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Biodiesel Production via Transesterification of Low Grade Cooking Oil over Heterostructure Nano Particles of Ni/Mg/Al$_2$O$_3$ Catalyst

N. M. Kamal, W. A. W. A. Bakar*, S. Toemen, R. Ali

Department of chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

P A P E R   I N F O

A B S T R A C T

Biodiesel which were synthesis from transesterification reaction in the present of heterogeneous base catalyst has been intensively studied over the last decades. This catalyst has an excellent result in producing high percentage conversions of biodiesel without further purification and cleaning process which contribute to the water pollution and high water content in biodiesel product. So, this study was conducted to synthesize and characterize series of heterostructure Ni/Mg/Al$_2$O$_3$ catalysts with different parameters to test their effectiveness towards the catalytic transesterification reaction. Series of Ni/Mg/Al$_2$O$_3$ catalysts were synthesized by wetness impregnation method supported on γ-alumina beads. Three parameters were studied include calcination temperatures, dopant ratios to base and numbers of alumina coating. The activity of the catalyst in transesterification reaction was evaluated at 65ºC of reaction temperature, 3 hours of reaction time, 6% w/w of catalyst loading and 1:24 molar ratio of oil to methanol. The potential catalyst was characterized by N$_2$ Adsorption Analysis, TEM (BIO-TEM) and CO$_2$-TPD. Meanwhile, the performance of the catalyst was evaluated using GC-FID. From the data obtained, Ni/Mg(20:80)/Al$_2$O$_3$ catalyst calcined at 800℃ and three times alumina coating have the highest weak and moderate basic sites that contribute to the highest percentage conversion of low grade palm oil to biodiesel compared to others. Besides that, BIO-TEM result showed that the particle was non-homogeneous shape with a mixture of square sheet and one dimensional heterostructure nano-rod particles was observed. The data obtained from CO$_2$-TPD and N$_2$ Adsorption Analysis (NAA) prove that high basicity of the Ni/Mg(20:80)/Al$_2$O$_3$ catalyst (2.80 mmol/g) and high surface area (125 m^2/g) had led to 78.53% of biodiesel conversion.

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1. INTRODUCTION

Depleting of fossil fuel due to its global usage has becoming a worldwide crisis. The demands of fossil fuels for transportations, industrial processes and power generations may lead to the total distinction of these most valuable energy resources [1]. To overcome the problem, new sustainable energy resources has been introduced, particularly by production of biodiesel from biomass, non-edible oil and animal fat are the best solutions and become one of the promising alternative energy [2].
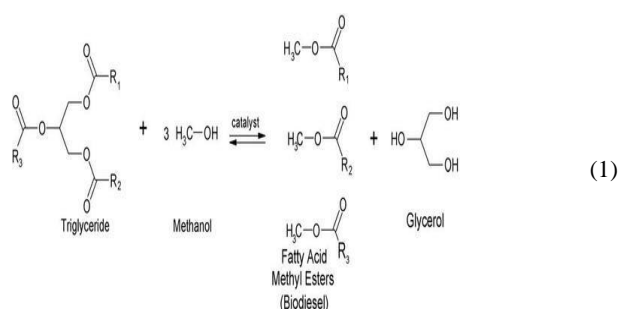
Biodiesel as one of alternatives fuel had been attracted researchers' and scientists' attention around the world due to the several advantages. Firstly, it was regard as a non-toxic and relatively produce a lower emission in contrast to petroleum based fossil fuel. Secondly, it was also eco-friendly in which it has no sulphur content that can cause acid rain formation [3]. Moreover, biodiesel has several good fuel properties such as good lubricity, carbon neutral and less emission of carbon dioxide in the atmosphere, a cetane number and cloud point which makes it volatile and easy to handle [4,5].

Biodiesel was synthesized from vegetable oils or animal fats and an alcohol, through a transesterification reaction [6]. This chemical reaction converts an ester into a mixture of esters of the fatty acids that makes up the oil. It was obtained from the purification of the mixture of fatty acid methyl esters (FAME) and the

*Corresponding Author Email: wazelee@kimia.fs.utm.my (W. A. W. A. Bakar)

catalyst was used to accelerate the reaction as given in Equation (1).

$$(1)$$

Previous studies suggested that the catalysts used in transesterification can be basic, acidic or enzymatic [7]. In industrial development, most common method to produce biodiesel is through transesterification of vegetable oil with methanol using liquid base catalysts such as NaOH, KOH and CH_3ONa [8, 9]. However, they are highly corrosive, and technically difficult to remove from the final product. Therefore, conventional homogeneous base catalysts need to be replaced by solid strong heterogeneous base catalysts, which are more environmentally friendly, low cost of production, less time consuming and can be recycle [10].

According to Kesic et al. [11] by introducing active species on porous support material like alumina gave high catalytic activity compared to the unsupported catalyst. A study reported that, the nature of alumina support played an important role on the catalytic activity. Among the support materials, Al_2O_3 shows higher activity, due to sufficient stability and dispersion properties and also enhanced surface reactants interaction [12].

It has been reported that the support materials can greatly affect the performance of catalysts. For example, immobilizing Ni nanoparticles inside the pore channels of order mesoporous alumina matrix by the confinement effect of the mesopores can prevent the sintering of Ni particles. However, among them, the addition of modifiers, including alkali, alkaline earth, and rare-earth metal oxides was widely reported to be an effective strategy which can provide more basic sites on the surface of the catalysts [13].

Therefore, the present study focus on introducing bimetallic catalyst $Ni/Mg/Al_2O_3$ used in transesterification of low grade cooking oil to biodiesel. The catalyst then was characterized to investigate the properties that lead to the highest performance in biodiesel production.

2. EXPERIMENTAL

2. 1. Materials   Low grade of palm cooking oil was purchased from the commercial market. Chemicals such

as $Ni(NO_3)_2.6H_2O$ (dopant), $Mg(NO_3)_2.6H_2O$(base), γ-Al_2O_3 3-5 mm (beads) and methanol (CH_3OH) were purchased from Sigma-Aldrich. All chemicals used were analytical reagent grade.

2. 2. Catalyst Preparation   In this study, aqueous incipient wetness impregnation method was applied to prepare series of catalysts. Nitrate salts were used as metal precursors since the solubility was high in water. 5 g of base (M' = Mg) was weighed in a small beaker and dissolved it in distilled water to obtained 5 mol/L of $MgNO_3$. The solution was stirred continuously for 15 minutes by a magnetic stirrer to homogenize the mixture at ambient temperature. The mixed catalyst solution was prepared for addition of second (M"= Ni) metal salt solution with base catalyst solution according to the molecular weight with different ratio (10:90, 20:80 and 30:70). After the solution was homogenized, 5g of Al_2O_3 with diameter of 4 mm to 5 mm was immersed in the solution mixture until the solution was evenly absorbed on the surface of the support. The support then was filtered and transferred onto glass wool. Next, the catalyst was aged in the oven for 24 hours at 80-90ºC. After that, it was calcined in the furnace at 600°C for 5 hours using a ramping rate of 5°C/min to eliminate all metal counter ions and water molecule. The similar procedure was repeated for all catalyst preparation at different calcinations temperature.

2. 3. Catalytic Activity   The catalytic activity of the potential catalyst was evaluated using the transesterification of low grade palm oil with methanol. Transesterification reaction was carried out in a three necked round bottom flask under refluxed with constant stirring. 6% w/w of catalyst loading with 1:24 ratio oil to methanol was added to the reaction mixture and heated at 65ºC for 3 hours. After the reaction was completed the mixture was distilled for 15 minutes to remove excess methanol. The reaction mixture was then centrifuged for 30 minutes at 3000 rpm. The top layer was the biodiesel and the lower phase was by-product (glycerol). Catalytic performance of the potential catalyst from the transesterification reaction was analyzed using GC-FID SP2560 (100 m x 0.25 mm x 0.20 um) with split ratio 100:1 and helium gas as carrier

2. 4. Catalyst Characterization   For NA analysis, Micromeritics ASAP 2010 was used to determine the surface area, pore volume and pore size of the potential catalyst. Prior to analysis, about 0.3g of the sample in powder form was degassed at 120°C in order to remove the previously adsorbed gases and evacuating the dead space by vacuum pump.

BIO-TEM specimen was prepared by dissolving small amount of the catalyst in powder form in appropriate amount of acetone in the 10 ml of glass

vial. The solution mixture was dispersed using ultrasonic bath for 2 hours to provide better dispersion before it has been dropped onto the surface of the carbon filmed copper grid. The specimen was then dried for 30 minutes at 80-90°C to let the evaporation of the solvent before analysis was started.

The CO_2-TPD was done using Micromeritics Autochem 2920 to study the amount of basic sites present on the surface of the catalyst. 40-50 mg of the catalyst was placed in a quartz U-tube and cleaned under helium flow for 20 mL/min at 150°C for one hour. The temperature was ramped down to 40°C and the CO2 gas was then flow continuously through the sample at 40°C for one hour. The gas flow was changed to He gas for another one hour at 80°C before subsequently ramped down to 40°C. The TPD was then carried out by ramp-up the temperature to 1000°C at 10°C/min and the response was recorded.

3. RESULTS AND DISCUSSION

3. 1. Catalytic Activity   The catalytic screening performance of Ni/Mg/Al$_2$O$_3$ is indicated in Table 1. The catalyst was prepared based on three different parameters which is numbers of alumina coating, dopant ratio to base and calcinations temperature. These three parameters were used in order to study the effect towards biodiesel conversion.

From the data displayed in Table 1, catalyst calcined at temperature of 700°C with 20:80 dopant ratios to base and two times alumina coating gave 78.53% biodiesel conversion which recorded the highest value compared to others. Overall, it can be seen that calcination temperature was the main parameter that has major effects in the biodiesel conversion. Calcination temperature affect largely on the structural and catalytic properties of the catalyst [14]. Therefore, the effect of the calcination temperature for Ni/Mg/Al$_2$O$_3$ catalyst on biodiesel conversion was investigated.
As illustrated in Figure 1, the data shows that as the calcination temperature increased, the biodiesel production was significantly increased. Mostly, at calcination temperature 600°C the biodiesel conversion was low compared to 700°C. This phenomenon occurred might due to the calcination temperature was not sufficient enough to activate the catalyst [15].

The study also reveals that 700°C was the optimum temperature where the biodiesel conversion recorded was the highest with 78.53%. Previous study reported that when catalyst showed the highest activity at certain calcination temperature might due to the improvement and the dispersion of metal oxide.

TABLE 1. Percentage conversion of low grade oil to biodiesel using Ni/Mg/Al$_2$O$_3$

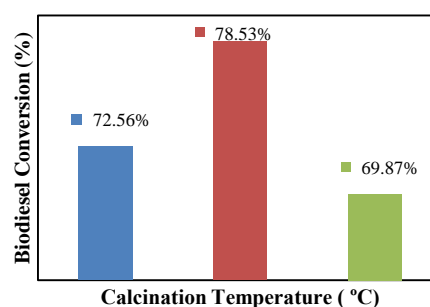| No of Coatings	Ratio Co-catalyst loading (wt%)	Calc. Temperature (°C)	Conversion (%)
One time	10:90	600	63.21
		700	69.37
		800	58.36
	20:80	600	61.25
		700	71.39
		800	62.35
	30:70	600	60.87
		700	68.32
		800	56.36
Two times	10:90	600	70.25
		700	71.32
		800	64.25
	20:80	600	72.56
		700	78.53
		800	69.87
	30:70	600	74.50
		700	73.50
		800	69.58
Three times	10:90	600	71.85
		700	71.52
		800	59.36
	20:80	600	70.31
		700	72.21
		800	70.51
	30:70	600	69.80
		700	70.39
		800	66.54

Figure 1. Effect of calcination Temperature of Ni/Mg(20:80)/Al$_2$O$_3$ with two times alumina coating

It also might be due to the changes that occurred on the surface structure (amorphous to polycrystalline structure) during the calcination process which lead to the generation of active species [16]. Furthermore, it strengthens the metal–support interaction and increase the number of medium strength basic sites on the catalyst surfaces [17].

After the calcination temperature of the catalyst was increased further to 800°C, the biodiesel conversion was significantly reduced. At calcination temperature 800°C, the biodiesel conversion was slightly lower which was 69.87% recorded. Some other studies reported a similar pattern. It has been reported that the performance of the catalyst was reduced due to the sintering effect and recrystallization metal oxide which gives in consequence decreasing of dispersion and catalyst activity, respectively [18].

Meanwhile, when dopant ratio to base was increased (as illustrated in Figure 2), the percentage conversion of biodiesel significantly decreased. Consistent with previous study which reported that, this phenomenon was due to the poor interactions between the active basic metal oxide and its support material [19]. The metals are easily migrated and sintered to form large metal particles which lead to the agglomeration on the surface of the catalyst. The agglomeration will cause a reduction in the active site and decreased the performance in catalytic activity [20].

The incorporation of nickel species as promoters could favour the Lewis basicity of the alumina supported catalyst, and mainly increase the strength basic sites, which could enhance the production of biodiesel [21]. Additionally, the increasing of the Ni species impregnated on the catalyst surface could also effectively hinder the formation biodiesel. It can be seen from the reducing of biodiesel conversion at 30:70 wt% of nickel to calcium.

For the effect of alumina coating, the present study discovered two times of alumina coating has been found as the optimum parameter for this effect. The conversion recorded slightly highest compared to others.
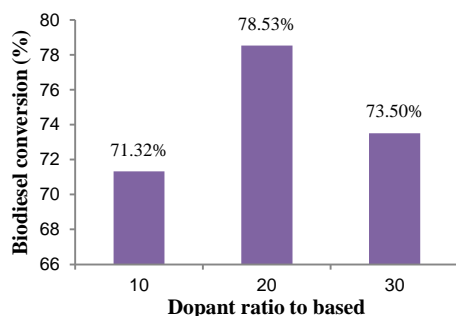
As illustrated in Figure 3, it shows that after three times alumina coating, the performance of the catalyst in transesterification reaction was decreased. This scenario occurred due to the limitation of the alumina beads to absorb the solution into its framework. Thus, two times of alumina coating was selected as the optimum parameter for this effect.

Table 2 shows the comparison between maximum yields of recent study with the previous reported research. As can be seen, all the alumina supported catalyst shows a good performance with the biodiesel yield was higher than 50%. The biodiesel yield was depending on the feedstock of the oil.

Mostly, the conversion was lower due to the low quality of the oil. For example, in this recent study the oil used was low grade cooking oil and the highest biodiesel yield was 75.20%. Another study that used waste cooking oil in the presence of $CaO/KI/Al_2O_3$ produced 83.08% biodiesel yield. Meanwhile, transesterification reaction that used high quality of oil like rapeseed oil with the presence of LiO supported in $CaAl_{14}O_{33}$ gave a higher biodiesel yield with 96%. Besides that, the supported catalyst used also differ in the characterization study especially in surface area, basicity and surface morphology. The differences in this factor may affect the biodiesel yield.
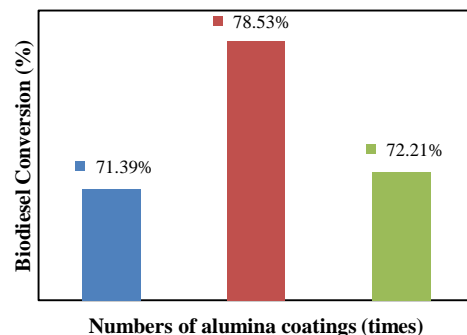

Figure 3. Effect of alumina coatings of Ni/Mg (20:80)/Al_2O_3 at calcination temperature of 700 °C

Figure 2. Effect of dopant ratio to base of Ni/Mg/Al_2O_3 with two times alumina coating at calcination temperature of 700°C

TABLE 2. Comparison between maximum yields of recent study with the other solid catalyst in previous research

Catalyst	Oil Feedstock	Yield (%)	References
$CaO/KI/Al_2O_3$	Waste cooking oil	83.08	[2]
LiO supported in $CaAl_{14}O_{33}$	Rapeseed oil	96.00	[22]
CaMgO alumina supported	Microalgae oil	75.20	[23]
Ni/Mg/Al_2O_3	Low grade cooking oil	78.53	Recent study

In order to study the relationship between catalytic activity and the characteristic of potential catalyst, Ni/Mg (20:80)/Al$_2$O$_3$ with 2 times alumina coating catalyst was selected. The catalyst was characterized to study on the surface area, surface morphology and the basic strength analysis at different calcinations temperature.

3. 2. N$_2$ Adsorption Analysis   Surface area of catalyst was recognized as an important factor in transesterification reaction. Thus, the activities of the catalyst calcined at different temperatures against their specific surface area were examined. A detail about the N$_2$ adsorption/desorption isotherms is illustrated in Figures 5. Meanwhile, the details on surface area, pore volume and pore sized at different calcinations temperature were recorded in Table 3.

From the results, Ni/Mg(20:80)/Al$_2$O$_3$ catalyst calcined at 700°C recorded the highest surface area of 139 m^2/g followed by 125 m^2/g for Ni/Mg(20:80)/Al$_2$O$_3$ calcined at 600 °C. As the temperature reached 800 °C the surface area reduced to 94 m^2/g.

It shows that, as the calcination temperature increased, the surface area decreased. The decreasing in surface area of the catalyst at high calcination temperature was probably because of the modification of the catalyst structure in which the particle started to agglomerate and form a crystalline structure [24]. It can be conclude that, when the catalyst calcined at high temperature, the particles also tend to agglomerate intensively. Meanwhile, when the calcination temperature increased the surface area of Ni/Mg(20:80)/Al$_2$O$_3$ decreased, but the pore diameter and pore size increased. This was attributed to the agglomeration of magnesium oxide species, as well as of nickel oxide.

Figure 4 compiles the N$_2$ adsorption-desorption isotherms of Ni/Mg(20:80)/Al$_2$O$_3$ calcined at 600-800°C. From the Figure above, the entire catalyst showed Type III isotherm which is associated with the non-porous or microporous with some presence of mesoporous properties and the presence of hysteresis loop. Besides that, the hysteresis loop can be classified as type H3 with denoted agglomerates and having slit-shaped pores [25].
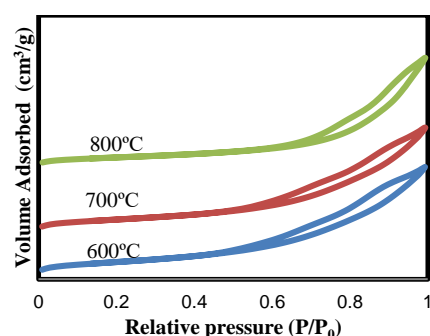

Figure 4. Nitrogen adsorption-desorption isotherms for Ni/Mg(20:80)/Al$_2$O$_3$ catalyst calcined at different temperatures of 600°C,700°C and 800°C for 5 hours

3. 3. Transmission Electron Microscopy (TEM)
TEM analysis was used to verify the morphology of potential catalyst calcined at different temperature. Figures 5a, 5b and 5c show the TEM images with magnification of x60.0k with 20 nm scale for Ni/Mg(20:80)/Al$_2$O$_3$ catalyst calcined at 600,700 and 800 for 5 hours with 2 times alumina coating.

As shown in Figures 5a-5c, the particle with in homogeneous shape which is a mixture of square sheet and one dimensional heterostucture nano-rod particles were observed. The images showed that the majority of the sample catalyst composed with smaller particles (rod shape) size in the range of 3-15 nm and some of the larger particles (square sheet like shape) with size of ~100 nm.

However, the size of the rod particles becomes larger when the catalyst was calcined at 800°C (Figure 5c). In addition, the irregular size (6-13 nm) of platelet shape was observed. The dark-field of TEM image of this catalyst shows the presence of agglomerated particles on the surface of the catalyst [26].
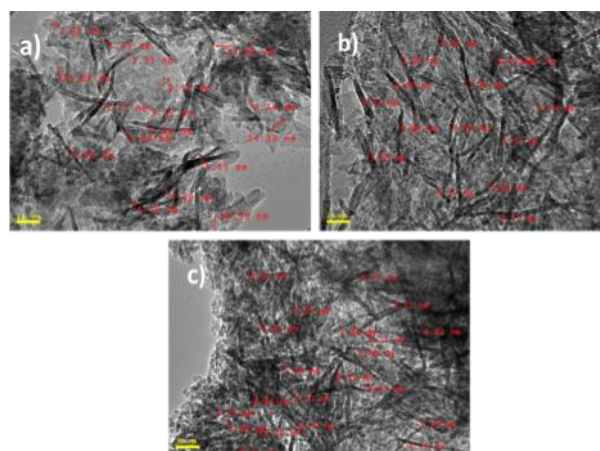
TABLE 3. BET surface area for Ni/Mg(20:80)/Al$_2$O$_3$ at different calcination temperatures and 3 times alumina coatings

Calcination temperature (°C)	BET Surface Area (m^2/g)	Pore volume (cm^3/g)	Pore size (A)
600	125	0.33	118
700	139	0.34	111
800	94	0.37	162

Figure 5. BIO-TEM image for Ni/Mg(20:80)/Al$_2$O$_3$ catalyst calcined at different temperatures of a)600°C, b)700°C and c) 800°C for 5 hours

From this observation, it can be concluded that when the calcinations temperature increased the surface of the catalyst was tending to agglomerate and reduce the surface area as reported in the BET results. This also contributes to the reducing of biodiesel conversion as reported in Table 1.

3. 3. CO_2-Temperature Programmed Desorption (CO_2-TPD)
Previous study found that an excellent transesterification process can be attributed to the presence of high basic sites on the surface of the prepared catalyst which can be measured using CO_2-TPD. The number of CO_2 molecules adsorbed per unit surface area can be considered as a measurement of the amount of basic sites on the surface of the catalyst [27].

The basic strength on the surface of the Ni/Mg (20:80)/Al_2O_3 catalysts shown in the Figure 6. It is illustrating that the CO_2-TPD plot for Ni/Mg (20:80)/Al_2O_3 catalyst at different calcination temperature range from 600 to 800ºC. The temperature range for CO_2 adsorption was related to the strength of the basic sites presence.

Furthermore, the temperature range whereby CO_2 was desorbed correlated to the strength of the basic sites. The adsorption of CO_2 from 50-200 ºC referred to the weak basic sites; while 200-400ºC referred to the moderate basic sites and temperature range of 400-800ºC correspond for strong basic sites [24]. The data summarized in Table 4 shows that the total amount of CO_2 desorbed (total basic sites) from the surface of the catalyst at calcination temperature 700ºC (2.80 mmol/g) showed the highest followed by 600ºC (2.79 mmol/g) and 800ºC. It can be concluded that, as the temperature of calcinations process increased, the total basic sites also increased. However, as the temperature reached to 800ºC, the total basic sites were dropped to 1.79 mmol/g compared to others.

The main factor that influenced transesterification activity is the alkalinity and the type of basic strength of the catalysts [28].
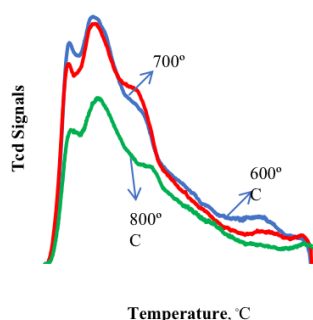
Figure 6. CO_2-TPD curves for Ni/Mg(20:80)/Al_2O_3 at calcination temperature of (a) 600°C, (b) 700°C and (c) 800°C, 5 hours and 3 times alumina coatings

TABLE 4. Total amount of CO_2 desorbed (total basic sites) from the surface of the catalyst at different calcination temperature

Calc. Temp. (°C)	Temp. at Maximum (°C)	Basic site (mmol/g)	Total basic site (mmol/g)
600	123.1	0.2274	2.79
	229.8	2.1077	
	830.2	0.0281	
	953.8	0.4257	
700	**124.0**	**0.1212**	**2.80**
	220.5	**2.5049**	
	812.7	**0.0216**	
	878.3	**0.1562**	
800	140.4	0.2870	1.79
	236.1	1.5009	
	960.2	2.984×10^{-13}	

From the data obtained, Ni/Mg (20:80)/Al_2O_3 catalyst calcined at 700°C has the highest weak and moderates basic sites that contribute to the highest percentage conversion of low grade cooking oil to biodiesel compared to others.

It is also shows the similar trend with the BET surface area analysis where, the temperature increased the surface area decreased. The data obtained from BET surface area analysis and the CO_2-TPD analysis proved that high basicity and high surface area of Ni/Mg (20:80)/Al_2O_3 catalyst led to the highest percentage conversion of low grade palm oil to biodiesel.

4. CONCLUSION

In conclusion the result reveal that Ni/Mg/Al_2O_3 calcined at temperature 700ºC, with ratio dopant to base 20:80 and 2 times alumina coating recorded the best performance in transesterification of low grade cooking oil to biodiesel. The calcination temperature was the highest influence parameter that contributed to the highest performance of the catalyst in transesterification reaction. In addition, this study confirmed that high surface area and high pore volume can improve the biodiesel performance in transesterification reaction. Based on surface morphology analysis in BIO-TEM indicated at calcination temperature 700 ºC the catalyst shows one dimensional heterostucture nano-rod particles. According to the CO_2-TPD results, the basicity of the catalyst functions as an important role in base-catalyzed biodiesel production. In this case Ni/Mg (20:80)/Al_2O_3 catalyst calcined at 700 ºC having the highest number of basic site which is determined as the prime contributor to the highest activity for the transesterification reaction.

5. ACKNOWLEDGEMENT

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Biodiesel Production via Transesterification of Low Grade Cooking Oil over Heterostructure Nano Particles of Ni/Mg/Al$_2$O$_3$ Catalyst

N. M. Kamal, W. A. W. A. Bakar, S. Toemen, R. Ali

Department of chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

چکیده

بیودیزل که از واکنش ترانس استریفیکاسیون در حال حاضر از کاتالیزور پایه ناهمگن ساخته شده است، در دهه های گذشته بطور گسترده ای مورد مطالعه قرار گرفته است. این کاتالیزور یک نتیجه عالی در تولید درصد بالا تبدیل بیودیزل بدون تصفیه بیشتر و فرایند تمیز کردن است که به کاهش آلودگی آب و محتوای آب بالا در محصول بیودیزل کمک می کند. بنابراین، این مطالعه به منظور تولید و دسته بندی کاتالیزورهای نانوساختار Ni/Mg/Al$_2$O$_3$ با پارامترهای مختلف برای تعیین اثربخشی آن ها در جهت واکنش کاتالیزوری ترانس استریفیکاسیون انجام شد. کاتالیزورهای سری Ni/Mg/Al$_2$O$_3$ با روش اشباع شدن رطوبت با دانه های γ-آلومینا سنتز شدند. سه پارامتر مورد مطالعه شامل دماسنج کلسیم، نسبت دوپینگ به مقیاس و تعداد پوشش آلومینا بود. فعالیت کاتالیزور در واکنش ترانس استریفیکاسیون در دمای 65 درجه سانتیگراد واکنش، 3 ساعت زمان واکنش، 6 درصد وزنی بر کیلوگرم بارگذاری کاتالیزور و نسبت مولی 1:24 روغن به متانول مورد بررسی قرار گرفت. کاتالیزور بالقوه با تجزیه و تحلیل جذب N$_2$، TEM(BIO-TEM) و CO$_2$-TPD مشخص شد. در همین حال، عملکرد کاتالیزور با استفاده از GC-FID مورد ارزیابی قرار گرفت. از داده های به دست آمده، کاتالیزور Ni/Mg/(20:80)/Al$_2$O$_3$ در دمای 800 درجه سانتیگراد کالسینه می شود و سه برابر پوشش آلومینا دارای بالاترین نقاط پایه ضعیف و متوسط هستند که به افزایش درصد تبدیل روغن نخل کم به بیودیزل در مقایسه با دیگران. علاوه بر این، نتایج BIO-TEM نشان می دهد که ذرات شکل غیرمعمول با مخلوطی از ورق مربع و ذرات نانو ذرات یک ساختار نانومتری مشاهده شده است. داده های به دست آمده از تجزیه و تحلیل جذب دی اکسید کربن (TPD و N$_2$ (NAA)نشان می دهد که پایه بالا Ni/Mg/(20:80)/Al$_2$O$_3$ کاتالیزور (2.80 mmol/g) و (125 m^2/g) سطح بالایی از سطح 78.53% درصد از تبدیل بیودیزل.

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