

Catalytic Performance and Characterization of Promoted K-La/ZSM-5 Nanocatalyst for Biodiesel Production

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ABSTRACT: The promoted K-La nanocatalysts supported on ZSM-5 zeolite were prepared via wetness impregnation method and tested for biodiesel production from soybean oil. The effects of different weight percentage of La, loading of K as a promoter and calcination conditions on structure and activity of catalyst were investigated. Results showed that the supported catalyst containing 7wt.% of La was promoted with 1wt.% of K is an optimal catalyst for biodiesel production. The best operational conditions were the CH₃OH/oil=12/1 molar ratio at 60°C with mechanical stirring 500 rpm for 3 h. The biodiesel yield reached 90% under the optimal operational conditions. It was found that K-La/ZSM-5 nanocatalyst have high basic sites and catalytic activity for biodiesel production. Characterization of catalysts was carried out by using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Temperature Programmed Desorption (TPD), X-Ray Diffraction (XRD), Fourier Transform-InfraRed (FT-IR) spectroscopy and N₂ adsorption-desorption measurements methods.

KEYWORDS: Biodiesel; Wetness impregnation; Calcination conditions; Operational condition; Characterization.

INTRODUCTION

With the increase of environment protection consciousness and decreasing of petroleum reserves, biodiesel, defined as the mono alkyl esters of fatty acids, has been the focus of a considerable amount of recent

research as an alternative renewable fuel. Fatty Acid Methyl Esters (FAMES), commonly known as biodiesel, are a nontoxic, biodegradable, eco-friendly and renewable substitute for common diesel fuel [1].

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Combustion of the biodiesel in engines causes pithy lesser emission of particulates, unborn hydrocarbons, carbon monoxide, carbon dioxide and SO_x than conventional diesel fuels. The general method for the preparation of biodiesel is transesterification reaction of oil and alcohol with homogeneous catalyst [1-4]. Commonly, biodiesel is produced using homogeneous acid and alkaline catalysts [5]. Most of the works have shown that the use of heterogeneous catalysts would result in high biodiesel yields, simpler and cheaper separation processes, a reduced water effluent load, and a higher grade of glycerol could be obtained. On the other hand, the main drawbacks are the high temperature and pressure, as well as the higher methanol to oil ratio needed for the transesterification reaction as compared with homogeneous systems [6-8]. A new trend in the preparation of biodiesel is to use "green" method based on heterogeneous catalyst [9, 10]. Although the solid phase catalytic methods are intensively studied, the industrial applications are limited. This fact offers that further research is necessary to solve current problems [11, 12]. Heterogeneous catalytic methods are usually mass transfer resistant, time-consuming and inefficient [13]. A variety of heterogeneous catalysts for the transesterification reactions were reported in the literature, including immobilized enzymes [14], calcium carbonate [15], alkali-earth metal compounds [15], sulphated zirconia [16], zeolites [19], alumina loaded with alkali metal salt [17-19], and calcium oxide loaded with lithium-ion [20]. Recent studies have also found functionalized mesoporous silica, such as tin-oxide-modified mesoporous SBA-15 [21], titanium-grafted mesoporous silica [22], and magnesium supported MCM-41 [23] effective for catalyzing transesterification reactions using a variety of triglycerides. Nanocatalysts have high specific surface and high catalysis activities may solve the above problems. They have become the focus of recent research [24, 25]. In general, the best catalysts must have several qualities i.e., catalyze transesterification and esterification, not be deactivated by water, be stable, do not give rise to leaching, be active at low temperature, and have high selectivity [26]. Thus far, the use of solid catalysts to produce biodiesel requires a better understanding of the factors that govern their reactivity. To improve the performance of these catalysts, it is essential to understand the correlations between acid and base

strength and catalytic activity. It is clear that the surface of these heterogeneous materials should display some hydrophobic character to promote the preferential adsorption of triglycerides and to avoid deactivation of catalytic sites by strong adsorption of polar by-products such as glycerol and water [27]. In the present work, novel La/ZSM-5 catalysts were prepared using the wetness impregnation method. The effect of the La ratio to support (wt.%), loading of promoter and calcination conditions on the catalytic performance were investigated. The effect of reaction variables, such as methanol to oil molar ratio, catalyst amount, reaction temperature and reaction time for biodiesel production were investigated. The prepared catalysts were characterized by FT-IR, TPD, XRD, SEM, TEM, and N_2 adsorption-desorption measurements methods.

EXPERIMENTAL SECTION

Catalyst preparation

All materials with analytical purity were purchased from Merck and used without further purification. At first, 5 g of ZSM-5 zeolite was washed with 30 mL of NaOH (2 M) for removal some atoms of Si in the framework of zeolite. In this media the ratio of Al/Si is < 6 and resulting is decreasing acidic property of zeolite. The obtained zeolite was dried at 100 °C for 2 h then heated at 600 °C for 4 h. The ZSM-5 was impregnated with an aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to generate a series of $x(\text{La})/\text{ZSM-5}$ catalysts ($x=2-10\text{wt}\%$). The catalysts were dried at 120 °C for 12 h after impregnation and then calcined in desired conditions. The promoted La/ZSM-5 catalysts were prepared with different amounts of KNO_3 to generate a series of promoted K-La/ZSM-5 catalysts. The promoted catalysts were dried in an oven (120 °C, 12 h) to give a material denoted as the catalyst precursor, subsequently calcined in a furnace to achieve the final catalyst.

Catalyst characterization

N_2 physisorption measurements

The specific surface area, total pore volume, and the mean pore diameter were measured using an N_2 adsorption-desorption isotherm at liquid nitrogen temperature (-196°C), using a NOVA 2200 instrument (Quanta chrome, USA). Prior to the adsorption-desorption measurements, all the samples were degassed

at 110 °C in an N₂ flow for 2 h to remove the moisture and other adsorbents.

Scanning Electron Microscopy (SEM)

The morphology of catalyst and precursor was observed by means of an S-360 Oxford Eng scanning electron microscopy.

Transmission Electron Microscopy (TEM)

TEM investigations were carried out using a Hitachi H-7500 (120 kV). The sample for TEM study was prepared by ultrasonic dispersion of the catalyst in ethanol. The suspension was dropped onto a carbon-coated copper grid.

Fourier Transforms Infrared (FT-IR) spectrometry

Fourier transform infrared (FT-IR) spectra of the samples were recorded using a Bruker Vector 22 spectrometer in the region of 400–4000 cm⁻¹ while the applied resolution was 1 cm⁻¹.

Temperature Programmed Desorption (TPD)

NH₃-TPD profile of ZSM-5 and La/ZSM-5 were recorded using a micromeritic TPD-TPR 290 system. The TPD analysis was performed using a mixture gas of 10%NH₃/90%He (v/v). The samples were heated from ambient temperature to 700 °C at a heating rate of 12 °C/min.

X-Ray Diffraction (XRD)

The XRD patterns of all the precursor and calcined samples were recorded on an Equinox 3000 (40 kV, 30 mA) X-ray diffractometer (Inel, France), using a Cu K_α radiation source (λ=1.542 Å) in the 2θ range of 5°-75°.

Transesterification reaction

The soybean oil was used in the transesterification reaction that provided from Mahidasht vegetable oil Company (Nazgol). The transesterification of 30 g oil was carried out in a 250 ml round bottomed flask fitted with a condenser and magnetic stirring system (reaction system). At first, the reaction system was heated to a selected temperature, when the mixture of methanol and the catalyst reached the desired temperature; oil was added with continuous stirring (300 rpm). After completion of the reaction, the solid catalyst was separated with filtration.

For the filtration test, the reaction mixture was filtered off after 20 minutes reaction time using a 0.2 μm PTFE filter. The obtained products were heated for remove excess methanol in T= 70 °C for 30 min then settled in a separating funnel. The upper phase consisted of fatty acid methyl esters (biodiesel) and the lower phase contained the glycerol as the by-product.

Catalytic test

The type and quantity of methyl esters in the biodiesel samples were determined using gas chromatography-mass spectrometry (GC Agilent 6890N model and Mass Agilent 5973N model) equipped with a Flame Ionized Detector (FID). A capillary column (HP-5) with 60 mm column length, 0.25 mm inner diameter and 0.25 μm film thickness was used with helium as the carrier gas. The temperature program for oven started at 50 °C and ramped to 150 °C at 10 °C/min. The temperature was held at 150 °C for 15 min and ramped to 340 °C at 10 °C/min. The holding time at the final temperature (340 °C) was 10 min. Also, the injector was used from kind Split/Splitless. The yield of biodiesel was calculated with equation (1):

$$y = \frac{\sum A - A_s}{A_s} \times \frac{C_s \times V_s}{m} \times 100 \quad (1)$$

Y=Yield, ΣA = total peak area of methyl ester, A_s = peak area of internal standard (methyl heptadecanoate), C_s = concentration of the internal standard solution, V_s = volume of the internal standard, m = mass of the sample

RESULTS AND DISCUSSION

Effect of La loading

A series of La/ZSM-5 catalysts with a different weight percent of La (2.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 wt.% based on the ZSM-5 weight) were prepared at calcination conditions: T=600 °C for 6 h and heating rate of 3 °C/min. All calcined catalysts were tested under same reaction conditions including methanol/oil=12/1, catalyst dosage 3wt.% of oil, reaction temperature 60 °C, the stirring rate of 500 rpm and reaction time of 3 h. The catalytic performance of all tested catalysts is shown in Fig. 1.

According to the obtained results, the catalyst containing 7wt.% of La showed the best catalytic performance for biodiesel production compared to the

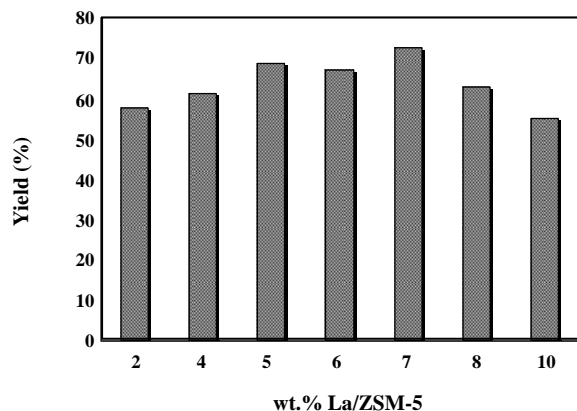


Fig. 1: Effect of La/ZSM-5 (wt.%) on the catalytic performance at reaction conditions: methanol /oil = 12/1, $T = 60\text{ }^{\circ}\text{C}$, the stirring rate=500 rpm and reaction time= 3 h.

other tested catalysts. This observation in catalytic performance can be explained as follows: Brønsted and Lewis acid sites are usually observed in calcined ZSM-5 zeolite [25]. The Brønsted acid sites are related to aluminum located in the framework of the zeolites, and Lewis acid sites are related to the Extra Framework Aluminum (EFAL) or distorted aluminum in the framework. EFAL is usually changing during the synthesis, calcination conditions and ion exchange process. Impregnation of lanthanum as an active metal phase to ZSM-5 zeolite provides bifunctional properties for ZSM-5, where showing both acid and basic sites [25]. Thus, lanthanum can remove stronger Brønsted acid sites located on the external surface and increases the basic property of the surface. So, the La/ZSM-5 catalysts were modified with lanthanum is very effective for the produce of biodiesel.

Effect of K loading on the catalytic performance

To investigate the effect of K loading on the catalytic performance of optimal La/ZSM-5 catalysts for biodiesel production, a series of K/La ratio were prepared (K/La= 0/5-6wt.%) and tested under the same reaction conditions (methanol/oil=12/1, catalyst to oil mass ratio of 3 wt.%, reaction temperature $60\text{ }^{\circ}\text{C}$, the stirring rate of 500 rpm and reaction time of 3 h). Fig. 2 shows the effect of K loading on the biodiesel yield and it indicates that the catalyst containing K/La=2wt.% has the maximum biodiesel production. Therefore, this catalyst was chosen as the optimal catalyst for the conversion of soybean oil to biodiesel. The promoted ZnO catalyst with Li has been

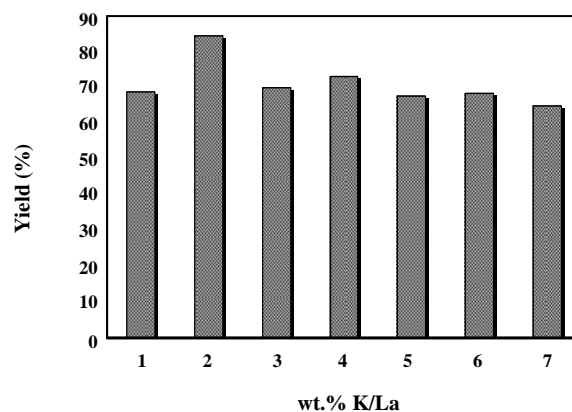


Fig. 2: Effect of K/La (wt.%) on the catalytic performance at reaction conditions: methanol /oil = 12/1, $T = 60\text{ }^{\circ}\text{C}$, the stirring rate= 500 rpm and reaction time=3 h.

prepared and using an impregnation method for the transesterification of soybean oil [28].

It was shown that the activity of these catalysts for the transesterification reaction is closely related to the amount of Li. Li/ZnO catalysts exhibited good catalytic activities, and the catalytic performance was greatly dependent on the loading amount of lithium. Similar conclusions were achieved by *Alonso et al.* [29] who studied a series of the catalyst with different amounts of lithium supported on CaO. It was found that a lithium amount above 4.5 wt.% is required to promote the catalytic activity of CaO in the transesterification of sunflower oil.

Effect of calcination temperature

As the calcination temperature increases, the molecules covering the surfaces are successively desorbed according to the strength of the interaction with the surface sites. The molecules weakly interact with the surfaces are desorbed at lower calcination temperatures, and those strongly interacting are desorbed at higher temperatures. The sites that appear on the surfaces by calcination at low temperatures are suggested to be different from those appearing at high temperatures. So, the optimal K-La/ZSM-5 catalyst precursor was calcined at 500, 550, 650 and 700 $^{\circ}\text{C}$ for 6 hours, separately (air atmosphere and heating rate of $3^{\circ}\text{Cmin}^{-1}$). Then, these calcined catalysts were tested at the same reaction conditions (methanol/oil=12/1, $T = 60\text{ }^{\circ}\text{C}$, the stirring rate of 500 rpm and reaction= time of 3 h). Moreover, the biodiesel yield of these calcined catalysts was measured, and the results were also presented in Fig. 3.

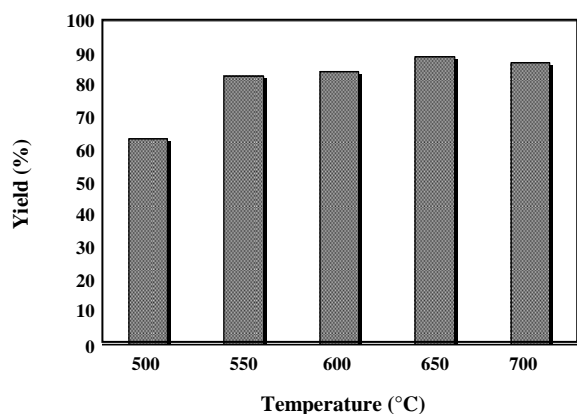


Fig. 3: Effect of calcination temperature on the catalytic performance of K-La/ZSM-5 catalyst at reaction conditions: methanol /oil = 12/1, T= 60 °C, the stirring rate of 500 rpm and reaction time of 3 h.

It was found that increases in calcination temperature increased the biodiesel yield at first, and decreasing above 650 °C. Calcination K-La/ZSM-5 catalyst at 650 °C is favorable for the interaction between ZSM-5 and active component, which it generates new active sites and phases on the catalysts surface, increases catalysts basicity and forms of new crystals. In this condition, it is suggested that a sufficient amount of active K_2O and La_2O_3 phases have been generated and modified surface. The nature of the surface basic sites varies with the severity of pre-treatment conditions. However, the surface sintering and the reduction of specific surface area, which leads to a reduction in catalytic activity, can react as the results of overheating of 650 °C [30, 31].

Effect of calcination time

Calcination condition is one of the important factors which can influence the texture, specific surface area and morphology of the catalyst. The influences of a range of calcination time were examined. At first, 5 samples of optimal K-La/ZSM-5 precursor were calcined separately in the air at 650 °C with a heating rate of 3 °C/min for 1, 2, 3, 4 and 5 hours, respectively. The biodiesel yield percents for these calcined catalysts in reaction conditions (methanol/oil= 12/1, T=60 °C, the stirring rate of 500 rpm and reaction time of 3 h) are shown in Fig. 4. As can be seen in Fig. 4, the optimum calcination time is 3 h at 650 °C with a heating rate of 3 °C/min and these conditions optimal K-La/ZSM-5 catalyst has the highest yield of biodiesel.

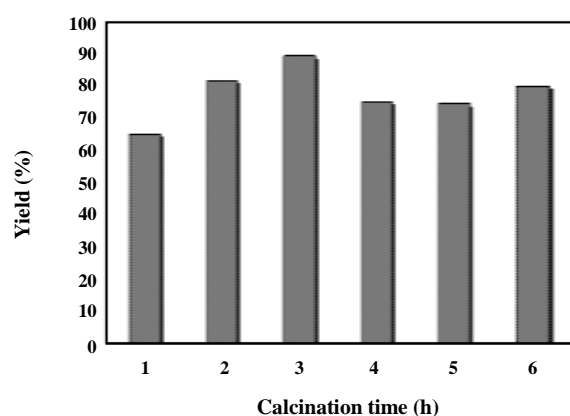


Fig. 4: Effect of calcination time (hour) on the catalytic performance of K-La/ZSM-5 catalyst at reaction conditions: methanol /oil = 12/1, T=60 °C, the stirring rate of 500 rpm and reaction time of 3 h.

The BET specific surface area and other surface characteristic results for the calcined catalysts at different calcination times are shown in Table 1. The results showed that the optimal catalyst which calcined at 650 °C for 3 h has a higher surface area value. As it mentioned, this catalyst showed a higher catalytic activity due to its higher BET surface area than the other prepared catalysts for biodiesel production. So, one of the origins of the higher activity of catalyst calcined in 3 h may be due to its higher BET surface area and pore volume than other prepared catalysts. As shown in Table 1 with the increase of calcining temperature, the catalyst gradually develops into crystal and its specific area increases. However, at high temperatures (>650 °C) the surface sintering and reduction of the specific surface area of the composite catalyst occurs, which leads to the decrease of the catalytic performance.

Characterization of optimal K-La/ZSM-5 catalyst was carried out using various techniques such as SEM, XRD and FT-IR methods. SEM images of both precursor and calcined K-La/ZSM-5 catalysts are displayed in Fig. 5 with irregular shapes.

SEM observations have shown differences in morphology of precursor and calcined catalysts. The image obtained from the catalyst precursor depicts several larger agglomerations of particles (Fig. 5a). After the calcination at 650 °C for 3 h and heating rate of 3 °C/min, the morphological and shape of the particle were more uniform and show that the agglomerate size in calcined catalyst is greatly reduced compared to the precursor (Fig. 5b).

Table 1: N_2 adsorption-desorption measurements of catalysts at different temperatures calcination ($^{\circ}C$) and precursor.

Calcination temperature ($^{\circ}C$)	S_{BET} (m^2/g)	D_p (nm)	V_p (cm^3/g)
500	165.3	19.13	0.48
550	167.1	19.17	0.50
600	173.1	19.28	0.52
650	183.3	19.56	0.55
700	179.4	19.34	0.53
precursor	145.3	16.23	0.43

S_{BET} : specific surface area, D_p : pore diameter, V_p : pore volume

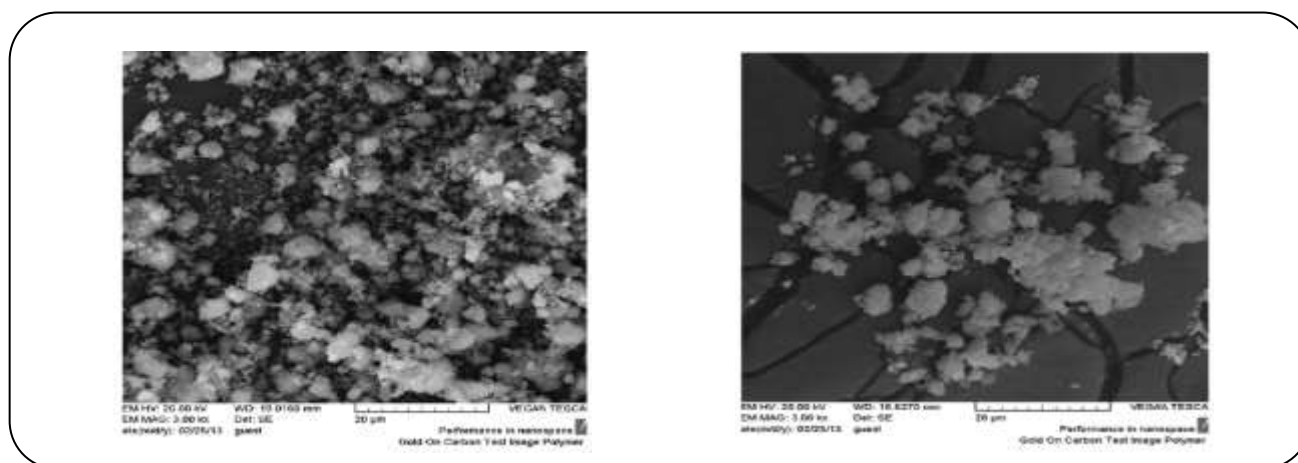


Fig. 5: The SEM images of K-La/ZSM-5 nanocatalyst, (a) precursor and (b) calcined catalyst.

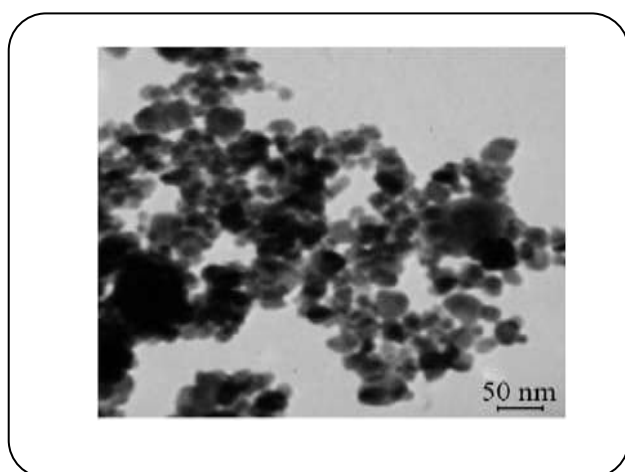


Fig. 6: TEM image of calcined K-La/ZSM-5 nanocatalyst.

Fig. 1S shows the XRD pattern of optimal K-La/ZSM-5 catalyst. The actually identified phases for this catalyst were the La_2O_3 (hexagonal), K_2O (cubic) and ZSM-5 (tetrahedral). From the XRD data and using the Debye-Scherrer equation, the crystallite size of optimal

K-La/ZSM-5 catalyst was calculated to be 43 nm [32]. The calcined K-La/ZSM-5 catalyst was characterized by TEM (Fig. 6).

According to this Fig, the crystal sizes were between 38–45 nm. This result confirmed the obtained results by using the Scherrer equation and SEM image. *Bancquart et al.* [33] compared the base-catalyzed activities of single metal oxides, La_2O_3 , MgO, CaO and ZnO, and the results confirmed that stronger basicity of the catalysts resulted in their higher activity for transesterification. *Sato et al.* [34] investigated the use of rare earth oxides catalysts and reported that rare earth oxides have similar basicity as CaO and that the strength of the basic sites of heavy rare earth oxides are dependent upon the radius of the rare earth cation. The basic properties of rare earth oxides are related to lanthanide contraction: the number and strength of basic sites of rare earth oxides increased with increasing radius of the rare earth cation. The basic property of K-La/ZSM-5 catalyst was evaluated (Fig. 2S). The strength of basic sites was deduced from the work

by Pasupulety *et al.* [35], where it was suggested that desorption temperature between 400-600 °C indicates basic sites of weak and medium strength, and desorption temperature range of 600-850 °C indicates strong basic sites. The catalytic activity of La/ZSM-5 catalyst in the biodiesel production increased with the addition of 2wt.% of K. At this media the K-La/ZSM-5 catalyst is more basic in comparison of La/ZSM-5 catalyst. The total amount of CO₂ desorbed for La/ZSM-5 catalyst is 1.1×10^{18} (atom/g). The peak in the 805 °C for K-La/ZSM-5 catalyst is desorption of CO₂ which was adsorbed on the basic sites. It can be seen that the total amount of CO₂ desorbed is 1.9×10^{20} (atom/g). The high basic sites of the catalysts enabled high yield biodiesel to occur. Also, when different K loading was used in the biodiesel production over La/ZSM-5 catalyst, it was possible to observe how promotion of catalyst with K, increased the basic strength and the number of basic sites of the La/ZSM-5, increasing also the catalytic activity for producing biodiesel. Sun *et al.* discussed the relationship between transesterification activity and surface basicity of La₂O₃/ZrO₂ catalyst and reported that the catalytic activities showed a correlation with their basic properties towards biodiesel production, which is that, the stronger basicity, the higher biodiesel yield was achieved. The La₂O₃ loaded on ZrO₂ was an active catalyst for the production of biodiesel from sunflower oil. After calcined at 600 °C for 4 h, the La₂O₃ catalyst loaded on ZrO₂ was found to be with the highest basicity and catalytic activity for the transesterification reaction [36]. FT-IR spectroscopy is used to get detailed information about the surface structure through the modes of vibration and results are displayed in Fig. 3S. The broadband at 3454 cm⁻¹ and 1636 cm⁻¹ is ascribed to the stretching and bending vibration of the OH groups of physically adsorbed water in the surface of catalyst that was chilled in an air atmosphere, respectively. The bands of hydroxyl groups of ZSM-5 zeolite are divided to terminal silanols (3740 cm⁻¹), outside the crystal lattice OH (3680 cm⁻¹) and hydroxyl groups at defect sites (3720 cm⁻¹) and the bridge OH as Al-Si-OH with the character Brønsted acid sites (3600-3650 cm⁻¹). The Lewis acid sites can be found in the region of 1490 cm⁻¹ and, the Brønsted acid sites in the 1540-1630 cm⁻¹ region [37]. The band at 844 cm⁻¹ is assigned to the Al-O-Al stretching mode, while the band in the range of 1095 cm⁻¹ is related to K₂O and La₂O₃

and the bending modes of Al₂O₃ [38]. Also, the band in the region of 440 cm⁻¹ can assign to Si-O-Si bending modes [37, 39]. The FT-IR spectra indicated that the surface of ZSM-5 was modified with La.

Effect of operating conditions

In biodiesel production, several process variables may influence the yield of biodiesel such as molar ratio of oil to alcohol and reaction temperature. The best combination of the process variables could save the production cost in an effective. To optimize the reaction conditions, the effects of these process variables were examined to evaluate the performance of optimal K-La/ZSM-5 nanocatalyst for the biodiesel production.

Effect of methanol to oil molar ratio on biodiesel yield

Methanol to oil ratio (molar ratio) is an important factor which affects the yield of the biodiesel [40]. To fully perceive the factors affecting the catalytic performance of optimal K-La/ZSM-5 nanocatalyst, a series of experiments were carried out at different methanol/oil from 9/1 to 12/1 molar ratios under the reaction conditions (T=60°C, the stirring rate of 500 rpm and reaction time of 3 h). The results are presented in Fig. 7.

Comparing the obtained results in Fig. 7 leads to the conclusion that in methanol/oil=12/1 the biodiesel yield percent increases. The biodiesel yield percents are varied by increasing methanol to oil ratio. It was observed that the feed ratio and mixing of feed play an important role in the transesterification of oil. It was necessary to stir the mixture to enhance the contact between reactants and active sites of the catalyst. According to the chemical dynamics, the transesterification could be accelerated by increasing the amounts of methanol. The high molar ratio of methanol to oil could enhance the conversion yield of biodiesel. The required molar ratio of methanol to oil was 3/1, in order to produce three moles of FAMEs from one a mole of triglycerides. In practice, the amount of methanol used to produce biodiesel is higher than the theoretical value. The stoichiometric molar ratio of methanol to oil was 3/1. But when the mass transfer was limited due to problems of mixing, the mass transfer rate seems to be much slower than the reaction rate, so the methanol/oil molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion and produce more methyl esters as a product. On the other

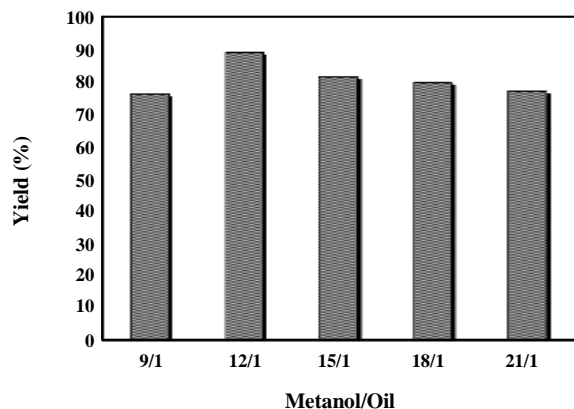


Fig. 7: Effect of oil/methanol on the catalytic performance of K-La/ZSM-5 nanocatalyst at reaction conditions: $T = 60\text{ }^{\circ}\text{C}$, the stirring rate of 500 rpm and reaction time of 3 h.

hand, increasing the amount of methanol reduces the concentrations of catalyst and reactant, which leads to delay of the reaction and aggravates recovery of solvents. The reaction was faster with a higher molar ratio of methanol to oil, whereas a longer time was required for the lower molar ratio to obtain similar conversion yields. However, it was laborious to recover solvent with a high ratio of methanol to oil, and emulsification could occur upon washing of products [39-43].

Effect of reaction time on biodiesel yield

Most of the studies have shown that reaction time significantly influence the transesterification reaction, especially the reactions catalyzed by heterogeneous catalysts [44]. To study the effect of reaction time on catalytic activity of optimal K-La/ZSM-5 catalyst, 4 series of experiments were carried out to investigate the performance of optimal K-La/ZSM-5 nanocatalyst with the variation in reaction time in the range of 1-5 h, at the optimal reaction conditions (methanol/oil=12/1, $T = 60\text{ }^{\circ}\text{C}$ and the stirring rate of 500 rpm). As shown in Fig. 8, increasing the reaction time has an influence on the biodiesel yield percent production. The biodiesel yield percent increased slightly by increasing the reaction time. Hence, the reaction time of 3 h is considered the optimum reaction time for biodiesel production [45, 46].

Increasing reaction time also increases the biodiesel yield, since the contact time between reactants increase, however, further increase of reaction time gave no significant effect on the yield of biodiesel since the equilibrium condition almost reached [47]. Also,

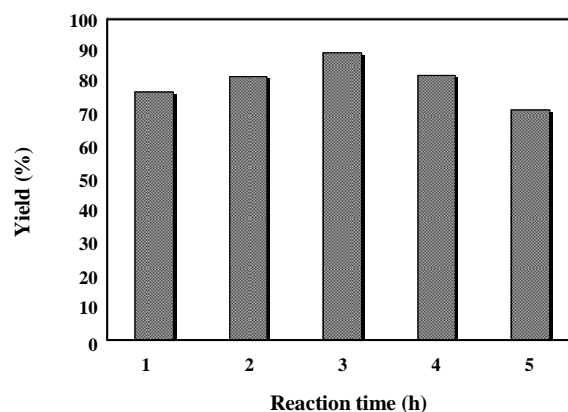


Fig. 8: Effect of reaction time on the catalytic performance of K-La/ZSM-5 nanocatalyst at reaction conditions: methanol/oil = 12/1, $T = 60\text{ }^{\circ}\text{C}$ and the stirring rate of 500 rpm.

it was observed that the reaction time of 3 h gave an optimum condition with a high yield of biodiesel.

Effect of reaction temperature on biodiesel yield

The effect of reaction temperature on the catalytic performance of optimal K-La/ZSM-5 catalyst studied at a range of temperatures between 45-65 $^{\circ}\text{C}$ under the same reaction conditions (methanol/oil=12/1, the stirring rate of 500 rpm and reaction time of 3 h). The results are presented in Fig. 9, showing that by increasing the reaction temperature, biodiesel yield percent increased.

In addition, for the reaction temperature at 60 $^{\circ}\text{C}$, the biodiesel yield percent was higher than the other reaction temperatures under the same reaction conditions. Previous studies [48-51] had proved that the yield of biodiesel could be increased by introducing an excess amount of methanol to shift the equilibrium to the right. A large amount of methanol is required to avoid the backward direction of transesterification from occurring. Besides, the reaction temperature was important in order to minimize the cost of production. When the reaction was carried out at 65 $^{\circ}\text{C}$, which is above the boiling point of methanol, the solvent vaporized and remained in the vapor phase in the reactor causing a reduction in the methanol in the reaction media. Because of high biodiesel yield percent, the temperature 60 $^{\circ}\text{C}$ was considered to be the optimum operating temperature. The reaction temperature had a significant effect on the reaction rate of transesterification. The oil conversion yield increased with rising temperatures because in the presence of heterogeneous nanocatalyst, the reaction mixture

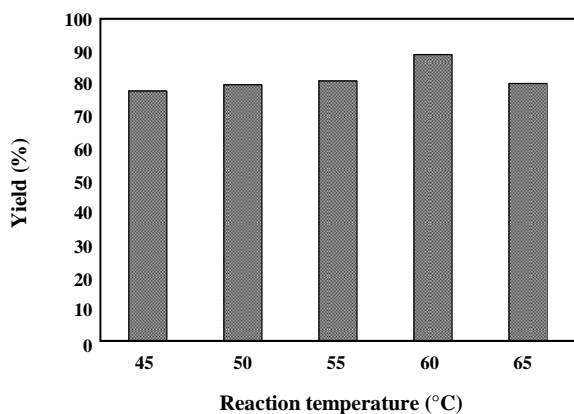


Fig. 9: Effect of reaction temperature (°C) on the catalytic performance of K-La/ZSM-5 nanocatalyst at reaction conditions: methanol /oil = 12/1, the stirring rate of 500 rpm and reaction time of 3 h.

constitutes a three-phase system, oil–methanol-catalyst, in which the reaction would be slowed down because of the diffusion resistance between different phases. However, the reaction rate can be accelerated at higher reaction temperatures and higher temperatures improved methanol dissolving and fastened the reaction. However, methanol vapor pressure rose with reaction temperatures with a rapid increase above 80 °C. Taking conversion rate, reaction equipment, and production operations into account, and a reaction temperature of approximately 60 °C was chosen for subsequent tests. Generally, a more fast reaction rate could be obtained at high temperatures, but at high temperatures, methanol was vaporized and formed a large number of bubbles, which inhibited the reaction on the three-phase interface. Therefore, the optimum reaction temperature was chosen 60 °C [41, 52]. The K-La/ZSM-5 nanocatalyst recovered and then is reused for the biodiesel production at optimal reaction conditions (T=60 °C, methanol/oil=12/1, the stirring rate of 500 rpm and reaction time of 3 h). As demonstrated in Fig. 10, after 4 times use, the biodiesel yield percent reached 88.1% for this nanocatalyst. The recovered catalyst was reused for other runs without significant degradation in catalytic performance.

Biodiesel kinematic viscosity and refractive index

Biodiesel viscosity and refractive index are very important parameters to appropriate with for its use in diesel engines. Because biodiesel is a blend of several

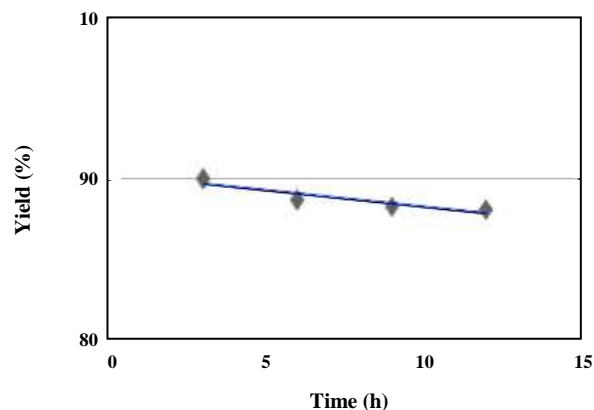


Fig. 10: The K-La/ZSM-5 catalyst regeneration study at reaction conditions: T = 60 °C, methanol /oil = 12/1, the stirring rate of 500 rpm and reaction time of 3 h

FAMES with each component contributing to the overall viscosity, it could be possible to find the relation between viscosity and the fatty acid methyl esters content of the biodiesel. Kinematic viscosity and refractive index value can be determinate by a fast, cheap and no destructive analysis with low-cost equipment [53,54]. As can be seen in Table 2, with increasing biodiesel yield, viscosity and refractive index decreased. In fact, it can be concluded that the viscosity and refractive index can be used as an important parameter in the production of biodiesel.

CONCLUSIONS

The K-La/ZSM-5 nanocatalyst was prepared and modified for biodiesel production. The best calcination conditions were found to be air atmosphere at 600 °C for 3 h with a heating rate of 3 °Cmin⁻¹. Due to fine particles and high specific surface area, the K-La/ZSM-5 (La=7wt.% and K=2 wt.%) catalyst exhibited the best catalytic performance for biodiesel production. The reaction conditions have a significant effect on the catalytic activity. The optimal operational conditions were found to be methanol to oil 12/1, a reaction temperature of 60 °C, and a reaction time of 3 h with mechanical stirring for 500 rpm. The characterization of catalysts was performed by powder XRD, TPD, TEM, SEM, and N₂ physisorption, also it is concluded that the preparation conditions has a marked effect on the morphology and texture of the catalysts.

Table 2: Effect of reaction temperature (°C) on the catalytic performance of K-La/ZSM-5 nanocatalyst.

Reaction temperature (°C)	Viscosity (mm ² /s)	Refractive index	Yield (%)
45	26.57	1.4642	78
50	25.31	1.4637	81
55	25.29	1.4635	82
60	25.24	1.4628	90
65	33.25	1.4639	80

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