

Cr and Ni Metals-Impregnated Natural Zeolites as Catalysts for Transformation of Glucose to 5-Hydroxymethylfurfural

Zeolit Alam Terimpregnasi Logam Ni dan Cr sebagai Katalis Transformasi Glukosa menjadi 5-Hidroksimetilfurfural

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The transformation of glucose sourced from agricultural waste into products with higher economic value has not been carried out optimally. One way to utilize glucose from the waste is to convert it into 5-hydroxymethylfurfural (HMF), an intermediate compound which can then be used as raw material for the manufacture of various other chemical compounds such as polymers or fuels. The results of the study using natural zeolite catalysts impregnated with Cr and Ni metals were proven to be able to convert glucose into HMF. Metal impregnation in zeolite is carried out through ion exchange with variations in heating temperatures of 60 °C and 90 °C. The impregnation efficiency of Cr and Ni is obtained in the range of 76-79%. The synthesis of HMF was carried out with pure glucose as a substrate in water: acetone (1:2) solvent using the hydrothermal method at 180 °C for 6 hours. The metal-impregnated zeolite heated at 60 °C showed better catalytic activity than the zeolite heated at 90 °C, with HMF yields of 22.7% for Cr and 38.68% for Ni metal impregnated zeolite. These results are better than studies using zeolite alone as a catalyst that have been previously reported, and show that Cr and Ni metals-impregnated zeolites can be used as catalysts for the transformation of glucose into HMF.

Keywords: catalyst, glucose, HMF, hydrothermal, natural zeolite

1. INTRODUCTION

Biomass is organic material that is relatively young and comes from plants, animals, waste products of agriculture, plantations, forestry, animal husbandry, and fisheries. Biomass with abundant availability is lignocellulose. The elementary composition of lignocellulosic biomass is 27–49% cellulose, 14–36.9% hemicellulose, and 16–32.9% lignin (Yu and Tsang 2017). Generally, lignocellulosic biomass is used as a source of fiber, animal feed, biochar briquettes, and renewable energy sources such as bioethanol. Lignocellulosic biomass also has the potential to be used as a source of glucose which can be converted into 5-Hydroxymethylfurfural (HMF) compound (Zhou et al., 2016).

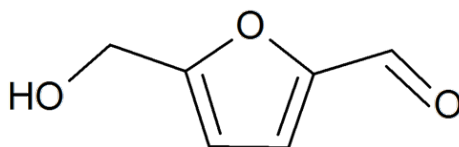


Figure 1 5-Hidroksimetilfurfural (HMF) compound

HMF compound (Figure 1) can be produced from the dehydration of glucose and fructose. HMF is an important chemical compound and can be converted into furan derivatives with various functions and chemical properties, such as 2,5-dimethylfuran which has a high-octane number (Aylak et al., 2016). According to Yu and Tsang (2017), the synthesis of HMF from glucose begins with the isomerization of glucose into fructose with a Lewis acid catalyst. After that, fructose undergoes a dehydration reaction to become HMF with Bronsted acid catalyst. Therefore, the production of HMF from glucose can take place with a Lewis acid catalyst and a Bronsted acid catalyst in one reactor. In order for the conversion reaction of glucose to HMF to take place efficiently, a catalyst with two types of acid sites is required.

The synthesis of HMF can be carried out using homogeneous and heterogeneous catalysts. Examples of homogeneous catalysts that have been reported are metal chloride salts and strong acids. Xin et al. (2017) have used the metal salt CrCl_2 as an efficient catalyst in converting glucose into HMF with a yield of 46.1%. Hu et al. (2012) also reported that the metal salt catalyst CrCl_3 was effective in converting glucose into HMF using ionic solvents with a yield of 71.3%. According to Lai et al. (2013) NiCl_2 metal salt can be used as a catalyst for the transformation of glucose into HMF with a yield of 30%. However, the use of homogeneous catalysts in chemical reactions has drawbacks such as the difficulty of the catalyst regeneration process, and the difficulty of separating the catalyst from the reactants or products. This research focuses on the development of heterogeneous catalysts in the synthesis of HMF.

One of the heterogeneous catalysts that is often used is zeolite. Generally, the zeolite used is synthetic zeolite because of its high purity and crystallinity. Zeolite has nano-dimensional pores on which cation exchange processes can occur on the surface, also has 2 acid sites, namely Lewis acid sites from Si or Al, and Bronsted acid sites from silanol groups. It can be said that zeolite is a multifunctional catalyst, and has a high selectivity (Ennaert et al., 2016). Zeolite catalysts are also called nanoreactors because of their shape and pore size. The shape and size can affect the selectivity, speed, and stability of the reaction (Kosinov et al., 2009). Synthetic zeolites have been applied as heterogeneous catalysts in converting glucose, fructose, and sucrose into HMF with yields of 34.01%, 51.72%, and 50.10%, respectively (Mostapha et al. 2016). Zeolite type H-mordenite has high catalytic activity in converting glucose to HMF with a yield of 14% (Li et al. 2015). According to Ngapa et al. (2016), Ende natural zeolite has a fairly high mordenite content. Aylak et al. (2016) reported that zeolite modified by chromium metal has high catalytic activity in converting glucose to HMF with a yield of 54.2%. In this study nickel and chromium metals-modified natural zeolite were used as catalysts to convert glucose into HMF.

2. MATERIAL AND METHOD

2.1. General details.

All manipulations were carried out using standard glassware and laboratory equipment. The success of metal impregnation on zeolites was observed using Shimadzu 8400S Fourier-transform infrared (FTIR) spectroscopy, Shimadzu AA-70 flame atomic absorption spectrometer (FAAS), and PANalytical X-ray diffraction (XRD) spectroscopy. Identity and yield of the HMF products were examined by High Performance Liquid Chromatography (HPLC) Shimadzu prominence CTO-20A. The materials used in this study were not further purified such as glucose (p.a), Ende natural zeolite, distilled water, 1M NaOH, 1M HCl, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, NH_4Cl , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, universal pH, acetone (p.a), methanol (p.a), and HMF standards.

2.2. Natural Zeolite Activation (Ngapa et al. 2016).

There are two types of zeolite activation carried out in this study, namely acid activation and alkaline activation. Acid activation was carried out with 50 g of filtered initial zeolite (ZA) with a size of 100 mesh soaked in 60 mL of 1M HCl for 3 hours. The mixture was stirred using a magnetic stirrer. After that, the mixture was washed with distilled water until the pH of the mixture became neutral. The mixture was dried in an oven at 120 °C for 3 hours. Base activation was carried out by soaking the zeolite in 1M NaOH. Then the activated zeolite was saturated with 40 mL 1M NaOH for 3 hours. The mixture was stirred with a magnetic stirrer. After that, the mixture was washed to neutral pH with distilled water. Zeolite was dried in an oven at 120 °C for 3 hours and obtained Na-zeolite from acid activation (Na-ZAA) and Na-zeolite with alkaline activation (Na-ZAB).

2.3. Synthesis of H-Zeolite catalyst from Natural Na-Zeolite (Nurhadi et al. 2001).

Na-zeolite was immersed in 1 M NH_4Cl with a ratio of 1:5 for 24 hours. The mixture was filtered and washed with distilled water until neutral. The mixture was dried in an oven at 120 °C for 3 hours and calcined at 500 °C for 5 hours. Samples of acid-activated H-zeolite (H-ZAA) and alkaline-activated H-zeolite (H-ZAB) were characterized using XRD.

2.4. Synthesis of Ni and Cr metals Zeolites (Modification of Hoang et al. 2017).

A total of 5 g of activated natural zeolite was mixed with 40 mL of 1% $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (or 1% $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) solution. The mixture was stirred with a magnetic stirrer and heated at various temperatures of 60 °C and 90 °C until the mixture formed a sol. The mixture was dried in an oven at 120 °C. Then, the dry sol was calcined for 3 hours at a temperature of 500 °C. Zeolite which has been modified with metal was characterized using XRD and FTIR.

2.5. Transformation of glucose into HMF (Modification of Pedersen et al. 2015).

A total of 0.15 grams of glucose was mixed with 0.02 grams of modified natural zeolite. The solvent used was water and acetone in a 1:2 ratio, with volumes of 10 and 20 mL. The mixture was heated at 180 °C for 6 hours in a hydrothermal autoclave. The synthesized HMF was characterized using HPLC with a hypersyl column C-18, UV-Vis detector with a wavelength of 254 nm with a mobile phase ratio of water:methanol (95:5). The sample was injected as much as 20 μL . Determination of the number of moles of HMF using HPLC by comparing the chromatogram with the standard. The amount of glucose that had not been converted was checked again using HPLC. Qualitative analysis was carried out by comparing the retention time between the sample and the standard, while quantitative analysis was carried out by calculating the concentration of HMF to determine the yield.

3. RESULTS AND DISCUSSION

3.1. Diffractogram of activated and H-zeolites.

Ende natural zeolite is a mixture of several crystalline phases, as shown by the acid and base activated zeolite diffractogram shown in Figure 2. After comparing the data from JCPDS (Joint Committee on Powder Diffraction Standards), Ende natural zeolite consists of a mixture of crystalline phases of mordenite and clinoptilolite. JCPDS No. 06-0239 states that the dominant peaks of mordenite phase zeolite are at $2\theta = 19.58^\circ$, 25.58° , 26.27° , and 27.68° . Ende's natural zeolite diffractogram shows that the dominant phase is mordenite with the appearance of high-intensity peaks at $2\theta = 19.57^\circ$, 25.55° , 26.58° , and 27.62° . The clinoptilolite phase according to JCPDS data No. 47-1870 was at $2\theta = 9.87^\circ$, 13.09° , 19.07° , and 22.17° . Ende's natural zeolite diffractogram shows clinoptilolite peaks at $2\theta = 9.67^\circ$, 13.09° , and 22.17° . The peak at $2\theta = 20.77^\circ$ may be from another crystalline phase, or from silica. XRD analysis of Ende natural zeolite also provides information about the degree of crystallinity as shown in Table 1. The degree of crystallinity increases with the treatment given to the zeolite. The degree of crystallinity of acid-activated zeolite showed greater crystallinity than base-activated zeolite, with the highest value indicated by H-zeolite in both treatments.

Natural zeolites generally contain impurities, such as iron oxides, metal oxides of the alkali and alkaline earth groups that cover the pores, so an activation process is necessary. Zeolite activation aims to open the pores of the zeolite and increase the percentage of crystallinity. Activation of zeolite with acid (HCl) and base (NaOH) is a chemical activation process. HCl solution is a strong acid which can dissolve metal oxides that are trapped in the pores of the zeolite, so that the pores of the zeolite become larger and the contact area is wide. The pore size and structure of zeolite have an impact on the catalytic activity, especially selectivity, depending on the pore size of the zeolite with the dimensions of the reactants and products. Molecules with dimensions lower than the zeolite pore can enter the pore, access the catalytic site and react within it. Molecules that diffuse through the pores of the zeolite will produce products (Hattori and Ono 2015). Activation with base aims to reduce impurities in the zeolite pores and to uniform the size of the zeolite pores. In addition, the activation of zeolite with base (NaOH) will make the active side of the zeolite more negative so that the ability of the zeolite as an absorbent is increasing. Acid and base activation did not change the significant peaks of the Ende zeolite which was generally dominant in mordenite. This can be seen in the Ende zeolite diffractogram (Figure 2a and Figure 2b), which shows that the mordenite peak is at an angle of 26.58° .

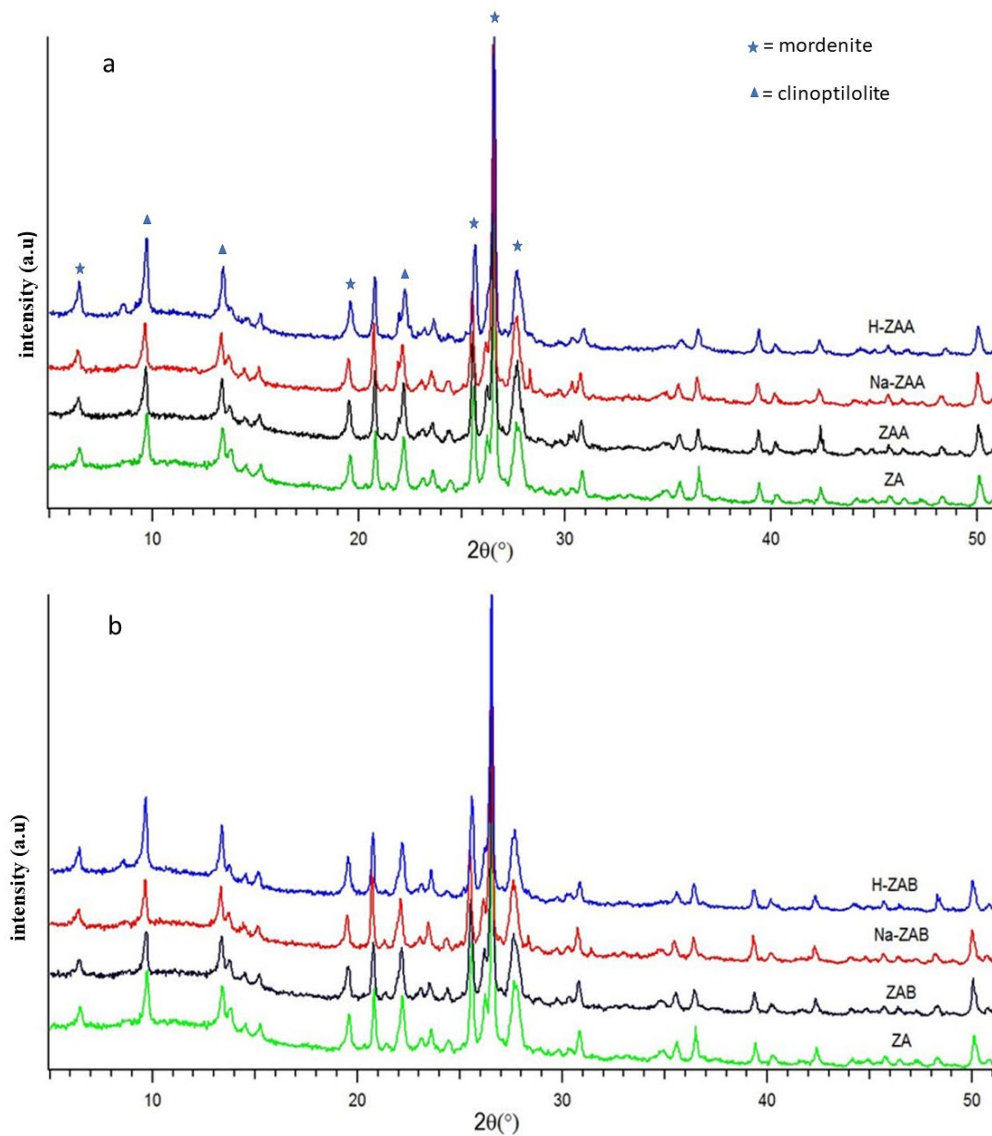


Figure 2 Diffractogram of acid-activated (a) and base-activated (b) natural zeolite

Table 1 Crystallinity data of Ende natural zeolite

Samples	Degree of crystallinity (%)	FWHM value
Natural zeolite (untreated, ZA)	54.64	0.34
Acid-activated zeolite (ZAA)	62.65	0.28
Na-acid zeolite (Na-ZAA)	66.38	0.24
H-acid zeolite (H-ZAA)	67.79	0.22
Base-activated zeolite (ZAB)	60.92	0.32
Na-base zeolite (Na-ZAB)	61.65	0.30
H-base zeolite (H-ZAB)	63.34	0.29

The percentage of crystallinity obtained from activated zeolite to the formation of H-zeolite continued to increase, both with acid activation and base activation (Table 1). The percent crystallinity correlated with the Si/Al ratio. A high percentage of crystallinity has a large Si/Al ratio. The acid-activated zeolite undergoes a dealumination process which reduces the amount of aluminum in the zeolite, reducing the amount of aluminum increases the Si/Al ratio and increases the percent crystallinity (Aboul-Fotouh et al. 2017). Zeolite with a high degree of crystallinity has a low FWHM value. The low FWHM value indicates that the zeolite has a homogeneous lattice spacing so that the atomic arrangement in the crystal lattice is neatly arranged (Wibowo et al. 2017).

The FWHM value of acid-activated H-zeolite is 0.22 which indicates that acid-activated H-zeolite has the highest percentage of crystallinity.

Na-zeolite is produced by mixing activated zeolite with 2 M NaOH solution. The higher the concentration of NaOH, the higher the number of Na^+ ions so that the active side of the zeolite is more negative. Furthermore, H-zeolite was synthesized by mixing Na-zeolite in 1 M NH_4Cl solution which aims to increase its Bronsted acid site. The formation of H-zeolite begins with the exchange of cations between NH_4^+ and Na^+ . The adsorption of ammonium cations occurs on the surface with hydroxyl groups, and also through the combination of the positive charge of the ammonium cation and the negative charge on the surface of the zeolite. The exchange of ammonium ions with alkaline cations is proportional to the number of ammonium ions added. The greater the concentration of the ammonium chloride solution used in the activation, the more alkali metal cations in the zeolite replaced by ammonium ions. The calcination process at a temperature of 550°C converts NH_4^+ ions into H^+ ions through the release of ammonia gas (NH_3) to form H-zeolite (Lanzafame, 2018). In addition, in the calcination process there is the release of water vapor in the zeolite pores, evaporation of organic compounds, and the process of crystal formation.

3.2. Nickel and Chromium Metal-Impregnated Natural Zeolites.

The zeolite used for metal impregnation is one that has high crystallinity, which is acid-activated H-zeolite (H-ZAA). The measurement of nickel and chromium concentrations in metal impregnated zeolite was carried out by atomic absorption spectrophotometer method. The efficiency of metal impregnation was observed through the leaching process, by measuring the initial mass of metal impregnated in the zeolite and the mass of metal remaining in the zeolite after the leaching process. The percentage of impregnation efficiency at 60°C and 90°C was 79.31% and 79.97%, respectively. For chromium, the percentage of impregnation efficiency at 60°C and 90°C was both 79.97%. The impregnation efficiency is not affected by the temperature during the sol formation process.

H-zeolite (H-ZAA), nickel metal (Ni-zeolite) and chromium metal (Cr-zeolite) modified zeolites were characterized using FTIR. Si-O-T vibrations ($\text{T}=\text{Si}, \text{Al}$) appear at an absorption of 1079 cm^{-1} for H-zeolite (Figure 2) and can experience a shift in absorption if there is a change in electron density. The change in electron density is due to metal substitution in the zeolite. An increase in electron density will result in a shift in absorption to a higher wave number value. Metal oxide vibrations will be observed at absorptions of $500 - 900\text{ cm}^{-1}$ (Sajjadi et.al 2014). Ni-O vibrations were observed at wave number 632 cm^{-1} and Cr-O vibrations were observed at 576 cm^{-1} . In general, the zeolite functional groups are well visible in all zeolite samples

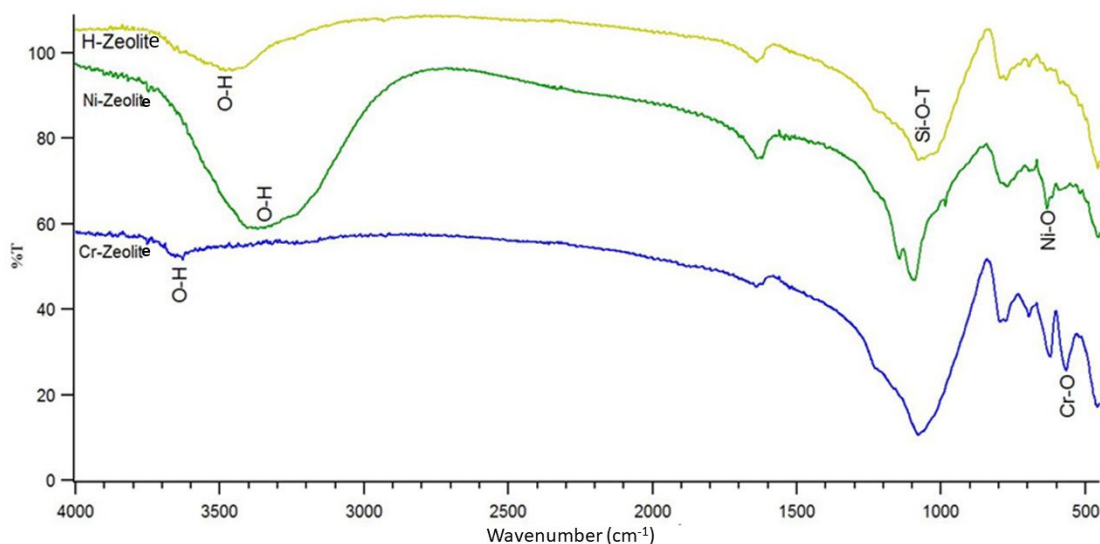


Figure 3 FTIR spectrum of H-zeolite, Ni-zeolite, and Cr-zeolite

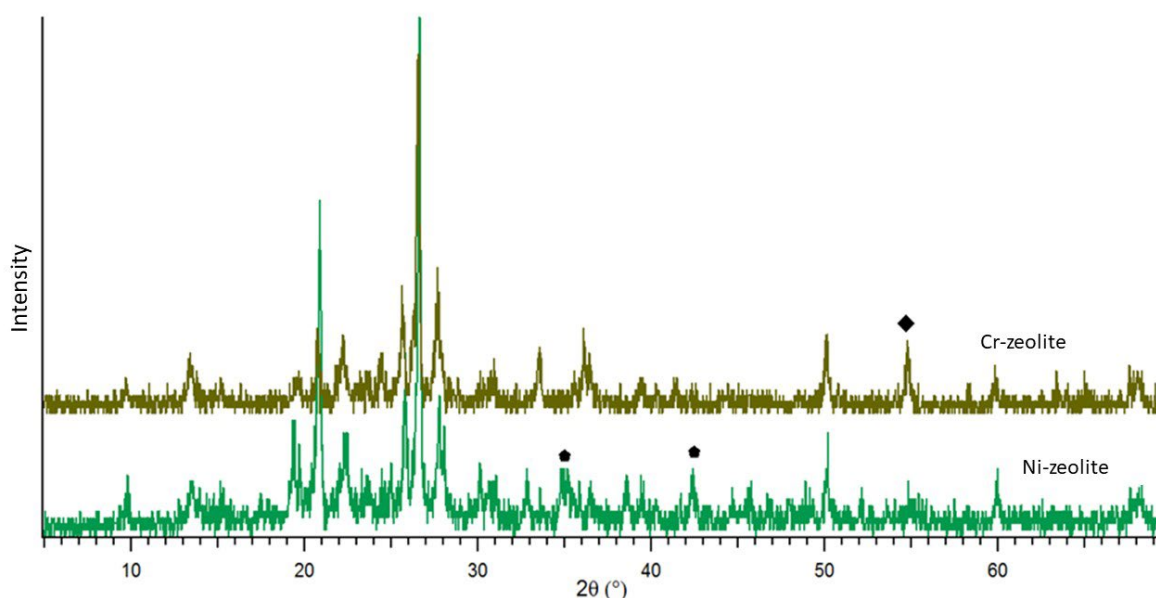


Figure 4 Diffractogram of Ni and Cr metals zeolites

The successful impregnation of Ni and Cr metals in zeolite was also indicated by the presence of NiO which appeared on 2θ 36° and 42° (JCPDS no. 04-0835), and Cr_2O_3 peak which appeared on 2θ 55° (JCPDS no. 38-1479) on the diffractogram from XRD analysis. The percentage of crystallinity of Ni-zeolite and Cr-zeolite are 64.24% and 65.88%, respectively, down slightly from the crystallinity of H-zeolite which is 67%. However, the diffraction pattern of all impregnated zeolite was still the same as that of H-zeolite indicating that the impregnation process did not change or damage the zeolite structure.

3.3. Modified Natural Zeolite Catalytic Activity on the Transformation of Glucose into HMF.

Based on the results of the HPLC analysis, the HMF compound appeared at a retention time of 7 minutes (Figure 5). It can be seen that all the catalysts used including H-zeolite can produce HMF compounds. The yield of HMF with H-zeolite catalyst of 24.8% produced using the hydrothermal method was greater than the results of Li et al. (2016) with an HMF yield of 14%. The salts of each metal were also tested as catalysts in the reaction, taking advantage of their Lewis acid properties. Ni salt shows better activity than Cr salt, this is because Ni is a better Lewis acid than Cr due to its higher electronegativity. The yield of HMF synthesized using all types of catalysts used is presented in Table 2.

Synthesis of HMF with nickel metal modified zeolite catalyst (Ni-zeolite60) produced a fairly high yield of HMF. This matter showed a positive correlation between Bronsted acid on the zeolite surface and Lewis acid from nickel metal which partially substitutes for H^+ in zeolite. However, in Ni-zeolite 90 percent the yield of HMF is smaller compared to the H-zeolite catalyst alone. This is thought to be caused by too much Ni metal which substitutes H^+ in zeolite so that the catalytic activity decreased which resulted in a decrease in the yield of HMF. Decrease in yield for HMF also occurs when metal salts are used as catalysts. However, the reduction in yield in the system with the modified zeolite catalyst was smaller when compared to the metal catalyst alone. This is caused by the H-zeolite thermally stable, so that even though it is modified with metal, the zeolite still maintains its thermal stability.

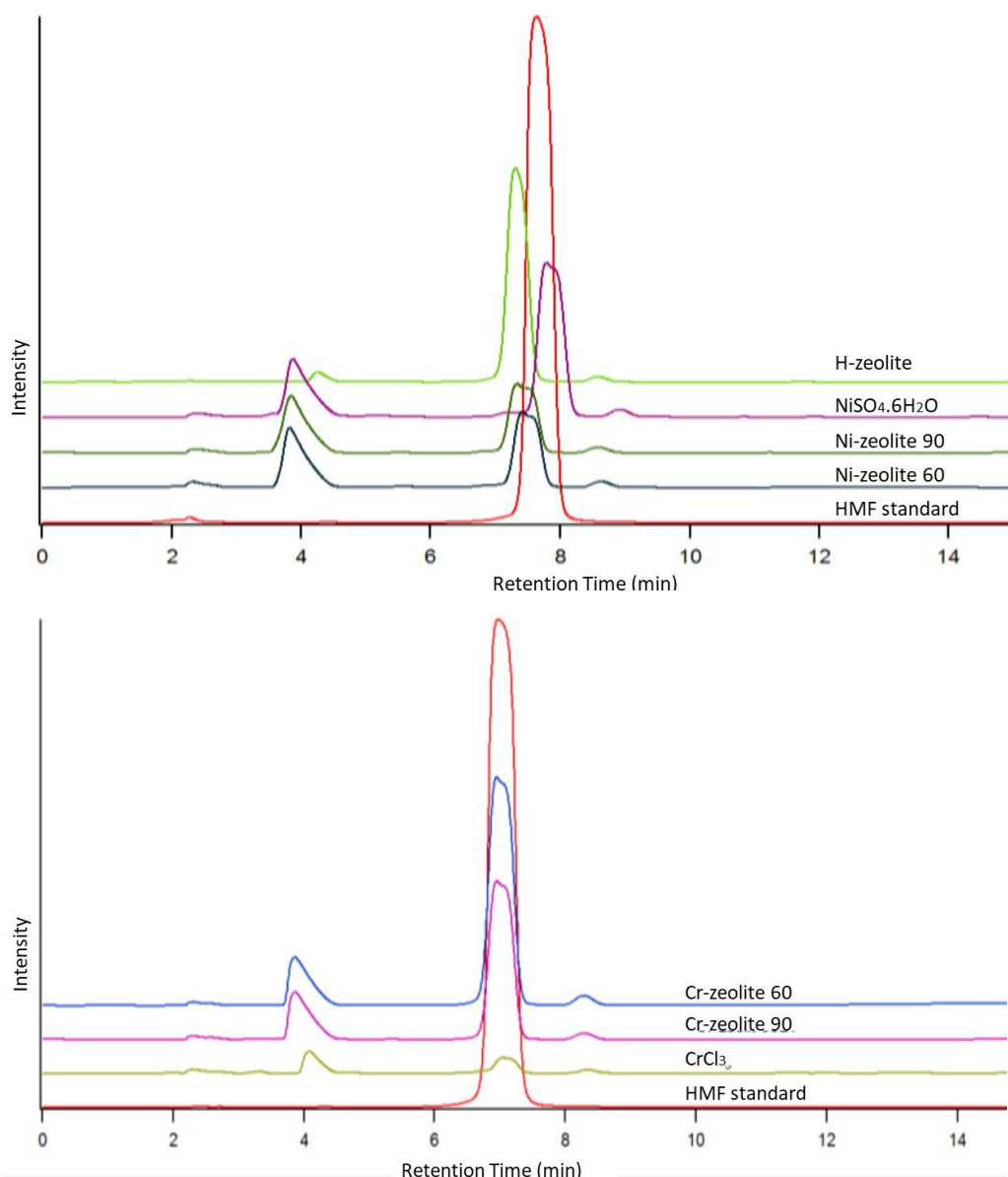


Figure 5 Chromatograms of HMF synthesized using various catalysts

Table 2 HMF yields synthesized by various type of catalysts

Catalyst	Yield (%)
H-zeolite	24.80
CrCl ₃ .6H ₂ O	1.67
Cr-zeolite 60	22.27
Cr-zeolite 90	21.69
NiSO ₄ .6H ₂ O	15.44
Ni-zeolite 60	38.68
Ni-zeolite 90	22.67

In this study, in addition to the HMF resulting from the transformation glucose, presumably humin is also produced. The formation of humin is influenced by substrate, reaction temperature, reaction time, and catalyst used. According to Siquera et al. (2013) synthesis of HMF at high temperatures and synthesis in aqueous solutions will produce by-products namely formic acid, levulinic acid, as well humin. The presence of humin was proven by the presence of brown precipitate in the autoclave after reaction. The use of metal chloride catalysts and temperatures exceeding 150 °C in HMF synthesis promotes the formation of humin. This is presumably due to the activation

energy to convert HMF to humin is lower than the activation energy fructose or glucose to form HMF. HMF activation energy becomes humin is 55 kJ/mol, while the activation energy of glucose to humin is 67 kJ/mol.

4. CONCLUSION

H-zeolite catalyst from Ende natural zeolite can transform glucose become HMF. Ende natural zeolite modified with nickel and chromium metals can be used as a catalyst for the transformation of glucose into HMF. Ni-zeolite 60 and Cr-zeolite 60 have a fairly good catalytic ability in comparison with the metal salt. Nickel-modified zeolite at 60 °C increase the catalytic ability of H-zeolite in transforming glucose become HMF.

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