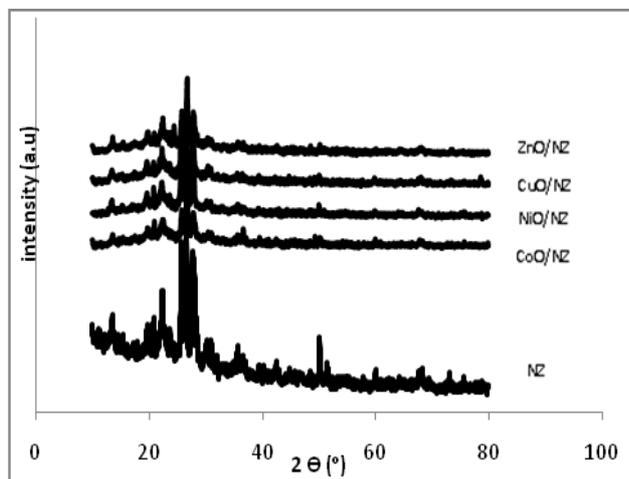


Fig.4. X-ray diffraction pattern of metal/natural zeolite.

3.2. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

To investigate the changes in physical and chemical properties of catalysts occurred during increasing activation temperatures, the weight loss of these materials under heating process were observed. Figure 5-9 shows the effect of metal loading on the TG and DSC curves of materials previously activated under heating up to 1000°C .

The initial weight loss observed at approximately 200°C corresponded to the desorption of water molecular from the catalysts samples. At higher temperature at about 200°C to 500°C can be attributed to the decomposition of nitrate entrapped in the narrow pores of the metal/zeolite catalyst. The slow change of weight after 500°C indicates the prolonged process of metal oxide/zeolite compound and/or gradual loss of the hydroxyl groups in the crystalline structure. According to the TGA/DSC profile, temperature at 500°C was selected for the calcination of the catalysts.

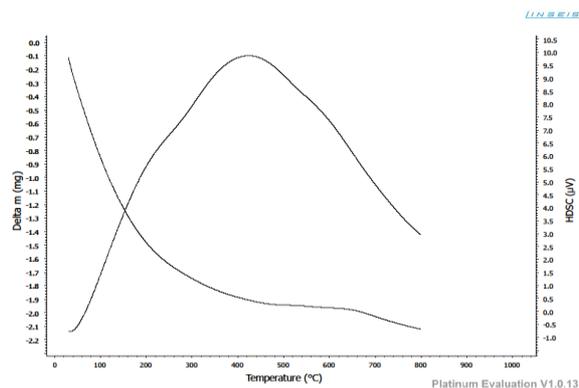


Fig.5. TGA/DSC pattern of natural zeolite

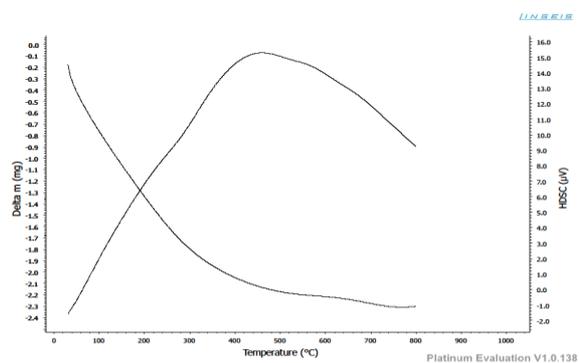


Fig.6. TGA/DSC pattern of NiO/NZ

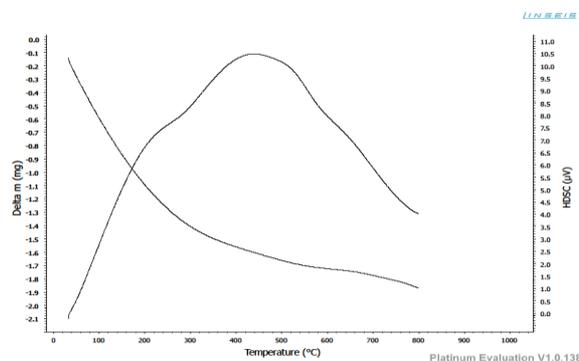


Fig.7. TGA/DSC pattern of CuO/NZ

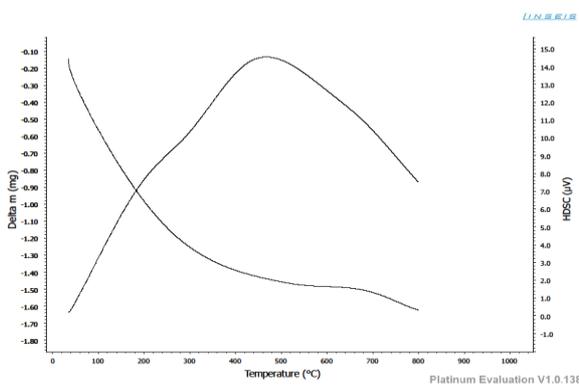


Fig.8. TGA/DSC pattern of CoO/NZ

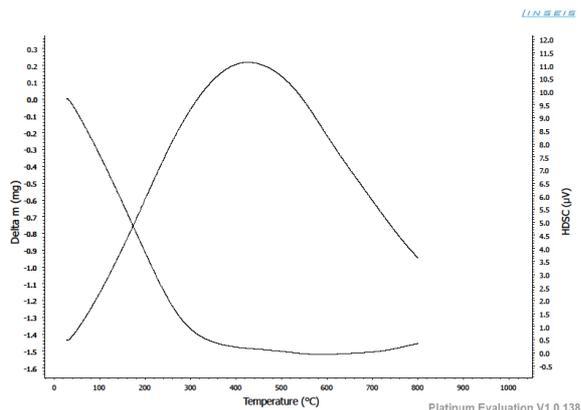


Fig.9. TGA/DSC pattern of ZnO/NZ

3.3. Specific surface area measurement

Specific surface area (S_{BET}), pore volume and pore size are shown in Table 1. It can be seen that the different transition metals supported on natural zeolite gave different specific surface area, but did not give significant changes in pore volume and pore size.

The transition metals might not enter the pore but only remained on the surface of the catalysts. Supported copper oxide on the zeolite has the highest surface area among the other transition metals. Copper metal was distributed well on the zeolite support so its specific surface area tends to higher than others.

Table 1. Specific Surface Area, Pore Volume and Pore Size of Metal/Natural Zeolite Catalysts

Samples	Specific surface area [$m^2.g^{-1}$]	Pore volume [$cc.g^{-1}$]	Pore size [\AA]
NZ	13.064	0.0033	2.099
NiO/NZ	15.471	0.0036	2.096
CuO/NZ	20.019	0.0039	2.092
CoO/NZ	18.092	0.0035	2.093
ZnO/NZ	17.234	0.0036	2.096

3.4. Acidity

Total acidity was determined using ammonia vapour while the surface acidity was determined using pyridine vapour. The nature of acid sites defined by the surface protons leading to the Bronsted sites or cationic centers due to unsaturation in coordination as the Lewis sites.

The result from the total and surface acidity of the samples are shown in Table 2. Metal loaded on zeolite tend to decrease the total acidity for all samples. While, the surface acidity for Cu and Zn supported on zeolite tend to increase slightly.

Table 2. Acidity of Metal/Natural Zeolite Catalysts

Samples	Total acidity [$mmol.g^{-1}$]	Surface acidity [$mmol.g^{-1}$]	Pores acidity [$mmol.g^{-1}$]
NZ	5.035	0.657	4.378
NiO/NZ	4.649	0.551	4.098
CuO/NZ	3.566	0.696	2.87
CoO/NZ	3.161	0.441	2.72
ZnO/NZ	3.707	1.018	2.689

Figure 10 shows NH_3 adsorbed on catalyst samples. The band at 1440 cm^{-1} is the characteristic peak of ammonium ion formed on the Bronsted acid sites and the absorption peak at $1300\text{--}1000\text{ cm}^{-1}$ is contributed by ammonia coordinately bonded to Lewis acid sites.

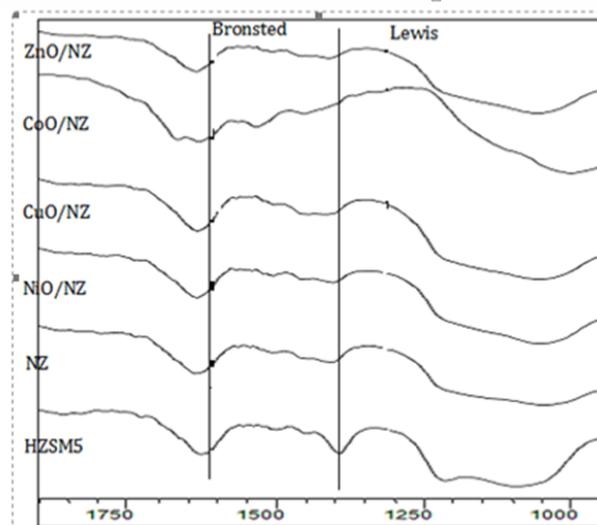


Fig. 10. FTIR spectra of NH_3 adsorbed on catalyst samples.

Figure 11 shows pyridine adsorbed on catalyst samples. The band at 1650 cm^{-1} is the characteristic peak of pyridine ion formed on the Bronsted acid sites in the surface of catalyst samples. This FTIR spectra indicated the presence of both Bronsted and Lewis acid sites on the catalyst samples.

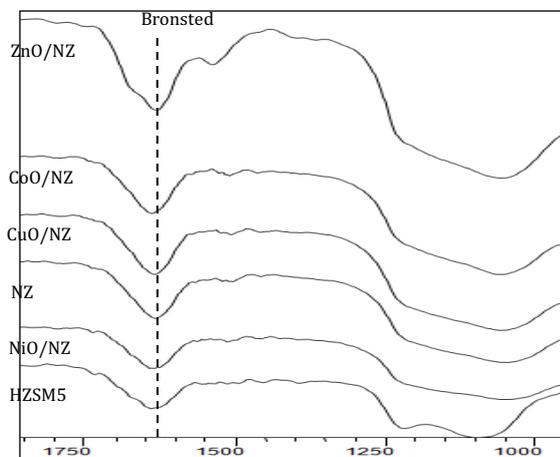


Fig. 11. FTIR spectra of pyridine adsorbed on catalyst samples.

3.5. Catalytic activity test

The catalysts were tested for ethanol to gasoline (ETG) conversion. All the prepared catalysts showed a good activity in ETG reaction. The conversion of reaction reached more than 80% at the reaction conditions studied. The liquid product contains major amount of aromatics followed by olefins, and a small fraction of parafins as shown in Figure 10.

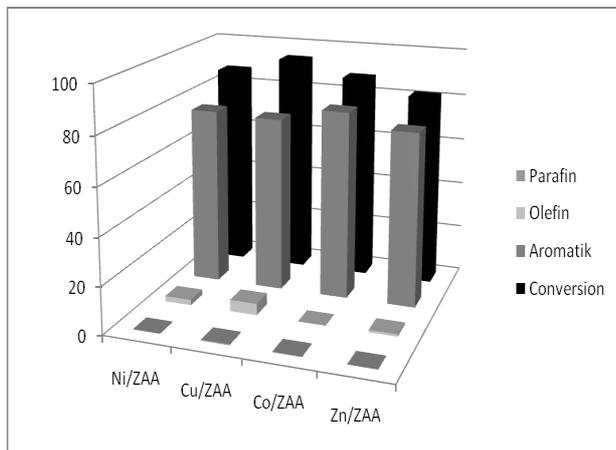


Fig. 10. Conversion and Product Distribution in Liquid Product

Among prepared catalysts, CuO/NZ catalyst revealed the highest conversion of ethanol, while ZnO/NZ performed the lowest activity. CuO/NZ catalyst shown highest selectivity of parafin and lowest of aromatic compared with other catalysts prepared. While, CoO/NZ catalyst shown highest selectivity of aromatics and lowest of parafins. Higher aromatics in gasoline fraction is less favored because it contributes knocking effect on the machine.

4 Conclusion

Different transition metals (Ni, Cu, Co and Zn) supported on zeolite by impregnation method resulted different physical and chemical properties, i.e. crystalinity, surface area, pore size, pore volume and acidity of the catalyst. The increasing of surface area and pore volume and the decreasing of pore size as the result of transition metals supported into zeolite gave better physical and chemical properties of catalyst. Copper metal was distributed well on the zeolite support so it has the highest surface area among the other transition metals. FTIR adsorption organic base indicated the nature acid site both of Bronsted and Lewis acid site on all the catalyst samples. The catalytic activity test showed the prepared catalysts gave conversion more than 80% and the major products were aromatics followed by olefins and a small fraction of parafins.

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