



Full Length Article

Efficient waste *Gallus domesticus* shell derived calcium-based catalyst for biodiesel productionNasar Mansir^{a,b,d}, Siow Hwa Teo^{a,b}, Umer Rashid^c, Yun Hin Taufiq-Yap^{a,b,*}^a Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia^b Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia^c Institute of Advanced Technology, Universiti Putra Malaysia, Serdang, Selangor, Malaysia^d Department of Chemistry, Faculty of Science, Federal University Dutse, 7156 Dutse, Jigawa State, Nigeria

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ABSTRACT

In this study, waste shells derived calcium-based catalysts were synthesized via wet-impregnation process in the presence of Mo-Zr mixed salt. The synthesized catalysts were characterized using CO₂-TPD, XRD, BET surface measurement, SEM and EDX spectrometry, respectively. This heterogeneous catalyst was used to synthesize biodiesel via transesterification of waste cooking palm oil (WCPO) to fatty acid methyl ester in the presence of methanol. The catalyst demonstrated a superior catalytic performance in transesterification reaction, yielded 90.1% in 3 h. Reusability of this waste shell derived catalyst was examined and results showed that the prepared catalysts are able to be reused up to 3 times with yield of more than 70% after the third cycles. Therefore, this new modified calcium-based catalyst exhibited outstanding activity and durability in the synthesis of biodiesel. The as-synthesized catalyst is recyclable and reusable, which successfully reduces the biodiesel production cost.

1. Introduction

Biodiesel is now considered as promising renewable source of energy alternative to fossil fuel due to its availability of feedstocks, biodegradable nature, less poisonous exhaust, free sulphur and possession of similar physical and chemical properties to that of fossil fuel [1,2]. Nevertheless, the conventional method adopted for the production of biodiesel in commercial scale, employed the use of food grade feedstocks *i.e.* soybean oil, palm oil, sunflower oil and *etc.* over the homogeneous catalytic system *i.e.* KOH, NaOH, H₂SO₄, HCl [3,4]. The current employed conventional method is no longer sustainable considering the high cost of food grade vegetable oils which account for more than 70% of the total cost of biodiesel production [5].

Low quality feedstocks *i.e.* waste cooking oil, jatropha oil and palm fatty acid distillate (PFAD) are more preferable as alternative options to edible oils for biodiesel production at commercial scale due to their low cost and high availability [6–10]. Nevertheless, the said feedstocks could not work on homogenous catalyst system due to the presence of high FFA content and other impurities (*i.e.* water and *etc.*) which would lead to the formation of soap emulsions that would eventually reduce the biodiesel yield [11–13]. The homogeneous catalytic system catalyst is difficult to separate after the reaction and additional waste water generated would cause pollution to the immediate environment

[14,15]. Hence, make biodiesel production very expensive and eventually difficult [16,17].

In the past a range of solid catalysts based on TiO₂, ZrO₂, SiO, Al₂O₃, Fe₂O₃, SrO, ZnO, MgO and CaO have been worked for the transesterification reaction [18–21]. CaO being easily available, less costly and non-toxic has been selected as one of the widely used among them. Most recently, research interest has been grown towards the production of biodiesel using economic and natural calcium carbonate (CaCO₃) *i.e.* waste shells of egg [5,22], scallop shell [23], obtuse horn [24] and *etc.* CaO derived from natural sources are considered as potential solid catalysts in transesterification reactions due to its strong basicity [5,22–28]. Fatty acid methyl ester (FAME) yield of 86% was obtained by Sirisomboonchai et al. [23] using transesterification reaction of waste cooking oil in the presence of scallop shell derived CaO catalyst. Tan et al. [22] produced waste cooking oil biodiesel using waste ostrich-and chicken-egg shells as heterogeneous calcium base catalysts in two step transesterification process achieving 96 and 94% of biodiesel yields, respectively. However, the process required pre-heating of CaO in methanol solution for additional 1 h to form methoxide mixture solution, which consider as waste of time. Moreover, corrosive H₂SO₄ is non environmental friendly to use as catalyst in the two step transesterification reaction.

The high moisture sensitivity and less reactivity towards

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transesterification of water containing oil is the major problem associated with pure CaO derived from natural sources, also it could partially soluble in alcohol and glycerol. The leaching of soluble Ca^{2+} ion is usually generated from the dissociation of CaO during the reaction with methanol [7]. Lee et al. [24] reported biodiesel yield of 86.75% from palm oil using obtuse horn derived CaO as a catalyst under the optimum reaction conditions. Nevertheless, due to the presence of impurities in oil, CaO alone is far from perfection as it can only transesterify low FFA ($< 3\%$) content oil and could lose the catalytic active phase component into the methanolic solution during the reaction process through leaching [29]. The leached CaO active phase will react with the FFA in the feedstock and result in soap formation and eventually deactivate the catalyst [24,29]. The stability as well as reactivity of pure CaO for the transesterification reaction could be improved by incorporation of mixed metal oxides [30–32]. Doping of carriers such as transition metal oxides could help in stabilizing the pure crystalline structure of CaO by forming additional bonds to connect Ca^{2+} and O^{2-} , hence reducing leaching of active phase into the product during the reaction [33].

Egg shells as calcium-based catalyst for biodiesel production were attained with edible oils [34,35]. Conversely, an edible oil as feedstock of biodiesel is not cost effective and it poses danger of food versus fuel competition and eventually result to hunger. Mo_2O_3 is a famous solid catalyst which has been effectively used for a wide variety of reactions including transesterification, alkylation and isomerisation [10,38,39]. Alternatively, ZrO_2 is also an interesting material because it possesses acidic, basic, oxidizing and reducing properties on the surface. The basicity of zirconium oxide would be enhanced by modified it with alkaline promoter *i.e.* magnesium metal, KOH and La_2O_3 [40–42]. Both solid materials having interconnection system of large pores and a hydrophilic surface would be best for biodiesel synthesis [43]. Therefore, our intention is to catalyze a non-food based oil *i.e.* high acid value of waste cooking palm oil (WCPO) using molybdenum and zirconium (Mo-Zr) modified calcium-based catalyst could be more economic and viable for biodiesel production. The oil is less expensive and widely available hence considered a prospective candidate to reduce the total production cost. To our best knowledge, never found even one report on transesterification of high acid value of WCPO for biodiesel production using Mo-Zr modified calcium-based catalyst.

Therefore, in this research, Mo-Zr modified calcium-based catalyst was synthesized by the wet impregnation method and tested for transesterification of high acid value oil. The effect of different Mo-Zr weight percentages loaded on CaO leaching into FAME was evaluated using Atomic absorption spectroscopy (AAS). The catalyst was further characterized by different analytical techniques *i.e.* CO_2 -TPD, XRD, BET, SEM and EDX, respectively to investigate their physiochemical properties.

2. Experimental

2.1. Materials

The ammonium heptamolybdate-tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 99.0%) and zirconium hydroxide (ZrO_4H_4 , 99.0%) were purchased from Merck and Sigma-Aldrich, Malaysia. Waste *Gallus domesticus* shells obtained from night market at Serdang, Malaysia. WCPO was collected from the cafeteria of Universiti Putra Malaysia. High performance liquid chromatography (HPLC) grade anhydrous methanol (99.7%), hexane (99.0%) and reference standards of FAME were purchased from Merck Co. Germany and fisher scientific company UK, respectively. The fatty acid profile composition of the WCPO was determined by gas chromatography-mass spectrometer, GCMS QP2010 Plus SHIMADZU. All solvents and reagents were used without any treatment. Other physico-chemical properties of the oil sample, *i.e.* acid value, FFA content, saponification value and water content were determined based on American Society for Testing and Material (ASTM) standard,

European Standard (EN) and Malaysian palm oil board (MPOB) method and the results are summarized in Supp. 1.

2.2. Catalyst preparation

2.2.1. Waste *Gallus domesticus* derived catalyst support

The waste shells were cleaned by washing with hot water, acetone and hexane to remove the oily material and other food residues, then dried in oven at $100\text{ }^\circ\text{C}$ for 3 h. After dried, the clean shells were crushed to become fine particles using an agate mortar. The powdered waste shells were subsequently calcined at a temperature of $900\text{ }^\circ\text{C}$ for 4 h in an opened-tube furnace. The synthesized CaO support (CS) was stored in a close tight bottle for subsequent use.

2.2.2. Modification of Ca-based catalyst

The precursor of metal oxides were dissolved homogeneously in distilled water (50 ml) and stirred vigorously for 1 h at a temperature of $80\text{ }^\circ\text{C}$ to ensure their total homogeneity before impregnated on waste *Gallus domesticus* derived CaO support. For incorporating 5 wt% Mo-Zr on CS support, aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (1.930 g) and of ZrO_4H_4 (0.175 g) compounds were weighted, respectively. Both metallic salts were mixed and stirred vigorously in 100 ml of deionised water for 1 h at a temperature of $80\text{ }^\circ\text{C}$. Afterward, the metallic mixture was impregnated over the synthesized CS (4.75 g) support and then, stirred vigorously at 450 rpm for 4 h at $24\text{ }^\circ\text{C}$. The obtained slurry was dried in an oven at $120\text{ }^\circ\text{C}$ for 24 h. The dried powder was calcined at $650\text{ }^\circ\text{C}$ for 4 h in an opened-tube furnace and donated it as XMo-Zr/CS, X represents to 5 wt% of Mo-Zr to CS [32]. By keeping the same atomic ratio of Mo : Zr = 3 : 2, the same procedure was repeated using 10, 15, 20 and 25 wt% of Mo-Zr as dopants in order to synthesize 10Mo-Zr/CS, 15Mo-Zr/CS, 20Mo-Zr/CS and 25Mo-Zr/CS catalysts.

2.3. Catalyst characterization

The distribution of basic sites densities of the synthesized catalysts were measured by Temperature Programmed Desorption Carbon Dioxide (CO_2 -TPD), in a Thermo Finnigan TPD/R/O 1100 series apparatus equipped with thermal conductivity detector (TCD). Before analysis, the sample was pre-treated at $800\text{ }^\circ\text{C}$ under the flow of helium at a rate of 30 ml min^{-1} with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ for degassing purpose and then allowed to cool down to a temperature of about $50\text{ }^\circ\text{C}$. The chemisorptions of CO_2 are usually performed with flowing CO_2 gas at a rate of 30 ml min^{-1} for 1 h. The excess CO_2 is then flushed with helium gas at a flow rate of 30 ml min^{-1} for 30 min. The CO_2 desorption is subsequently proceed under helium as carrier gas from 50 to $900\text{ }^\circ\text{C}$ with a ramp of $10\text{ }^\circ\text{C min}^{-1}$ and soak for 10 min [37]. The amount of desorbed CO_2 from catalyst was detected and determined by TCD.

The X-ray Diffraction (XRD) patterns of the catalysts were obtained by using Shimadzu model XRD6000 power X-ray diffractometer. The Cu, $\text{K}\alpha$ radiation electrons with a wavelength of 1.54 \AA were accelerated at 27.7 kW and 30 mA in an evacuated X-ray tube with Ni filter over a range of 10° to 80° with a step of 0.04° at screening speed of $2\theta\text{ min}^{-1}$. The crystallite size of the catalyst powder was computed using Debye-Scherrer's equation.

The catalyst's total surface area, pore size and pore volume were determined by the corresponding nitrogen adsorption-desorption isotherms (at $-196\text{ }^\circ\text{C}$) using the Brunauer-Emmett-Teller (BET) technique with a micrometrics ASAP 2020 3Flex version 1.02.

The surface morphology of the synthesized catalyst samples was studied by the use of Scanning Electron Microscope (SEM) (Hitachi S-3400 Japan model). The catalysts were coated with gold using a Sputter Coater before analysis.

Metallic compositions of the synthesized catalyst were evaluated by Energy Dispersive X-ray (EDX) spectroscopy Shimadzu EDX 720 model equipped with rhodium X-ray source tube. The powdered sample was

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