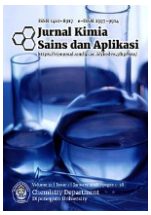
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Hydrothermal Conversion of Glycerol over Cu-Modified Acid-Activated Natural Zeolite: Effect of Cu Loading and Reaction Time on Catalytic Performance

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Abstract

The conversion of glycerol into value-added chemicals represents an attractive approach for improving the economic sustainability of biodiesel production. In this study, Cu-modified acid-activated natural zeolite (Cu-ANZ) catalysts were prepared and evaluated for hydrothermal glycerol conversion, with particular attention to the formation of a product tentatively assigned to lactic acid based on its HPLC retention time relative to that of a lactic acid standard. Natural zeolite was activated using hydrochloric acid and subsequently modified by Cu impregnation at loadings of 2.5–15 wt%. The catalysts were characterized using FTIR, XRD, SEM-EDX, and BET analyses, while the reaction products were analyzed by HPLC after hydrothermal conversion of glycerol at 230°C in the presence of NaOH. FTIR and XRD analyses indicated that the modification treatments altered the physicochemical properties of the natural zeolite while preserving its fundamental structural features and crystallinity. SEM-EDX analysis confirmed the presence of Cu in the modified catalyst and showed a higher Si/Al ratio for Cu-ANZ than for the untreated natural zeolite. BET analysis showed that the surface area increased from 27.010 to 32.826 $m^2\ g^{-1}$ after the overall modification process. The relative HPLC peak area (RHPA) increased with Cu loading up to 10 wt%, reaching its maximum, then decreased at higher Cu loadings. Investigation of reaction time showed an increase in the RHPA with longer reaction durations, with a pronounced increase observed between 100 and 180 min and the highest value observed at 300 min. These findings indicate that Cu loading and reaction time influence the relative HPLC response associated with the product tentatively assigned to lactic acid during hydrothermal glycerol conversion and provide insights into the potential application of Cu-modified acid-activated natural zeolite in this reaction.

1. Introduction

The increasing production and utilization of biodiesel have spurred the development of renewable energy as an alternative to fossil fuels [1, 2, 3]. However, large-scale biodiesel production via the transesterification process also generates significant amounts of crude glycerol as a byproduct [4, 5, 6]. It is estimated that glycerol accounts for 10% of biodiesel production [1, 7, 8, 9]. In Indonesia, the implementation of a large-scale biodiesel program has led to a continuous increase in glycerol production [3, 9, 10]. The oversupply of glycerol reduces its market value and creates challenges for its utilization and disposal [5, 6, 11]. In many cases, crude glycerol is treated as a low-value byproduct despite its potential as a renewable carbon feedstock for producing value-added chemicals [5, 6].

Conversion of glycerol into various chemicals is an important strategy to improve the economic sustainability of biodiesel production [6, 7, 11]. Among the possible products, lactic acid has attracted

considerable attention because of its applications in the food, pharmaceutical, cosmetic, and chemical industries [1, 7, 8, 12]. In addition, lactic acid is the main precursor for the manufacturing of polylactic acid, a biodegradable polymer whose demand continues to increase worldwide [1, 2, 8, 12]. Currently, microbial fermentation of feedstocks based on carbohydrates is the primary method of producing lactic acid [1, 8, 13]. Although commercial production of lactic acid through microbial fermentation or biochemical pathways has long been practiced, these processes have several drawbacks, including the need for relatively expensive enzymes, complex purification steps, and lengthy reaction times [7, 8, 12, 14]. The dependence of this process on sugar- and starch-based feedstocks may create competition with food resources, ultimately leading to higher production costs and difficulties in developing production [1, 8, 13]. On the other hand, the lactic acid synthesis pathway using a catalytic reaction with glycerol, a readily available and affordable waste material, has various advantages, including shorter reaction times, easier product recovery, and the use of an inexpensive byproduct stream [7, 8, 12, 15].

Under alkaline hydrothermal conditions, glycerol can be catalytically converted to lactic acid in several successive steps [1, 2, 11]. An intermediate compound is formed at the start of this reaction, followed by pyruvaldehyde, which eventually undergoes a Cannizzaro-type rearrangement to become lactate [2, 11, 12]. The efficiency of this process is greatly affected by the existence of active base sites that facilitate the formation and conversion of the intermediates [2, 12, 16]. Even though homogeneous bases like NaOH and KOH can provide substantial catalytic activity, their use is often associated with problems of catalyst recovery and corrosion [12, 17, 18]. Heterogeneous catalysts are receiving growing interest because they offer easier separation and potential reuse while maintaining catalytic efficacy under hydrothermal conditions [5, 12, 18].

Copper (Cu)-based catalysts have been widely investigated as a cost-effective alternative to noble metals such as Pt, Pd, and Au for glycerol conversion reactions [1, 2, 7, 15]. Compared with many transition metals, Cu catalysts generally exhibit high selectivity for oxygenated products because they tend to maintain the three-carbon structure of glycerol while minimizing undesirable C–C bond-cleavage reactions [1, 14, 16]. The catalytic performance of Cu is often attributed to the presence of various oxidation states and their interaction with the catalyst support, which together influence the formation and conversion of reaction intermediates [14, 16, 19]. Consequently, various Cu-based catalytic systems have been investigated for the production of lactic acid and other chemicals from glycerol [2, 7, 16].

Natural zeolites are commonly used as catalytic supports because of their low cost, abundance, and hydrothermal stability [20, 21]. Acid activation is commonly employed to modify the physicochemical properties of natural zeolites by removing impurities and altering their aluminosilicate structure [10, 22]. Such treatment may also change the Si/Al ratio, thereby affecting the acidity and surface characteristics of the material [10, 23]. Furthermore, the properties of the modified zeolite may influence the dispersion of Cu species during catalyst preparation [24]. Under hydrothermal conditions, the combined properties of Cu species and the zeolite support may therefore influence glycerol conversion and product distribution [25, 26].

Several studies have reported the use of Cu-supported catalysts for the conversion of glycerol under alkaline conditions [2, 16, 27]. Acid-activated natural zeolites have also been considered attractive catalyst supports because of their low cost, availability, and stability under hydrothermal conditions [10, 21]. However, information on the influence of Cu loading on the physicochemical properties of Cu-modified acid-activated natural zeolite and its behavior during hydrothermal glycerol conversion remains limited [26]. Previous studies have reported Cu supported on various materials [2, 16], whereas the use of acid-activated natural zeolite as a support provides an alternative using a low-cost, naturally abundant material. In addition, excessive metal loading may lead to particle agglomeration and partial pore blockage, which can affect the properties and behavior of the catalyst [16, 28].

The hydrothermal conversion of glycerol has been investigated at a reaction temperature of 230°C under alkaline conditions in several studies [1, 2, 16]. Accordingly, 230°C was selected as the fixed reaction temperature in the present study to evaluate the effects of Cu loading and reaction time under consistent hydrothermal conditions. Therefore, this study investigates the physicochemical characteristics of Cu-modified acid-activated natural zeolite and examines the influence of Cu loading and reaction time on the relative HPLC peak area of a product tentatively assigned to lactic acid during hydrothermal glycerol conversion. The contribution of this study is to provide experimental information on the relationship between Cu loading, catalyst physicochemical characteristics, and the observed reaction-product response under the investigated hydrothermal conditions.

2. Experimental

2.1. Materials

Glycerol, sodium hydroxide (NaOH), hydrochloric acid (HCl), copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), nitrogen gas (N_2), silver nitrate ($AgNO_3$), and distilled water were used in this study. Natural zeolite was employed as the catalyst support material. Before use, natural zeolite was crushed and sieved to produce a 100-mesh powder. Every chemical was utilized without additional purification.

2.2. Preparation of Cu-Modified Acid-Activated Natural Zeolite Catalyst

The 100-mesh natural zeolite powder was activated by the acidification method. The acid activation process was conducted by immersing the zeolite in 1 M HCl solution under continuous stirring for 2 h. The activated zeolite was filtered and washed repeatedly with distilled

water until no chloride ions were detected in the filtrate, as confirmed by the absence of a white precipitate upon addition of $AgNO_3$ solution. The resulting material was then dried in a furnace at 200°C for 3 h to obtain acid-activated natural zeolite.

Cu-modified acid-activated natural zeolite catalysts were prepared by impregnation. Acid-activated natural zeolite was mixed with $Cu(NO_3)_2{\cdot}3H_2O$ solution at various Cu loadings of 2.5, 5, 7.5, 10, 12.5, and 15% (wt%). The mixture was heated at 100°C under continuous stirring for 2 h. Subsequently, the obtained slurry was filtered, washed with hot distilled water, and dried at 110°C for 24 h. The dried catalyst was then calcined at 300°C [29] for 3 h with a heating rate of 2°C min^{-1} [28]. Natural zeolite, acid-activated natural zeolite, and Cu-modified acid-activated natural zeolite were denoted as NZ, ANZ, and xCu-ANZ, respectively, where x represents the Cu loading percentage.

2.3. Catalyst Characterization

The physicochemical properties of the prepared catalysts were characterized using several analytical techniques. Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu Q-ATR) was used to examine surface functional groups. Crystalline structures of the catalysts were identified by X-ray diffraction (XRD; Shimadzu XRD-6100). Surface morphology and elemental composition were examined using Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy (SEM-EDX, JEOL JCM-7000). Additionally, the specific surface area of the catalyst was determined using Brunauer–Emmett–Teller (BET) analysis. FTIR and XRD analyses were performed on a representative Cu-ANZ catalyst containing 7.5 wt% Cu, while SEM-EDX and BET analyses were conducted on the 10 wt% Cu catalyst, which showed the highest relative HPLC peak area (RHPA) among the catalysts evaluated under the investigated reaction conditions.

2.4. Hydrothermal Conversion of Glycerol and Product Analysis

Hydrothermal conversion of glycerol was carried out in a 150 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical experiment, 100 mL of glycerol solution containing NaOH and 0.52 g of catalyst was introduced into the reactor. The molar ratio of glycerol to NaOH was maintained at 1:1.1. Cu-ANZ catalysts with Cu loadings of 2.5, 5, 7.5, 10, 12.5, and 15% were employed in the reaction system. Prior to heating, the reactor was purged with nitrogen gas for 10 min to establish an inert atmosphere and subsequently sealed. The hydrothermal reaction was conducted at 230°C for 2 h under continuous stirring at 300 rpm. Once the reaction had finished and the reactor had cooled to room temperature, the liquid products were separated from the solid catalyst by filtration.

To investigate the effect of reaction time on the RHPA, additional experiments were performed using the 10 wt% Cu catalyst, which showed the highest RHPA in the catalyst-loading experiments, at reaction times of 20, 40, 60, 80, 100, 180, and 300 min while maintaining the same reaction conditions. The resulting liquid products were analyzed using High-Performance Liquid Chromatography (HPLC, Shimadzu LC-2030) equipped with a UV–Vis detector operated at a wavelength of 210 nm. The analysis was performed at a flow rate of 0.7 mL/min using 50 mM KH_2PO_4 as the mobile phase, with an acquisition time of 10 min. A standard lactic acid solution was analyzed under the same HPLC conditions to determine its retention time. Peaks detected in the reaction products with retention times close to that of the lactic acid standard were tentatively assigned to lactic acid. The corresponding peak area was used to calculate the RHPA, which was then used to compare the HPLC responses across the investigated reaction conditions. RHPA was calculated as stated in Equation 1.

$$RHPA\ (\%) = \frac{A_{LA-assigned}}{\sum_{i=1}^{n} A_i} \times 100\% \quad (1)$$

Where, $A_{\text{LA-assigned}}$ is the peak area of the peak tentatively assigned to lactic acid (LA), and $\sum_{i=1}^{n} A_i$ is the sum of the peak areas of all detected peaks in the corresponding chromatogram.

3. Results and Discussion

3.1. FTIR Analysis of Natural Zeolite and Cu-Modified Catalysts

Figure 1 shows the FTIR spectra of NZ, ANZ, and Cu-ANZ catalysts. In all samples, surface hydroxyl groups and bound water molecules dominate this region of the spectrum, resulting in a broad O–H stretching band around 3440 cm^{-1} [22, 30]. Also, the band around 1637 cm^{-1} corresponds to the bending vibrations of adsorbed water, indicating the presence of moisture within the zeolite structure [22, 31]. The most prominent absorption band was observed in the region of 1047–1088 cm^{-1}, which is commonly assigned to the asymmetric stretching vibration of Si–O–Si and Si–O–Al bonds in the aluminosilicate framework [22, 30]. A noticeable shift of this band from 1047 cm^{-1} for NZ to 1078 cm^{-1} for ANZ was observed after acid activation, suggesting changes in the local aluminosilicate environment that may be associated with partial dealumination [22].

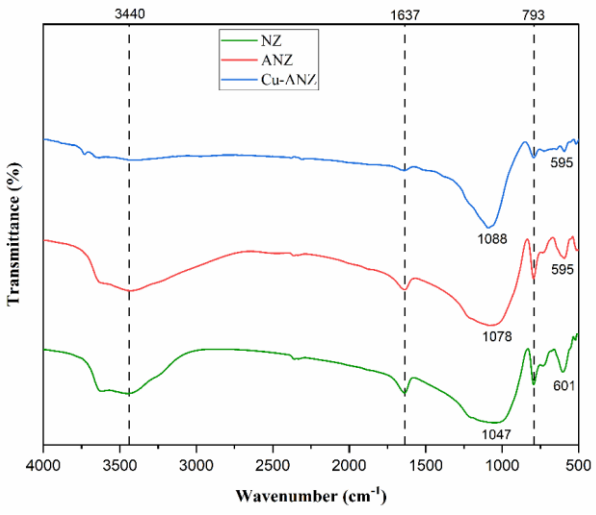


Figure 1. FTIR spectra of NZ, ANZ, and Cu-ANZ

Following Cu impregnation, the band further shifted to 1088 cm^{-1}. This additional shift suggests a change in the local bonding environment after Cu modification; however, FTIR alone does not allow the specific nature of the interaction between Cu species and the zeolite framework to be conclusively established [31]. Additional bands observed at approximately 793 cm^{-1} and 595–601 cm^{-1} are associated with the symmetric stretching vibration of Si–O–Si bonds and the characteristic double-ring vibration of zeolitic structures, respectively [31, 32]. The persistence of these bands after acid activation and Cu modification suggests that the fundamental zeolite framework remained intact throughout the catalyst preparation process [22, 31].

3.2. XRD Analysis of Catalyst Crystallinity

Figure 2 presents the XRD patterns of NZ, ANZ, and Cu-ANZ catalysts. The diffraction patterns of all samples exhibit major reflections at approximately 2θ = 22.5°, 25.7°, and 27.8°, consistent with the crystalline characteristics reported for natural zeolite materials [23, 33]. The persistence of these major reflections after acid activation and Cu modification suggests that the crystalline zeolitic structure was largely preserved throughout the catalyst preparation process [22, 31]. However, because phase identification via reference-pattern matching or quantitative phase analysis was not performed, the specific zeolite mineral phase cannot be conclusively assigned from the present XRD data alone.

Compared with NZ, the XRD pattern of ANZ showed no substantial change in the positions of the major diffraction peaks, suggesting that acid activation did not cause major changes in the crystalline structure of the zeolitic material [22, 33]. The observed preservation of the major diffraction features is consistent with the FTIR results, which suggest that the fundamental aluminosilicate framework was retained after acid activation [22, 23].

Following Cu modification, the Cu-ANZ catalyst retained the major diffraction peaks observed for the parent material, suggesting that the modification procedure did not cause substantial changes in the crystalline structure of the support [24, 34]. No distinct diffraction peaks attributable to crystalline Cu-containing phases were detected. This may be related to the amount of Cu species being below the XRD detection limit, their high dispersion, small crystallite size, or the presence of poorly crystalline or amorphous Cu-containing species [24]. Taken together, the XRD results indicate that the major crystalline features of the zeolitic material were retained after acid activation and Cu modification, with no substantial changes in the positions of the major diffraction peaks [31, 34].

3.3. Surface Morphology and Elemental Composition (SEM-EDX)

Table 1 presents the elemental composition of NZ and Cu-ANZ determined by EDX analysis. The elemental composition analysis revealed an increase in Cu content from 0.08 atomic % in NZ to 6.34 atomic % in Cu-ANZ, confirming the presence of Cu species in the analyzed Cu-ANZ catalyst after the impregnation procedure [31, 34]. The Si/Al ratio also increased from 4.96 for NZ to 6.69 for Cu-ANZ, indicating a difference in the elemental composition of the analyzed materials. Acid activation of natural zeolites has been reported to promote partial dealumination and the removal of exchangeable cations and impurity oxides, which may increase the Si/Al ratio and alter the surface composition [22, 23, 33].

Therefore, the higher Si/Al ratio observed for Cu-ANZ is consistent with compositional changes that may occur during acid activation. However, because EDX analysis was not performed on the intermediate acid-activated zeolite (ANZ), the individual contribution of acid activation to the observed increase in the Si/Al ratio cannot be directly established, and the observed difference may also reflect the subsequent Cu modification procedure. These results are consistent with the FTIR observations, which suggest changes in the local aluminosilicate environment after the modification treatments [22, 23, 31].

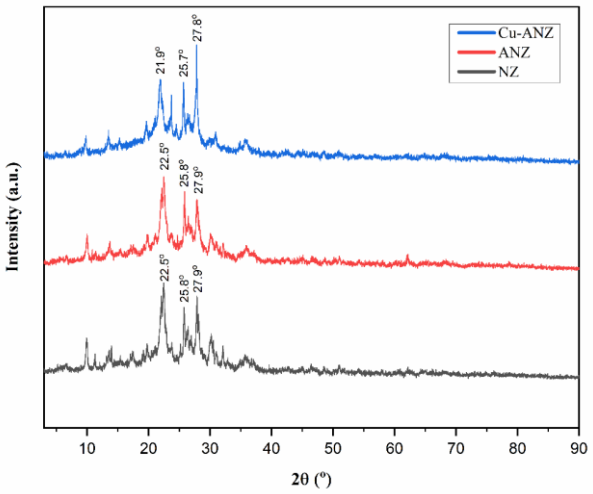


Figure 2. XRD patterns of NZ, ANZ, and Cu-ANZ catalysts showing the structural changes after acid activation and Cu modification

Table 1. Surface elemental composition (atomic %) and Si/Al ratio of NZ and Cu-ANZ catalysts obtained from EDX analysis

Material	C (atomic%)	O (atomic%)	Al (atomic%)	Si (atomic%)	Cu (atomic%)	Si/Al ratio
NZ	45.04	48.04	0.97	4.81	0.08	4.96
Cu-ANZ	20.44	59.15	1.63	10.91	6.34	6.69

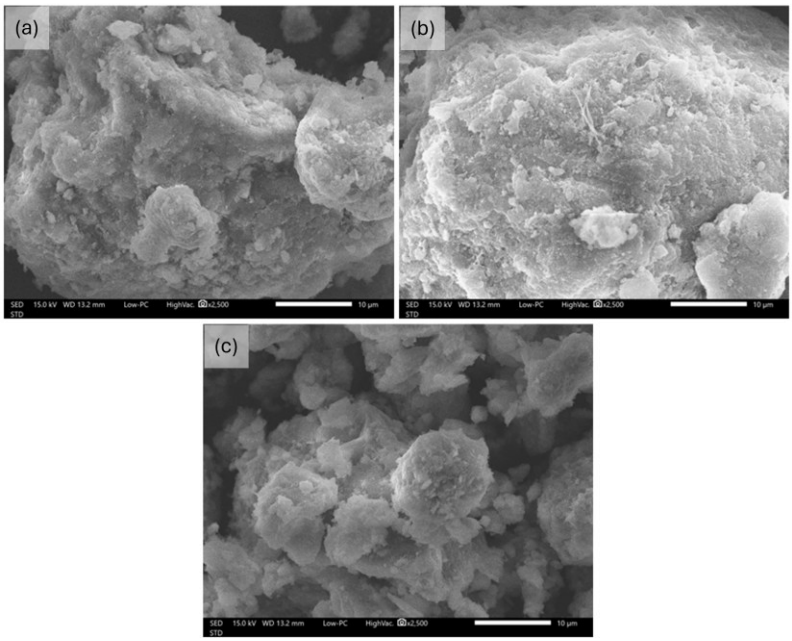


Figure 3. SEM images of (a) NZ, (b) ANZ, and (c) Cu-ANZ catalysts obtained at 2500× magnification, showing surface morphology changes after acid activation and Cu modification

The SEM images shown in Figure 3 reveal noticeable differences in surface morphology following acid activation and Cu modification. The NZ sample exhibited relatively compact and irregular particles, whereas the ANZ sample displayed a rougher surface texture, which may be associated with changes in the surface caused by the acid treatment, such as the removal of impurities and modification of the zeolitic framework [10, 20]. After Cu impregnation, the Cu-ANZ catalyst showed a more heterogeneous surface morphology, indicating further morphological changes following Cu modification [10]. Despite these morphological differences, the catalyst particles retained their aggregated structure, suggesting that the modification procedures did not cause severe morphological degradation [10, 20].

Collectively, the SEM and EDX results reveal differences in surface morphology and elemental composition following the catalyst modification procedures, including the higher Cu content detected in Cu-ANZ [31, 34]. The SEM observations and EDX results together indicate that the modification procedures altered the surface characteristics of the natural zeolite without causing severe morphological degradation [22, 23, 26]. However, the individual contributions of acid activation and Cu modification to the observed changes in elemental composition cannot be distinguished from the available EDX data because ANZ was not analyzed by EDX.

3.4. Surface Area Characteristics Based on BET Analysis

Figure 4 presents the nitrogen adsorption data of NZ and Cu-ANZ as a function of relative pressure, while the corresponding BET specific surface areas are summarized in Table 2. The BET specific surface area increased from 27.010 $m^2 g^{-1}$ for NZ to 32.826 $m^2 g^{-1}$ for Cu-ANZ, indicating that the entire catalyst modification procedure was associated with an increase in the measured specific surface area.

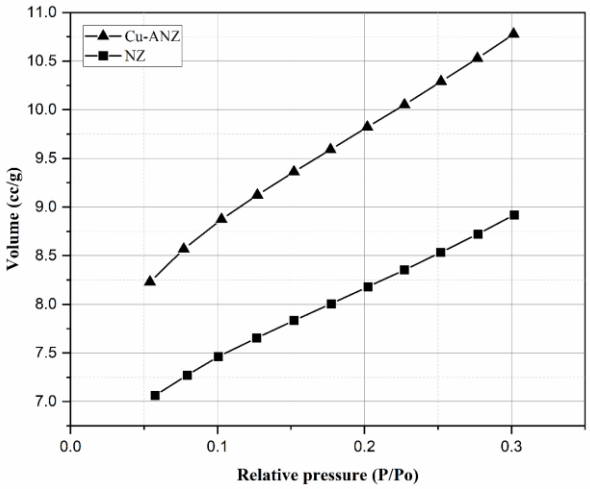


Figure 4. Nitrogen adsorption data of NZ and Cu-ANZ as a function of relative pressure

Table 2. BET surface area of NZ and Cu-ANZ catalysts

Material	BET surface area ($m^2 g^{-1}$)
NZ	27.010
Cu-ANZ	32.826

Acid activation of natural zeolites has been reported to remove impurities and promote partial dealumination, which can modify the surface characteristics and increase the accessible surface area of the material. Such effects may contribute to the increase in BET surface area observed after the entire modification process in the present study. The higher Si/Al ratio observed for Cu-ANZ compared with NZ is also consistent with compositional changes reported for acid-treated natural zeolites [22, 23, 33]. However, because BET and EDX analyses were not performed on the intermediate ANZ sample, the individual contribution of acid activation to the observed increase in surface area and Si/Al ratio cannot be directly established.

Despite the incorporation of Cu species, the BET specific surface area of Cu-ANZ was higher than that of NZ, representing an increase of approximately 21.5% [10, 22, 23, 35]. This observation indicates that the overall modification procedure did not reduce the measured specific surface area. Although pore volume and pore size distribution were not determined in the present study, the higher specific surface area may provide greater surface accessibility for interactions between the reactants and catalyst surface during hydrothermal glycerol conversion [12, 22, 23]. However, the extent to which this difference contributes to the observed RHPA cannot be established from the present data alone.

3.5. Effect of Cu Loading during Hydrothermal Glycerol Conversion

Figure 5 shows the RHPA of the peak tentatively assigned to lactic acid at different Cu loadings during hydrothermal glycerol conversion over Cu-ANZ catalysts. The RHPA generally increased with Cu loading from 2.5 wt% to 10 wt%, although the increase was not strictly linear across the investigated catalysts. The highest RHPA was obtained with the catalyst containing 10 wt% Cu under the applied reaction conditions. At higher Cu loadings of 12.5 and 15 wt%, the RHPA decreased markedly. Based on the RHPA, the 10 wt% Cu-ANZ catalyst was therefore selected as the optimum catalyst composition among the investigated catalysts for the subsequent reaction-time experiments.

The increase in RHPA with Cu loading up to 10 wt% may be related to the role of Cu species in the catalytic transformation of glycerol. Copper-containing catalysts have been reported to facilitate the transformation of glycerol toward lactic acid under alkaline hydrothermal conditions, with Cu species playing an important role in glycerol dehydrogenation and subsequent transformation reactions [2, 12]. The observed increase in RHPA is therefore consistent with the reported beneficial role of Cu-containing catalysts in glycerol-to-lactic-acid conversion. Tang *et al.* [7] also demonstrated the effectiveness of Cu-containing complex oxide catalysts for the selective conversion of glycerol to lactic acid. However, the number and nature of catalytically active sites were not determined in the present study. Thus, the increase in RHPA cannot be directly attributed solely to an increase in the concentration of active Cu sites.

The decrease in RHPA at Cu loadings above 10 wt% indicates that increasing the Cu content beyond this level did not further increase the HPLC response under the investigated reaction conditions. Previous studies on Cu-supported catalysts have shown that catalytic performance may exhibit an optimum with increasing Cu loading. At excessive Cu loadings, Cu aggregation or reduced metal dispersion can limit the effective utilization of Cu species [36]. Such behavior may provide a possible explanation for the lower RHPA observed at 12.5 and 15 wt% Cu in the present study. However, Cu dispersion and particle aggregation were not directly characterized for the catalysts investigated at different Cu loadings; therefore, this explanation remains tentative.

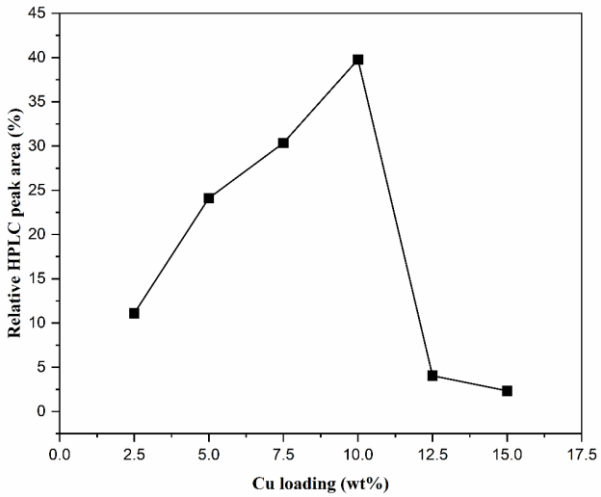


Figure 5. Relative HPLC peak area tentatively assigned to lactic acid at different Cu loadings during hydrothermal glycerol conversion over Cu-ANZ catalysts

The maximum RHPA observed for the 10 wt% Cu catalyst is consistent with the optimum Cu loading reported for other Cu-based catalytic systems. Han *et al.* [25] reported an optimum Cu loading of 10 wt% for Cu-loaded porous metal oxide catalysts, while Yan *et al.* [36] also identified 10 wt% Cu as the optimum loading for Cu catalysts supported on dealuminated Y zeolite. Although the catalyst supports and reaction systems differed from those used in the present study, these reports demonstrate that an optimum Cu loading can arise from a balance between the availability of Cu species and their effective utilization on the catalyst support. In the present study, the 10 wt% Cu-ANZ catalyst was therefore selected as the optimum catalyst composition based on the highest RHPA observed under the investigated reaction conditions and was used for the subsequent investigation of reaction-time effects.

3.6. Effect of Reaction Time on Lactic Acid Formation

Figure 6 presents the HPLC chromatograms of the lactic acid standard solution and the reaction product obtained from hydrothermal glycerol conversion over the Cu-ANZ catalyst. The chromatogram of the standard solution exhibited a characteristic peak at a retention time of approximately 5 min, while a corresponding peak was also observed in the reaction product chromatogram at a similar retention time [15, 27]. This agreement in retention time supports the tentative assignment of the selected peak in the reaction product to lactic acid under the applied HPLC conditions. Therefore, the peak area associated with this retention time was used as an indicator of the relative amount of the product tentatively assigned to lactic acid for evaluating the effect of reaction time.

The influence of reaction time on the HPLC peak area of the product tentatively assigned to lactic acid is shown in Figure 7. The HPLC peak area increased continuously with increasing reaction time, indicating an increase in the relative amount of the product tentatively assigned to lactic acid during hydrothermal glycerol conversion [2, 27]. At reaction times between 20 and 100 min, only a gradual increase in peak area was observed. This behavior

suggests that the reaction was still progressing through the formation and transformation of intermediate compounds generated from glycerol degradation [17].

A substantial increase in the HPLC peak area was observed when the reaction time was extended from 100 to 180 min. This sharp increase suggests that prolonged reaction time promoted the transformation of reaction intermediates toward the product tentatively assigned to lactic acid [2]. The formation of lactic acid from glycerol is generally understood to proceed through a series of dehydrogenation, dehydration, and rearrangement reactions involving intermediate species such as glyceraldehyde, dihydroxyacetone, and pyruvaldehyde [2, 12, 27]. Therefore, the accumulation and subsequent transformation of these intermediates may contribute to the pronounced increase in the HPLC peak area observed at longer reaction times [2].

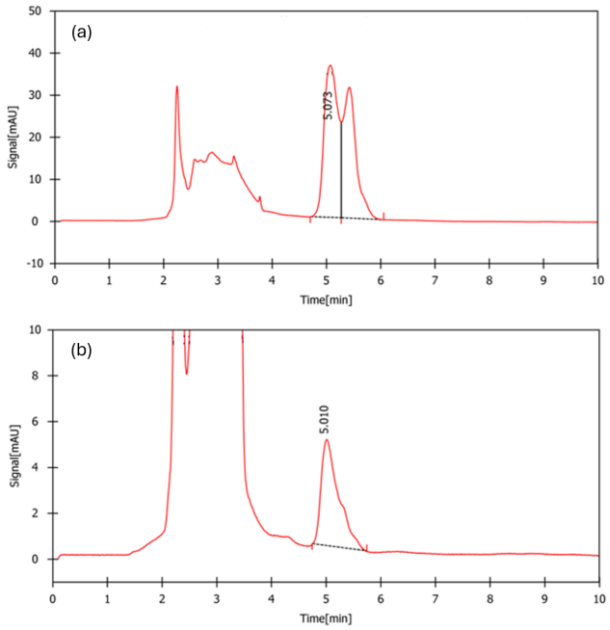


Figure 6. HPLC chromatograms of (a) lactic acid standard and (b) reaction product obtained over the Cu-ANZ catalyst for assignment of lactic acid peak

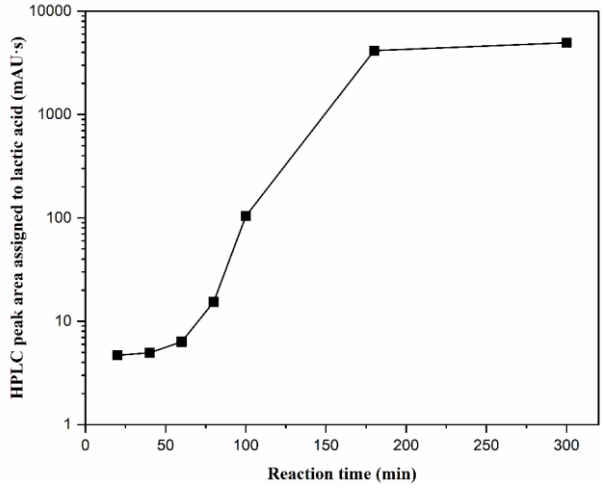


Figure 7. Effect of reaction time on HPLC peak area of the peak tentatively assigned to lactic acid during hydrothermal glycerol conversion over the Cu-ANZ catalyst

Further extending the reaction time from 180 to 300 min resulted in only a slight increase in the HPLC peak area associated with the product tentatively assigned to lactic acid. This observation suggests that the increase in the peak area associated with this product became less pronounced after 180 min [14, 27]. Similar trends have been reported in hydrothermal glycerol conversion studies, where prolonged reaction times enhance the transformation of intermediate products toward lactic acid, with the increase becoming less pronounced at longer reaction times [27].

The results indicate that reaction time substantially influenced the HPLC peak area associated with the peak tentatively assigned to lactic acid during hydrothermal glycerol conversion. Among the investigated conditions, reaction times of 180–300 min yielded the highest HPLC peak areas for the peak tentatively assigned to lactic acid, with the highest at 300 min.

4. Conclusion

The hydrothermal conversion of glycerol over Cu-modified acid-activated natural zeolite (Cu-ANZ) was investigated. FTIR and XRD analyses indicated that acid activation and Cu impregnation modified the physicochemical characteristics of natural zeolite while preserving its fundamental aluminosilicate framework and crystallinity. SEM-EDX analysis confirmed the presence of Cu in the modified catalyst and revealed an increase in the Si/Al ratio from 4.96 to 6.69 after the overall modification process. BET analysis showed that the catalyst modification increased the specific surface area from 27.010 to 32.826 $m^2 g^{-1}$. The relative HPLC peak area (RHPA) of the peak tentatively assigned to lactic acid increased with Cu loading up to 10 wt% Cu and decreased at higher Cu loadings. The 10 wt% Cu-ANZ catalyst therefore showed the highest RHPA among the catalysts investigated and was selected for subsequent reaction-time experiments. The decrease in RHPA at higher Cu loadings may be associated with changes in Cu dispersion or aggregation, although these effects were not directly characterized in the present study. Increasing the reaction time resulted in a progressive increase in the HPLC peak area associated with the peak tentatively assigned to lactic acid. A pronounced increase was observed between 100 and 180 min, while only a slight further increase occurred from 180 to 300 min. The highest HPLC peak area was obtained at 300 min. The findings indicate that Cu loading and reaction time influenced the HPLC response associated with the product tentatively assigned to lactic acid under the investigated hydrothermal conditions.

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