IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.16 No.2 (June 2015) 19- 29
ISSN: 1997-4884

University of Baghdad
College of Engineering

Preparation and Characterization of Nay Zeolite for Biodiesel Production

Ammar S. Abbas and Rowaida N. Abbas
Chemical Engineering Department, College of Engineering – University of Baghdad

Abstract

Iraqi kaolin was used for the preparation and characterization of NaY zeolite for biodiesel production via esterification reaction. Oleic acid was used usually as a typical simulated feedstock of high acid number for the esterification reaction.

The chemical composition for the prepared Nay zeolite is as following: $(Ca_2.6Na_1.K_{0.1})(Al_6.3Si_{17.7})O_{48}.16H_2O$, the silica to alumina ratio in the prepared catalyst was found equal to 2.6 and Na_2O content was 12.26 wt. %, with relative crystallinity equal to 147.4 % obtained by the X-ray diffraction. The surface area result shows that the prepared catalyst has 330 m^2/g. While, the measured pore volume by nitrogen adsorption was equal to 0.35 cm^3/ g. SEM images show notable differences between the kaolin crystal and prepared NaY crystal.

The effect of NaY zeolite, as a loaded catalyst in the esterification of oleic acid reaction did not show any significant change of oleic acid conversion for catalyst load more than 5 wt. %. The reused NaY zeolite is loses 31 % of its activity because of that the pores are filled with water and other organic molecules and that may cause poisoning the catalyst.

Key Words: NaY, zeolite, esterification, characterization, catalyst.

Introduction

The energy consumption in the global has been increasing steadily for a variety of reasons, which include enhancements in quality of life, population increase, industrialization, rapid economic growth of developing countries, increased transportation of people, goods, etc. [1].

In the recent years, there has been increased focus on global warming and the depletion of resources caused by the heavy consumption of fossil resources, have become major global issues. The use of biofuel such as biodiesel can help firmness this problem as biofuels are renewable sources of energy [2].

Biodiesel has gained international attention as a source of alternative fuel due to characteristics like high degradability, no toxicity, low emission of carbon monoxide, particulate matter and unburned hydrocarbons [3]. Biodiesel is a mixture of alkyl esters, contains 10 to 15% oxygen by weight and sulfur-free, it can be used in conventional compression ignitions engines, which need almost no modification. As well, biodiesel can used as heating oil and as fuel [4].

Catalysts investigated for the transesterification are either acids or bases, both homogeneous and heterogeneous, or they are enzymes [5]. Conventionally, commercial biodiesel produced by using traditional liquid base catalysts [6]. However, there is a considerable incentive for the substitution of liquid bases by solid bases for the following reasons: (a) energy intensive product/catalyst separation, (b) corrosiveness and (c) the costs associated with the disposal of spent or neutralized caustics [7]. In other words, the use of heterogeneous catalysts allows a more environmentally friendly process to be used for biodiesel production. In addition, the use of heterogeneous catalysts could enable the design of an efficient, continuous process and improve the economics of biodiesel production [8]. Furthermore, the use of heterogeneous catalysts do not produce soaps through free fatty acid neutralization [9], which simplifies the post-treatment (i.e. separation and purification) processes. Because of these advantages, research on the transesterification or esterification reaction using heterogeneous catalysts for biodiesel production has increased over the past decade [10].

Heterogeneous catalysts now being tried extensively for biodiesel synthesis. These catalysts are poised to play an important role in future for biodiesel production at industrial level[11].

The use of homogeneous catalysts leads to soap production. Besides, in the homogeneous process the catalyst consumed, thus, reducing the catalytic efficiency. This causes an increase in viscosity and the formation of gels. In addition, the method for the removal of the catalyst after reaction is technically difficult and a large amount of wastewater produced in order to separate and clean the products, which increases the overall cost of the process [12].

During homogeneous catalytic transesterification the glycerol produced is of low quality and requires lengthy process and distillation for purification [13]. All these processing increases the cost of the end-products: biodiesel and glycerin. Moreover, the homogeneous base catalyzed transesterification process encountered problems to handle multiple feedstock. On the other hand, heterogeneous catalytic transesterification process overcomes these problems because methanol or ethanol does not mix with solid heterogeneous catalyst. After the transesterification reaction, it is relatively easy to separate the catalyst from biodiesel and glycerol [14].

The heterogeneous catalytic transesterification is included under Green Technology due to the following attributes [15]: (1) the catalyst can be recycled (reused), (2) there is no, or very less, amount of wastewater produced during the process and (3) separation of biodiesel from glycerol is much easier.

The main advantages of the process described as the production of high-quality glycerol and no need for disposal of salts resulting from the catalyst. However, the overall economic advantages have to be proved in long-term running. Additional benefit with solid based catalyst is the slighter consumption of catalyst. As per studies, for production of 8000 tons of biodiesel, 88 tons of sodium hydroxide may be required [16], while only 5.7 tons of solid supported MgO is sufficient for production of 100,000 tons of biodiesel [17].

Heterogeneous catalyst offers easier production process, improve product quality, and reduce corrosion and toxicity problems. Furthermore, it can used for low quality feedstock, which contains high FFA [18].

Low-cost feedstock needs pretreatment (esterification) to remove FFAs before base catalyzed transesterification reaction. The esterification path is relatively simple reversible reaction as shown in equation 1.

… (1)

In the reaction (Eq. 1), FFA is converting to FAME. When homogenous acid (e.g., sulfonate acid, phosphorus acid and hydrochloric acid) used, esterification reaction is a process that FFA supply hydroxide and methanol supply proton without intermediate process. Different to homogeneous catalysis, heterogeneous catalytic is a process known to follow a carbonium ion mechanism. The mechanism of solid acid-catalyzed esterification consists of following steps as shown in Figure 1. Firstly, solid catalysts provided protons, and carbonyl carbon was protonated. Next, nucleophilic attack of CH_3OH on the carbonium ion formed a tetrahedral intermediate. Finally, FAME produced after proton migrated and the intermediate broke down, and proton was reformed [19].

The esterification reaction path is slightly different in various acidic species types. The whole reaction process is through proton-exchange. Tesser et al. [20] proposed a kinetic model based on the following hypotheses: (1) major part of the active sites are occupied by methanol in a protonated form, and the rest part are also occupied; (2) fatty acid, water and methyl ester reach proton-exchange equilibrium with the protonated methanol; (3) inside the resin particles, an Eley-Rideal mechanism occurs between protonated fatty acid and the methanol. Deviate from the mechanism shown in figure 1, steps of protonation of carbonyl carbon, nucleophilic attack, proton migration and breakdown of intermediate are undergoing in a proton exchange way.

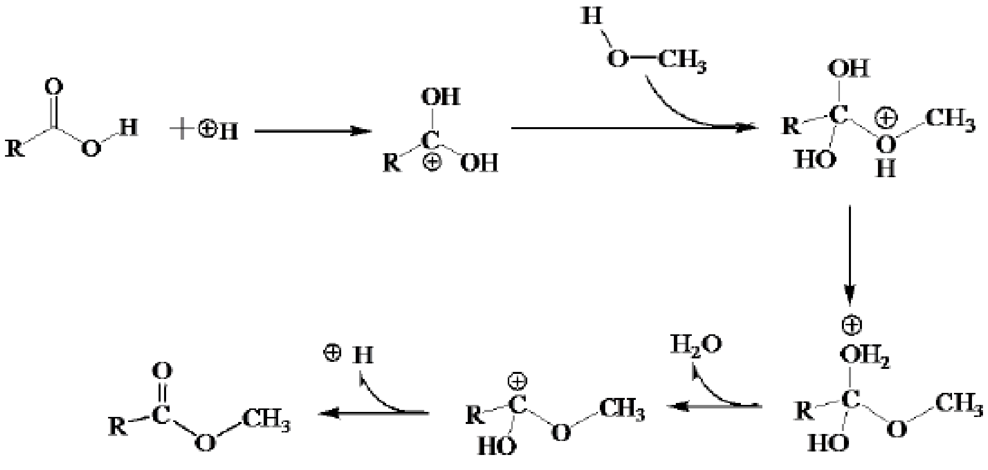

Fig. 1, Solid acid-catalyzed reaction mechanism of esterification [20]

The aim of this research is the preparation and characterization of NaY zeolite from Iraqi kaolin suitable for esterification of oleic acid. The characterization of the prepared zeolite catalyst includes composition, X-ray diffraction (XRD), surface area and pore volume and scanning electron microscopic (SEM). Finally, the prepared NaY will tested as a catalyst for the oleic acid esterification at selected conditions to study the load effect of catalyst and its age.

Experimental Work

Catalyst Preparation

Iraqi kaolin (chemical composition listed in table 1) sieved to a particle size less than 75µm.

Table 1, Chemical analysis of Iraqi kaolin

Component	Wt. %
SiO_2	49.64
Fe_2O_3	1.72
Al_2O_3	34.05
CaO	1.10
Na_2O	0.46
L.O.I.	12.28

The sieved kaolin was mixed with 40 % sodium hydroxide solution using (kaolin/NaOH = 1/1.5) and fused at 850˚C for 3 hours. 50 g of fused kaolin and 63 g of sodium silicate were pressed in 500 ml of de-ionized water under constant stirring at 50˚C for 1 hour by electric magnetic stirrer, and then the slurry with pH 13.3 was placed in 1000 ml glass jar and subjected to ageing at 50 ^{o}C for 24 hours in a programmable electrical furnace.

The product slurry crystallized at 100 ^{o}C for 48 h in a programmatic electrical furnace. The yield crystalline repeatedly washed with water until pH arriving to 11.7, and then the crystalline mass dried at 100 ^{o}C for 16 hours by using programmatic electrical furnace.

Catalyst Characterization

X-Ray Diffraction and X-Ray Florescence

X-ray diffraction and x-ray florescence analyses achieved in Department of Geological Science – College of Sciences in University of Baghdad.

Chemical Analysis

The percent of silica and alumina in prepared zeolite catalyst and the chemical analysis measured in State Company of Geological and Mineral – Ministry of Industry and Minerals.

Surface Area and Pore Volume

Determination of prepared catalyst surface area and pore volume obtained at Oil Development and Research Center-Ministry of Oil, using BET method by Thermo-Finnegan type apparatus.

SEM (Scan Electron Microscopy)

Scan electron microscopy achieved in Ministry of Science and Technology.

Esterification of Oleic Acid

The desired amount of catalyst (NaY zeolite) for every experiment was calcinated at 300 °C up to 3 hours to eliminate any possible amount of water.

The reactor (kept in water bath) was loaded with 30 ml of oleic acid (with specific gravity of 0.895) and mixed with the same amount of Iraqi commercial ethanol (88 wt. %), start agitation with 300 rpm to have a good mixing of the compounds and eliminate possible mass transfer problems.

The reaction mixture preheated to the reaction temperature and then addition a certain amount of NaY zeolite to ensure the desired catalyst load. After one hour the mixture reaction was taken and centrifuged for 10 min to improve the separation of the phases (catalyst, and other phases). Then, two to three drops of phenolphthalein was added to the organic phase and titrated with 0.2 molarity of NaOH in order to obtain oleic acid conversion, the equations for calculating conversion from each catalyst concentration (2, 5 and 10 wt. % NaY) are obtained as:

$$conv. = \frac{initial\ acid\ No. - organic\ layer\ acid\ No.}{initial\ acid\ No.} \ldots (2)$$

The acid number of oleic acid obtained according to ASTM D-664. The reactor setup details and the selected best conditions for the reaction for the esterification of oleic acid over NaY zeolite reported in previous work [21].

Results and Discussion

Characterization of Prepared Catalyst

X-Ray Diffraction and X-Ray Florescence

The purity of solid crystal measured by comparing the X-ray diffractgram pattern of sample with X-ray pattern of standard that can be obtained from international zeolite association [22].

X-ray diffraction pattern was determined for prepared NaY zeolite as shown in Fig. 2.

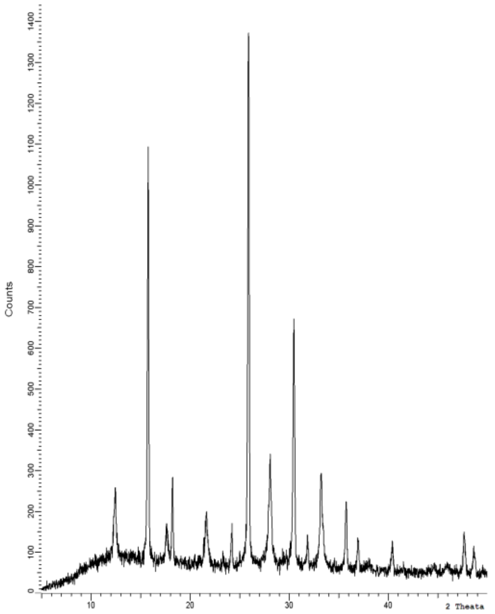

Fig.2, X-ray diffraction spectrum for the prepared NaY zeolite

A relative crystallinity of NaY zeolite was obtained by comparing the summation of integrated peak intensities of sample and reference, the values of the peak intensities were used for determination the area under the peaks of the strongest intensities [23], and the values of the area under the peaks were used for estimation of relative crystallinities % by equation 3 and it was equal to 147.4 % for the prepared NaY zeolite.

$$relative\ crystallinity\ of\ NaY = \frac{Sx}{Sr}\ X\ 100 \quad \ldots (3)$$

Where:

Sx= sum of integral peak intensities for sample NaY

Sr= sum of integral peak intensities for the reference NaY

The comparison between lattice spacing of prepared NaY zeolite with standard synthesis faujasite is shown in table 2.

Table 2, Comparison of lattice spacing, between prepared Catalyst and standard synthesis faujasite-Na

Prepared NaY		Standard synthesis faujasite Na	
Angle (2-Theta) deg.	d, spacing (Å)	Angle (2-Theta) deg.	d, spacing (Å)
12.47	7.09	12.59	7.02
18.24	4.85	18.65	4.36
21.64	4.1	21.80	4.07
25.91	3.4	26.64	3.30
28.07	3.17	28.27	3.15
32.7	2.7	32.04	2.7
33.31	2.5	33.56	2.66
35.74	2.5	35.90	2.53
37.0	2.4	37.72	2.4
40.4	2.23	40.3	2.23
44.11	2.05	44.36	2.04

The comparison between the lattice spacing shows that the prepared NaY zeolite is approximately comparable with the standard.

As shown in the result of XRD for the prepared NaY zeolite (Fig. 2), the ions such as calcium, sodium, potassium, aluminum, silicon, oxygen, may be exist in addition to water. The increasing in silica content, sodium content, potassium content increasing the acidity of the prepared catalyst. While increasing in calcium content decreasing the acidity of the catalyst.

The result of XRD shows that the prepared catalyst has an amount of moisture; therefore, drying needed before using the catalyst in the esterification reaction.

The chemical composition for the prepared catalyst is $(Ca_2.6Na_1.K_{0.1})(Al_6.3Si_{17.7})O_{48}.16H_2O$.

The positive ions such as Na^+, Ca^+ and K^+ are more rarely elements belonging to other columns of the periodic classification such as $La3^+$. Groups of atoms such as ammonium cation $NH4^+$ are also common structures which balance the negative charge of the zeolite framework. However, the nature of the cation determines the acidic catalytic power of the zeolite. The higher Brønsted acidity of a zeolite is obtained when the extra framework cation is hydrogen H^+ [24].

Chemical Analysis

The silica to alumina ratio in the prepared catalyst was found equal to 2.6, this result is in a good agreement with Davis and Davis [25] who reported that the ratio of silica to alumina in NaY is about 2.4. The silicon to aluminum ratio is one of the parameters that govern the zeolite's reactivity.

Based on the general formula of the zeolite the number of charged entities within the structure is closely related to the amount of aluminum atoms. The more AlO_4^- groups in the zeolite, the more negative charge that needs to be balanced and consequently, the more positive counter-ions. On top of assuring the electro-neutrality of the structure, those positive ions play an important role in the reactivity of the zeolite due to their location outside of the Al-O-Si framework. As explained above, their number is closely related to the number of AlO_4^- units and consequently to the Si/Al ratio. If the silicon-to-aluminum ratio has a strong influence on the reactivity (and catalytic power) of the zeolite, it also has a huge impact of its affinity towards water. Indeed, the higher Si/Al ratio, the more hydrophobic the zeolite and vice-versa [26].

Decreasing the Si/Al ratio increases the affinity of the zeolite towards water and in the case of a reaction between organic species catalyzed by the acid properties of the zeolite, water molecules are more likely to adsorb on the surface of the zeolite causing a deactivation of the catalyst and thus a drop in conversion. On the other side, increasing the Si/Al ratio decreases the affinity of water towards the catalyst which is more available to interact with organic species and efficiently play the role of acid catalyst for the organic reaction [24].

Na_2O content of prepared NaY zeolite was analyzed and it was 12.26 wt. %. This result is in agreement with the result published Mohammed and Dahyool [27]. They recorded that NaY zeolite contains approximately 12.5 wt% Na_2O. It is important for the fresh zeolite to contain very low amount of sodium, sodium decrease the hydrothermal stability of zeolite and it is also react with the zeolite acid sites and reduces catalyst activity. Sodium is commonly reported as the weight percentage of sodium or soda (Na_2O) on catalyst [28].

Surface Area and Pore Volume

The surface area of prepared catalyst was measured by nitrogen physical adsorption at liquid nitrogen temperature using the BET (Brunauer, Emmett, and Teller) method, and equal to 330 m^2/g.

A high surface area is obvious due to the micro porosity of prepared powdered zeolite [29]. An increase in surface area generally increases the catalyst activity.

Furthermore, high surface area usually has a high percentage of small pores, which are hydrothermally less stable than large pores [30].

Pore volume is a measure the void space in the catalyst. It is measured by nitrogen adsorption and expressed in cm^3/g. For the prepared catalyst, it was equal to 0.35 cm^3/g.

SEM (Scan Electron Microscopy)

SEM characterization techniques were performed on the kaolin and the prepared catalyst. SEM image of kaolin and NaY can be seen in figure 3 (a and b, respectively). It is clear the notable differences between the kaolin crystal and prepared NaY crystal.

Since that, the SEM picture is like the fingerprint of the prepared crystal, it is very convenient to compare the prepared NaY zeolite crystal with prepared NaY zeolite by Zaidi and Rohani [31].

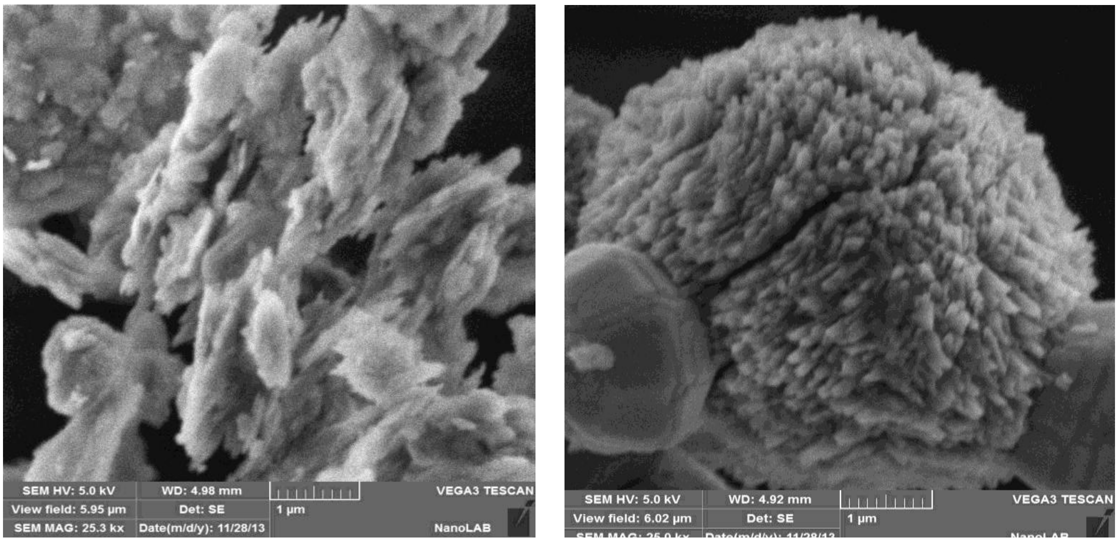

Fig. 3, SEM for Iraqi kaolin, prepared NaY zeolite and prepared zeolite

Effect of Catalyst Load on the Oleic Acid Conversion

The catalyst load effect on the oleic acid conversion at selected operating conditions shown in figure 4, which demonstrated the relationships between the oleic acid conversion and time at various catalyst load.

Generally, the oleic acid conversion increased with increasing the catalyst load. The reaction rate of esterification is directly proportional to the amount of a catalyst, due to the increase of active site numbers, so the catalyst used to enhance the reaction rate and conversion.

At catalyst weight present more than 5 wt. % the effect of catalyst load did not show any remarkable effect on oleic acid conversion, that may be due to increasing the surface area of zeolite catalyst that causes more accumulation of water in the pores as a result of the hydrophilic action of the zeolite [32]. This accumulation of water increasing backward reaction.

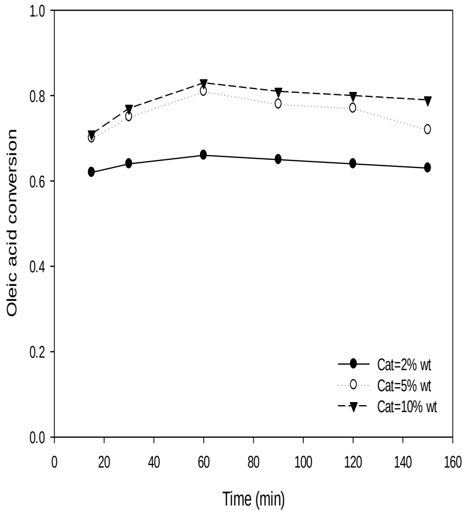

Fig. 4, Effect of catalyst load (NaY) on oleic acid conversion by esterification reaction, at the temperature 70° C

Marchetti and Errazu [33] reached to 26% conversion of oleic acid by using NaY zeolite with a molar ratio 6/1 and the amount of catalyst 2.6 wt. %, while the conversion in our work reached to 66 % at 2 wt. % of NaY and 70 °C, and this may be casus by the transition metals (such as Fe^{+2}), that found in Iraqi kaolin.

Catalyst Reuse

The solid catalyst needs regenerated when they used for a period in order to have good performance. Stopping the reaction and regeneration the catalyst is an expensive non-conventional operation [34].

The used NaY catalyst (for 3 hours) reused after drying it at 100 °C for 24 hours (without regeneration). The conversion decreased from 0.81 (for fresh catalyst and 1 hour reaction time) to 0.56 (for reused catalyst), as shown in figure 5.

The conversion decreases about 0.25 (about 31 %) due to poisoning of the catalyst by the trapped water and other reactant and product molecules.

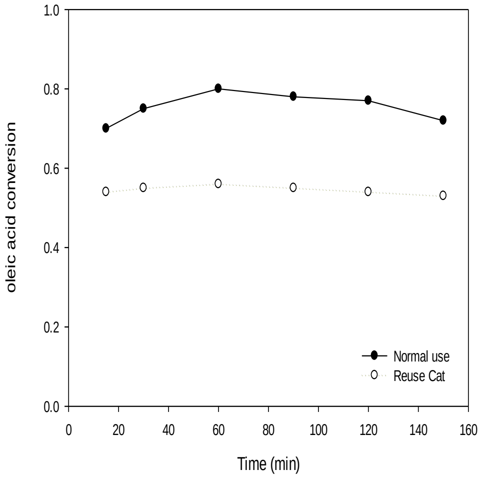

Fig. 5, Effect of the reaction time on oleic acid conversion by the esterification reaction using fresh and reuse NaY at the temperature 70°C

Marchetti et.al [35] using resins as a catalyst for esterification reaction. Temperature was set at 45 °C, the molar ratio of alcohol to oil was 6/1, and the speed of agitation was 200 rpm. The percentage of catalyst changed irrelevantly due to the some loss when the reactor washed and refilled; however, this variation has no effect on the equilibrium conversion allowing for the comparison of the results obtained. The conversion decreases from 0.8 for the fresh catalyst to 0.2 for first, second and third reuses.

Conclusions

According to the results obtained from this study, the following conclusions obtained:

1- From the results of x-ray diffraction pattern, silica to alumina mole ratio (2.6), sodium content (12.26 wt. %), surface area (330 m^2/g) and pore volume (0.35 cm^3/g) for the prepared NaY zeolite, and by the comparison SEM with the standard NaY zeolite, it is possible to say that the prepared catalyst in this work is matching the standard.
2- The conversion of oleic acid increasing with the amount of NaY zeolite catalyst from 2 to 10 wt. %.
3- The best NaY catalyst load weight ratio is 5% for esterification reaction of oleic acid.
4- The fresh NaY zeolite catalyst gives conversion as high as 81 % during only one hour reaction,
5- The reused NaY zeolite catalyst loss about 31 % of its activity for esterification reaction of oleic acid.

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