

# Bifunctional Effects of $\text{MoO}_3/\text{S-ZrO}_2$ and $\text{Mo}_2\text{C}/\text{S-ZrO}_2$ Catalysts in Transesterification of Groundnut Oil

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## ABSTRACT

Successful doping via impregnation and carburization under  $\text{CH}_4/\text{H}_2$  atmosphere were respectively employed to achieve the formation of  $\text{MoO}_3/\text{S-ZrO}_2$  and  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$  catalysts. The synthesis of both materials was confirmed as illustrated by the binding energies associated with XPS spectra of C1s, Mo 3p and Mo 3d states. In addition to compatible BET surface areas of 120 and  $97\text{m}^2\text{g}^{-1}$ , both catalysts were found to exhibit appreciable densities of surface Mo species as revealed by the  $\text{N}_2$ -adsorption data. These species enhanced catalytic activity and prompted the catalyst to exhibit bifunctional properties during transesterification of groundnut oil. When compared with the support system (i.e.  $\text{S-ZrO}_2$ ), the overall catalytic performance at  $60^\circ\text{C}$ , 0.5g of catalyst and 1:6 (oil: methanol) followed the trend  $\text{S-ZrO}_2 < \text{MoO}_3/\text{S-ZrO}_2 < \text{Mo}_2\text{C}/\text{S-ZrO}_2$ . Another appreciable result is the conformity of the derived biodiesel with international specifications approved by ASTM for B100 and other fuel grades of methyl esters.

**Keywords:** Transesterification; Bifunctional;  $\text{S-ZrO}_2$ ;  $\text{MoO}_3/\text{S-ZrO}_2$ ;  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$ .

## 1.0 INTRODUCTION

There is a recent unanimous agreement by stake holders from academia, industry and critical researchers that energy production and effective utilization are good indicators of socio-economic status of a country (Noyan et al., 2023; Yolcan et al., 2023). The human population surge in the recent years and associated future escalations have linear relationship with global energy requirements for both household and industrial applications. No doubt, the fossil fuels, especially crude oil and natural gas, remained the major sources of energy and chemicals for sustainable development of various sectors of human endeavor. However, the fossil fuels are associated with certain negative effects that negated their full-reliance as fuels for the future. Noticeably, the fossil fuels production is associated with catastrophic episodes with consequent loss of lives and properties. For example, the Piper Alpha catastrophe of the night of 6<sup>th</sup> July, 1988 was responsible for 167 deaths and a property damage of £1.7 billion (i.e. equivalent of £6 billion in 2023) (Swuste et al., 2018; Acheampong et al., 2021). Emissions from fossil fuels-based power plants have been responsible for acid rain and other dangers related with  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$  and  $\text{CO}_2$  interaction with water and environment. In fact, statistics recorded that approximately 13-16% of Hg emissions in the USA are consequences with coal production (Broczka et al., 2024; Liu et al., 2024). Other dangers of fossil fuels include triggering global warming, oil spill, price uncertainties and uneven distribution in addition to the non-renewable features.

These negative factors accounted the need for the consideration of other fuel alternatives. Specifically, biofuels from biomass valorization are good candidates with strong potentials to add value to the global energy cycle. Among there bio fuels, biodiesel has been identities as feasible in terms of production chemistry, quality evaluation, compatibility with diesel engines and production cost. These factors are responsible for the growing feature of the global biodiesel market. In the year 2021, the biodiesel market was found to be 32.09 billion United States dollars, but an annual growth rate of 3.209 billion United States dollars (i.e. 10% per annum) was predicted for the period 2022-2030 (GVR, 2024; Suhara et al., 2024). The trend was also projected to be linear for decades beyond the 2030 (i.e. at least for 2040 and 2050). From the chemistry point of view, the biodiesel preparation method (i.e. transesterification) involved the transformation of triglyceride esters in oil and/or fats into corresponding mono-alkyl esters by reaction with simple alcohols (i.e. commonly methanol and ethanol). The reaction is equilibrium mediated and the selection of reaction conditions such as temperature, catalyst, reactor configuration, degree of stirring, alcohol-to-oil ratio and oil feed compositions are very critical in achieving desirable yields of the biodiesel product. Several heterogeneous catalytic materials that cover oxides (acidic and basic), zeolites and heteropoly acids were evaluated for the reaction (Galadima and Muraza, 2020). However, challenges such as low yield of the methyl esters, catalyst leaching into glycerol/biodiesel, activity-decay overtime and low-purity of the final product have accounted for the

continuous search for more affordable materials (Ahmed et al., 2018; Galadima et al., 2024). In line with this scope, the current study explored the prospects of  $\text{MoO}_3$  and  $\text{Mo}_2\text{C}$  materials doped over  $\text{S-ZrO}_2$  (i.e. sulphated zirconia) as candidates for methyl esters production via transesterification of locally manufactured groundnut oil. Further steps were taken to establish the physicochemical properties of the developed catalysts as well as the compatibility of the biodiesel product with approved standards.

## 2.0 EXPERIMENTAL STUDIES

### 2.1 Sampling

The groundnut oil employed for this research was obtained from Kotorkoshi market (i.e. Coordinates: 12.1409°N, 6.8177°E) in Zamfara State of North-Western, Nigeria. Two (2) liters of the locally processed oil were secured and transported in cleaned and dried high density polyethylene plastic containers. Subsequently, the oil was filtered to eliminate solid impurities that may interfere with the reaction. The filtrate oil was stored under laboratory conditions (approximate temperature range: 26-30°C) prior to further studies.

### 2.2 Catalyst Preparation

The parent sulphated zirconia support (i.e.  $\text{S-ZrO}_2$ ) was designed to contain 10% (w/w) of  $\text{SO}_4^{2-}$  species. The  $\text{MoO}_3$  particles were doped onto the  $\text{S-ZrO}_2$  surfaces via wetness-impregnation method. A loading of 25% (w/w) of  $\text{MoO}_3$  to  $\text{S-ZrO}_2$  was developed under the conditions of 200  $\text{cm}^3$ , 120°C and 2h distilled water, temperature and stirring time, respectively. The developed  $\text{MoO}_3/\text{S-ZrO}_2$  material was calcined at 500°C in air, cooled and stored under lab-scale conditions. Subsequently, the  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$  was obtained via  $\text{CH}_4/\text{H}_2$  carburization of  $\text{MoO}_3/\text{S-ZrO}_2$  under the conditions of 25% (v/v) of  $\text{CH}_4$  in  $\text{H}_2$ , 650°C and 1.5h. Both catalysts (i.e.  $\text{MoO}_3/\text{S-ZrO}_2$  and  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$ ) were later characterized.

### 2.3 Catalyst Characterization

The prepared Catalyst systems were characterized using two different methods (i.e.  $\text{N}_2$ -physisorption and x-ray photo electron spectroscopy). For the physisorption experiments, BET surface area and pore properties were derived following catalyst out gassing for 6h, liquid  $\text{N}_2$ -adsorption at 77K and data extrapolations with the aid of a BELCAT approved porosimeter. On the other hand, the x-ray photo electron spectroscopy (xps) studies were performed with the aid of a Thermo Fisher Scientific spectrometer (model: Nexsa G2). Extrapolated values were exposed as binding energies (i.e. eV).

### 2.4 Transesterification Studies

Transformation of the groundnut oil into biodiesel was conducted with aid of an improvised laboratory scale reactor that was previously validated. Typical reaction conditions include 1:6 (molar ratio of oil to methanol), 60°C reaction temperature, and 0.5g of catalyst, 1.5h reaction time and constant stirring. The two reaction products (i.e. biodiesel and glycerol) were separated via gravity method. Fuel quality parameters of the biodiesel were subsequently measured in line with the ASTM approved standards.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Catalyst Characterization

The physicochemical properties of the two main catalysts (i.e.  $\text{MoO}_3/\text{S-ZrO}_2$  and  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$ ) were established by both  $\text{N}_2$ -physisorption and xps studies. Specifically, the results of physisorption are documented as Figures 1 and 2. Both materials exhibited similar adsorption patterns as indicated in Figure 1. However, the transformation of  $\text{MoO}_3/\text{S-ZrO}_2$  to  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$  triggered a noticeable reduction in BET surface area from  $120\text{m}^2\text{g}^{-1}$  to  $97\text{m}^2\text{g}^{-1}$ . This specific factor could be connected to the high temperature (i.e. 650°C) employed during carburization with  $\text{CH}_4/\text{H}_2$  mixture (Galadima, 2012). Under such treatment conditions, the surfaces of  $\text{MoO}_3/\text{S-ZrO}_2$  could experience shrinkages due to particles agglomeration and re-orientation. As carefully observed in both Figures 1 and 2, the pore volume characteristics of both catalysts are closely related in terms pore-filling and adsorption/desorption patterns. However, massive increase was noticed from  $0.0143\text{cm}^3\text{g}^{-1}$  for the  $\text{MoO}_3/\text{S-ZrO}_2$  to  $0.1810\text{cm}^3\text{g}^{-1}$  for the  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$  system. The trend illustrated that agglomeration of particles could not be ruled out, pores development was prominent. These observations are in good conformity with the nature of the BJH pore volume features depicted in Figure 2. Additionally, reaction involving catalysts based on Mo are associated with the availability of the Mo atoms at the surfaces (Galadima, 2012). In this direction, Figure 1 reported the density of Mo species on the surfaces of both  $\text{MoO}_3/\text{S-ZrO}_2$  and  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$ . The reduction in BET surface area was positive in enhancing the concentration of available Mo atoms/ $\text{nm}^2$  that can participate in the reaction. Specifically, the surface Mo atoms increased from 8.70 atoms/ $\text{nm}^2$  for the  $\text{MoO}_3/\text{S-ZrO}_2$  to 12.60 atoms/ $\text{nm}^2$  for  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$  (i.e. depicting 30.95% increase).

The xps spectral results were extrapolated for three key states (i.e. C 1s, Mo 3p and Mo 3d) for the  $\text{Mo}_2\text{C}/\text{S-ZrO}_2$  material to confirm its successful development from the  $\text{MoO}_3/\text{S-ZrO}_2$  system (see Figure 3). Specifically, the C 1s spectra exhibited pronounced peaks around 283-284eV which are good characteristics of carbidic carbon

in  $\beta$ - $\text{Mo}_2\text{C}$  (Huang et al., 2024; Xu et al., 2023). New feature observed beyond these binding energies are clear indication of surface-CH-species associated with the carburization process. In the Mo 3p spectra, binding peaks that are consistent with both  $\text{Mo}_2\text{C}$  and  $\text{MoO}_3$  were observed. Thus, the possibility of partial re-oxidation of

the  $\text{Mo}_2\text{C}$  after carburization could not be ruled out. These details were further revealed by the attributed binding energy values of Mo 3d states (especially for the  $3d_{5/2}$ ). Overall, the xps results confirmed the formation of  $\text{Mo}_2\text{C}$  from  $\text{MoO}_3$ , but with partial re-oxidation due to catalyst exposure to air.

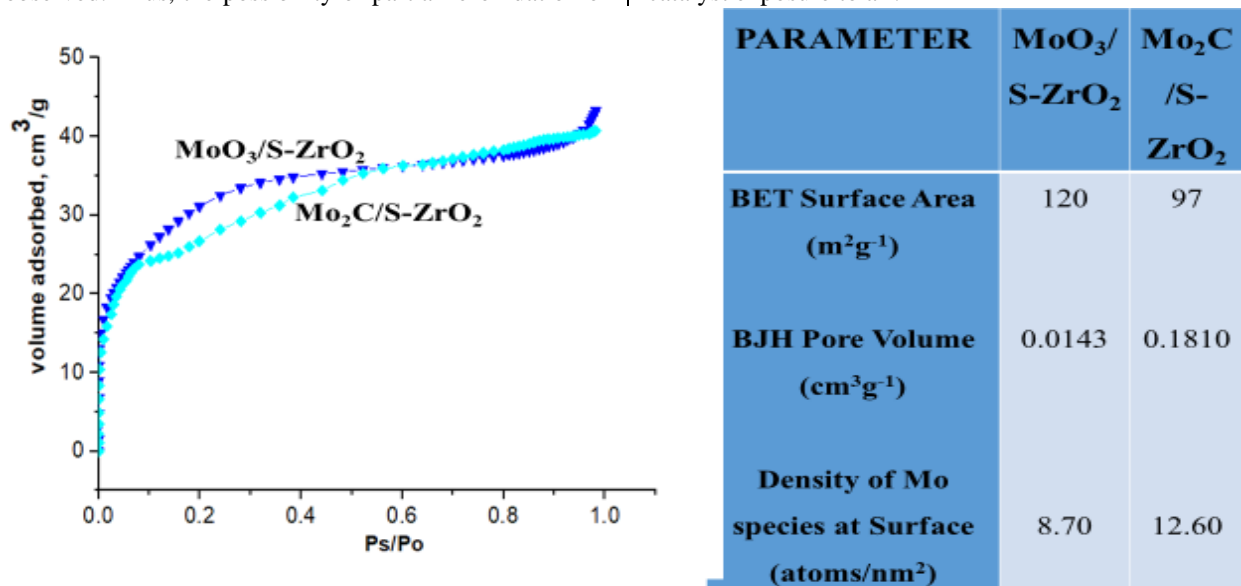


Figure 1. Data for isotherm from N<sub>2</sub>-physorption studies of the precursor and catalyst

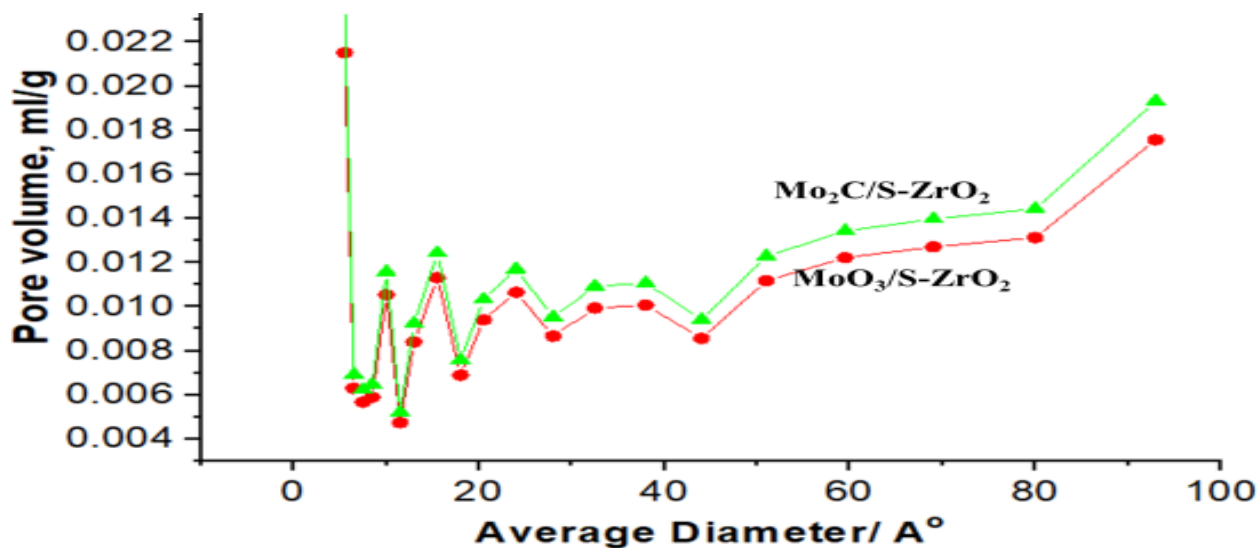


Figure 2. Data for pore volume distribution from N<sub>2</sub>-physorption studies of the precursor and catalyst

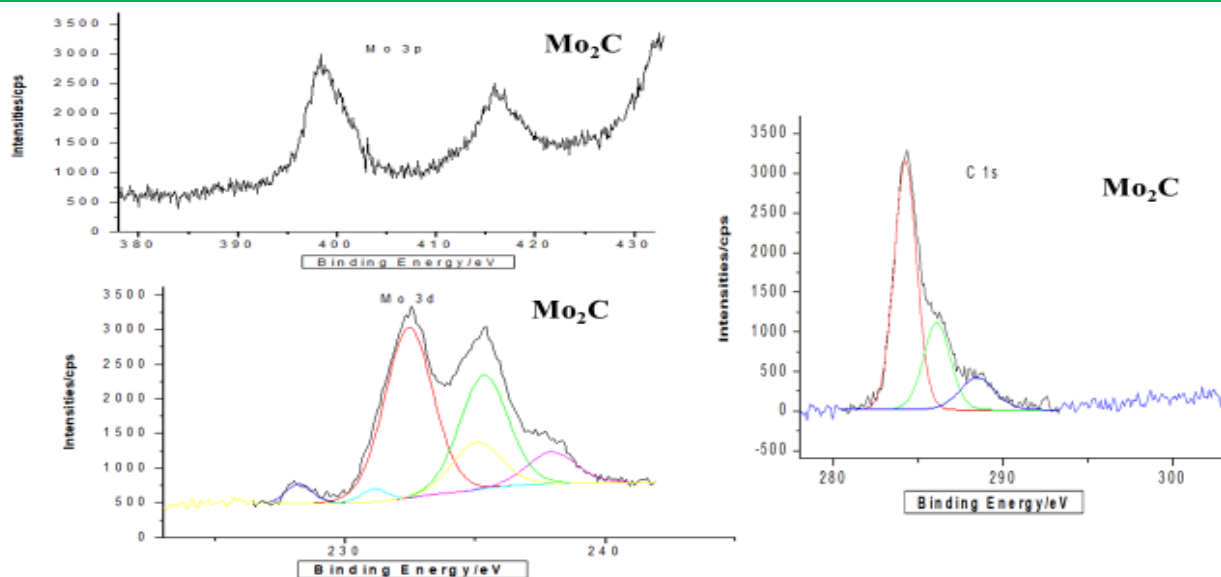


Figure 3. C 1s, Mo 3p and Mo 3d X-ray photoelectron spectra (XPS) of the carbided catalyst (i.e. Mo<sub>2</sub>C/S-ZrO<sub>2</sub>)

## 2.4 Transesterification Results

The effects of the support (i.e. S-ZrO<sub>2</sub>) and the two developed catalyst (i.e. MoO<sub>3</sub>/S-ZrO<sub>2</sub> and Mo<sub>2</sub>C/S-ZrO<sub>2</sub>) on the transesterification of groundnut oil into biodiesel (i.e. methyl esters) are presented in Table 1. The results demonstrated that the support actively participated in the reaction, possibly due to the presence of SO<sub>4</sub><sup>2-</sup> species that can allow the formation of both Lewis and Bronsted acid sites in S-ZrO<sub>2</sub> material (Fernandez-Morales et al., 2019). These acid sites can have positive effects of triggering bond clearages in triglyceride esters of the parent groundnut oil. Similarly, their effects could promote the abstraction of -OH group from methanol followed by elevated coupling reactions with consequential role of both methyl esters and glycerol production.

Table 1. Role of various catalysts during transesterification

Catalyst	Biodiesel Yield (%)	Recovered Catalyst (%)
S-ZrO <sub>2</sub>	50.25	98.8
MoO <sub>3</sub> /S-ZrO <sub>2</sub>	78.30	99.6
Mo <sub>2</sub> C/S-ZrO <sub>2</sub>	95.45	99.7

Table 1 further showed recovery efficiency of the various catalysts during the reaction. While both MoO<sub>3</sub>/S-ZrO<sub>2</sub> and Mo<sub>2</sub>C/S-ZrO<sub>2</sub> were fully recovered, up to 1.2% of S-ZrO<sub>2</sub> could not be recovered at the end of the reaction. Apparently, the SO<sub>4</sub><sup>2-</sup> species in the S-ZrO<sub>2</sub> material underwent leaching during the process thereby triggering a reduction in the amount or recovered catalyst. On the other hand, the doping of both MoO<sub>3</sub> and Mo<sub>2</sub>C onto the S-ZrO<sub>2</sub> caused surface stabilization of the support and

consequently eliminated the leaching of SO<sub>4</sub><sup>2-</sup> species during the reaction. A comparative role of the transesterification activity of the various catalysts is depicted as Figure 4. The activity followed the order S-ZrO<sub>2</sub> < MoO<sub>3</sub>/S-ZrO<sub>2</sub> < Mo<sub>2</sub>C/S-ZrO<sub>2</sub> revealing the activity to be a function of the availability of Mo species at the Surface of the catalyst. With reference to Figure 1, the Mo<sub>2</sub>C/S-ZrO<sub>2</sub> has the highest concentration of Mo atoms/nm<sup>2</sup> when compared to the MoO<sub>3</sub>/S-ZrO<sub>2</sub> material. Additionally, the transesterification results revealed the participation of both Mo species and S-ZrO<sub>2</sub> during the reaction. Thus, both MoO<sub>3</sub>/S-ZrO<sub>2</sub> and Mo<sub>2</sub>C/S-ZrO<sub>2</sub> demonstrated bifunctional roles. In essence, metal and acidic sites in these materials were responsible for the improved catalytic transesterification performance.

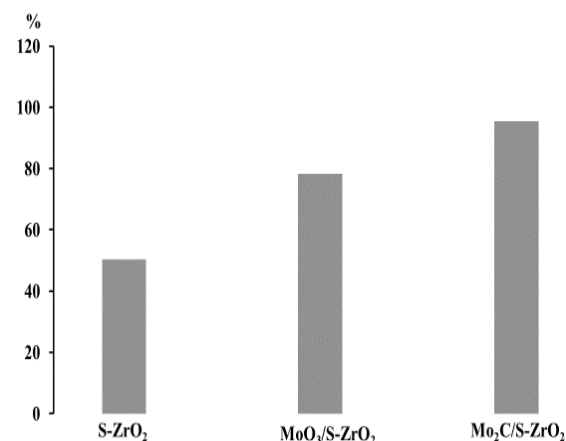


Figure 4. Effect of the various catalysts and support on the transesterification activity of groundnut oil

### 3.2 Fuel Product Quality

Biodiesel fuel for application in automobiles or other means of energy generation must meet certain standards

in terms of quality and specifications. Table 2 depicted the data derived from quality assessment of biodiesel produced with all the catalytic systems.

**Table 2. Results of quality specification studies**

Standard	S-ZrO <sub>2</sub>	MoO <sub>3</sub> /S-ZrO <sub>2</sub>	Mo <sub>2</sub> C/S-ZrO <sub>2</sub>	ASTM limit
Methanol Content, Max %	0.03	0.022	0.024	0.20 (EN14110)
Water and Sediments, Vol.%, max	0.01	0.02	0.01	0.05 (D2709)
Glycerol, % max	0.005	0.004	0.003	0.02 (D6584)
Acid number, mgKOH/g, max	0.05	0.04	0.04	0.5 (D664)
Flash point, °C, min.	100	98.0	98.0	93 (D93)

According to these results presented in Table 2, five key quality parameters were evaluated to establish the potential application of the produced biodiesel as B100 or other grades. The parameters assessed include methanol content, water and sediments, glycerol content, acid number and flash point. The values of these parameters must be maintained at certain limits to avoid engine damages and other unbearable effects (Galadima et al., 2023; Galadima et al., 2024). Generally, all the values obtained are within the standards approved by ASTM for good grade biodiesel fuel. Among the various products, the biodiesel produced with Mo<sub>2</sub>C/S-ZrO<sub>2</sub> catalyst exhibited the best quality control properties especially due to low content of glycerol and water and sediments, catalytically, the metal was effective in facilitating the transesterification process without side reaction interferences.

### 4.0 ONCLUSION

The continuous rise in global energy demand remained a serious issue with great concerns. Biofuels are currently being developed to complement the role of fossil fuels and other renewables in the global energy cycle. Biodiesel is one of these biofuels witnessing expansion in demand and market size over the years. Accordingly, several studies are underway to formulate very efficient and reliable catalysts for biodiesel production from oils and/or fats and simple alcohols like methanol. Results obtained from this investigation revealed that both Mo<sub>6</sub>O<sub>3</sub>/S-ZrO<sub>2</sub> and Mo<sub>2</sub>C/S-ZrO<sub>2</sub> behaved as bifunctional materials in upgrading glyceride esters of groundnut oil into mono-alkyl esters (i.e. biodiesel). The activity exhibited good linear relationship with the surface density of Mo atoms. Specifically, the Mo<sub>2</sub>C/S-ZrO<sub>2</sub> possessing the highest Mo concentrations (i.e. 12.60

atoms/nm<sup>2</sup>) produced the highest biodiesel yield of 95.45%. More importantly, all the designed catalysts produced biodiesel with specifications that are compatible with international standards. This later factor further escalates the potentials of the designed catalysts as transesterification candidates.

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