



Transesterification of palm oil on $K_yMg_{1-x}Zn_{1+x}O_3$ catalyst: Effect of Mg–Zn interaction

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ABSTRACT

The Mg–Zn interaction effect of $K_yMg_{1-x}Zn_{1+x}O_3$ heterogeneous type catalyst and its performance on transesterification of palm oil have been studied using the response surface methodology and the factorial design of experiments. The catalyst was synthesized using the co-precipitation method and the activity was assessed by transesterification of palm oil into fatty acid methyl esters. The ratio of the Mg/Zn metal interaction, temperature and time of calcination were found to have positive influence on the conversion of palm oil to fatty acid methyl ester (FAME) with the effect of metal to metal ratio and temperature of calcination being more significant. The catalytic activity was found to decrease at higher calcination temperature and the catalyst type $K_2Mg_{0.34}Zn_{1.66}O_3$ with Mg/Zn ratio of 4.81 gave FAME content of 73% at a catalyst loading of 1.404 wt.% of oil with molar ratio of methanol to oil being 6:1 at temperature of 150 °C in 6 h. A regression model was obtained to predict conversions to methyl esters as a function of metal interaction ratio, temperature of calcination and time. The observed activity of the synthesized catalyst was due to its synergetic structure and composition.

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1. Introduction

Fatty acid methyl ester (FAME), also called biodiesel, is a clean-burning alternative fuel, produced from renewable resources such as vegetable oils, animal fats and waste cooking oils. It is a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, obtained by the process of transesterification of the oil (triglyceride) with primary alcohol (methanol) in the presence of a catalyst [1]. This can be used alone or blended with conventional petro-diesel in unmodified diesel engine vehicles [2]. Considering the increasing decline in crude oil reserves, alternative energy sources have become of great importance. More so, there has been an increasing campaign for cleaner burning fuels in order to safeguard the environment and protect man from inhalation of toxic substances. The exhaust from petroleum diesel is known to be carcinogenic in nature, since they contain polycyclic aromatic hydrocarbons (PAHs) [3].

Recently, there has been a surge in the prices of petroleum products worldwide leading to economic instability in some countries. Hence, there is a global search for alternative sources of fuel which would be cheaper, safer, and more importantly, environmental friendly. Thus, researchers have concentrated on the development of biodiesel and optimization of the process to meet the standards and specifications required for it to be commercially viable

using various types of catalyst [4–7]. Many studies have been conducted on the use of homogeneous catalyst such as NaOH or KOH [8] for transesterification and are widely known to give higher conversion to methyl esters but with many shortcomings. Among these include free fatty acid in feedstock which formed saponified products, water in raw materials interferes with the reaction, glycerol separation is usually difficult, and purification of methyl esters require repeated washing with water which when discharged make the environment unsafe [9]. All these make the homogeneous process cumbersome and uneconomical [10,11]. Thus, there is the need to develop a solid catalyst that will address some of these disadvantages. Heterogeneous catalyst, however, has been used in various processes, for example, alkali metal (Li, Na, and K) promoted alkali earth oxides (CaO, BaO, and MgO), as well as K_2CO_3 supported on Al_2O_3 (K_2CO_3/Al_2O_3), has been used for transesterification of canola oil with molar ratio of alcohol to oil at 11.48:1, catalyst loading 3.16 wt.% of oil at 60 °C for 2 h, more than 85% yield was obtained. However, there was K leaching and catalyst modification is required [12]. It has been reported that zinc and magnesium oxides are widely used as catalyst support in transesterification and other chemical processes [13,14]. For example, transesterification over Lanthanum promoted zinc oxide ($ZnO-La_2O_3$) catalysts of unrefined or waste oil with 3:1 ratio of zinc to lanthanum, temperature between 170–220 °C using 126 g of oil and 180 g methanol gave 96% yield at reaction time of 3 h using 3 g of catalyst [15]. In the same vein, MgO and ZnO have been studied by various authors for their structure and properties [16]. MgO has been investigated in environmental friendly process of Baeyer–Villiger oxidation [17], ZnO in oxonation and oxygen–ionic transport [18,19]

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and its catalytic [20,21] and photocatalytic [22] behaviour, have been studied. Similarly, activated CaO was used for rapeseed oil with 0.1 g cat., 3.9 g Met., 15 g oil, reaction temperature and time of 60 °C and 3 h respectively to obtain 90% yield [23,24]. Moreover, the utilization of heterogeneous catalyst in transesterification reactions appeared very promising because they could become cheaper materials in substitution of noble metal supported on alumina, silica and other inert solids in addition to the ease of separation of the products. Mg–Zn mixed oxides have been widely employed in a wide band gap quasi-ternary alloy by molecular epitaxy [25]. The crux of this research is to synthesize a heterogeneous catalyst from a combination of these metals (Mg, Zn and K being used as fluxing material) with the form of $K_yMg_{1-x}Zn_{1+x}O_3$ structure. This is due to the fact that their independent structures and properties have been investigated and were chosen for this study because they are of interest in a large field of applications [7,17–19,21,26,27]. They possess desirable properties such as basicity, catalytic properties, surface area and good porosity.

The specific objective requires the performance test of the activity of the catalyst so synthesized in the transesterification of palm oil and study of interaction effects. The efficiency of the catalyst developed would be evaluated in terms of the conversion of palm oil to methyl esters. Depending on the possibility of altering the combination of Mg/Zn ratio in $K_yMg_{1-x}Zn_{1+x}O_3$ as it was proposed by us ($y=2$ and $0.1 < x < 0.9$) at different calcination temperatures and time on the transesterification reaction, different types of combinations were obtained, characterized and the performance discussed.

2. Materials and methods

2.1. Materials

Commercial edible grade palm oil was purchased from the supermarket at Nibong Tebal, Malaysia. Analytical reagent grade 99.9% methanol (HPLC) purchased from Merck (Malaysia) was used for the transesterification reactions. Analytical grade of (pro analysis) KOH ($\geq 85\%$), Mg ($(NO_3)_2 \cdot 6H_2O$ ($\geq 99\%$)), Zn ($(NO_3)_2 \cdot 6H_2O$ ($\geq 98\%$)) and KNO_3 (99%) used to synthesize the catalysts were purchased from Sigma-Aldrich Pty Ltd., Malaysia. Methyl heptadecanoate (99.5%) used as internal standard for gas chromatography (GC) analysis was purchased from Sigma-Aldrich (Malaysia) and *n*-hexane (96%) used as a solvent for GC analysis was purchased from Merck (Malaysia). These reagents were used without further purification for catalyst synthesis and activity.

2.2. Catalyst preparation

The heterogeneous catalyst, $K_yMg_{1-x}Zn_{1+x}O_3$ ($0.1 \leq x \leq 0.9$), was prepared by co-precipitation from the nitrates of the metal compounds. Based on 20 g of salt, 50 mL of mixed salt solution containing 1.65576 M of Zn ($(NO_3)_2$), 0.34424 M of Mg ($(NO_3)_2$) and 2 M of KNO_3 were prepared and mixed in a flask and stirred thoroughly at 600 rpm with a magnetic stirrer. The metals were precipitated using 2 M KOH. K was introduced into the composition as a fluxing agent and to maintain electrical neutrality for the heterogeneous catalyst. The mixture was aged to 80 °C and was stirred continuously for 6 h until the solution is homogenized. Basic strength was determined by the indicator method. The solution was filtered and dried at oven temperature of 85 °C for 12 h. The above procedure describes the synthesized catalyst where the ratio of Mg: Zn varied from a minimum of 1:1.2 to 1:19 maximum and for catalyst sample $K_2Mg_{0.34}Zn_{1.66}O_3$, $x=0.66$ and Mg:Zn = 1:4.8. This was followed by calcination at 460 °C for 4.41 h and was employed for the transesterification activity immediately. These values were arrived after careful selection based on preliminary experimental results and after reviewing related literature [2]. In order to understand the performance of the synthesized catalyst in the production of FAME, two

separate batches of MgO and ZnO were precipitated from their nitrate compounds (all preparations at the same conditions), calcined and employed for transesterification activity.

2.3. Catalyst characterization

The surface area, pore volume and pore size distribution of the developed catalyst were measured by data from nitrogen adsorption at 77 K adsorption/desorption using ASAP 2020 Micrometrics instrument by Brunauer–Emmett–Teller (BET) method. Powder X-ray diffraction patterns recorded on a diffractometer (Phillips PW 1710) with Cu K α radiation were used to check the purity and to determine the unit cell parameters of developed oxides catalyst. The particle microstructure was studied on a Philips XL30S model Scanning Electron Microscopy (SEM). The element composition was analyzed by using an energy dispersive X-ray detector (EDX) mounted on the microscope. Fourier transform infrared (FT-IR) analysis to determine the active surface functional groups. The spectra were recorded in the range 4000–400 cm^{-1} .

2.4. Design of experiments

The optimization of the variables affecting the preparation of the catalyst prior to its activity was carried out using the Central Composite Design (CCD) and Response Surface Methodology (RSM). The response measured FAME content % of triglyceride (TG) conversion to methyl esters (ME) after 6 h. For the catalyst, the factors chosen were calcination temperature, CT, calcination time Ct, and ratio of interaction of the metals. All the activity tests were at atmospheric pressure, based on preliminary experiments which gave indication that the catalyst was active even at the reactor pressure. The use of higher pressures would largely increase the cost of the process both in terms of equipment and energy, thus this was avoided. The methanol: TG molar ratio was fixed at 6:1 on the basis of literature data indicated above [2]. Also, the temperature used for the activity was 150 °C, and the catalyst loading of 1.404 wt.% of oil equivalent to 1.2 g. The activity parameters were chosen by considering the operating limits of the experimental apparatus and the properties of the reactants. As for the catalyst, the CT upper level was 700 °C, and the lower level was 400 °C while the Ct upper and lower levels were 6 h and 4 h respectively as determined by preliminary experiments and from literature [28]. Tables 1 and 2 show the factors and corresponding levels for the experimental design matrix. The last column on Table 2 shows the conversion to ME obtained experimentally for each run. To elucidate the performance of the catalyst a series of 20 experimental runs obtained from Design of Experiment software was carried out which allows interaction between factor parameters. All preparations were conducted under the same conditions and the order in which the runs were made was randomized to avoid systematic errors.

2.5. Statistical analysis

The experimental data obtained above and presented on Table 2 were analyzed using the response surface methodology (RSM) provided by Design-Expert software version 6.0.6 (Stat-Ease Inc., USA). The quality of the fit of the model was evaluated using the coefficients of

Table 1
Factors and corresponding levels for the response surface design.

Factors	ID	Units	Low actual	High actual	Low coded	High coded
Mg/Zn ratio	A	–	4.81	15.39	–1.000	1.000
Cal. temp. (CT)	B	°C	460	639	–1.000	1.000
Cal. time (Ct)	C	h	4.41	5.59	–1.000	1.000

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