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Zeolite and Its Potential as a Catalyst: A Study of Alternative Mineral Development in the Process of Converting Sugar Compounds into 5-Hydroxymethylfurfural

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Abstract

Synthesis of 5-hydroxymethylfurfural (HMF) from sugar compounds in the form of glucose using natural zeolite catalysts Ende-Nusa Tenggara Timur (NTT) through activation and modification of Cr metal impregnation processes has been carried out. This study aims to determine the potential of Ende natural zeolite as a catalyst in converting sugar compounds into HMF. The results showed that natural zeolite from Ende without activation, the process of activating acid-base compounds, and zeolite with the Cr metal embedding method had the potential as a catalyst for the transformation of sugar compounds into HMF. The resulting yield of glucose substrate was around 50.17%. Using a Cr-zeolite catalyst resulted in an HMF yield for glucose substrate of 26.78%. Overall, Ende natural zeolite can be used as a catalyst for synthesizing HMF without modification and with Cr metal impregnation.

1. Introduction

Utilization of natural mineral resources, which are abundant in Indonesia, is one of the opportunities for research innovation. Thus, besides making an important contribution to developing advanced materials research, these natural resources can also maximize their potential and usefulness [1]. One abundant natural resource is natural zeolite minerals. Data from the Geological Agency, Department of Energy and Mineral Resources shows that natural zeolite reserves in the Ende-East Nusa Tenggara (NTT) district are around 20 million tons. The large zeolite content in this area has not been utilized optimally [2].

Sugar compounds such as fructose and glucose are used in the compound 5-hydroxymethylfurfural (HMF) synthesis process. HMF acts as a platform compound for the production of various chemicals such as dimethylfuran (DMF), levulinic acid, 2,5-furandicaboxylic acid (FDA), 2,5-diformylfuran (DFF), 3,5-dihydroxymethylfuran, and other important molecules other. Compounds derived from HMF can be used as precursor molecules for producing raw chemical materials: furfural alcohol, plastics, medicines (such as antiviral hepatitis precursors), and liquid hydrocarbon fuels [3]. The structure of HMF is shown in Figure 1.

HMF can be produced through the dehydration of fructose, a process in which fructose loses three water molecules to form HMF. However, when starting from glucose, HMF production requires an additional isomerization step, which converts glucose into fructose before undergoing dehydration to yield HMF. Both isomerization and dehydration reactions occur in the presence of a catalyst [4]. The catalyst used in these reactions can either be in the same phase as the reactants, known as a homogeneous reaction, or in a different phase, referred to as a heterogeneous reaction. Various metal chloride catalysts, such as $CrCl_3$, $AlCl_3$, $CuCl_2$, and $MnCl_2$, are commonly used to facilitate the conversion of glucose into HMF [5]. Although homogeneous catalysts, such as metal chlorides, effectively promote the reaction, they have significant drawbacks, including their non-reusability and the challenges associated with separating them from the reaction mixture, making them less practical compared to heterogeneous catalysts [6].

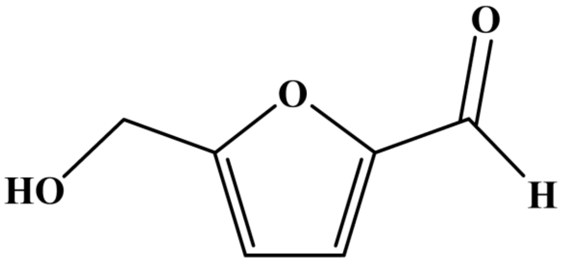

Figure 1. HMF structure

Heterogeneous catalysts that have potential in the HMF production process are natural zeolites. Zeolites have Lewis acid and Brønsted acid sites. Using heterogeneous catalysts such as zeolites can overcome the shortcomings of using homogeneous catalysts because zeolite catalysts are more easily separated from the product and can be reused in subsequent synthesis processes. The zeolite catalyst is used in research by Weigang *et al.* [7] and is a synthetic zeolite catalyst [8]. Synthetic zeolites have advantages, including high crystallinity, minimum amounts of metal oxides, and high catalytic activity. However, the weakness of synthetic zeolite is that it cannot withstand high temperatures, and making synthetic zeolite requires high costs. Therefore, this research used natural zeolite as a catalyst source. Apart from being abundant, natural zeolite also has good thermal stability. Natural zeolite in Indonesia, which is in high abundance but not optimal utilization, is Ende natural zeolite from East Nusa Tenggara.

One effort to increase the catalytic activity of natural zeolite is through the activation process, hydrothermal transformation, and modification of Ende natural zeolite [9]. This method is carried out by changing the ratio of Si and Al, then adding active sites by metal impregnation. The use of Cr metal in the form of $CrCl_3$ is known to be able to catalyze the synthesis of HMF. Therefore, impregnating Cr metal on Ende-NTT natural zeolite is very important. Apart from looking at the potential of natural zeolites as catalysts in the transformation reaction of sugar compounds into HMF, this research also aims to increase the added value and function of natural zeolites in Indonesia [10].

2. Experimental

2.1. Materials

The ingredients used in this research were standard HMF (Sigma Aldrich), fructose (Merck), glucose (Merck), NaOH (Merck), HCl (Merck), DMSO (Merck), NH_4Cl (Merck), $CrCl_3.6H_2O$ (Merck).

2.2. Tools

The tools used included glassware, porcelain cups, mortar, 100 mesh filter, Whatman 40 filter paper, magnetic stirrer, oven, furnace, and bath. The analytical tools used were advanced liquid chromatography (HPLC; Shimadzu LC-20AD), atomic absorption spectrophotometer (AAS; Shimadzu AA-7000), X-ray diffraction spectroscopy (XRD; PANalytical Empyrean), and scanning electron microscope (SEM; ZEISS EVO MA10).

2.3. Preparation, Activation, and Synthesis of Natural Na-zeolite

Ende natural zeolite (Z) was ground until it passed a 100-mesh sieve. Next, the zeolite was soaked in distilled water at room temperature for 24 hours, then filtered and dried at 100°C for 3 hours. Next, the zeolite was chemically activated using a 1.5 M HCl solution for acid activation. Then, the zeolite was dried at 110°C for 2 hours to obtain acid-activated zeolite (ZA). The zeolite sample was soaked in 3 M NaOH solution for 24 hours, and then the sample was washed with distilled water until the filtrate pH was neutral. After that, it was dried in an oven at 110°C for 3 hours, and the result was called Na-ZA.

2.4. Synthesis of H-zeolite Catalyst from Na-zeolite

H-zeolite was synthesized by adding 500 mL of 1 M NH_4Cl to Na-ZA and leaving it for 36 hours at 100°C. The H-ZA product was filtered, washed until the pH was neutral, and dried in an oven at 110°C for 3 hours. Next, the product was calcined at 500°C for 5 hours and characterized using XRD.

2.5. Glucose Conversion Process into HMF with Zeolite Catalyst

The transformation process of fructose and glucose into HMF was carried out using the reflux method in an oil bath supplied with N_2 gas. A total of 0.01 g of ZA catalyst was added to 15 mL of DMSO. Then 0.15 g of substrate (fructose/glucose) was added to the mixture and stirred using a magnetic stirrer at a speed of 600 rpm at a temperature of 120°C for 2 hours for fructose and 6 hours for glucose. The product was characterized using HPLC at a wavelength of 284 nm, with a mobile phase of water:methanol in a fixed composition of 95:5, a flow rate of 1 mL/minute, and an injection volume of 20 µL. This research was conducted repeatedly by replacing the zeolite catalysts sequentially with ZB, Na-ZA, Na-ZB, H-ZA, and H-ZB. All conversion results were compared against the HMF standard. The H-zeolite catalyst, which demonstrated the best catalytic activity, was further modified through Cr metal impregnation.

2.6. Cr Metal Impregnation Process on H-zeolite

A total of 5 g of H-zeolite was added to 125 mL of distilled water, and 3.3 gr of $CrCl_3{\cdot}6H_2O$ mixed while stirring for 24 hours. Then, the sample was filtered and washed with distilled water, and the precipitate was dried in an oven at 110°C for 24 hours. The impregnated catalyst was calcined by placing it in a furnace for 3 hours at a temperature of 500°C. Next, the Cr-zeolite catalyst was characterized using SEM and XRD. Impregnation efficiency was evaluated using the AAS analysis. Next, the Cr-zeolite catalyst obtained was applied to transform fructose and glucose into HMF using the same method as previously using a zeolite catalyst.

2.7. Glucose Conversion Process into HMF Using Cr-Metal-Modified Zeolite Catalyst

The glucose transformation process used a reflux method, filling an oil bath with N_2 gas. A total of 0.01 g of Cr-zeolite catalyst was added to 15 mL of DMSO. Then, 0.15 g of glucose substrate was added to the mixture and stirred using a magnetic stirrer at a speed of 600 rpm at a temperature of 120°C for 2 hours for fructose and 6 hours for glucose. The product was characterized using HPLC at a wavelength of 284 nm, with a mobile phase of water: methanol in a fixed composition of 95:5, a flow rate of 1 mL/minute, and an injection volume of 20 µL.

3. Results and Discussion

3.1. Preparation and Activation of Zeolite

The initial preparation involves grinding the zeolite into a fine powder that can pass through a 100-mesh sieve. Changing the size of natural zeolite aims to homogenize the size and enlarge the contact surface to maximize the adsorption capacity [11]. In general, large quantities of water vapor and metal oxides reduce the catalytic and ion exchange capabilities of natural zeolites. Therefore, to enhance the quality of natural zeolite, a preparation and activation process is necessary [12].

The results of the XRD analysis performed on Ende natural zeolite before the activation and transformation process revealed that the natural zeolite is a mixture of mordenite and clinoptilolite, as indicated by the characteristic peaks at an angle of 2θ according to the JCPDS (Joint Committee on Powder Diffraction Standards) database. The peak intensities for mordenite-type zeolite appear at angles 2θ = 19.63°, 22.25°, 25.87°, and 27.67°, whereas for clinoptilolite-type zeolite, the peaks are observed at angles 2θ = 9.87°, 13.46°, 21.36°, and 23.49°. The XRD diffractogram of the natural zeolite is presented in Figure 2.

Mordenite zeolite has the potential to be used as a catalyst because it can act as an acid through an activation process (acid and base) and calcination at high temperatures [13]. The XRD analysis diffractogram after the activation process is shown in Figure 3. Zeolite activation is conducted chemically by adding 1.5 M HCl and 1.5 M NaOH. This process aims to dissolve the metal oxides on the zeolite surface, thereby increasing its surface area [14]. The activation treatment does not significantly alter the 2θ angle, as the natural zeolite structure remains relatively stable. This structural stability is attributed to the high content of metal oxides, which contribute to the zeolite's resistance [15]. The stable structure ensures the zeolite retains its functional properties for catalytic and adsorption applications.

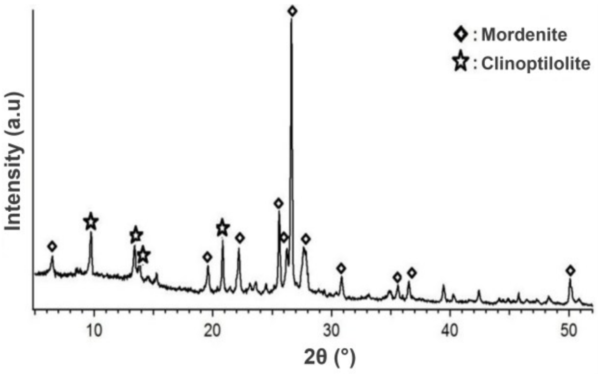

Figure 2. Diffractogram of natural zeolite before activation

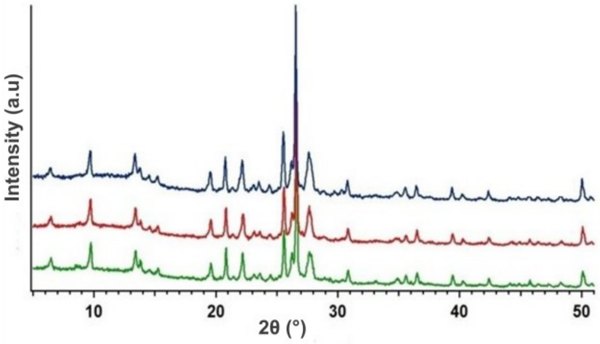

Figure 3. Diffractogram of natural zeolite: (a) untreated, (b) acid-activated, and (c) base-activated

3.2. H-zeolite Catalyst from Na-zeolite

The dehydration process of 3 water molecules from fructose to become HMF requires a Brønsted acid catalyst [16]. Therefore, modifying the activated zeolite into the H-zeolite form is necessary. The H-zeolite formation process cannot be carried out directly from the activated zeolite form due to the instability of the interaction of H^+ ions with O in the zeolite framework. This means the formation process occurs through ion exchange between Na^+ ions in Na-zeolite and ammonium ions (NH_4^+) in the acid salt solution (NH_4Cl). Following the ion exchange, the heating and calcination process removes NH_3 gas, while water remains in the zeolite pores, leaving only H^+ ions. These H^+ ions interact with the oxygen atoms in the zeolite to form an H-zeolite catalyst [17].

Figure 4 presents Na-ZAA, Na-ZAB, H-ZAA, and H-ZAB diffractograms. This figure indicates that the activation and calcination processes for ZAA and ZAB do not significantly alter the 2θ angles. The observed changes were limited to variations in intensity, which are believed to affect the degree of zeolite crystallinity. Consequently, in addition to possessing a stable structure, Ende natural zeolite demonstrates good thermal resistance.

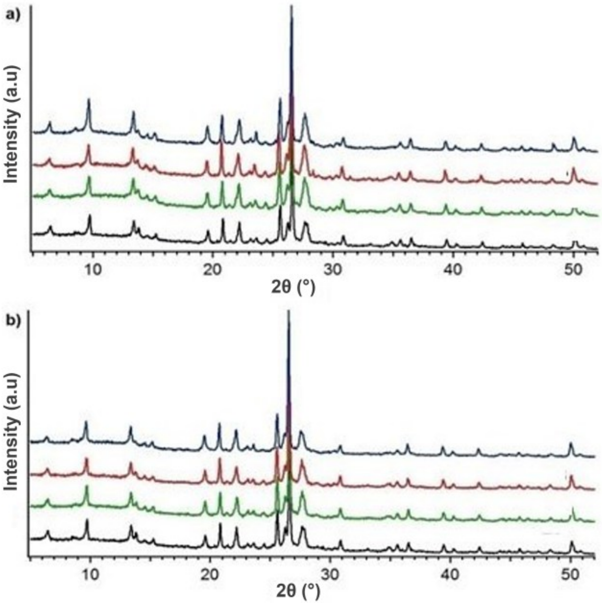

Figure 4. Diffractograms of (a) ZA, ZAA, Na-ZAA, and H- ZAA, and (b) ZA, ZAB, Na-ZAB, and H-ZAB

Table 1. Crystallinity of Ende natural zeolite with acid activation

Sample	Degree of crystallinity (%)
ZA	57.37
ZAA	52.04
Na-ZAA	60.19
H-ZAA	58.64

Table 2. Crystallinity of Ende natural zeolite with base activation

Sample	Degree of crystallinity (%)
ZA	57.37
ZAB	59.19
Na-ZAB	59.01
H-ZAB	58.65

Table 1 shows that Na-ZAA has the highest degree of crystallinity at 62.91%. This crystalline nature is expected in a catalyst. The acid activation process on natural zeolite (ZAA) reduced the degree of zeolite crystallinity from 59.73% to 54.40%, while the alkaline activation process (ZAB) did the opposite, increasing the zeolite crystallinity to 61.29% (Table 2). This is because, during acid activation, dealumination occurs in the zeolite sample, which results in the collapse of some of the Al-O bonds in the zeolite, whereas during base activation, the zeolite structure rearranges, and the formation of mesopores occurs [18].

The treatment of adding NaOH to ZAA increased the crystallinity of Na-ZAA quite high, from 54.40% to 62.91% (Table 1), while in ZAB, the increase in Na-ZAB crystallinity was not significant from 61.29% to 61.52% (Table 2). This is because when NaOH is added, a distribution process of Na^+ ions occurs, where these Na^+ ions play a role in forming silicate compounds, which can increase the crystalline properties of the zeolite [19]. However, the distribution of Na^+ ions in ZAB is thought to be less than in ZAA. After adding the acid salt NH_4Cl to Na-ZAA and Na-ZAB and then carrying out the calcination process at a temperature of 550°C, the two zeolite products H-ZAA and H-ZAB showed a decrease in the degree of crystallinity of H-ZAA to 61.46% (Table 1) and H-ZAB to 60.05% (Table 2). This is because the exchange of Na^+ ions with NH_4^+ ions causes the levels of Na^+ ions, which play a role in forming silicate compounds, to decrease.

3.3. Synthesis of HMF from Sugar Materials Using Zeolite Catalysts

The transformation of glucose into HMF compounds is conducted via the reflux method. This conversion initiates with an isomerization process whereby glucose is first transformed into fructose, followed by a dehydration reaction resulting in the formation of HMF by eliminating three molecules of water (Figure 5) [20].

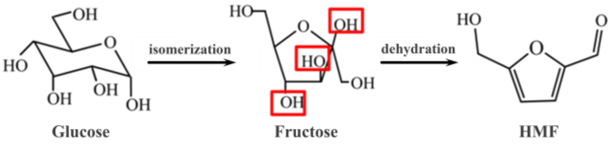

Figure 5. Transformation of glucose into HMF

Qualitative analysis of HMF was conducted by comparing the retention time of the synthesized HMF with that of a standard sample. Quantitative analysis was performed by calculating the yield based on comparing peak areas between the synthesized and standard HMF samples. This transformation was effectively executed, as indicated by the chromatogram peak observed at a retention time of 7.6 minutes, closely matching the standard sample. This observation confirms the successful conversion of glucose into a compound structurally similar to HMF, verifying its identity as HMF. In research by Wustoni *et al.* [21], the retention times for fructose and glucose alone were 5.8 and 6.8 minutes, respectively. At this stage, the $CrCl_3$ catalyst is used as a comparison. Based on research by Xue et al. [22], the $CrCl_3$ catalyst has the best catalytic ability for the glucose transformation process into HMF.

Natural zeolite catalysts exhibit limited activity due to the absence of Brønsted acid sites necessary to facilitate the dehydration process. Consequently, modifying Ende natural zeolite holds promise for enhancing HMF production, as this modification introduces Brønsted acid sites through the conversion to H-zeolite form, along with Lewis acid sites associated with silicon and aluminum atoms within the zeolite framework.

Transforming glucose into HMF requires a bifunctional catalyst to assist the isomerization and dehydration processes. The yield of HMF synthesized from various catalysts is shown in Table 3. The $CrCl_3$ catalyst has the best ability for glucose conversion with a yield of 50.17%, while using a zeolite catalyst gives an HMF yield of 26.78 with glucose as the starting material. This is because the $CrCl_3$ catalyst has bifunctional catalyst properties, which can help the isomerization and dehydration processes. The Lewis acid site (Cr^{3+}) can help the process of isomerization of glucose into fructose; this catalyst has a halide nucleophile site (Cl^-), which plays a role in helping the dehydration process of fructose into HMF [23]. The Lewis acid site (Cr^{3+}) in $CrCl_3$ has high acidity because it has empty d orbitals. Lewis acids can facilitate the ring opening of glucose, forming a complex with acyclic glucose at its hydroxyl group (C1 and C2). The presence of empty d orbitals in Lewis acids makes electron transfer from O1 to O2 and proton transfer from C2 to C1 easier [23].

Zeolite catalysts also have bifunctional properties, which can help the isomerization and dehydration processes convert them into H-zeolite form. H^+ protons act as Brønsted-Lowry acids, which can help the dehydration process, while Si and Al atoms act as Lewis acid sites, which help the isomerization process. The isomerization process can be influenced by the Lewis acidity level of the catalyst used. Although zeolites also have Lewis sites, the acidity of the Si and Al Lewis sites on zeolites is much lower than that of Cr on the $CrCl_3$ catalyst [10]. This causes a small yield of synthetic HMF for the starting material glucose.

3.4. Cr-zeolite Catalyst

Impregnation is the process of introducing a metal into the zeolite micropores through an adsorption process [24]. The Cr metal impregnation process was carried out on H-zeolite. The catalytic ability of HZAA for glucose transformation is better than that of the H-ZAB catalyst. Therefore, the Cr metal impregnation process was carried out on the H-ZAA catalyst. The impregnation method used is ion exchange.

Percent impregnation efficiency was evaluated by the amount of metal embedded in the zeolite using AAS observations. The efficiency of Cr impregnation on zeolite using the ion exchange method is 33.52%. Metal impregnation into zeolite can be analyzed using XRD diffractograms. In the Cr-zeolite diffractogram, the peak observed at a 2θ angle of 28.06° corresponds to the characteristic peak of Cr_2O_3, as referenced in JCPDS No. 38-1479. This confirms the substitution of Cr^{3+} ions into the H-ZAA framework. During this process, Cr^{3+} ions migrate from the framework and occupy the cavities and surface of H-ZAA, resulting in the appearance of a new peak in the diffractogram, identified as the characteristic peak of Cr_2O_3. The transformation of the metal chloride $CrCl_3 \cdot 6H_2O$ into the oxide form Cr_2O_3 occurs due to the calcination process at high temperatures.

The surface morphology of H-ZAA and Cr-zeolite was observed using a SEM. The results of SEM characterization with a magnification of 20,000× (Figure 6) show that the morphology of the H-ZAA and Cr-zeolite catalysts consists of layered crystalline lamellar particles, and there are more cavities between the lamellas. H-ZAA has a more regular particle structure, whereas the Cr- zeolite catalyst shows that the particle structure is less regular, forming many agglomerations. The irregularity of the particles in Cr-zeolite is thought to be caused by the formation of Cr_2O_3 metal oxides from the previous impregnation process. Apart from looking at the morphology of the catalyst, SEM analysis can also determine the average particle size of each catalyst. The particle sizes of the H-ZAA, Cr-zeolite, and Fe-zeolite catalysts are 231.95 nm, 242.60 nm, and 264.57 nm, respectively.

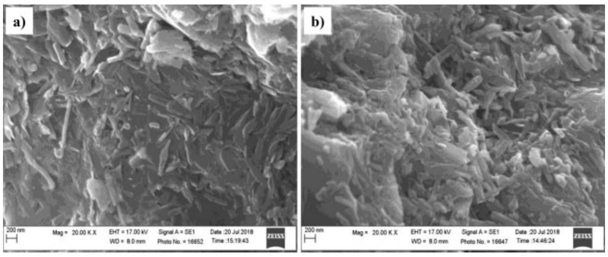

Figure 6. Catalyst surface morphologies of a) H-ZAA and b) Cr-zeolite

Table 3. Yield of HMF using several catalysts

Catalyst	% Yield of glucose starting material
Ende natural zeolite	7.54
H-zeolite	13.14
$CrCl_3.6H_2O$	50.17
Cr-zeolite	26.78

3.5. HMF Products from Glucose Using Catalysts

The modified Cr-zeolite catalyst was subsequently utilized to catalyze the conversion of glucose into HMF. Similar to earlier stages, qualitative analysis of HMF involved comparing the retention time of synthesized HMF with that of a standard sample, while quantitative analysis entailed calculating the yield based on peak area comparisons between the synthesized and standard HMF samples. The retention time of the synthesized HMF (7.7-7.8 minutes), which closely matches the standard HMF (7.8 minutes), suggests that the chromatogram peak observed in the synthesized sample corresponds to an HMF compound.

The yield of HMF synthesized from various catalysts is shown in Table 3. Table 3 shows that the Cr-zeolite catalyst can provide a synergistic effect for the glucose starting material because it can increase the yield of HMF compared to using only the H-ZAA catalyst. According to Shimizu *et al.* [25], the decrease in HMF yield from glucose using the CrOx-zeolite catalyst was caused by the side reactions that occurred. This reaction can be a humin formation reaction. Humin formation can be indicated by a change in product color from brown to black. This can be seen from the synthesis product catalyzed by Cr-zeolite using glucose as the starting material. The synthesized product is blackish-brown, indicating the formation of humin. This fact is also supported by Silaghi *et al.* [26]; the activation energy for the transformation of glucose into humin is much lower (71 ± 19 $kJ.mol^{-1}$) compared to fructose (114 ± 6 $kJ.mol^{-1}$).

4. Conclusion

Ende natural zeolite is a mixture of mordenite and clinoptilolite, with the dominant peak belonging to mordenite based on comparison with JCPDS. Ende zeolite without and with metal modification can act as a catalyst in synthesizing sugar compounds into HMF. Modifying Ende natural zeolite with Cr metal impregnation has a synergistic effect as a catalyst from the increased yield of HMF produced.

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References

[1] Yantus A. B. Neolaka, Ganden Supriyanto, Heri Septya Kusuma, Adsorption performance of Cr(VI)-imprinted poly(4-VP-co-MMA) supported on activated Indonesia (Ende-Flores) natural zeolite structure for Cr(VI) removal from aqueous solution, *Journal of Environmental Chemical Engineering*, 6, 2, (2018), 3436-3443 https://doi.org/10.1016/j.jece.2018.04.053

[2] Nuryono Nuryono, Ali Agus, Sri Wedhastri, Y. M. S. Maryudhani, Deni Pranowo, Yunianto Yunianto, Ebrahim Razzazi-Fazeli, Adsorption of Aflatoxin B1 in Corn on Natural Zeolite and Bentonite, *Indonesian Journal of Chemistry*, 12, 3, (2012), 279-286

[3] Aziz Rahman Aylak, Solmaz Akmaz, Serkan Naci Koc, Glucose conversion to 5-hydroxymethylfurfural with chromium exchanged bentonite and montmorillonite catalysts in different solvents, *Chemical Engineering Communications*, 207, 8, (2020), 1103-1113 https://doi.org/10.1080/00986445.2019.1641489

[4] Mela Faradika, Sri Sugiarti, Purwantiningsih Sugita, Potensi Zeolit Alam Ende-NTT sebagai Katalis Transformasi Senyawa Gula Menjadi 5-Hidroksimetilfurfural (HMF), *Jurnal Kimia Valensi*, 5, 1, (2019), 15-22

[5] Hu Li, Song Yang, Anders Riisager, Ashok Pandey, Rajender S. Sangwan, Shunmugavel Saravanamurugan, Rafael Luque, Zeolite and zeotype-catalysed transformations of biofuranic compounds, *Green Chemistry*, 18, 21, (2016), 5701-5735 https://doi.org/10.1039/C6GC02415G

[6] Remi Ayu Pratika, Karna Wijaya, Wega Trisunaryanti, Hydrothermal treatment of SO_4/TiO_2 and TiO_2/CaO as heterogeneous catalysts for the conversion of Jatropha oil into biodiesel, *Journal of Environmental Chemical Engineering*, 9, 6, (2021), 106547 https://doi.org/10.1016/j.jece.2021.106547

[7] Fan Weigang, Verrier Charlie, Queneau Yves, Popowycz Florence, 5-Hydroxymethylfurfural (HMF) in Organic Synthesis: A Review of its Recent Applications Towards Fine Chemicals, *Current Organic Synthesis*, 16, 4, (2019), 583-614 http://dx.doi.org/10.2174/1570179416666190412164738

[8] Zehui Zhang, Kejian Deng, Recent Advances in the Catalytic Synthesis of 2,5-Furandicarboxylic Acid and Its Derivatives, *ACS Catalysis*, 5, 11, (2015), 6529-6544 https://doi.org/10.1021/acscatal.5b01491

[9] M. Sakti La Ore, Karna Wijaya, Wega Trisunaryanti, Wahyu Dita Saputri, Eddy Heraldy, Nasih Widya Yuwana, Poedji Loekitowati Hariani, Arief Budiman, Sri Sudiono, The synthesis of SO_4/ZrO_2 and Zr/CaO catalysts via hydrothermal treatment and their application for conversion of low-grade coconut oil into biodiesel, *Journal of Environmental Chemical Engineering*, 8, 5, (2020), 104205 https://doi.org/10.1016/j.jece.2020.104205

[10] Yunxiang Qiao, Nils Theyssen, Zhenshan Hou, Acid-catalyzed dehydration of fructose to 5-(hydroxymethyl) furfural, *Recyclable Catalysis*, 2, 1, (2015), 36-60 http://dx.doi.org/10.1515/recat-2015-0006

[11] Wenze Guo, Zheng Zhang, Jasper Hacking, Hero Jan Heeres, Jun Yue, Selective fructose dehydration to 5-hydroxymethylfurfural from a fructose-glucose mixture over a sulfuric acid catalyst in a biphasic system: Experimental study and kinetic modelling, *Chemical Engineering Journal*, 409, (2021), 128182 https://doi.org/10.1016/j.cej.2020.128182

[12] Maria Luisa Testa, Gianmarco Miroddi, Marco Russo, Valeria La Parola, Giuseppe Marcì, Dehydration of Fructose to 5-HMF over Acidic TiO_2 Catalysts, *Materials*, 13, 5, (2020), 1178 https://doi.org/10.3390/ma13051178

[13] Dwi Kurniawati, Jumaeri Jumaeri, Silvester Tursiloadi, Osi Arutanti, Muhammad Safaat, Modification of Indonesian Natural Zeolite (Clipnotillite-Mordenite) for Synthesis of Solketal, *Iranian Journal of Catalysis*, 11, 3, (2024),

[14] Irvan Irvan, Bambang Trisakti, Seri Maulina, Rivaldi Sidabutar, Iriany Iriany, Mohd Sobri Takriff, Adsorption-desorption system for CO_2 removal in biogas using natural zeolite-based adsorbent, *Journal of Engineering Science and Technology*, 13, 10, (2018), 3058-3070

[15] Yateman Arryanto, *Zeolit dan Masa Depan Bangsa: Roadmap Revitalisasi Peranan Zeolit Alam dalam Ketahanan Pangan dan Kedaulatan Bangsa*, Imperium, Yogyakarta, 2012,

[16] Junifa Layla Sihombing, Ahmad Nasir Pulungan, Poppy Lindawati, Adittiya Prayoga, Intan Ayu Safitri, Clara Nur Wandani, Lastri Anita Silitonga, Ambarwati Ambarwati, Puji Prayugo, Ary Anggara Wibowo, Optimization of Indonesia biodiesel production from rubber seed oil using natural zeolite modification, *Jurnal Pendidikan Kimia*, 10, 2, (2018), 387-392 https://doi.org/10.24114/jpkim.v10i2.10919

[17] Changquan Zhang, Suqin Li, Utilization of iron ore tailing for the synthesis of zeolite A by hydrothermal method, *Journal of Material Cycles and Waste Management*, 20, 3, (2018), 1605-1614 https://doi.org/10.1007/s10163-018-0724-7

[18] O. B. Kotova, I. N. Shabalin, D. A. Shushkov, L. S. Kocheva, Hydrothermal synthesis of zeolites from coal fly ash, *Advances in Applied Ceramics: Structural, Functional and Bioceramics*, 115, 3, (2016), 152-157 https://doi.org/10.1179/1743676115y.0000000063

[19] Shuangqing Su, Hongwen Ma, Xiuyun Chuan, Hydrothermal synthesis of zeolite A from K-feldspar and its crystallization mechanism, *Advanced Powder Technology*, 27, 1, (2016), 139-144 https://doi.org/10.1016/j.apt.2015.11.011

[20] Terence E. Warner, Mads Galsgaard Klokker, Ulla Gro Nielsen, Synthesis and Characterization of Zeolite Na–Y and Its Conversion to the Solid Acid Zeolite H–Y, *Journal of Chemical Education*, 94, 6, (2017), 781-785 https://doi.org/10.1021/acs.jchemed.6b00718

[21] Shofarul Wustoni, Rino R. Mukti, Agus Wahyudi, Ismunandar, Sintesis Zeolit Mordenit dengan Bantuan Benih Mineral Alam Indonesia, *Jurnal Matematika & Sains*, 16, 3, (2011), 158-160

[22] Zhimin Xue, Ming-Guo Ma, Zhonghao Li, Tiancheng Mu, Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts, *RSC Advances*, 6, 101, (2016), 98874-98892 https://doi.org/10.1039/C6RA20547J

[23] Xinli Tong, Yang Ma, Yongdan Li, Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes, *Applied Catalysis A: General*, 385, 1, (2010), 1-13 https://doi.org/10.1016/j.apcata.2010.06.049

[24] Daniel E. Resasco, Surapas Sitthisa, Jimmy Faria, Teerawit Prasomsri, M. Pilar Ruiz, Furfurals as chemical platform for biofuels production, in: *Solid Waste as a Renewable Resource*, Apple Academic Press, New York, 2015, https://doi.org/10.1201/b18712

[25] Ken-ichi Shimizu, Rie Uozumi, Atsushi Satsuma, Enhanced production of hydroxymethylfurfural from fructose with solid acid catalysts by simple water removal methods, *Catalysis Communications*, 10, 14, (2009), 1849-1853 https://doi.org/10.1016/j.catcom.2009.06.012

[26] Marius-Christian Silaghi, Céline Chizallet, Joachim Sauer, Pascal Raybaud, Dealumination mechanisms of zeolites and extra-framework aluminum confinement, *Journal of Catalysis*, 339, (2016), 242-255 https://doi.org/10.1016/j.jcat.2016.04.021