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Synthesis and Characterization of CaO-Zeolite Catalyst by Sonochemical Engineering Method

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Abstract

Calcium Sulfate Dihydrate was an active site embedded in natural zeolite and categorized as a heterogeneous catalyst. The research aimed to prepare and synthesize CaO-Zeolite catalyst by sonochemical impregnation and stirrer was used as a control. CaO-Zeolite catalyst characterization was identified via Scanning Electron Microscopy- Energy Dispersive X-Ray (SEM-EDX). The activation experiments were performed at 120°C for 5 h and a calcination temperature of 300 ˚C for 2 h. The synthesized catalysts of sonochemical occured at 20 minutes, 20 kHz, and 1200 Watt, and occurred at 120 minutes, 1500 rpm, and 1000 watts for stirrer impregnation. The experimental results revealed that the catalysts prepared by the sonochemical method better than the stirrer. Ca wt.% increased from 0.86 wt.% NZ (natural zeolite) to (11.3 wt.%, 14.15 wt.%, and 23.48 wt.%) of sonochemical and (11.82 wt.%, 13.95 wt.% and 20.64 wt.%) of the stirrer. The results demonstrated that Ca wt.% by sonochemical dispersed at support surface (zeolite) more effective than stirrer. The alumina and silica content were significantly reduced inversely proportional to increased Ca. The highest sonochemical value of Si/Al was obtained at 4.49 and 4.46 at stirrer impregnation. The acid strength of the bronsted acid site increased proportionally to increase in Si/Al ratio. The more acidic the catalyst, the more active the catalyst obtained.

Keywords: CaO-Zeolite catalyst, Sonochemical Impregnation, Ca weight percentage, Acid Strength.

Abstrak (Indonesian)

Kalsium Sulfat Dihidrat merupakan sisi aktif yang diembankan pada zeolit alam dan dikategorikan sebagai katalis heterogen. Tujuan penelitian ini adalah mempersipakan dan mensintesa CaO-Zeolit dengan impregnasi sonokimia dan stirrer sebagai pembanding. CaO-Zeolit diidentifikasi dengan Scanning Electron Microscopy- Energy Dispersive X-Ray (SEM-EDX). Proses aktivasi dilakukan pada 120°C selama 5 jam dan temperatur kalsinasi 300°C selama 2 jam. Katalis yang disintesis dengan sonokimia berlangsung selama 20 menit, dengan frekuensi 20 kHz dan 1200 watt, sedangkan katalis yang disintesis dengan pengaduk (*stirrer*) berlangsung selama 120 menit, 1500 rpm dan 1000 watt. Hasil penelitian menunjukkan bahwa katalis yang disintesis oleh metode sonokimia lebih unggul dibandingkan dengan metode stirrer. Persen berat Ca dari 0.86 % zeolit alam menjadi 11.3 % berat, 14.15 % berat, 23.48 % berat dengan metode sonokimia, sedangkan dengan metode stirrer didapat hasil 11.82 % berat, 13.95 % berat dan 20.64 % berat. Hasil ini menunjukkan bahwasannya % berat Ca dengan metode sonokimia dalam waktu 20 menit terdispersi pada permukaan zeolit lebih efektif dari pada secara stirrer selama 120 menit. Kandungan Alumina dan silika kecendrungan menurun seiring dengan meningkatnya komponen Ca. Nilai tertinggi Si/Al pada sonokimia sebesar 4.49 dan pada stirrer 4.46. Semakin tinggi perbandingan Si/Al, semakin kuat asam bronsted. Semakin kuat asam suatu katalis maka semakin aktif katalis tersebut.

Kata Kunci: Katalis CaO-Zeolit, Impregnasi Sonokimia, Persentase Berat Ca, Kekuatan Asam.

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INTRODUCTION

The consumption of catalysts in a chemical process reaction is beneficial to accelerate the reaction time, reduce the reaction temperature, selective process, desired reaction, productivity [1], improve process efficiency entirely in catalytic pyrolysis, and increase the yield and gaseous production [2]. Any catalyst's main factors that impact the pyrolysis process are enlarged specific surface area, pore volume, pore size, and acidity. Using catalysts in the catalytic process could enhance the yield of syngas production, improve energy efficiency and reduce tar components effectively[3].

The addition of acidic metal oxides led to improving the gaseous and solid yield, the other side decreasing the liquid yield [4]. Acidic metal oxides such as Al_2O_3, SiO_2, and SiO_2–Al_2O_3. On the other side, metal oxides such as MgO and CaO are also classic base catalysts, where oxide ions behave as bases and metal cations behave as Lewis acids [4]. CaO, SiO_2, MgO, Fe_2O_3, and Al_2O_3 were categorized as high alkaline metal compositions [5].

The researchers continually study and develop heterogeneous catalysts to keep sustainable processes [6]. Due to heterogeneous catalysts could be recycled, improved selectivity, and simple catalyst separation, their utilization minimizes the reaction time in biodiesel production [7] and the pyrolysis process [1]. As a heterogeneous catalyst, Calcium Oxide is widely available, efficient cost is used frequently, has excellent catalytic performance, and requires moderate reaction conditions in application [8].

The addition of CaO catalyst could support the formation of syngas more effectively in the bagasse microwave pyrolysis process and increase syngas yield [1]. The performance of CaO can improve syngas production and absorb the CO_2 produced [9].

The synthesis of CaO catalyst embedded in porous materials (zeolite) is advantageous in cost and process. Zeolite can load active catalysts, providing a large surface area [10], accessible volume, and effective pore size distribution[11,12]. Optimization catalyst in pyrolysis of biomass waste to biofuel could be microporous zeolite, highly acidic, enhanced surface area [13]. However, to the best of our knowledge, it is needed to enhance the ability of catalytic pyrolysis by modifying catalyst pathways such as CaO-Zeolite by developing the active site with high acidity and utilizing the proper method of impregnation. The high acidity of Bronsted in zeolite could enhance the gas yield and decrease the liquid oil yield [14].

The industry's two main precipitation methods are commonly precipitation and impregnation [15]. Ultrasonic technology is a constantly evolving method for synthesizing catalysts due to low consumption of chemical reagents, cavitation phenomena saving energy, and environment-friendly methods [16]. The sonochemical synthesizing catalyst method with the principle of ultrasonic technology [17]. Ultrasonic impregnation has proven to be a superior method in synthesizing catalysts to improve adsorption capacity, lower time [18], enlarge the specific surface area and pore volume [19], superior in the mass transfer process, improve more active sites [20], and assisted precipitation technique. The shockwave of ultrasound (cavitation phenomena) can generate more active components (metal oxide) and disperse more homogeneously on the external surface [21]. The shockwave of ultrasound (acoustic) break agglomeration of catalyst particles has been proven to enhance the physicochemical properties of the catalysts [22], create smaller particle size [23], more specific surface area [24], and active component entering into the support pores by high pressure.

The research aimed to prepare and synthesize CaO-Zeolite by sonochemical impregnation method. The additional high alkali metal composition was embedded on the zeolite surface to develop more active catalyst sites and enhance the Bronsted acid site of the catalyst. The sonochemical method’s objective selected for this research was to enlarge the surface area of active sites embedded on zeolite to dispersive uniformly at the external surface of zeolite, and improve more active sites, pore volume, and pore sizes. For comparison, the catalyst of CaO-Zeolite was also prepared by stirrer impregnation. The samples were characterized by Scanning Electron Microscope (SEM) to study the surface morphology of CaO-Zeolite, composition, distribution, and dispersion state of the active component. The preparation process was optimized, by using the time of impregnation, and comparison time of sonochemical impregnation and stirrer impregnation.

MATERIALS AND METHODS

Materials

In this work, the natural zeolite was provided by Lampung (Indonesia). Hydrogen Chloride (HCl) and Aquadest were purchased from the BRATA CHEM, Palembang-Indonesia. Calcium Sulfate Dihydrate) (Merck) was purchased from the Shagufta Lab Scientific- Jakarta, and $AgNO_3$ was purchased from the ROFA laboratory Center, Bandung, under the Pudak Scientific brand.

Table 1. Parameter sample based on Stirrer Impregnation and Sonochemical Impregnation.

Items	Impregnation Methods	Times (minutes)	Ratio Calcium Sulfate Dihydrate: Zeolite
Sample #I	Magnetic Stirrer	120	1:3
Sample #II			1:1
Sample #III			3:1
Sample #IV	Sonochemical	20	1:3
Sample #V			1: 1
Sample #VI			3:1

Catalyst Preparation

In the first step, as zeolites activation, the natural zeolite 100 grams was crushed into smaller ones and dispersed into 1000 ml distilled water by magnetic stirrer for 2 h. The mixture was filtered and dried by oven at 120°C for 5 h to be feedstock. Ground the feedstock that had been treated to ensure a more homogenous texture. Afterward, the feedstock 40 g was dipped to ion exchange with 200 ml HCl 1 M to obtain a protonated catalyst and increase the Bronsted acid site concentration. The process was accomplished in a beaker glass for 2 h ambient temperature without agitation treatment (stagnant condition). Next step, the feedstock was separated by filtration and rinsed by distilled water until free from Cl^-, which was tested with $AgNO_3$ solution [25]. Finally, the feedstock (filtrate) was dried in the oven at 120°C for 5 h and calcinated for 2 h at 300°C to be an activated zeolite before catalysts impregnation.

Synthesis of CaO-Zeolite using sonochemical and stirrer impregnation method

The synthesis stage was carried out by the sonochemical and stirrer methods. Comparison of Calcium Sulfate Dihydrate with zeolite was 1:3, 1:1, 3:1. Synthesis of CaO-Zeolite used the sonochemical method. The ratio of Calcium Sulfate Dihydrate to Zeolite was 40 ml of ethanol added and then impregnated using sonochemistry for 20 minutes. The mixture was filtered and dried in an oven at 120°C for 5 hours, then calcined at 400°C for 5 hours. Afterward, the sample was characterized. For the synthesis of CaO-Zeolite using the stirrer method, the operating conditions used were the same as sonochemical impregnation, with the same ratio of Calcium Sulfate Dihydrate to zeolite. The difference was the impregnation using a stirrer for 120 minutes.

Catalyst characterization

The catalyst was characterized by a scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX). The surface morphology of samples was obtained by a Hitachi S 4700 SEM analyzer at different scales and magnifications. Meanwhile, the component compositions were detected by EDX.

RESULTS AND DISCUSSION

SEM-EDX Analysis

Two methods, sonochemical impregnation, and stirrer impregnation were used to prepare CaO-Zeolite. **Figure** 1 showed images of SEM analysis showing the surface morphology of CaO-Zeolite by the stirring impregnation method. In **Figure** 1(a), the morphology of the zeolite sample before activation was still a rock plate with an irregular shape. The surface morphology of natural zeolite was still covered with a black shadow on the surface, wavy, uneven surface. Many impurities covered the zeolite surface, and many cations were carried from various elements on the surface.

In **Figure** 1(b), the morphology had a spherical but irregular shape. Regarding the SEM image, it could be seen that there was a color combination where the darker color has indicated the zeolite surface itself. In contrast, the white color indicated the Ca embedded on the zeolite surface. In general, the use of a buffer also serves to spread the active phase of the catalyst. The spread has been done to expand the contact surface between the active reactant phases without reducing the intrinsic activity of the active phase.

In **Figures** 1(d), the morphology of the zeolite surface appears lighter, and the distribution of the particle size of the active side was needle-shaped, spherical, and crystalline. Related to the Ca ratio was greater than the zeolite. On the surface of the zeolite were also visible cracks on the surface. This phenomenon was influenced by many actives Ca sites embedded in the zeolite. Another occurrence factor of defects in the catalyst was a decrease in crystallinity. Si/Al was decreasing due to the presence of Ca, which has a larger ratio, so the zeolite framework had become unstable, explaining that the decrease in crystallinity was caused by the presence of Al which came out of the zeolite framework.

The morphology of CaO-Zeolite that was synthesized by stirring impregnations in Figures 1(b)-(d) described that the distribution of particles on the surface of the zeolite was uneven, granular, and tends to stick to the surface. This phenomenon was caused by the tendency of un-maximum pore diffusion to occur during the adsorption. The overall picture of the catalyst morphology using a stirrer for samples (I), (II), and (III) described that the surface morphology of the catalyst after activation was flatter than the surface morphology of natural zeolite.

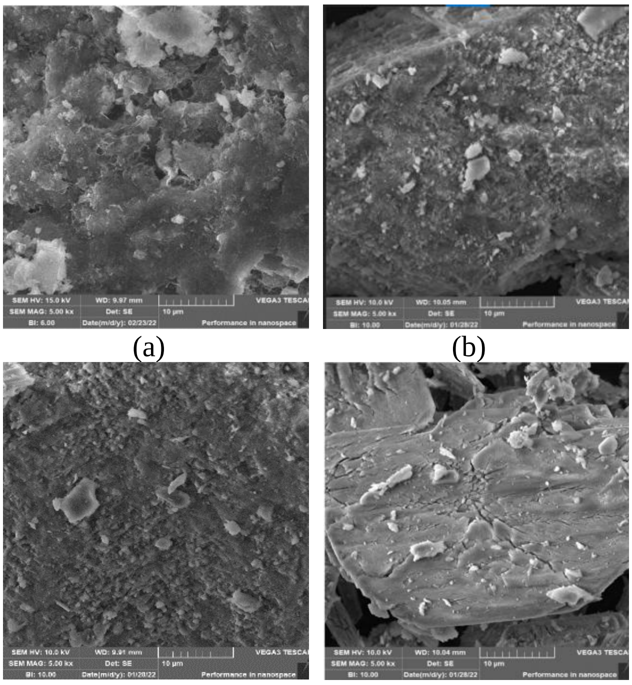
(a) (b)
(c) (d)

Figure 1. SEM images of 5.00 kx by stirrer impregnation method (a) natural zeolite - Lampung, (b) Sample (I) (c) Sample (II) (d) Sample (III)

Figure 2 showed images of SEM analysis showing the surface morphology of CaO-Zeolite by the sonochemical impregnation method. In Figure 2(a), the morphology of the natural zeolite was still a rock plate with an irregular shape. The surface morphology of natural zeolite was covered with a black shadow on the surface, wavy, uneven surface. Indicated that most impurities are covered on the external zeolite surface, and many cations have carried from various elements on the surface of the zeolite.

In **Figures** 2(b)-(d), the surface morphology of the catalyst after activation had a flatter surface and unwavy. It can also be seen that the active substances were evenly distributed in the pores of the zeolite surface. The catalyst activity was significantly improved through ultrasonic impregnation [17]. The surface morphology of the catalyst after activation had no agglomeration at one point on the zeolite surface.

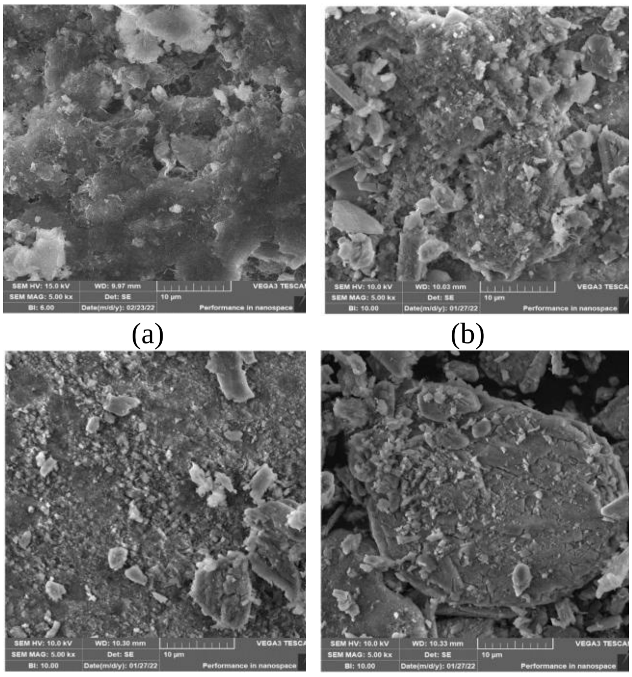
(a) (b)
(c) (d)

Figure 2. SEM images of 5.00 kv by sonochemical impregnation method (a) natural zeolite - Lampung, (b) Sample (IV) (c) Sample (V) (d) Sample (VI)

Figure 2(b) showed that the distribution of the active site Ca scattered on the surface of the zeolite was not entirely. There were still visible pores on the surface of the zeolite, which were not covered by the active side Ca. **Figure** 2(c) showed that Ca distribution on CaO-Zeolite was more homogenous, and the catalyst particle size was smaller than in **Figure** 2(b). Possibly the active site was more absorbed on the surface of the zeolite, along with the ratio of Calcium Sulfate Dihydrate loaded to zeolite.

Figure 2(d) showed the surface of the zeolite was flatter than in **Figures** 2(b) and **Figure** 2(c), probably due to the main active component of Calcium Sulfate Dihydrate many embedded in the surface of the zeolite. The effects of ultrasound irradiation improved catalyst properties by facilitating interaction between metal and support, allowing oxygen motion with the oxide site [26]. Shockwave generated metal–support interaction and accelerated mass transfer which created homogenous dispersion [27].

EDX Analysis

Herewith, attached in **Table** 1, natural zeolite before activation. The Ca content was still in low % weight before activation. The ratio of Si/Al at the natural zeolite was 5.28 and Si/Ca was 36.05.

Table 1. Natural Zeolite Before Activation

Element	Weight (%)
Si	31
Al	5.87
Ca	0.86

The results of the zeolite activation and dealumination are shown in **Table** 2.

Table 2. Ca component – EDX analysis

Sample Item	Ca Component (% weight)
Sample (I)	11.82
Sample (II)	13.95
Sample (III)	20,64
Sample (IV)	11.3
Sample (V)	14.15
Sample (VI)	23.48

Regarding the EDX result, it concluded that % mass Ca was increased at activated zeolite compared to % mass Ca of natural zeolite. Ca component at natural zeolite is 0.86%.

Ca components had been impregnated in the activated zeolite pores. The highest Ca was obtained from sonochemical impregnation at sample (VI) with a result of 23.48 % Ca weight. For the stirrer method, the Ca component was obtained in sample (III) with the result of 20.64%. Meanwhile, regarding the results from **Table** 2. Ca components at the sonochemical impregnation method were obtained as equivalent as and higher than the stirrer method. The effect of sonochemical impregnation increased Ca have embedded in the zeolite. This is made possible by the shockwave and cavitation bubbles of ultrasound waves [28]. The bubbles collapsed in the liquid-solid interface, so the localized temperature of the zeolite surface increased. The interaction between Ca ions from calcium sulfate dihydrate and zeolite was enhanced, which favored electron transferring and oxygen vacancy formation. The using time of sonochemical was lower than the stirrer impregnation method. The time for the stirrer method was 120 minutes, and the sonochemical method was 20 minutes.

The relation between the ratios of calcium sulfate dihydrate to zeolite has presented in **Figure** 3.

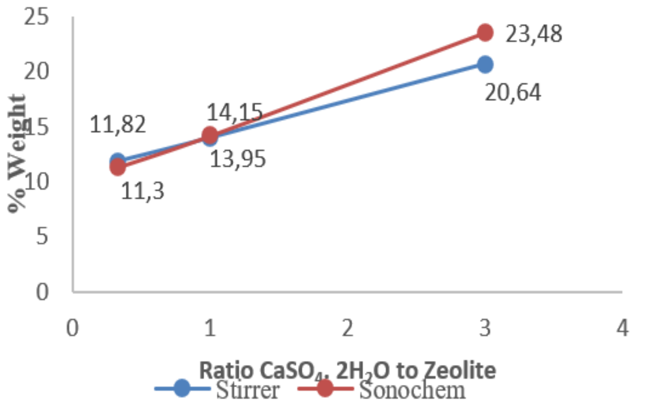

Figure 3. Ca distribution to zeolite with a stirrer and sonochemical impregnation method

In addition, **Table** 3 and **Table** 4 show Si and Al components after activation. The data showed that the higher the ratio of Ca added to the zeolite, the more mass % of Ca in the activated zeolite. The conclusion was that the higher ratio was proportional to the amount of Ca entering the pores of the zeolite both stirrer and sonochemical.

Based on **Table** 3 and **Table** 4, there was a decrease in Si and Al content from both impregnation methods compared to the Si and Al values in the natural zeolite. The content of the mass % value of Si in natural zeolite is 31, and the mass % value of Al in natural zeolite is 5.87. This phenomenon indicated that the activation and dealumination process had taken place. The phenomena showed that zeolite released many aluminas during activation and called as dealumination process. Dealumination was caused by the treatment of the presence of HCl.

The addition of sulfuric acid/ HCl will increase the dealumination process. Dealumination was a process of replacing aluminium with hydrogen, which involves changing the structure of the Si-O-Al aluminosilicate to a silica structure in the form of a silanol group - Si-OH. Bentonite is usually Ca^{2+} bentonite treated with an inorganic acid to substitute divalent calcium ions with monovalent hydrogen ions and increase the specific surface area and porosity [29].

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Table 3. Si and Al Components (stirrer impregnation) EDX analysis

Component	NZ % wt.	Sample (I) % wt.	Sample (II) % wt.	Sample (III) % wt.
Si	31	15.15	15.45	4.64
Al	5.87	4.89	3.64	1.04
Ca	0.86	11.82	13.95	20.64
Si/Al	5.28	3.09	4.24	4.46
Si/Ca	36.05	1.28	1.18	0.22

From the trend of the data, the alumina content was significantly reduced both from stirrer impregnation and sonochemical impregnation. Meanwhile, the silica content of sonochemical significantly resulted in a number of values of 12.1 %, 12.2 %, and 0.84%, and for stirrer was also fluctuate, the silica was up and down in number values of 15.15%, 15.45%, and 4.64%.

Table 4. Si and Al Components (sonochemical impregnation) EDX analysis

Component	NZ % wt.	Sample (IV) % wt.	Sample(V) % wt.	Sample (VI) % wt.
Si	31	12.1	12.2	0.84
Al	5.87	2.69	2.84	0.25
Ca	0.86	11.3	14.15	23.48
Si/Al	5.28	4.49	4.29	3.36
Si/Ca	36.05	1.07	0.86	0.04

The effect of Ca addition to zeolite can be seen in resulted value number of Si/Al in Table 3 and Table 4. The highest sonochemical value of Si/Al was obtained in sample (IV) with 1:3 ratio value of 4.49. Meanwhile, the highest stirrer value of Si/Al was obtained in sample (III) with 3:1 ratio value of 4.46. The strength of the bronsted acid site would increase proportionally to increase in Si/Al ratio. The more acidic the catalyst, the more active the catalyst obtained. The high bronsted acidic site in zeolite could enhance the catalytic cracking process of tar and increase the syngas composition [5]. The higher Si/Al ratio leads to higher catalytic activity [30]. The pore size, pore volume, surface area, and acidity were the main features of any catalyst that affect the pyrolysis process [14].

As the data in Table 3 and Table 4 showed the alumina content that tends to decrease and was inversely proportional to the increase in the Ca component. Meanwhile, for the stirrer impregnation, the highest Si/Ca value was obtained at sample (I) and for the sonochemical impregnation, the highest Si/Ca value was obtained at sample (IV). This condition indicated that the more Ca deposited on zeolite, the value of Si/Ca significantly reduced both from stirrer and sonochemical impregnation. Generally, there were key features of catalysts that could enhance the pyrolysis process in syngas production which were microporous materials, transition metal, and alkali metal [4]. The catalysts CaO and MgO could react with water to produce alkaline aqueous, which could be useful for H_2 production, and thus to increase the gaseous yield [1]. On the other side, CaO has the ability to absorb the CO_2 produced and enhanced syngas production [5]

Based on **Table** 3 and **Table** 4, there was a decrease in Si and Al content from both impregnation methods compared to the Si and Al values in the natural zeolite. The content of the mass % value of Si in natural zeolite is 31, and the mass % value of Al in natural zeolite is 5.87. This phenomenon indicated that the activation and dealumination process had taken place. The phenomena showed that zeolite released many aluminas during activation and called as dealumination process. Dealumination was caused by the treatment of the presence of HCl. The addition of sulfuric acid/ HCl will increase the dealumination process. Dealumination was a process of replacing aluminium with hydrogen, which involves changing the structure of the Si-O-Al aluminosilicate to a silica structure in the form of a silanol group - Si-OH. Bentonite is usually Ca^{2+} bentonite treated with an inorganic acid to substitute divalent calcium ions with monovalent hydrogen ions and increase the specific surface area and porosity [29].

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CONCLUSION

The experimental results revealed that the characterization of the catalysts prepared by the sonochemical method was better than the stirrer. The catalyst activity was significantly improved through ultrasonic impregnation. The surface morphology of the catalyst after activation had no agglomeration at one point on the zeolite surface. Ca wt % increased from 0.86 wt% NZ (natural zeolite) to (11.3 wt%, 14.15 wt%, and 23.48 wt%) of sonochemical and (11.82wt%, 13.95 wt% and 20.64 wt%) of the stirrer. The results demonstrated that Ca wt% by sonochemical dispersed at support surface (zeolite) more effective than stirrer. The alumina and silica content were significantly reduced inversely proportional to increased Ca. The highest sonochemical value of Si/Al was obtained at 4.49 and 4.46 at stirrer impregnation. The strength of the bronsted acid site increased proportionally to increase in Si/Al ratio. The higher Si/Al ratio leads to higher catalytic activity [30]. The more acidic the catalyst, the more active the catalyst obtained.

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