Environment-Friendly Heterogeneous Alkaline-Based Mixed Metal Oxide Catalysts for Biodiesel Production

Authors:

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The critical problem arising from the depletion of fossil fuels has stimulated recent interests in alternative sources for petroleum-based fuel. An alternative fuel should be technically feasible, readily available, sustainable, and techno-economically competitive. Biodiesel is considered as a potential replacement of conventional diesel fuel, which is prepared from non-edible and high-acid feedstock via transesterification technology. The focus of this study is to investigate the catalytic activity of mixed metal oxides (MMOs) as catalysts for biodiesel production by using non-edible jatropha oil as feedstock. Various types of MMOs (CaO-MgO, CaO-ZnO, CaO-La?O?, and MgO-ZnO) were synthesized via a co-precipitation method. In this study, transesterification activities are closely related to the physicochemical properties of catalysts. The presence of different active metals in the binary system greatly influenced the surface area, basicity, and the stability of catalysts. The catalytic activity of MMO catalysts was increased in the order of CaO-ZnO (94% ± 1%) > CaO ~ CaO-MgO ~ CaO-La?O? (~90% ± 2%) > MgO-ZnO (83% ± 2%) > MgO (64% ± 1%) > ZnO (41% ± 2%) > La?O? (23% ± 1%). In addition, the MMO catalysts, especially CaO-ZnO, demonstrated high reusability and catalyst stability for four cycles of transesterification reaction of jatropha oil.

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Abstract: The critical problem arising from the depletion of fossil fuels has stimulated recent interests in alternative sources for petroleum-based fuel. An alternative fuel should be technically feasible, readily available, sustainable, and techno-economically competitive. Biodiesel is considered as a potential replacement of conventional diesel fuel, which is prepared from non-edible and high-acid feedstock via transesterification technology. The focus of this study is to investigate the catalytic activity of mixed metal oxides (MMOs) as catalysts for biodiesel production by using non-edible jatropha oil as feedstock. Various types of MMOs (CaO-MgO, CaO-ZnO, CaO-La_2O_3, and MgO-ZnO) were synthesized via a co-precipitation method. In this study, transesterification activities are closely related to the physicochemical properties of catalysts. The presence of different active metals in the binary system greatly influenced the surface area, basicity, and the stability of catalysts. The catalytic activity of MMO catalysts was increased in the order of CaO-ZnO (94% $\pm$ 1%) > CaO ~CaO-MgO ~CaO-La_2O_3 (~90% $\pm$ 2%) > MgO-ZnO (83% $\pm$ 2%) > MgO (64% $\pm$ 1%) > ZnO (41% $\pm$ 2%) > La_2O_3 (23% $\pm$ 1%). In addition, the MMO catalysts, especially CaO-ZnO, demonstrated high reusability and catalyst stability for four cycles of transesterification reaction of jatropha oil.

Keywords: biodiesel; transesterification; non-edible oil; mixed metal oxides; solid catalyst

1. Introduction

Increasing crude oil demand, deleterious environmental impacts, and restrictions imposed by environmental agencies have created a desire to develop new sustainable fuel. Biodiesel has been gaining attention as an alternative energy due to its similar combustion properties with petroleum. Furthermore, this type of biofuel is superior than that of petroleum diesel, with improved physical and chemical properties, such as higher flash point and cetane number, ultralow sulphur content, better lubricity, and smaller carbon footprint [1,2].

The conventional processing route for biodiesel is transesterification reaction of edible vegetable oil (sunflower, soybean, rapeseed, palm oil) in the presence of alkali catalyst (NaOH/KOH) [3,4]. With regards to better economic efficiency for biodiesel production, there are three main interconnected factors that dictate biodiesel productivity and market demand: (i) availability of feedstock; (ii) performance of catalyst, and (iii) production cost [5].

Biodiesel feedstocks cost more than 75% of the overall manufacturing expenditure [6]. Thus, selecting the suitable biological feedstock is crucial as the price of feedstock is based primarily on the

region, climate, and availability of biomass resources and resource edibility [7]. The sustainability of edible oil as a biodiesel feed is under threat and, thus, non-edible oil, such as jatropha oil, is considered to be a promising alternative. Jatropha has a high oil yield with its high heating value (HHV) of 39 MJ/kg, which is on par with most of the edible oils [8–10]. Other than biodiesel feedstock, the transesterification reaction requires a robust heterogeneous (solid) catalyst for an easier processing route. Hetero-technology is expected to be well-suited for all types of biodiesel raw materials with different quality.

Generally, the transesterification process is catalysed by using a homogeneous alkali catalyst system, such as NaOH and KOH. Although the homogeneous system renders high reactivity under mild conditions, it also results in many limitations, such as unfavourable side reaction (saponification), which reduces the biodiesel yield, limited usage for feedstock with high free fatty acid (FFA), and extra washing processes for the biodiesel product [1]. Therefore, transformation from a homogeneous to a heterogeneous system has been developed to adapt the natural characteristic of biodiesel feedstock and existing transesterification technology. The high reusability and eco-friendly nature of the heterogeneous base catalyst is capable of producing a higher purity of biodiesel and glycerol [2]. In the present study, new types of heterogeneous catalysis technology have been developed to eliminate the poor process with homogeneous catalysts. Utilization of heterogeneous catalysts for biodiesel production shall offer some relief to the biodiesel producers by improving their ability to process alternative and cheaper feedstock with simplified processing and a cheaper manufacturing process with prolonged catalyst lifetime [11]. The mixed metal oxide (MMO) catalysts, with binary metal oxide systems, are the promising transesterification catalysts with easy separation and render high yields [12–14].

Mixed metal oxide catalysts are an interesting class of combinatorial metal oxide solid catalysts that can be derived from various types of metal from the periodic groups such as alkali metal, alkali-earth metal, transition metal, rare earth metal, or noble metal. The combination of oxide phases has generated valuable functionalities and characteristics that are suitable for the transesterification reaction of various types of biodiesel feedstock. Different catalyst synthesis methods, such as co-precipitation, sol-gel, wet impregnation, and solid-state mixing may render different physicochemical properties that fit in as transesterification catalysts [15–20]. Dai and Wang's research group used $LiAlO_2$ and Li_4SiO_4 mixed metal oxides for transesterification of triglyceride (soy bean oil and microalgae oil) into biodiesel. Both catalysts showed high catalytic activity with >97% and >75% of conversion for soybean and microalgae-based biodiesel, respectively [21–23]. Transesterification of high-FFA jatropha oil is also possible by using various type of mixed metal oxides catalyst with incipient wetness or impregnation method. The catalytic activity of Li-CaO show better activity as compared to parent catalyst (CaO). However, soap formation was found to be the main problem which reduced the activity of these two catalysts. Endalew et al. [24] have studied a series of lanthanum-based mixed metal oxide (La_2O_3-ZnO, La_2O_3/Al_2O_3, and La-Ca-MnO_3) catalysts. They found that these catalysts contain low base strength and, thus, required higher temperature, higher pressure, longer reaction time and higher reactant ratios to promote the activity of the catalysts [24].

Based on several studies mentioned above, mixed metal oxides have been found to be very active for transesterification reactions. Unfortunately, there is no literature reporting the catalytic behaviour on the series of alkaline-based mixed metal oxides for transesterification of jatropha oil. Thus, in the present study, a series of alkaline-based mixed metal oxide catalysts have been developed for transesterification of jatropha oil. These alkaline-based MMO catalysts include CaO-MgO, CaO-ZnO, MgO-ZnO, and CaO-La_2O_3, which combine between an alkaline-earth, transition, and rare-earth metal, were investigated by studying the effect of the composition of the binary metal system, basic characteristic, surface area, and stability of MMO catalysts. Furthermore, the catalytic activity of MMOs catalysts was tested via methanolysis of crude jatropha oil.

2. Methods

2.1. Preparation of Mixed Metal Oxide (MMO) Catalysts

The alkaline-based binary metal oxide catalysts (CaO-MgO, CaO-ZnO, CaO-La$_2$O$_3$, and MgO-ZnO) were synthesized by using a co-precipitation method. Two aqueous solutions with corresponding metals were first prepared. The first solution of 1 M aqueous metallic cation of Ca(NO$_3$)$_2$·4H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, or La(NO$_3$)$_3$·6H$_2$O was dissolved in deionized water. The second basic carbonate solution with concentration of 2 M was prepared by dissolving appropriate amounts of Na$_2$CO$_3$ in deionized water. In the synthesis procedure, the carbonate solution was slowly dropped (10 mL/min) to the aqueous metallic cation under vigorous stirring at room temperature. During the gel formation, the mixture was adjusted to pH 10 by 1 M NaOH solution. The mixture was then stirred for 24 h at 60 °C. The solid obtained was then filtered and washed with distilled water until the filtrate was near to pH 7. The precipitate was then dried in an oven at 100 °C overnight, followed by calcinations at 800 °C for 6 h for CaO-MgO, CaO-ZnO, and MgO-ZnO catalysts. The CaO-La$_2$O$_3$ precursor was calcined at 950 °C for 6 h.

2.2. Characterization of MMO Catalysts

The crystalline phases of synthesized MMO catalysts were analyzed by using a powder X-ray diffraction analysis utilizing diffractometer model XRD 6000 (Shimadzu, Kyoto, Japan) employing Cu–Kα radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. Specific surface area of the catalysts was obtained by the Brunauer-Emmer-Teller (BET) method using a Thermo Finnigan Sorptomatic 1900 series nitrogen adsorption desorption analyzer (Thermo Scientific, Waltham, MA, USA). The total basicity and basic strength of the catalysts were measured by a temperature-programmed desorption by CO$_2$ (CO$_2$-TPD) method using a Thermo Finnigan TPDRO1100 apparatus (Thermo Scientific, Waltham, MA, USA) equipped with a thermal conductivity detector. Morphological characteristic of the samples were determined by scanning electron microscope (LEO 1455 VP SEM, Cambridge, UK) and the compositional analysis of the synthesized catalyst surface was tested via an energy dispersive spectrometer (EDX) technique. The chemical stability of the binary metal oxide catalysts was investigated by analyzing the active metal content (Mg and Ca) in the biodiesel product via an atomic absorption spectrophotometer (AAS-S series; Thermo Scientific, San Jose, CA, USA).

2.3. Transesterification Reaction of High Acid Jatropha Oil

The catalytic activity of alkaline-based MMO catalysts was evaluated using the transesterification of crude jatropha oil (FFA content, 12 wt %, Bionas Sdn. Bhd., Kuala Lumpur, Malaysia) with methanol. Transesterification was carried out in a stainless steel reactor equipped with a temperature probe, overhead stirrer, and temperature controller (Figure 1). A certain amount of CaO-MgO/CaO-ZnO/MgO-ZnO/CaO-La$_2$O$_3$ mixed metal oxide catalysts were added into the reaction mixture of 20.0 g jatropha oil, along with the required volume of methanol. Then the reaction mixture was heated to a constant temperature (120 °C) under maximum agitation. At the end of the experiment, the catalyst was separated from the product by centrifugation, and the reaction mixture was then loaded into a rotary evaporator to remove excess methanol. The produced biodiesel (fatty acid methyl esters) and unconverted oil were isolated by distillation.

The composition of final biodiesel (fatty acid methyl ester) was analyzed according to European-regulated procedure EN14103 using gas chromatography (Perkin Elmer, Brussels, Belgium) with a flame ionization detector (FID) detector equipped with a HP INNOWax capillary column (30 μm × 320 μm × 0.25 μm film thickness).
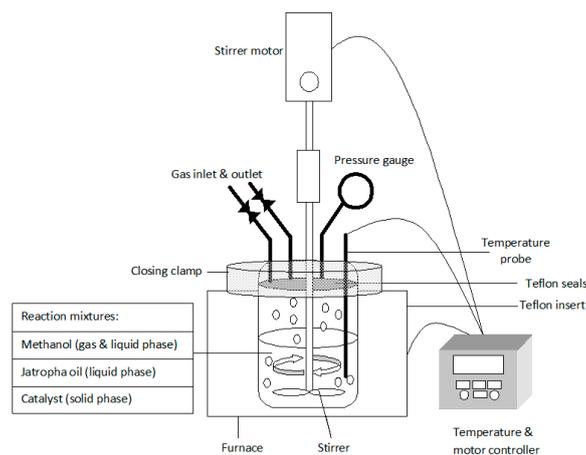
Figure 1. Schematic diagram of the high-temperature reactor.

3. Results and Discussion

3.1. Physicochemical Properties of Mixed Metal Oxide (MMO) Catalysts

X-ray diffraction analyses of MMO catalysts were performed to determine the existential state of binary oxide phases in the MMO system. The XRD patterns (Figure 2) of co-precipitated CaO-MgO, CaO-ZnO, MgO-ZnO, and CaO-La$_2$O$_3$ showed the characteristic peaks of individual metal oxide crystalline phases. New formation of a homogeneous solid solutions phase was absent in the binary system. For calcium-based MMO catalysts (CaO-MgO, CaO-ZnO, CaO-La$_2$O$_3$), two types of diffraction patterns were observed. The first type of characteristic peak was attributed to the CaO phase (JCPDS File No. 37-1497), while the second type corresponded to another joined oxide, such as MgO, ZnO, and La$_2$O$_3$ (JCPDS File No. 4-0829, 36-1451, and 2-668, respectively). The diffraction patterns observed in CaO-La$_2$O$_3$ catalyst showed an intense and dominant La$_2$O$_3$ phase and a low intensity of Ca crystallite peaks. This suggested that La^{3+} ions in the host lattice were partially substituted by Ca^{2+} ions [25] and resulted in habitation of CaO crystal growth and vigorous dispersion CaO crystals. The XRD patterns of MgO-ZnO MMO catalyst showed the existence of individual MgO and ZnO phases in the binary system. The presence of separated oxide phases for all mixed-metal oxide catalysts were greatly influence by the synthesis technique (co-precipitation) and also the synthesis parameters (concentration of metal salt solution, precipitation agent, temperature, aging, or stirring time) [26].
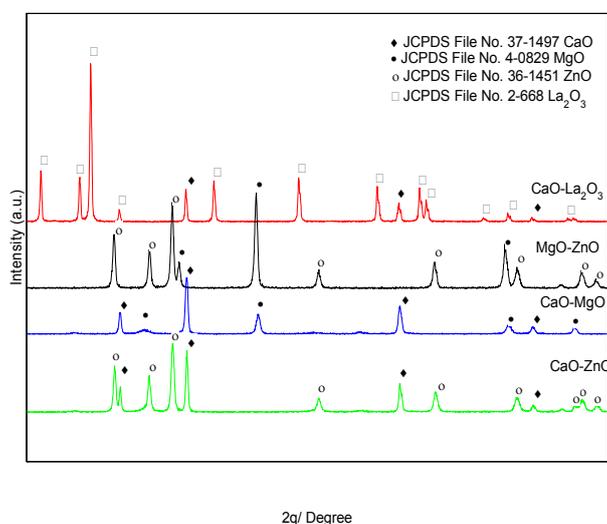

Figure 2. XRD patterns of different MMO catalysts.

The BET surface area of the MMO catalysts: CaO-MgO, CaO-ZnO, MgO-ZnO, and CaO-La$_2$O$_3$ were 5.8, 5.7, 9.5, and 7.7 m^2/g, respectively. The low surface areas of the MMO catalysts were closely related to the calcination temperature. A high calcination temperature and longer time of treatment is necessary for MMO catalysts to increase the basicity or active sites of the catalyst. This is because the metal oxides need suffient energy to be decomposed into metal carbonate, However, this scenario has led to sintering of fine crystals, thus promoting cluster agglomeration [27], and resulted in a reduction of surface area in bimetal oxides [24]. As observed in Figure 3, the SEM images of alkaline-based MMO catalysts showed large and aggregated particles on the catalyst surface. Furthermore, elemental analysis of the active metal was determined via EDX analysis. The results showed that the experimental M$_1$/M$_2$ ratio were 1.14, 0.93, 1.56, and 0.98 atomic % for CaO-MgO, CaO-ZnO, MgO-ZnO, and CaO-La$_2$O$_3$, repectively, which is in agreement with the intended ratio M$_1$/M$_2$ ratio = 1.
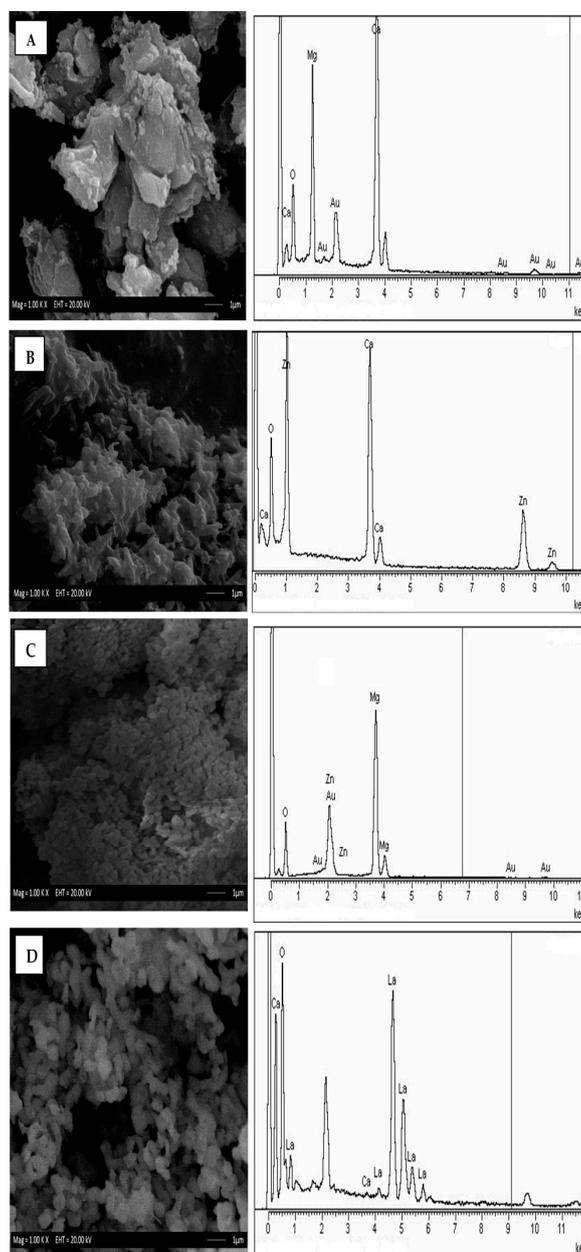

Figure 3. SEM images and EDX analysis of MMO catalysts: (**A**) CaO-MgO, (**B**) CaO-ZnO, (**C**) MgO-ZnO, and (**D**) CaO-La$_2$O$_3$.

Basicity of catalyst is one of the crucial characteristics to influence the performance of transesterification, whereby the transesterification activity greatly depends upon the number and the strength of basic sites present in a catalyst [28–30]. Thus, the basicity characteristic of MMO catalysts were analyzed using temperature-programmed desorption of TPD-CO_2. The basicity profiles of alkaline-based MMOs and pure metal oxide catalysts are displayed in Table 1. Results showed that calcium-based mixed-metal oxides (CaO-MgO, CaO-ZnO, and CaO-La_2O_3) render strong basic strength (with an intense desorption peak at 500–700 °C), which corresponded to the association of Ca^{2+}-O^{2-} pairs located in a particular position of the binary system. The combination of metal oxide systems for MMO catalysts rendered higher amounts of basic sites compared to single metal oxides (CaO, MgO, La_2O_3, and ZnO). The results showed that CaO-MgO, CaO-ZnO, MgO-ZnO, and CaO-La_2O_3 with amounts of basic sites of 1210.5, 1383.0, 333.1 and 737.8 µmol of CO_2/g, while MgO, ZnO, and La_2O_3 give lower amounts of basicity, which is less than 200 µmol of CO_2/g. In fact, CaO itself renders the highest basicity at 290.42 µmol of CO_2/g among the pure oxide, whereby it showed comparable basicity content to the binary MgO-ZnO system with the presence of strong basic strength. Thus, combination of Ca^{2+} with other group metals synergically alter the electronic properties of the catalyst's surface by increasing electron transfer from metal ions (M^{n+}) to the oxide phase in metal-metal oxide systems and, thus, increase the electron density of the oxide phase for better basicity behaviour [31,32].

Table 1. Basicity profile of bulk oxide and mixed metal oxide catalysts.

Catalysts	Amount of Basic Sites	
	T_{max} (300–500 °C) Medium Basic Strength	T_{max} (>500 °C) Strong Basic Strength
ZnO	-	-
MgO	50.3	-
CaO	-	290.4
La_2O_3	-	179.9
MgO-ZnO	73.2	257.9
CaO-MgO	-	1210.5
CaO-ZnO	-	1383.0
CaO-La_2O_3	-	737.8

The basic strength of MMO catalysts were indirectly influenced by the electron transfer from the metal groups. It was assumed that positive metal ions (cations) generated from the binary metal oxide system possess Lewis acidity, whereby the high negativity oxygen ions (anions) were prone to nucleophilic attack (proton acceptors) and act as Brønsted bases. The higher the electro-negativity in the oxide phase means the stronger the basic strength that exists in the active site of the catalyst. During the methanolysis of oil, the strong basic active sites provide sufficient adsorptive sites for methanol, in which the (O-H) bonds readily break into methoxide anions and hydrogen cations (Figure 4). The methoxide anions were then reacted with triglyceride molecules to yield methyl esters [33,34].
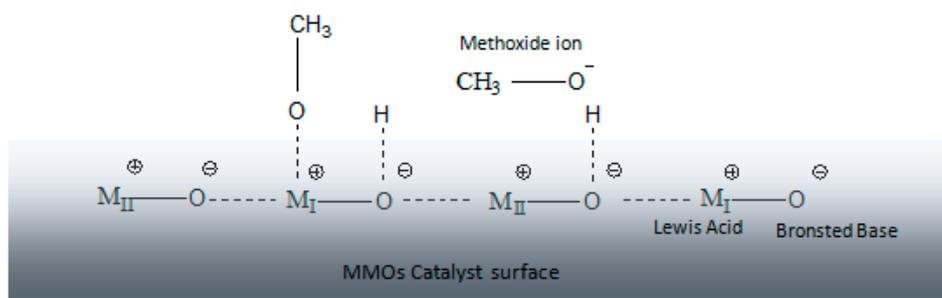

Figure 4. Surface Rreaction of MMO catalysts.

3.2. Transesterification Activity of the MMO Catalysed Reaction

The catalytic performance of MMO catalysts (CaO-MgO, CaO-ZnO, CaO-La$_2$O$_3$, and MgO-ZnO) have been studied and compared with the individual oxide catalysts (CaO, MgO, ZnO, and La$_2$O$_3$) under reaction conditions: catalyst amount of 3 wt %, methanol/oil ratio of 25:1, 120 °C within 3 h. It is interesting to observe CaO-ZnO (94% yield) shows the highest catalytic activity as compared to other alkaline-based MMO catalysts (Figure 5). As compared to the catalytic activity of single CaO (91%) and ZnO (41%), the synergism effect CaO-ZnO has significantly improved the catalytic performance. Although the CaO-ZnO basicity is weaker than CaO (Table 2), the amount of basic sites is still higher than CaO. Thus, this will enhance the catalytic performance of CaO-ZnO.
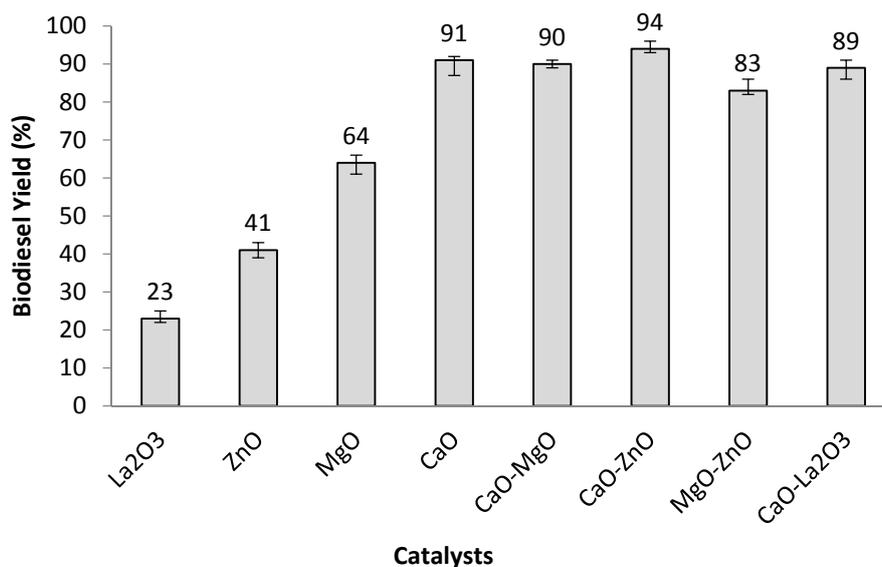

Figure 5. Comparative transesterification studies for MMOs and single metal oxide catalysts.

With the presence of a high acid value (12 wt % FFA) in crude jatropha oil, it has been presumed that unfavorable side reactions (saponification) between free fatty acids and the active metal (Ca^{2+} or Mg^{2+}) happen during the transesterification. As expected, the single alkaline-earth metal oxide (MgO and CaO) showed the existence of soap in the final product. This result is in accordance with a previous study [35]; poor stability of the CaO catalyst is prone to deactivation by acid and forms soap in the reaction. Consequently by coupling two different oxides in one catalyst system, the physicochemical properties of MMO catalysts are superior than pure alkaline oxide with less influence by FFA in the oil feedstock. The mixture of both alkaline metal oxide with transition metal and rare earth metal by co-precipitation methods rendered positive feedback with less soap formation and even gives a high biodiesel yield.

The transition metal oxide (ZnO) and rare-earth metal oxide (La$_2$O$_3$) catalysts are of interest due to their activity in simultaneous transesterification and esterification of high-FFA containing vegetable oils. They are found to be water-tolerant compared to alkali and alkaline metal oxide catalysts [24]. Thus, it is observed that CaO-ZnO catalysts are dual-functional due to the presence of combining Lewis base and Lewis acid metal oxides. This has led to the prevalence of Lewis base and acid catalytic sites in a single catalyst for simultaneous esterification and transesterification reactions. Thus, combination of an active alkaline metal oxide with ZnO is a wise choice for the transesterification reaction, as it can be conducted under mild reaction conditions.

Based on the present study, the CaO-ZnO catalyst showed the highest biodiesel yield (94%) via transesterification of high-acid crude jatropha oil (12 wt % FFA) under reaction conditions of: catalyst amount, 3 wt %; methanol/oil ratio = 25:1; temperature of 120 °C; and time of 3 h. Comparative

study for the Ca-Zn binary metal oxide system was depicted in Table 1. Most of the studies were focused in transesterification of refined vegetable oil with low FFA content. Thus, the slightly lower content of biodiesel for the present study was due to the occurrence of the unfavarouble saponification reaction of FFA with the base catalyst and, thus, formed soap byproducts instead of biodiesel yield [36]. Although the present CaO-ZnO catalyst showed lower activity than the literature, this catalyst is capable of sustaining and resisting poisioning of FFAs in low-quality oil with a considerably good yield of product.

Table 2. Summary studies of Ca-Zn mixed metal oxide catalyst for biodiesel production.

Catalyst	Catalyst Synthesis Method	Feedstock and Transesterification Condition	Biodiesel Yield (%)	Reference
CaO·ZnO	Ball milling of CaO and ZnO powder mixture (CaO:ZnO = 1:2)	Methanolysis of sunflower oil, at 60 °C and 1 bar, using molar ratio of sunflower oil to methanol of 1:10 and with 2 wt % of catalyst based on oil weight, 3 h	99%	[37]
CaO·ZnO	Conventional co-precipitation (Ca:Zn = 0.25:1)	Transesterification of palm kernel oil under conditions at 60 °C, catalyst amount = 10 wt %, methanol/oil molar ratio = 30, reaction time = 1 h	>94%	[38]
K2O/CaO-ZnO	CaO-ZnO prepared by co-precipitation was promoted by K2O via impregnation method (Ca:Zn = 1:3)	Tranesterification of soybean oil under reaction temperature of 60 °C, catalyst loading of 2 wt %, methanol to oil molar ratio of 15:1, and reaction time of 4 h	81%	[39]
CaO-ZnO	Co-precipitation method (Ca:Zn ratio = 1:1)	Transesterification of high-acid crude jatrophas oil (12 wt % of FFA) under reaction conditions: catalyst amount,3 wt %; methanol/oil ratio = 25:1; 120 °C; 3 h	94%	Present study

3.3. Catalyst Reusability

From an economic point of view, the most important features for a catalyst to be industrially competent are stability and reusability. Although single CaO showed comparable catalytic activity as a MMO catalyst, some studies reported that the Ca^{2+} active metal of the CaO catalyst easily leached into the methanolic solution, which reduces the catalytic activity [35]. Furthermore, strong surface basicity of CaO favours the neutralization reaction with FFA to form large-molecule calcium soap. This inhibits the continuous cycle of the reaction.

This scenario was affirmed in the present reusability study (Figure 6), in which jatropha-based biodiesel yield obtained from CaO-catalyzed transesterification was reduced badly from 91% to 58% after four cycles. In contrast, MMO catalytic activities only drop slightly as compared to that of the CaO catalyst. The biodiesel yield capable to maintain around 80% for four runs using calcium-based MMO catalysts (CaO-MgO, CaO-ZnO, CaO-La$_2$O$_3$), with CaO-ZnO being the most stable MMO catalyst. In the case of magnesium-based MMOs catalyst (MgO-ZnO), the yield also dropped sharply after the fourth cycle because of the higher solubility of magnesium in the methanol FFA medium [40,41], which led to the poor reusability performance. As shown in Figure 7, the reusability profile was well correlated with the leaching test in biodiesel products via AAS analysis. The Ca content in the first-run biodiesel product (catalysed by CaO) was very high (156 ppm), followed by 87 ppm and 67 ppm for second and third runs, respectively. This finding was compatible with other studies, which decreased CaO activity for continuous runs due to the leaching of Ca^{2+} active sites. For calcium-based MMO catalysts, low concentrations of Ca (<30 ppm) were found in biodiesel yield for four cycles. It is also shown that the leaching of CaO-ZnO is the lowest amongst the alkaline-based MMO catalysts. This indicated the stronger stability of the binary metal oxide systems. The biodiesel derived by the MgO-ZnO catalysed reaction showed high Mg content (68 ppm) in the first cycle, while second and

third cycle products rendered lower Mg content (<15 ppm). This might due to the presence of unstable amorphous MgO on the catalyst surface and easily be detached and solubilised during reaction.
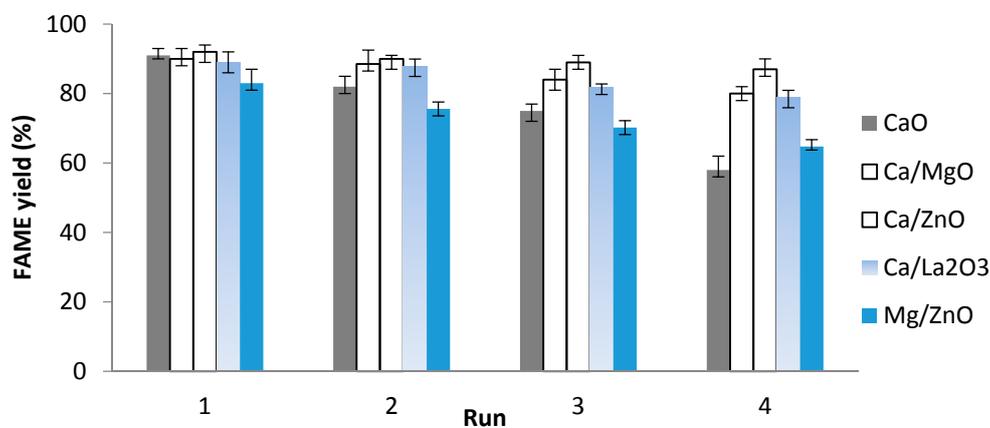

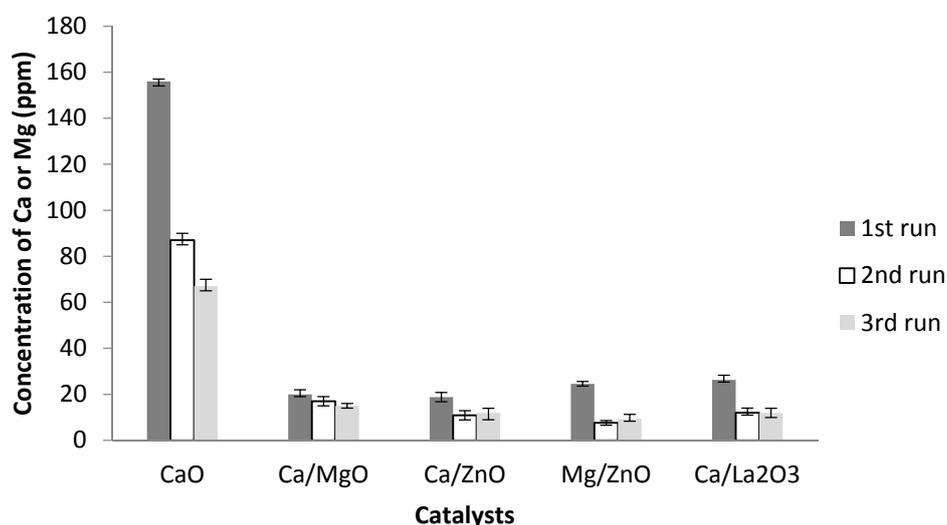**Figure 6.** Reusability studies of CaO and alkaline-based MMO catalysts.

Figure 7. Elemental analysis of leached Ca^{2+} and Mg^{2+} in biodiesel medium.

Furthermore, the loss of transesterification activity of catalysts at continuous usage may be due to the blockage of active sites by adsorbed intermediates or product species, such as diglyceride, monoglyceride, and glycerine, and the contamination by O_2, H_2O, and CO_2 in the air. These adsorbed intermediates sometimes led to the formation of magnesium diglyceroxides or calcium diglyceroxides that poisoned the active phase of the catalysts and, thus, reduced the transesterification rate [42].

Although MMO-catalysed transesterification renders lower leaching of active Ca or Mg active metal (<15 ppm), the concentration is still above the biodiesel standard. Thus, simple water washing was done prior to a fuel properties study. For the biodiesel to be used in diesel engines, it has to meet the biodiesel standards ASTM D6751 and EN14214. Results showed that the biodiesel prepared by the MMO-catalysed process complied with the biodiesel standard. The density and kinematic viscosity of biodiesel at 40 °C is in the range of 891.8–890.7 kg/m^3 and 3.8–3.9 mm^2/s, respectively. The pour point and flash point of biodiesel were −6.0 to −7.0 °C and 140–160 °C, respectively, which indicated high adaptability for various weather conditions. Furthermore, the moisture content (<1.0 wt %,), acid value (0.5 mg KOH/g), and FFA (<1.0 wt %) in this biodiesel was low after washing. In conclusion, this biodiesel is suitable for use in diesel engines.

4. Conclusions

In summary, a series of solid base MMO catalysts (CaO-MgO, CaO-ZnO, CaO-La$_2$O$_3$, and MgO-ZnO) were studied via transesterification of non-edible jatropha oil. It was clearly shown that the alkaline-based MMO catalysts possess higher catalytic activities compared to those of single-metal oxides. As compared to single-metal oxides (CaO, MgO, ZnO, and La$_2$O$_3$), the MMO catalysts (especially Ca-based catalysts) showed high basicity density and strong basic strength, which pose excellent properties for the transesterification reaction. As a result, Ca-based MMO catalysts had the highest catalytic activity (>90% biodiesel yield) and good reusability with low metal leaching. Amongst these catalyst, CaO-ZnO is the most potential catalyst for transesterification of high-acid feedstock without any pretreatment. CaO-ZnO showed a higher biodiesel yield (94%) with negligible catalytic deactivation after four cycles.

Author Contributions: J.C. Juan and Y.H. Taufiq-Yap conceived and designed the experiments; H.V. Lee performed the experiments; H.V. Lee and Hwai Chyuan Ong analyzed the data; H.V. Lee wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Luque, R.; Lovett, J.C.; Datta, B.; Clancy, J.; Campelo, J.M.; Romero, A.A. Biodiesel as feasible petrol fuel replacement: A multidisciplinary overview. *Energy Environ. Sci.* **2010**, *3*, 1706–1721. [CrossRef]
2. Ganjehkaviri, A.; Mohd Jaafar, M.; Hosseini, S.; Musthafa, A. Performance Evaluation of Palm Oil-Based Biodiesel Combustion in an Oil Burner. *Energies* **2016**, *9*, 97. [CrossRef]
3. Vyas, A.P.; Verma, J.L.; Subrahmanyam, N. A review on FAME production processes. *Fuel* **2010**, *89*, 1–9. [CrossRef]
4. Leung, D.Y.; Wu, X.; Leung, M. A review on biodiesel production using catalyzed transesterification. *Appl. Energy* **2010**, *87*, 1083–1095. [CrossRef]
5. Taufiq-Yap, Y.H.; Lee, H.V. Higher Grade Biodiesel Production by Using Solid Heterogeneous Catalysts. In *Advances in Biofuels*; Pogaku, R., Sarbatly, R.H., Eds.; Springer: New York, NY, USA, 2013; pp. 153–176.
6. Meng, X.; Yang, J.; Xu, X.; Zhang, L.; Nie, Q.; Xian, M. Biodiesel production from oleaginous microorganisms. *Renew. Energy* **2009**, *34*, 1–5. [CrossRef]
7. Bryan, R.M. Biodiesel production, properties and feedstocks. *Vitro Cell. Dev. Biol. Plant* **2009**, *45*, 229–266.
8. Jain, S.; Sharma, M. Prospects of biodiesel from Jatropha in India: A review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 763–771. [CrossRef]
9. Chavan, S.B.; Kumbhar, R.R.; Madhu, D.; Singh, B.; Sharma, Y.C. Synthesis of biodiesel from Jatropha curcas oil using waste eggshell and study of its fuel properties. *RSC Adv.* **2015**, *5*, 63596–63604. [CrossRef]
10. Deng, X.; Han, J.; Yin, F. Net Energy, CO$_2$ Emission and Land-Based Cost-Benefit Analyses of Jatropha Biodiesel: A Case Study of the Panzhihua Region of Sichuan Province in China. *Energies* **2012**, *5*, 2150–2164. [CrossRef]
11. Ruhul, A.M.; Kalam, M.A.; Masjuki, H.H.; Fattah, I.M.R.; Reham, S.S.; Rashed, M.M. State of the art of biodiesel production processes: A review of the heterogeneous catalyst. *RSC Adv.* **2015**, *5*, 101023–101044. [CrossRef]
12. Taufiq-Yap, Y.H.; Lee, H.V.; Hussein, M.Z.; Yunus, R. Calcium-based mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. *Biomass Bioenergy* **2011**, *35*, 827–834. [CrossRef]
13. Taufiq-Yap, Y.H.; Lee, H.V.; Yunus, R.; Juan, J.C. Transesterification of non-edible Jatropha curcas oil to biodiesel using binary Ca–Mg mixed oxide catalyst: Effect of stoichiometric composition. *Chem. Eng. J.* **2011**, *178*, 342–347. [CrossRef]
14. Lee, H.V.; Taufiq-Yap, Y.H.; Hussein, M.Z.; Yunus, R. Transesterification of jatropha oil with methanol over Mg-Zn mixed metal oxide catalysts. *Energy* **2013**, *49*, 12–18. [CrossRef]
15. Wachs, I.E. Recent conceptual advances in the catalysis science of mixed metal oxide catalytic materials. *Catal. Today* **2005**, *100*, 79–94. [CrossRef]

16. Gawande, M.B.; Pandey, R.K.; Jayaram, R.V. Role of mixed metal oxides in catalysis science—Versatile applications in organic synthesis. *Catal. Sci. Technol.* **2012**, *2*, 1113–1125. [CrossRef]

17. Climent, M.J.; Corma, A.; de Frutos, P.; Iborra, S.; Noy, M.; Velty, A.; Concepción, P. Chemicals from biomass: Synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts: The role of acid–base pairs. *J. Catal.* **2010**, *269*, 140–149. [CrossRef]

18. Xie, W.; Zhao, L. Heterogeneous CaO–MoO$_3$–SBA-15 catalysts for biodiesel production from soybean oil. *Energy Convers. Manag.* **2014**, *79*, 34–42. [CrossRef]

19. Santiago-Torres, N.; Romero-Ibarra, I.C.; Pfeiffer, H. Sodium zirconate (Na$_2$ZrO$_3$) as a catalyst in a soybean oil transesterification reaction for biodiesel production. *Fuel Process. Technol.* **2014**, *120*, 34–39. [CrossRef]

20. Sawangkeaw, R.; Tejvirat, P.; Ngamcharassrivichai, C.; Ngamprasertsith, S. Supercritical Transesterification of Palm Oil and Hydrated Ethanol in a Fixed Bed Reactor with a CaO/Al$_2$O$_3$ Catalyst. *Energies* **2012**, *5*, 1062. [CrossRef]

21. Dai, Y.-M.; Wu, J.-S.; Chen, C.-C.; Chen, K.-T. Evaluating the optimum operating parameters on transesterification reaction for biodiesel production over a LiAlO$_2$ catalyst. *Chem. Eng. J.* **2015**, *280*, 370–376. [CrossRef]

22. Dai, Y.-M.; Chen, K.-T.; Chen, C.-C. Study of the microwave lipid extraction from microalgae for biodiesel production. *Chem. Eng. J.* **2014**, *250*, 267–273. [CrossRef]

23. Wang, J.-X.; Chen, K.-T.; Wu, J.-S.; Wang, P.-H.; Huang, S.-T.; Chen, C.-C. Production of biodiesel through transesterification of soybean oil using lithium orthosilicate solid catalyst. *Fuel Process. Technol.* **2012**, *104*, 167–173. [CrossRef]

24. Endalew, A.K.; Kiros, Y.; Zanzi, R. Heterogeneous catalysis for biodiesel production from Jatropha curcas oil (JCO). *Energy* **2011**, *36*, 2693–2700. [CrossRef]

25. Liu, S.; Ma, J.; Guan, L.; Li, J.; Wei, W.; Sun, Y. Mesoporous CaO–ZrO$_2$ nano-oxides: A novel solid base with high activity and stability. *Microporous Mesoporous Mater.* **2009**, *117*, 466–471. [CrossRef]

26. Yan, S.; Kim, M.; Mohan, S.; Salley, S.O.; Ng, K.Y.S. Effects of preparative parameters on the structure and performance of Ca-La metal oxide catalysts for oil transesterification. *Appl. Catal. A Gen.* **2010**, *373*, 104–111. [CrossRef]

27. Boynton, R.S. *Chemistry and Technology of Lime and Limestone*; Interscience: New York, NY, USA, 1966.

28. Fraile, J.M.; García, N.; Mayoral, J.A.; Pires, E.; Roldán, L. The basicity of mixed oxides and the influence of alkaline metals: The case of transesterification reactions. *Appl. Catal. A Gen.* **2010**, *387*, 67–74. [CrossRef]

29. Di Serio, M.; Ledda, M.; Cozzolino, M.; Minutillo, G.; Tesser, R.; Santacesaria, E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Ind. Eng. Chem. Res.* **2006**, *45*, 3009–3014. [CrossRef]

30. Zhang, P.; Han, Q.; Fan, M.; Jiang, P. Magnetic solid base catalyst CaO/CoFe$_2$O$_4$ for biodiesel production: Influence of basicity and wettability of the catalyst in catalytic performance. *Appl. Surf. Sci.* **2014**, *317*, 1125–1130. [CrossRef]

31. Hattori, H. Solid Base Catalysts: Generation, Characterization, and Catalytic Behavior of Basic Sites. *J. Jpn. Pet. Inst.* **2004**, *47*, 67–81. [CrossRef]

32. Corma, A.; Hamid, S.B.A.; Iborra, S.; Velty, A. Lewis and Brönsted basic active sites on solid catalysts and their role in the synthesis of monoglycerides. *J. Catal.* **2005**, *234*, 340–347. [CrossRef]

33. Refaat, A. Biodiesel production using solid metal oxide catalysts. *Int. J. Environ. Sci. Technol.* **2011**, *8*, 203–221. [CrossRef]

34. Om Tapanes, N.C.; Gomes Aranda, D.A.; de Mesquita Carneiro, J.W.; Ceva Antunes, O.A. Transesterification of Jatropha curcas oil glycerides: Theoretical and experimental studies of biodiesel reaction. *Fuel* **2008**, *87*, 2286–2295. [CrossRef]

35. Boey, P.-L.; Maniam, G.P.; Hamid, S.A. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chem. Eng. J.* **2011**, *168*, 15–22. [CrossRef]

36. Atadashi, I.M.; Aroua, M.K.; Abdul Aziz, A.R.; Sulaiman, N.M.N. Production of biodiesel using high free fatty acid feedstocks. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3275–3285. [CrossRef]

37. Kesica, Z.; Lukic, I.; Zdujic, M.; Liu, H.; Skala, D. Mechanochemically Synthesized CaO·ZnO Catalyst For Biodiesel Production. *Procedia Eng.* **2012**, *42*, 1169–1178. [CrossRef]

38. Ngamcharussrivichai, C.; Totarat, P.; Bunyakiat, K. Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. *Appl. Catal. A Gen.* **2008**, *341*, 77–85. [CrossRef]

39. Istadi, I.; Prasetyo, S.A.; Nugroho, T.S. Characterization of K2O/CaO-ZnO Catalyst for Transesterification of Soybean Oil to Biodiesel. *Procedia Environ. Sci.* **2015**, *23*, 394–399. [CrossRef]

40. Gryglewicz, S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Bioresour. Technol.* **1999**, *70*, 249–253. [CrossRef]

41. Gryglewicz, S. Alkaline-earth metal compounds as alcoholysis catalysts for ester oils synthesis. *Appl. Catal. A Gen.* **2000**, *192*, 23–28. [CrossRef]

42. Sharma, Y.C.; Singh, B.; Korstad, J. Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review. *Fuel* **2011**, *90*, 1309–1324. [CrossRef]