Preparation, characterization, kinetic and thermodynamic studies of MgO-La₂O₃ nanocatalysts for biodiesel production from sunflower oil

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Abstract

A series of MgO-La₂O₃ nanocatalysts were prepared via a co-precipitation method and used for biodiesel production from sunflower oil. The results showed that with increasing Mg/La weight percent the catalytic activity increases obviously. Also the results showed that the catalyst with Mg/La=60wt.% (based on weight of La) is an optimal nanocatalyst. The best operational conditions were the CH₃OH/oil=18/1 at 338 K with mechanical stirring 700 rpm for 5 h. Furthermore, the optimal nanocatalyst showed high catalytic activity for biodiesel production and the biodiesel yield reached 97.7% under the optimal conditions. Furthermore, this nanocatalyst was used for 4 runs in biodiesel production without significant decrease of catalytic performance. Also kinetic and thermodynamic of reaction has been studied in the presence of optimal nanocatalyst. From the kinetic and thermodynamic studies, $E_a=77.6 \text{ kJ.mol}^{-1}$, $A=3.5 \times 10^7 \text{ lit.mol}^{-1}\text{s}^{-1}$, $\Delta_r H^\theta=162 \text{ kJ.mol}^{-1}\text{K}^{-1}$, $\Delta_r S^\theta=0.54 \text{ kJ.mol}^{-1}\text{K}^{-1}$ were obtained. Characterization of catalysts was carried out by using scanning electron microscopy (SEM), X-ray diffraction (XRD), temperature programmed desorption (TPD), Fourier transform-infrared spectroscopy (FT-IR) and N₂ adsorption–desorption measurement methods.

Keywords

Biodiesel; kinetic; thermodynamic; operational conditions; nanocatalyst

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1. Introduction

The high energy demand in the industrialized world as well as the pollution problems caused due to the use of fossil fuels make it increasingly necessary to develop a new renewable energy source. Biodiesel is a suitable alternative renewable fuel for diesel engines. It has played an earthshaking role in easing global pressures associated with diminishing fossil fuel reserves, easing down greenhouse gas emissions and climate change [1-4]. Biodiesel can be produced from fats or triglycerides in vegetable oils through a process called transesterification of an acid and base catalyst by using a homogeneous or heterogeneous catalytic process [5]. Fig. 1, shows the overall stoichiometry for transesterification of triglycerides in oil with alcohol in the presence catalysts. The stoichiometry requires 3 mol of alcohol and 1 mol of triglyceride to give 3 mol of fatty acid esters and 1 mol of glycerine. Where R_1 , R_2 and R_3 are alkyl chains derived from fatty acids and R_4 is the alcohol alkyl chain [6,7].

Fig. 1 the transesterification reaction

Homogeneous base catalysts such as KOH and NaOH showed a high catalytic activity in the transesterification to produce fatty acid methyl ester irrespective of their basic [8]. However these homogeneous catalysts lead to an almost complete conversion of triglyceride and yield of biodiesel facile catalyst recovery the use of a heterogeneous catalyst is more desirable [9]. Heterogeneous catalysts can be separated easily from reaction products. It yields high conversion with low reaction temperature and long reaction time. Nevertheless, ethanol can prevail in regions where it is less expensive than methanol, due to its easier production and accessibility.

The process is called methanolysis, when the used alcohol is methanol [10,11]. Many kinds of basic catalysts suggested for the transesterification including alkali metal oxides and also mixed metal oxides for high activity of catalyst. Alkaline earth metal oxides such as CaO, calcium methoxide and MgO have been shown to have excellent catalytic activity and stability for the production of biodiesel. Mg-Al mixed oxides and analogues with other divalent (Ca, Zn) and trivalent cations (La, Ga), prepared from mixed hydroxides with hydrotalcite have been reported as good basic catalysts could be used for biodiesel production. Especially, Mg–Al hydrotalcite and Mg-Al-Zr mixed oxide have been successfully applied to biodiesel synthesis [3, 12-14]. Mixed oxides of magnesium or lanthanum such as Zr/La₂O₃, CaO-MgO, CaO-La₂O₃, Zr/MgO, were also found to be promising solid catalysts for the transesterification reaction [15-18]. The superlative active catalyst based on Mg having the high basic site concentration that was calcined at 993 K for 4 h [19]. The aims of this work were to investigate the effects of different Mg/La weight percent and calcination temperature on catalytic performance for biodiesel production. Further results are also reported the effects of operational conditions such as CH₃OH to oil ratio, reaction temperature on the catalytic performance of MgO-La₂O₃ catalysts. In addition, the kinetic study for determination of activation energy, pre-exponential coefficient of the reaction using the Arrhenius equation and thermodynamic constants including: ΔG , ΔS and ΔH have been investigated. Characterization of catalysts was carried out by using SEM, XRD, TPD, FT-IR and N₂ adsorption–desorption measurement methods.

2. Experimental

2.1. Catalyst preparation

All the catalysts tested in this study, were prepared using a co-precipitation procedure. In the co-precipitation method, aqueous solutions of Mg(NO₃)₂.6H₂O (1 M) and La(NO₃)₃.6H₂O (1 M) with different weight percent were premixed and the resulting solution heated to 343 K in a

round bottomed flask fitted with a condenser. Aqueous Na_2CO_3 (1 M) was added drop wise to the mixed nitrate solution with stirring while the temperature was maintained at 70 °C until pH 12.0 was achieved. The resulting precipitate was then left in this medium for 20 min and the aged suspension was then filtered and washed several times with warm distilled water. The precipitate was then dried in an oven (353 K, 16 h) to give a material denoted as the catalyst precursor which was, subsequently calcined in static air in a furnace to give the final catalyst. This catalyst was labeled as $\text{MgO-La}_2\text{O}_3$.

2.2. Characterization of sunflower oil

The sunflower oil was provided from Iranian Nazgol Company, and its characterization parameters are shown in Table 1. The Cannon–Fenske Routine viscometer (Cole-Parmer Co., US) in a glycerin bath fixed at specified temperature ± 1 K which can be used for high viscosity measurements was employed to measure kinematic viscosity variation of samples according to ASTM D445 (Standard test method, 2012) and EN 14214 standard test method. In the present work, density of samples was measured by Anton Paar DMA 4100 M device. The refractive index for biodiesel and used oil were measured by refractometer D-22976 model with an accuracy of ± 0.001 at 313 K (The refractive index should be read to at least four decimal places). The refractive index measurements were conducted 4 times for each sample, and the results were averaged.

Table 1. Composition and characterization of used sunflower oil	
Physical propertie	values
Density at 298 K (gcm^{-3})	0.9240
Acid value (mg KOHg^{-1})	0.10
Alkali value (mg KOH g^{-1})	194.91
Mean molecular weight (gmol^{-1})	863.47
Refractive index at 313K	1.4649
Kinematic viscosity at 313K (cSt)	24.58

2.3. Transesterification of sunflower oil with methanol

The transesterification of 10 g oil was carried out in a 250 ml round bottomed flask fitted with a condenser and magnetic stirring system (reaction system). The operation conditions was as follows: methanol/oil molar ratio of (3/1, 6/1, 9/1, 12/1, 18/1, 21/1), catalyst/oil weight ratio of 2–5 wt.% reaction temperature (323–343 K) under stirring by a magnet at 700 rpm . A detailed of procedures has been provided elsewhere [16].

2.4. Catalytic tests

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 detailed description of the experimental setup and procedures has been provided elsewhere [1].

2.5. Catalyst characterization

2.5.1. X-Ray diffraction (XRD)

The XRD patterns of all samples were recorded by Inel EQUINOX 3000 (40 kV, 30 mA) X-ray diffractometer, using a Cu K α radiation source ($\lambda=1.542$ Å) and a nickel filter in the 2θ range of 5°-70°.

2.5.2. N₂ adsorption-desorption measurements

The specific surface area, the total pore volume and the mean pore diameter were measured using a N₂ adsorption-desorption isotherm at liquid nitrogen temperature (-196 °C), using a NOVA 2200 instrument (Quantachrome, USA). Prior to the adsorption-desorption measurements, all the samples were degassed at 110 °C in a N₂ flow for 3 h to remove the moisture and other adsorbates.

2.5.3. Scanning electron microscopy (SEM)

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

2.5.4. Temperature programmed desorption (TPD)

TPD profile of MgO–La₂O₃ nanocatalysts were recorded using a micromeritic TPD–TPR 290 system. The TPD for each sample (100 mg) was performed using a mixture gas of 10%CO₂/90%He (v/v). The samples were heated from 473 to 1373 K at a heating rate of 10 K min⁻¹.

2.5.5. Fourier transform infrared spectroscopy (FT-IR)

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

3. Results and discussion

3.1. Effect of Mg/La weight percent

To understand the influence of Mg/La wt.% on the catalytic performance, a series of Mg/La catalysts with different weight percent of Mg/La (Mg/La =10, 20, 30, 40, 50, 60, 70, 80 and 90) were prepared at the following calcination conditions: T=823 K, 4 h and heating rate of 5 Kmin⁻¹. All prepared catalysts were tested under the same reaction conditions including: methanol/oil =15/1, catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h, the results are shown in Table 2. According to the obtained results, the catalyst with Mg/La=60 wt.% showed the best catalytic performance for biodiesel production. Thus, this catalyst was chosen as the optimal catalyst for the conversion of oil to biodiesel. As can be seen in Table 2, with increasing biodiesel yield, viscosity and refractive index of biodiesel

were decreases. In fact, it can be concluded that the viscosity and refractive index can be used as important physical parameters in the production of biodiesel.

Table 2. Effect of Mg/La wt.% on the catalytic performance			
Mg/La wt. %	viscosity	refractive	Yield (%)
10	19.59	1.4650	18.8
20	9.97	1.4620	36.5
30	6.65	1.4592	59.5
40	6.23	1.4573	68.3
60	3.74	1.4453	91.4
70	3.98	1.4492	88.2
80	4.24	1.4522	84.8
90	5.25	1.4542	73.2

Reaction conditions: CH₃OH/oil =15/1, catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h

Characterization of the basic property of Mg-La catalysts were carried out by CO₂-TPD technique. Usually, two desorption peaks are observed in the CO₂-TPD profiles of catalysts, as shown in Fig. 2; there are in the low and high temperatures. At this media the Mg-La catalyst (Mg/La=60 wt.%) is more basic in comparison of Mg-La (Mg/La=10 wt.%) catalyst (Fig.2). The total amount of CO₂ desorbed for Mg-La (Mg/La=10 wt.%) is 2.4×10^{19} (atom g⁻¹). Also it can be seen that the total amount of CO₂ desorbed for Mg-La (Mg/La=60 wt.%) is 6.8×10^{19} (atomg⁻¹). The high basic sites of the catalysts enabled high yield biodiesel to occur. Also, when different Mg loading were used in Mg-La catalyst, it was possible to observe how promotion of catalyst with increasing of Mg wt.%, increased the basic strength and the number of basic sites of the Mg-La (Mg/La=60 wt.%), increasing also the catalytic activity for producing biodiesel.

Fig 2. CO₂-TPD profiles of Mg/La=10wt.% and Mg/La=60wt.% catalyst

The preparation of a promoted Li catalyst with MgO for biodiesel synthesis has been investigated by optimizing the catalyst composition and calcination temperatures. The results show that the formation of strong base sites is particularly promoted by the addition of Li, thus resulting in an increase of the biodiesel synthesis. The catalyst with the Li/Mg molar ratio of 0.08 and calcination temperature of 823K exhibits the best performance. The biodiesel conversion decreases with further increasing Li/Mg molar ratio above 0.08, which is most likely attributed to the separated lithium hydroxide formed by excess Li ions and a concomitant decrease of BET values [20].

Sato et. al [21] 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 is 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. Sun et. al [22] 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 La_2O_3 loaded on ZrO_2 was an active catalyst for the production of biodiesel from sunflower oil. After calcined at 823 K for 4 h, the La_2O_3 catalyst loaded on ZrO_2 was found to be with highest basicity and catalytic activity for the transesterification reaction. Our obtained results from CO_2 -TPD is confirm with these results. A comparative study on the activity of $\text{MgO-La}_2\text{O}_3$ and MgO and La_2O_3 to produce biodiesel was conducted. The MgO catalyst was used for biodiesel production at 533 K and the biodiesel yield reached 98% at 533 K, this reaction temperature is high for biodiesel production and it is uneconomical reaction condition in comparison the reaction temperature of $\text{MgO-La}_2\text{O}_3$ catalyst (338 K) and biodiesel yield is 97 %. The results from TPR and BET analysis are shown that there is an interaction between Mg and La species (synergic effect) in the $\text{MgO-La}_2\text{O}_3$ catalyst, which resulted is high basicity, high BET surface area and high catalytic activity in biodiesel production []. The La_2O_3 catalyst was used for biodiesel production at 453 K, also it is high reaction temperature and the biodiesel yield reached 97 % in this reaction temperature [23].

3.2. Effect of calcination temperature

The activity of the catalyst was explicitly related to its specific surface area and crystalline structure [24]. In order to investigate the effect of calcination temperature, 5 samples of the optimal Mg-La (Mg/La=60wt.%) catalyst precursor were heated for 4 h (in the air atmosphere and heating rate of 5 K min^{-1}) at 723, 773, 823, 873 and 923 K, separately. Then, these calcined catalysts were tested at the same reaction conditions ($\text{CH}_3\text{OH/oil} = 15/1$, catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h). According to the results are shown in Table 3, increasing in calcination temperature increased

the biodiesel yield at first, and decreasing it above 873 K. The catalyst calcined at 873 K showed the highest activity with > 96% yield of biodiesel.

Table 3. The effect of calcination temperature on yield of biodiesel

calcination temperature (K)	viscosity	refractive	Yield (%)
723	5.70	1.4579	68.5
773	5.38	1.4575	71.8
823	3.74	1.4453	91.4
873	3.46	1.4474	96.2
923	4.55	1.4497	81.1

Reaction conditions: CH₃OH/oil =15/1, catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h

The surfaces of material are covered with carbon dioxide, water, and in some cases, oxygen as they are handled in air also in calcination procedure the phases of precursor converted to oxides phases that they are active sites for reactions. To have basic sites exposed on the surfaces, calcination at high temperatures is required. Beside of changing in phases of catalyst, removal of water and carbon dioxide, rearrangement of surface and bulk atoms occurs during calcination, which changes the number and nature of the basic sites. Therefore, the optimum calcination temperature varies with the type of reaction. As the calcination temperature increases until to optimum temperature, the molecules covering the surfaces are successively desorbed according to the strength of the interaction with the surface sites. The sites that appear on the surfaces by calcination at low temperatures are suggested to be different from those appearing at high temperatures. If simple desorption of molecules occurs during pretreatment, the basic sites that appear at high temperatures should be strong. However, rearrangement of surface and bulk atoms also occurs during calcination, which may change the number and nature of the surface basic sites with increasing the calcination temperature these results confirm with CO₂-TPD profiles in Fig. 2. Catalyst activity is a function of its specific surface area, base strength and base site concentration. High specific surface area, strong base strength and high concentration of base

sites are characteristics of an active transesterification catalyst. The surface density of base sites, which is a combination of surface area and overall number of base sites, represents a relevant parameter to explain the catalytic behavior in transesterification reactions when different metal oxide solids show similar numbers of strong and very strong base sites [25].

4. Effect of reaction conditions

Here, the effects of the several parameters such as the molar ratio of methanol to oil, time and temperature reaction and the amount of the catalyst on the yield of biodiesel were also investigated.

4.1. Effect of feed molar ratio

The stoichiometric ratio for the transesterification of with methanol requires 3 mol of methanol and 1 mol of oil as an equilibrium reaction. An excess of methanol is able to promote the conversion of oil to biodiesel [26]. The effect of methanol/oil molar ratio (feed molar ratio) has been studied at the same reaction conditions such as: catalyst dosage=3wt.% (based on weight of oil), reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h and the results are presented in Table 4. As shown in table 4 the yield of biodiesel increases with increasing the molar ratio of methanol to oil also when the molar ratio of methanol to oil was 3/1 the yield of biodiesel is only 31.7 %. Increasing the molar ratio of methanol to oil from 3/1 to 18/1 caused the yield of biodiesel reach to 96.9 %. Enhancing the methanol/oil molar ratio between 12/1 and 18/1, the growth rate of yield of biodiesel becomes not high. The higher molar ratio of methanol to oil increases the cost of reaction and the separation is also hardly. Hence, the most result is obtained for a methanol/oil molar ratio of 18/1.

Table 4. Effect of feed molar ratio of on yield of biodiesel.

CH ₃ OH/Oil	viscosity	refractive	Yield (%)
3/1	6.93	1.4623	31.7
6/1	6.71	1.4603	47.3
9/1	5.44	1.4551	71.7
12/1	3.59	1.4493	95.2
15/1	3.46	1.4474	96.2
18/1	3.31	1.4443	96.9
21/1	3.73	1.4498	93.4

Reaction conditions: catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h

The ratio methanol/oil influence the refractive index and viscosity of the produced biodiesel. The refractive index and viscosity of the biodiesel were decreased with the increasing of methanol/oil molar ratio (Table 4).

4.2. Effect of catalyst wt.% (catalyst dosage)

Also, the catalyst amount used in transesterification influence the reaction rate significantly though it doesn't change the equilibrium conversion for reversible reactions [24]. Interestingly, as seen in Table 5, by increasing percent of weight MgO-La₂O₃ catalyst (catalyst/oil) from 1% to 3% wt.%, the yield of biodiesel reached to substantial increase, noticeable point of this plot is reduced as the yield of biodiesel with further increase in catalyst amount (>3wt.%). A possible explanation is that at higher catalyst amount leads the reaction mixture becomes increases the viscosity, which could resist the mass transfer in the liquid–liquid–solid system [27]. Therefore, 3wt.% catalyst/oil with the biodiesel yield 96.9 % was found to be an optimum catalyst amount for the present transesterification reaction of sunflower oil with methanol.

Table 5. Effect of catalyst wt.% on yield of biodiesel

% wt. catalyst	viscosity	refractive	Yield (%)
1	5.41	1.4556	71.9
2	4.18	1.4515	86.2
3	3.31	1.4443	96.9
4	4.09	1.4509	87.6
5	4.33	1.4523	83.5

Reaction conditions: CH₃OH/oil =18/1, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 4 h

4.3. Effect of the reaction temperature

Heterogeneous catalysts, due to the phase difference from reagents, usually needed high temperature and pressure and longer reaction period to yield the significant conversion, of a similar kind reaction conditions demand complicatedly designed costlier reactor which in turn may increase the biodiesel production cost [1,57]. The temperature reaction has an important influences in transesterification reactions. The transesterification reaction rate can be hastened at higher reaction temperature. In this study, The Optimum condition reaction temperature for reaching to maximal yield of biodiesel in percent MgO-La₂O₃ catalyst was determined by performing the transesterification of sunflower oil in the temperature range of 323–343 K. Table 6. Below 343 K the yield of biodiesel increased with the temperature. The yield of biodiesel was 79.1 % at 323 K. When the reaction temperature reached 338 K, the 96.9 % of yield of biodiesel was obtained. Higher temperature results in more frequent collisions of methanol and triglyceride molecules, and the reaction becomes faster. When the reaction temperature was over the boiling point of methanol, somewhat of methanol evaporated from the reaction system, and the reaction was difficult controlled [6]. Thus, the temperature range of 323–338 K is more suitable for the present transesterification reaction (Table 6).

Table 6. Effect of the reaction temperature on yield of biodiesel.

reaction temperature K	viscosity	refractive	Yield (%)
323	5.35	1.4550	72.3
328	4.79	1.4532	80.6
333	4.23	1.4519	85.7
338	3.31	1.4443	96.9
343	3.84	1.4501	92.7

Reaction conditions: CH₃OH/oil =18/1, catalyst dosage 3 wt.% of oil, the stirring rate of 700 rpm and reaction time of 4 h

4.4. Effect of the reaction time

Reported the transesterification reaction is normally very slow at the beginning due to the immiscibility of the methanol and oil [28]. Table 7, shows the effect of reaction time on the biodiesel production from 1 to 6 h, CH₃OH/oil =18/1, catalyst dosage 3 wt.% of oil, reaction temperature 338 K and the stirring rate of 700 rpm. When the reaction time was 5 hours the biodiesel yield reached 97.7%. The results show that transesterification of sunflower oil with methanol is able to occur fast initially and gradually reach the equilibrium in 5 hours. When the time was over 5 hours, the biodiesel yield changed a little. Hence, 5 hours is considered the optimal reaction time for this reaction. As shown in Table 7, the yield of biodiesel was increased with decreasing of viscosity and refractive index.

Table 7. Effect of the reaction time on the yield of biodiesel

reaction time (h)	viscosity	refractive	Yield (%)
1	6.62	1.4598	51.3
2	5.21	1.4545	74.9
3	3.87	1.4503	92.5
4	3.31	1.4443	96.9
5	3.24	1.4433	97.7
6	3.33	1.4445	96.5

Reaction conditions: CH₃OH/oil =18/1, catalyst dosage 3 wt.% of oil, reaction temperature 338 K and the stirring rate of 700 rpm

The optimal catalyst containing 60 %wt of Mg based on La and was calcined at 873 K for 4 hours used four many runs in the transesterification reaction at reaction conditions: $\text{CH}_3\text{OH}/\text{oil} = 18/1$, catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 500 rpm reaction time of 5 h . Also the yield of biodiesel reduced from 97.7 to 95.3 % after fourth run. (Fig 3). In general, it seem with consecutive use of catalyst decrease active catalytic sites that appropriate with the loss of active species on the catalyst surface and covered surface by heavy product such as glycerol [3] . Unfortunately, the reusability of the catalyst decreased quite gradually, and after 7 runs yield of biodiesel was down from 97.7 % to 66 % (Fig 3).

Fig. 3 Recycling experiments of $\text{MgO-La}_2\text{O}_3$ based catalysts, $\text{CH}_3\text{OH}/\text{oil} = 18/1$, catalyst dosage 3 wt.% of oil, reaction temperature 338 K, the stirring rate of 700 rpm and reaction time of 5 h

5. Catalyst characterization

In this study, structure and feature of $\text{MgO-La}_2\text{O}_3$ catalyst was characterized by different techniques such as BET, SEM, FT-IR and XRD.

5.1. Analysis Brunauer–Emmet–Teller (BET)

All catalyst samples were degassed at 383 K in a N₂ flow for 4 hours for removal any adsorbed molecules from the pores and surfaces. Table 8 depicts the effects of calcination temperature and calcination time on the Surface area and porosity of MgO–La₂O₃ catalyst. The specific surface area, and also pore volumes and mean pore diameters were measured by BET and BJH methods, respectively. As indicated in Table 8, the MgO–La₂O₃ catalyst was calcined at 873 K for 4 h shows the highest specific surface area, pore volume and pore diameter. As is well known, Mg-La catalyst without calcination is partially hydrated and carbonated to form (Mg-La)₂(OH)₂CO₃ which are inactive. So, optimal calcination temperature and time to achieve maximum yield of biodiesel (97.7 %) is 873 K for 4 h. According to previous reports, there is relationship between the calcination temperature, surface area and the catalytic activity for mixed metal oxides (MMOs). Also, the catalytic activity and surface area of catalyst was decreased at higher calcination temperature [12,29]. Results in Table 8 shows, calcination of catalyst at 973 K for 4 h leads to a decrease in the BET surface areas, pore volumes and pore diameters. Also based on results in Table 8, all calcined catalysts are in the mesopores stat. BET analysis are shown the specific surface area, pore volume and pore diameter of catalyst was decreased, and so the yield of biodiesel reduced from 97.7 to 95.3 % after fourth run.

Table 8. Surface area and porosity data for MgO–La₂O₃ catalysts at different calcinations conditions

calcination temperature (K)	S _{BET} (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	PD (nm)
723	116.3	0.2345	15.79
773	124.5	0.2398	15.95
823	135.6	0.2457	16.04
873	151.7	0.2954	17.75
923	147.0	0.2698	17.31
973	139.0	0.2486	16.09
Before fourth run	138.7	0.2930	17.25
Before calcination	99.7	0.2012	15.01

S_{BET}: specific surface area

PD: pore diameter

PV: pore volume

5.2. X-Ray diffraction (XRD)

Powder X-ray diffraction (XRD) method was used for identification the phase and crystallite size of the MgO–La₂O₃ catalyst. The XRD patterns were recorded by a Philips X' Pert (40 kV, 30 mA) X-ray diffractometer, using a Cu K α radiation source ($\lambda=1.542$ Å) and a nickel filter in the 2 θ range of 5°-70°.

The XRD patterns of calcined MgO–La₂O₃ catalysts at 873 K for 4 hours, precursor (uncalcined) and catalyst after 4 cycle reused are shown in Fig. 4. The precursor was largely found to be amorphous by XRD. The presence of amorphous phase in the XRD patterns of these precursor makes the other phases undetectable, and this is because of iron hydroxide and carbonate phases curve an in Fig. 4a. After calcined MgO–La₂O₃ catalysts (curve b in Fig. 4b) at 873 K, new diffraction peaks of MgO at 2 θ (35-40 °, 40-45 °, 60-65 °, 60-65 °), La₂O₃ (2 θ = 26.0, 29.0, 29.8, 39.4, 52.0, 53.7, 55.3, 55.7, 60.3, 62.1, 72.0, 73.3, 75.2 and 79.0°) with different crystal structures emerges. This result is agreement with previous reported [12,16,30,31]. The identified phases for the calcined catalyst were MgO (cubic crystalline phase) and La₂O₃ (hexagonal phase). According to Scherer equation " $D=K \lambda/\beta \cos\theta$ " the average particle sizes was obtained with the calculation of the parameters of the tallest peaks.

Fig. 4 X-ray diffraction pattern of the MgO—La₂O₃ catalyst: precursor (4a), calcined at 873 K for 4 hours (4b) and after a fourth run (4c)

Where $K=0.9$, D represents crystallite size, λ represents the wavelength of Cu K $_{\alpha}$ radiation, and θ represents the corrected half-width of the diffraction peak. Hence, the crystal size of the MgO—La₂O₃ catalyst was calculated by this equation and they are in nano dimension (20 nm) [32].

4.3. Scanning electron microscopic (SEM) analysis

Scanning electron microscopic (SEM) analysis was remarkable method for showing the surface morphologies and the determination of particle sizes of heterogeneous catalysts. Fig 5. Shows SEM images of precursor and calcined MgO-La₂O₃ catalyst that was calcined at 873 K for 4 h. As Fig. 5b reveals, the average particle size of calcined MgO-La₂O₃ catalyst is 21.1 nm which is confirm with calculated particle sizes from Debye-Scherrer equation in XRD pattern. As seen from SEM images in Fig 5b, after calcinations of catalyst, the porosity and homogeneity of

surface and number of active sites was increased with remove any adsorbed species and hydroxides.

Fig. 5 Scanning electron microscope images of MgO–La₂O₃ catalyst: before calcination (a) and (b) after calcinations

Reported that the calcined catalyst show higher catalytic activities and selectivities in different organic reactions than their uncalcined counterparts as they contain a higher number of basic sites [32,33]. Fig. 5a and 5b demonstrate before and after calcination of MgO-L₂O₃ catalyst, respectively. The experiments demonstrated that calcination temperature influences on the morphology, active sites of catalyst and yield of biodiesel. After calcination the nano size provides shorter paths to access active sites for molecules which reduce the internal diffusion significantly. Moreover, the larger BET surface area presents much more accessible active sites than uncalcined catalyst.

4.4. Fourier transform infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was used to identify the function groups and feature of $\text{MgO-La}_2\text{O}_3$ catalyst. The samples were scanned in the range of 400 to 4000 cm^{-1} . Fig. 6 shows FT-IR spectras of the catalyst $\text{MgO-La}_2\text{O}_3$ at different states. The peak at 1445 cm^{-1} can be attributed to the stretching vibration of surface CO_3^{-2} group, which suggested small amount of CO_2 was adsorbed on the surface of Mg-La precursor on spectra (6a) the bands at 1238 and 1163 cm^{-1} are assigned to the stretching vibration of Mg-O-La groups [17]. The broad peak near 3400 is assigned to the formation of $-\text{OH}$ group on catalyst surface [10]. The 1466 and 1367 cm^{-1} bands are related with the bending vibration of the metal oxides group such as magnesium oxide and La oxide (Fig. 6b). The FT-IR spectrums of catalyst were calcined at 873 K for 4 hours and after being re-used Fig. 6b, Fig. 6c, respectively, and look identical to each other. As can be seen, they have similar adsorption bands. Two new bands at 2930 and 2835 cm^{-1} emerge. These new bands are assigned to the stretching vibration of composition containing of mixed metal oxides [17,30].

Fig. 6 FT-IR spectrums of the MgO–La₂O₃ catalyst: uncalcined (6a), calcined at 873 K for 4h (6b) and after fourth run (6c)

5. Kinetic and thermodynamic studies of MgO–La₂O₃ nanocatalyst for biodiesel production

Transesterification of vegetable oil with methanol is believed to proceed via a stepwise, reversible reaction catalyzed by acid or base catalysts [34]. Generally; the heterogeneously catalyzed transesterification is a very complicated reaction involving a liquid-liquid-solid (three phase) system where reactions occur on the surface of the solid catalyst. Therefore, the chemical reaction rate on the catalyst surface, the external and internal mass transfer rate of reactant and product molecules, the absorption rate of reactant molecules on active sites of the catalyst, and the desorption rate of products could impact the overall rate. One or more of these rates may be the limiting rate [35-38]. Generally, the mechanism transesterification consists of three consecutive and reversible reactions, that triglycerides (TG) reacts reversibly with methanol to produce diglycerides (DG), which further reacts reversibly with methanol to generate monoglycerides (MG), and finally, monoglycerides reacts reversibly with methanol to give to monoalkyl esters (biodiesel) and glycerol [39-41]. Equations 1-3 summarize the reaction of transesterification. Where k_1 to k_3 are the constant rate involved in the kinetics of reactions in biodiesel development.

According to previous reported pseudo-first and pseudo-second order reactions for the transesterification reaction of sunflower oil have been proposed [40-41]. In the remainder of this paper we evaluated the comparison between models prediction pseudo first order and pseudo

Second order. The main goal of the present study is to validate the adequate model of experimental data for obtaining kinetic constants (activation energy “E_a”, frequency factor “A”).

5.1. Pseudo-first order kinetics model

The kinetic model used is based on the following assumptions:

(i) The transesterification chemical reaction occurred in the oil phase and therefore sunflower oil was considered as the limiting reactant. (ii) Transesterification reaction was conducted in a huge excess of methanol (C_{MeOH} is constant). (iii) The slowly step and determinative rate is reaction triglyceride with one molecule of methanol to form diglyceride (DG) and one molecule of methyl ester. Equation 1. Therefore, based on the above assumptions, the transesterification reaction rate of triglyceride can be expressed as:

$$r = \frac{-d[TG]}{dt} = k[TG][CH_3OH] \quad (4)$$

$$k' = k[CH_3OH] \longrightarrow r = \frac{-d[TG]}{dt} = k'[TG] \quad (5)$$

Integrating both sides by taken initial concentration of triglyceride as TG₀ at time t= 0 and concentration after time 't' as TG_t, on integration the Eq. (5) can be written as Eq. (6).

$$\Rightarrow \ln[TG_0] - \ln[TG] = k' \cdot t \quad (6)$$

Since the TG concentration is related to the conversion degree of TG, X_{TG}:

Where is expressed as:

$$X_{TG} = \frac{[TG_0] - [TG]}{[TG_0]} \gg 1 - \frac{[TG]}{[TG_0]} \quad (7)$$

$$\Rightarrow [TG] = [TG_0] [1 - X_{TG}]$$

(8)

With replacement Eq. (8) into Eq. (6) can be written as Eq. (9).

$$\Rightarrow -\ln(1 - X_{TG}) = k'.t \quad (9)$$

Where k is the rate constant of triglyceride (TG), k' is $k [\text{CH}_3\text{OH}]$. The kinetic modeling used in this study is based on the assumptions given by Emeji et. al, Ghoreishi et. Al [42,43]. Conversion degree of TG at temperature ranging from 323–338 K was investigated. Fig. 7 shows the differential plot of $-\ln(1 - X_{TG})$ versus reaction time based pseudo-first order kinetics model and the experimental data.

Fig. 7 Plots of $-\ln(1-X_{TG})$ versus time during transesterification reaction for Pseudo-first order kinetic model. (Reaction conditions: $\text{CH}_3\text{OH}/\text{oil}=18/1$, catalyst dose= 3 wt.% of oil and reaction temperature, 323–338 K).

5.2. Pseudo-second order kinetics model

In this section, a second-order kinetics model for transesterification reaction of sunflower oil with methanol catalyzed by $\text{MgO-La}_2\text{O}_3$ will be proposed based on Langmuir-Hinshelwood model. The Langmuir-Hinshelwood model assumes the reaction occurs between neighboring

adsorbed reactant species. In this proposed mechanism, both alcohol and triglyceride molecules are chemisorbed on active sites of the catalyst. The kinetic rate constants for Langmuir-Hinshelwood mechanism comprising 9 steps (3 steps absorption, 3 steps reaction, 3 steps proceeds desorption) are shown in Fig. 8. As depicted in Fig. 8, in LHHW kinetic mechanism the first step is the adsorption of methanol and triglyceride on the surface of the catalyst, to produce adsorbed diglyceride and methylester. Subsequently this adsorbed methanol reacts with adsorbed diglyceride or monoglyceride to form adsorbed monoglyceride, and glycerol respectively along with methylester. Also presents the expressions for equilibrium rate constants k_1 - k_{18} , for the 9 reaction steps in Langmuir-Hinshelwood mechanisms respectively. Methanol and triglyceride adsorption onto the catalyst surface is identified as the slowly and the rate determining step, because triglyceride molecules are large molecules and rate transesterification reaction is slowest in this steps (a and b). The above assumptions, given by Kapil et al, Kavashima et al and Pappu et al [37,44,45]. So, Based on this assumptions, can be written the rate law of transesterification reaction for sunflower oil Catalyzed by MgO–La₂O₃.

Fig 8. Stepwise transesterification reactions in Langmuir-Hinshelwood mechanism

, CH₃OH, TG*, DG*, MG*, ME* represent the intermediates from the reactions between adsorbed methanol and adsorbed TG, DG, MG and ME the catalyst surface.

According to the proposed reaction mechanism, the adsorption of TG is the rate-limiting step (a, b steps in Fig 8). Based on step (a), the rate law can be expressed by Eq 10:

$$r_A = k_1 [TG] [CH_3OH] [*]^2 \quad (10)$$

(*), in Eq 10 is in fact concentration of active sites catalyst. And based on step (b), we have:

$$r_A = k_3 [TG^*CH_3OH^*] \quad (11)$$

$$k_1/k_2 = [TG^* CH_3OH^*] / [TG] [CH_3OH] [*]^2 \quad (12)$$

With replacement Eq. (12) into Eq. (11) can be written as Eq. (13)

$$r_A = k_1 k_3/k_2 [TG] [CH_3OH] [*]^2 \quad (13)$$

If $k' = k_1 k_3/k_2$ can be written as Eq. (14)

$$r_A = k' [TG] [CH_3OH] [*]^2 \quad (14)$$

As can be seen, both steps (a, b) have the Similar kinetic law. Eq. (10) and Eq. (14).thus, each of these steps can be treated as a rate determining step.

$$k'' = k' [*] \quad (15)$$

Eventually, according to above equation can be written as Eq. (16)

$$r_A = k'' [TG] [CH_3OH] \quad (16)$$

Based on this rate law for evaluation the concentration of methanol and triglyceride in different times of reaction can be written as Eq. (17)

Equation 17, indicates chemical reaction between the triglyceride and one molecule of methanol for proceeds production. Also, terminal concentration of triglyceride and methanol was calculated according to Eq. (18)

$$(TG) = (TG)_0 - x, (CH_3OH) = (CH_3OH)_0 - x \quad (18)$$

Substituting equation (18) into (16) and differential, we have:

$$dx/dt = k'' [(TG)_0 - x][(CH_3OH)_0 - x] \quad (19)$$

Finally, for second order kinetic and integration gives:

$$y(t) = \frac{1}{(CH_3OH)_0 - (TG)_0} \ln \frac{(TG)_0 [(CH_3OH)_0 - x]}{(CH_3OH)_0 [(TG)_0 - x]} = k'' t \quad (20)$$

Where $(TG)_0$, $(CH_3OH)_0$, k'' and x are concentration of triglyceride and methanol at $t = 0$, rate constant and the concentration of triglyceride reactant respectively. According to Eq. (20), k'' is slope equal with can be obtained by plotting $y(t)$ reaction time t .

Fig. 9 Plots of $\frac{1}{(CH_3OH)_0 - (TG)_0} \ln \frac{(TG)_0 [(CH_3OH)_0 - x]}{(CH_3OH)_0 [(TG)_0 - x]}$ vs time during trans esterification of sunflower oil for Pseudo-first order kinetics model. (Reaction conditions: $CH_3OH/oil=18/1$, catalyst dose= 3 wt. % of oil and reaction temperature, 323 –338 K).

Table 9 depicts a comparison between two kinetics models prediction at same temperatures. According to results in Table 8, there is a better fitting with the pseudo second order kinetics model ($R^2 > 0.99$). Hence, the kinetics parameters such as activation energy (E_a) and pre-exponential factor (A) calculated based on pseudo-second order kinetics model [34,46].

Table 9. comparison between R^2 and variance two kinetics models

Pseudo first order					Pseudo second order				
T(K)	k(min ⁻¹)	variance (σ)	intercept	R^2	T(K)	k (litmol ⁻¹ . min ⁻¹)	variance (σ)	intercept	R^2
323	0.0063	0.0054	0.0424	99.14	323	0.0006	0.000054	0.005	99.20
328	0.0087	0.0063	0.0143	99.67	328	0.0009	0.000038	0.0041	99.71
333	0.0111	0.0054	0.0141	98.77	333	0.0015	0.000449	0.0081	98.77
338	0.0136	0.039	0.0402	98.14	338	0.0021	0.000385	0.0101	99.45

5.3. Rate constant, activation energy and pre-exponential factor

The reaction rate constant is a temperature-dependent term and has been found to be described by Arrhenius equation [47].

$$k = A e^{-E_a/RT}$$

(21)

Taking the natural logarithm for Eq.(21) obtain Eq.(22):

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (22)$$

A plot of $\ln k$ versus $1/T$ yields a straight line with intercept and slope of $\ln A$ and $-E_a/R$, respectively, that R is the universal gas constant (8.314 kJ.mol⁻¹K⁻¹) and T is the absolute temperature in Kelvin. So, the pre-exponential factors and effective activation energies calculated from Eq.(22) are inscribed in Table. Table 10 shows a list of reported pre-exponential factor, activation energy (E_a) various oil types. According to this table, the obtained values of

pre-exponential factor and activation energy are 77.6 kJ.mol^{-1} and $3.5 \times 10^7 \text{ lit.mol}^{-1}\text{s}^{-1}$, respectively.

Fig. 10. Plot of $\ln k$ vs $1/T$ (K)

Table 10. Reported pre-exponential factor, activation energy(E_a)

Oil type	Reaction order	$E_a(\text{kJ.mol}^{-1})$	Frequency factor (A)	Ref.
waste cottonseed	pseudo first	40.08	8.1×10^4	1
waste vegetable	pseudo first	31.71	3.4	43,48
Spirulina platensis	pseudo first	14.51	2.3	49
sunflower	pseudo second	67.03	9.2×10^8	50
sunflower	pseudo second	43.90	-	51
palm	pseudo second	51.00	-	52
palm	pseudo second	42.36	-	53
sunflower	pseudo second	77.60	3.5×10^7	This study

6. Thermodynamic parameters

In general, transesterification reaction results in the formation of three moles of methyl esters [54-57] as shown in Eq (23).

Equilibrium constant for the sunflower oil transesterification reaction with methanol (K_{eq}) based on the total reaction above can be written as:

$$K_{eq} = a_{ME}^3 \cdot a_G / a_{TG} \cdot a_{CH_3OH}^3 \quad (24)$$

$a_{ME}, a_G, a_{TG}, a_{CH_3OH}$ are activity coefficient methyl ester, glycerol, triglyceride and methanol, respectively. In reaction biodiesel production can be written as:

$$G, CH_3OH \cong \text{pure} \gg a_G, a_{CH_3OH} \cong 1$$

So, with assumption $a_{ME} \cong [ME]$, $a_{TG} \cong [TG]$ equilibrium constant can be expressed as:

$$K_{eq} = \frac{[ME]^3}{[TG]} \quad (25)$$

to calculate Gibbs free energy reaction we have:

$$\Delta_r G = \Delta_r G^\theta + RT \ln K \quad (26)$$

In time equilibrium $\Delta_r G = 0$ and Eq. (26) can be written as:

$$\Delta_r G^\theta = -RT \ln K \quad (27)$$

Taking the natural logarithm of Eq. (27) and substituting $\Delta_r G^\theta = \Delta_r H^\theta - T \Delta_r S^\theta$ in Eq. (27) can be written as:

$$\ln K = -\frac{\Delta_r H^\theta}{R} \left(\frac{1}{T} \right) + \frac{\Delta_r S^\theta}{R} \quad (28)$$

A plot of $\ln k$ versus $1/T$ yields values of slope and intercept $-\frac{\Delta_r H^\theta}{R}$ and $\frac{\Delta_r S^\theta}{R}$ respectively.

So, for evaluation equilibrium constant and thermodynamic parameters we needs to calculate concentration of methyl ester and triglyceride at different temperatures Based on Eq.(29).

$$\text{yield \%} = \frac{M_E}{M_C} \times 100 \quad (29)$$

Where M_E and M_C are mass experimental and theoretical of methyl ester respectively. Finally, substituting concentration methyl ester and triglyceride at Eq. (24) we obtain at equilibrium constant. The results exhibited in Table 11. According to Eq. (28) and using linear plot of $\ln K_{eq}$

versus $1/T$ which shown in Fig. 11 the values of $\Delta_r G^\theta$, $\Delta_r H^\theta$ and $\Delta_r S^\theta$ can be calculated. A positive value of $\Delta_r H^\theta$ shows that the transesterification reaction is an endothermic reaction a negative value of $\Delta_r G^\theta$ indicates that the reaction was spontaneous in direction form the products (Table 12).

Table 11. The Effect of the reaction temperature on equilibrium constant

Tem (K)	Yeild (%)	[ME](mol.lit ⁻¹)	[TG] (mol.lit ⁻¹)	K _{eq}	ln K _{eq}
323.15	83.2	2.62	0.172	105.5	4.6
328.15	92.9	2.93	0.079	318.9	5.7
333.15	95.9	3.02	0.039	706.1	6.5
338.15	97.7	3.08	0.020	1537.3	7.3

Fig. 11 Plot of $\ln K_{eq}$ vs different $1/T$ (K)

Table 12. Thermodynamic parameters evaluated in biodiesel production				
Tem (K)	$\ln K_{eq}$	$\Delta_r G^\theta$ (kJ. mol ⁻¹ K ⁻¹)	$\Delta_r S^\theta$ (kJ. mol ⁻¹ K ⁻¹)	$\Delta_r H^\theta$ (kJ. mol ⁻¹ K ⁻¹)
323.15	4.6	-12.5	0.54	162
328.15	5.7	-16.1		
333.15	6.5	-18.1		
338.15	7.3	-20.7		

7. Conclusions

The aims of this study were the synthesis, characterization and catalytic activity of MgO-La₂O₃ nanocatalyst for biodiesel production and influence of operation conditions on the yield of biodiesel. The measured properties of the biodiesel were viscosity and refractive index; the experimental data showed that viscosity and refractive index decreases by the increase of biodiesel yield. Viscosity and refractive index are recommended as reliable physical properties to estimate of biodiesel yield and reduce analysis cost. The optimum calcination temperature was obtained 873 K for 4 hours which in this temperature, the catalyst showed maximum activity (97.7%) and highest specific surface area. The suitable operational conditions were CH₃OH/oil=18/1, catalyst dosage=3wt.% of oil, reaction temperature, 323–338 K and reaction time 5 h. Further, this catalyst had excellent reusability for several uses (4 cycles) without significant loss in activity. The kinetic and thermodynamic studies were performed. The fitting of the data based on pseudo-first and pseudo-second order models indicated that the reaction is a forward second order reaction. From the kinetic and thermodynamic studies, $E_a = 77.6$ kJ. mol⁻¹, $A = 3.5 \times 10^7$ lit. mol⁻¹s⁻¹, $\Delta_r H^\theta = 162$ kJ. mol⁻¹K⁻¹, $\Delta_r S^\theta = 0.54$ kJ. mol⁻¹K⁻¹ were obtained.

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**Preparation, characterization, kinetic and thermodynamic studies of $\text{MgO-La}_2\text{O}_3$
nanocatalysts for biodiesel production from sunflower oil**

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Graphical Abstract

$\text{MgO-La}_2\text{O}_3$ nanocatalysts were prepared. The activity of optimal catalyst was studied at different operational conditions. $E_a=77.6 \text{ kJ.mol}^{-1}$, $A= 3.5 \times 10^7 \text{ lit.mol}^{-1}\text{s}^{-1}$, $\Delta_r H^\theta=162 \text{ kJ.mol}^{-1}\text{K}^{-1}$, $\Delta_r S^\theta=0.54 \text{ kJ.mol}^{-1}\text{K}^{-1}$ were obtained