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KOH-Modified Nano-ZnO from Hydration-dehydration as Efficient Catalyst in the Basic Transesterification of Rice Bran Oil

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ABSTRACT

Amphoteric zinc oxide has low toxicity and solubility and KOH was proved to be very effective in enhancing catalytic performance of many substances. In this research, nano-zinc oxide (Nano-ZnO) was prepared through environmental-friendly hydration-dehydration method, modified with 5-25 % KOH by wet impregnation and used in esterification/transesterification of rice bran oil (RBO) to form biodiesel. The catalyst was characterized by Branneur-Emmer-Teller (BET) surface analysis, X-Ray powder Diffraction (XRD) and basic strength determination by Temperature Programmed Desorption (TPD)-CO_2 and the biodiesel prepared was characterized by Nuclear Magnetic Resonance (NMR) spectroscopy. The result shows this method produced nano-ZnO having average crystallite size of 30-40 nm at an optimum temperature of 400°C and the wet impregnation method used disperses KOH well into the ZnO crystal lattice and improves its basic strength. Basic heterogeneous transesterification was carried out at 65 °C, 5% catalyst, 9:1 methanol to oil ratio and 3 hours-time. It shows the formation of biodiesel and that there is increase in basic strength of modified catalyst causing increase in catalyst activity and biodiesel yield. Optimum 96 % conversion was obtained from 15 % KOH-modified catalyst, proving that ZnO can be prepared by hydration-dehydration and its modification with KOH produced effective catalyst in transesterification for biodiesel preparation.

Keywords: Catalyst modification, TPD-CO_2, nano-zinc oxide, transesterification, biodiesel

INTRODUCTION

In recent years, the development of alternative fuels, like bioethanol, biodiesel and biokerosine from renewable resources, has received considerable attention. Worldwide energy demand, particularly for liquid transportation fuels, continues to rise as populations grow and become more affluent. Concurrently, concern over climate change, declining petroleum reserves, and national security has encouraged the research and possible applications of biofuels (Del Río *et al*., 2012).The utilization of biomass to produce fuels is a promising way to sustainably produce clean energy and alleviate our societal and economic dependence on fossil fuels. But, the production of fuels from biomass requires the development of new technology, chemical pathways, optimum conditions and efficient, less toxic catalysts to convert the oxygenated renewable feedstock into molecules with the appropriate molecular weight and structure for use as liquid fuels. Also, continued use of fossil fuels is generating concern because of the large amounts of carbon dioxide released into the atmosphere which cause global warming (Serrano-ruiz & Ramos-fern, 2012). Then there are technical problems associated with homogeneous catalysts like non-recyclability, contamination with metal ions due to leaching, release of large quantity of water from washing to purify biodiesel which contains high concentration of organic contaminants, saponification, difficulty in product separation, etc.

The use of amphoteric substances in transesterification reactions for biodiesel can have the advantage of simultaneous esterification /transesterification; using their acid sites for esterification of free fatty acids present in oil to ester, at the same time when their basic sites are being used for transesterification of glycerides to ester. This can prevent two-step process of free fatty acid (FFA) removal before transesterification which is needed as pre-treatment for substrates containing higher FFA. Many studies have reported different methods used in the synthesis and characterization of ZnO with various structures, shapes and morphologies for numerous catalytic and electronic applications (Alba-Rubio *et al.* 2010; Sayyadnejad *et al.* 2008; Coutts *et al.* 2010; Cho *et al.* 2011; Ahmadi *et al.* 2013; Moezzi *et al.* 2013; Khan *et al.* 2009) and most of the literature focused mainly on its synthesis and application in electronic, gas sensing purification, etc with only few investigating its catalytic application. But zinc oxide has very low toxicity and solubility levels which are good properties needed in heterogeneous catalyst as there is less danger of pollution and enable ease of phase separation after product formation. Zinc oxide alone has low activity in transesterification reaction, so its properties need to be modified and some researches were reported in that attempt (Wan *et al*. 2014; Yan *et al*. 2008; Yoo *et al*. 2010). KOH alone is very good homogeneous catalyst with excellent yield in transesterification reactions for biodiesel, but there are so many problems of phase, catalyst and glycerol separation associated with homogeneous catalysts. The use KOH supported on some substances for heterogeneous application was also investigated and it was reported to show remarkable improvement on the catalytic activity of substances used (Takase *et al*. 2014). But information from the available literature shows no detailed work was carried out on the modification of zinc oxide with KOH for the transesterification. RBO oil is reported to have high FFA (Lin *et al*. 2009) content and is largely unexploited (Sinha *et al*. 2008) especially in Africa, making it a good candidate for use in biodiesel and the application of ZnO in simultaneous esterification-transesterification can be promising for high FFA containing oils as there is the possibility that both its acid and basic sites present can be used in the process.

This work aims to introduce new catalyst through simple and environmentally using modified ZnO that can produce biodiesel and help eliminate the problems associated with the use of homogeneous catalysts.

MATERIALS AND METHODS

All apparatus used in the experiment were soaked in dilute acid solution, washed with detergent, rinsed with distilled water and dried in the oven at 95 °C. Analytical grade reagents from commercial sources were used. Both commercial zinc oxide, KOH and methanol were purchased from QRëC^{TM}, while commercial rice bran oil was bought from a local super market. The oil was if used as received without further purification or treatment.

Hydration-Dehydration

This method is used to immobilize active sites, create vacant pores and defect sites in order to improve the catalytic activity of materials as reported by (Asikin-Mijan *et al*. 2015). Hydration was done by weighing about 12.0 g of commercial ZnO into a 250 ml round bottom flask, adding 150ml distilled water and refluxing at 95 °C for 24 hrs. Hydrated ZnO was produced which was vacuum-filtered and dried in oven at 105 °C overnight in order to remove the excess water. Dehydration of the samples was done to prepare the nano-zinc oxide by calcination at higher temperatures by decomposing the hydrated ZnO to nano-ZnO through heating in the furnace at 400 °C for 2 hrs. These are the prepared samples which were characterized in order to obtain the optimum calcination temperature for the modification. 0%KOH zinc oxide is obtained at this stage.

BASIC SITES MODIFICATION OF THE CATALYST.

The modification is carried out to disperse KOH on the surface of the amphoteric ZnO in order to improve its basic sites through wet impregnation method as described by (Pugnet *et al*. 2010) and (Yang and Xie 2007). Exactly 4.2 mg of the prepared nano-zinc oxide obtained from hydration-dehydration was measured and transferred into 200ml beaker and 25 ml distilled water added. 5% KOH (mol/mol) was accurately measured and transferred into the beaker and the set-up mounted onto hot plate with magnetic stirrer. The mixture was maintained at 90°C stirred with gentle evaporation until the water dried off and then transferred to oven (Memmert GmbH) and kept at 105°C for 5 hrs for complete drying. The sample was then transferred to furnace and calcined at 400°C for two hours. This is the basic sites modified catalyst used in transesterification for biodiesel. 5, 10, 15, 20 and 25 % KOH (mol/mol) modified catalysts were prepared in similar way.

Characterization of the Catalyst

After the preparation and modification, the catalyst samples were characterized by Brunauer-Emmer-Teller (BET) nitrogen adsorption surface area analysis and X-Ray Powder Diffraction (XRD) analysis. The basic sites analysis was carried-out through TPD-CO_2.

The surface area analysis was carried out using Micromeritics PulseChemiSorb 2705 based on the principle of nitrogen gas adsorption-desorption on the porous surfaces of the sample. Initially, 10 mg of each sample was measured, degassed for 1 hr at 473 K under nitrogen gas flow condition. The samples were then evacuated to 10^{-2} Torr and immersed in the liquid nitrogen. The specific surface area was then estimated from the amount of adsorbed nitrogen gas. The isotherms were applied into BET equation and used to determine the specific surface area. Powder X-ray diffraction patterns were recorded on a Bruker D8 having Siemens Diffractometer D5000 with Cu-Kα radiation (λ=1.5406 Å, 40 kV, 40 mA). The samples were ground into small particles for smooth surface, pressed into sample holder and scanned at the rate of 0.05s/step and 2θ range of 10 to 70°. The X-ray Powder Diffraction (XRD) pattern obtained was used to identify the calcined powder crystalline phases and estimate crystallites size using the Scherrer formula. TPD-CO_2- was carried out for instrumental analysis of the active basic sites. It was performed on AutoChem II 2920 instrument (Micromeritics Corporation). Exactly 25 mg of each sample was put into a quartz sample tube and pretreated under a helium stream at 400 ^oC for 1 hr. The sample was then cooled to 35 ^oC, and at this temperature a flow of mixed gas of CO_2 and helium was subsequently introduced into the quartz tube for 1 h. Then the temperature was raised to 120 ^oC and the gas flow was changed to the helium gas flow again for 1 h to remove loosely adsorbed carbon dioxide molecules from the catalyst surface. The sample was then heated to 500 ^oC under helium flow to desorb CO_2, which was detected using an online thermal conductivity detector.

Biodiesel Preparation (Transesterification)

The biodiesel was prepared at relatively modest conditions of methanol to oil molar ratio of 9:1 and 5% w/w of catalyst is used (Patil *et al.* 2009). 250 ml double necked round bottomed flask is fitted with condenser, thermometer and mounted onto retort stand. 4.2 mL of methanol is measured into the round flask followed by 0.5 g of the catalyst. The mixture was then vigorously stirred for 20 min with the aid of magnetic stirrer to form a uniform alkoxide mixture. 11 ml of rice bran oil was then added and the set up heated in paraffin oil at 65^{o}C with magnetic stirring for 3 hrs. The product was cooled, allowed to stand overnight and centrifuged at 1500 rpm for 20 mins. Three layers were distinct. The small upper layer of unreacted methanol was removed while the middle layer of biodiesel was carefully decanted from the lower layer which contains glycerol and the settled solid catalyst. The analysis was carried out at 20 ^oC.

Analysis of the Transesterification Products

The substances obtained after the transesterification were characterized by Nuclear Magnetic Resonance (NMR) spectroscopy for both confirmation of the functional groups and percentage yield determination. NMR spectra of biodiesel samples were obtained using Bruker 400 MHz Avance II spectrometer. The samples were prepared by mixing one to two drops of the biodiesel sample with 0.5ml of 99% deuterated chloroform in 5mm sample tubes. The solution was shaken to achieve homogeneity, appropriately attached to the spinner with the aid of the gauge and then inserted into magnet chamber.

RESULTS AND DISCUSSION

The results from the characterization of modified catalysts and analysis of esterification /transesterification products are presented and discussed as follows.

KOH-Modified ZnO

The KOH-modified zinc oxide was characterized by BET, XRD and TPD-CO_2, the results are presented as follows.

BET Surface Area Analysis

The BET surface area results obtained shows that a very high surface area of 16.75 m^2/g zinc oxide was obtained from the hydration dehydration process as compared with other methods (Hariharan 2006; Li and Haneda 2003; Moezzi *et al.* 2013) and other heterogeneous catalysts like CaO, BaO and MgO (Patil *et al.* 2009). After the modification, the surface area was moderately reduced to 12.35 for 5%KOH-ZnO, 11.63 m^2/g for 10%KOH-ZnO, and 11.47 m^2/g for 15%KOH-ZnO. It then shows rapid deterioration of the surface area as the amount of KOH used is increased with 6.38 m^2/g and 4.29 m^2/g for 20%KOH-ZnO and 25%KOH-ZnO respectively. This is likely because as the amount of KOH is increased, it fails to adsorb properly on the ZnO interstitial layers and then ordinarily occupy the inter-spacings of the ZnO structures (Uekawa *et al.* 2004).

X-Ray Powder Diffraction (XRD) Analysis

The XRD spectra obtained is presented in Figure 1, it shows the dominant characteristic peaks related to the hexagonal wurtzite zinc oxide at 2θ positions of 31.8, 34.4, 36.3, 47.5, 56.6, 62.8, 66.5, 67.9 and 69.1. The KOH peaks could be observed at 27^o, 31^o, 31.9^o, 33^o and 43^o (Takase *et al.* 2014) and (Ilgen and Akin 2009). The XRD spectra obtained from 5% KOH modified is the same with that of pure ZnO, but from 10% KOH, the result shows the peak at 33^o related to KOH and 27^o peak was observed in 20% and 25% KOH-modified samples. Their intensity KOH peaks is quite weak and does not increase with increase in the amount of KOH, suggesting a proper dispersion and successful incorporation in to the crystalline lattices of the ZnO through this method. The crystallite size calculation using Scherer’s equation indicated that, in all the KOH-modified ZnO catalysts, the crystal remain approximately at 30-40 nm. This is indicating that there was no crystal growth when the KOH is attached to the ZnO crystalline lattice and that KOH is properly dispersed within the ZnO nano-structures (Ilgen & Akin 2009).

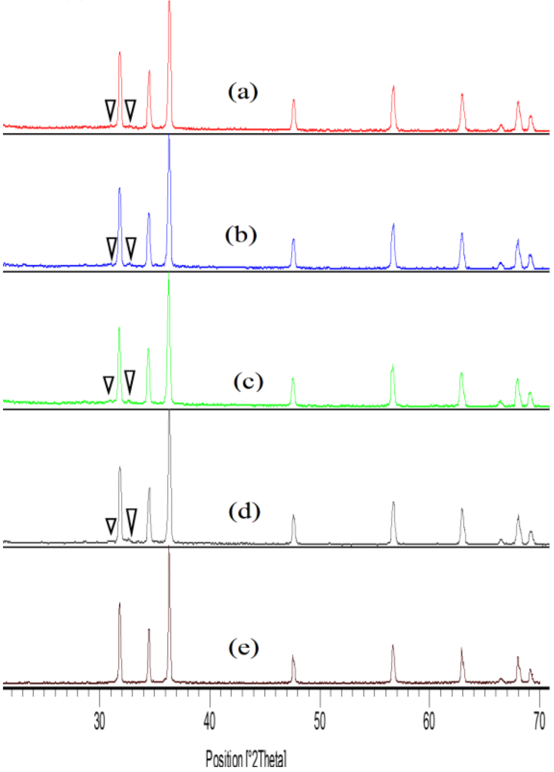

Figure 1: XRD diffraction patterns of a 10 % KOH, b 15 % KOH, c 20 % KOH d 25 % and e 5/0 % KOH zinc oxide samples.

Temperature Programmed Desorption (TPD)-CO_2

Result of the TPD as shown in Table 1 indicates the presence of basic sites in all the samples analyzed. Before the basic modification, ZnO has very low basic sites of 0.0182 mmol/g. But after modification with 5%KOH, it sharply increased to 0.06336 mmol/g. The basic sites continues to increase with increase in KOH amount used in the modification; 10%KOH; 0.08541, 15%KOH; 0.25164, 20%KOH; 0.25318 and the highest of 0.27537 mmol/g was obtained from 25%KOH. But the increase in the basic site does not change significantly after 15%KOH modification, suggesting that above 15%, the excess KOH is not used to create active sites on the ZnO surfaces. Therefore 15% can be said to be optimum amount for the modification and this may be suggesting that the active sites are largely due to the active basic sites created by modification rather than the quantity of the KOH used which is in agreement with both BET and XRD results.

Table 1: Summery of basic sites obtained from different methods

Catalyst	Basic sites	Method	Reference
KOH/ZnO	251.64 μmolg^{-1}	TPD-CO_2	This study
MgO/ZnO	333.10 μmolg^{-1}	TPD-CO_2	(Lee *et al.* 2013)
Zeolite/ZnO	0.33 mmolg^{-1}	TPD-CH_3CN	(Penzien *et al.* 2004)
KI/Al_2O_3	1.37 mmolg^{-1}	Titration	(Evangelista *et al.* 2012)
CaO/MgO	1210.50 μmolg^{-1}	TPD-CO_2	(Taufiq-yap *et al.* 2011)
CaMaZn	563.00 μmolg^{-1}	TPD-CO_2	(Limmanee *et al.* 2013)

Biodiesel Analysis

Biodiesel was prepared and characterized by ^1H NMR, results obtained are presented below.

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra of biodiesel samples from zinc oxide modified under various KOH concentrations were recorded and presented in Figure 2. The NMR spectra obtained have shown the presence of peaks related to methyl esters that are present in biodiesel, while the percentage conversion of triglycerides (TG) oil to methyl esters (biodiesel) was calculated by taking the ratio of peak area of methoxy protons from methyl esters which appears at 3.7 ppm and that of methylene proton from fatty esters which appears at 2.3 ppm. The spectra of rice bran oil can be seen to have peaks at 4.2 ppm which are associated with to the oil glycerides (Gelbard *et al.* 1995; Morgenstern *et al.* 2006; Satyarthi *et al.* 2009).

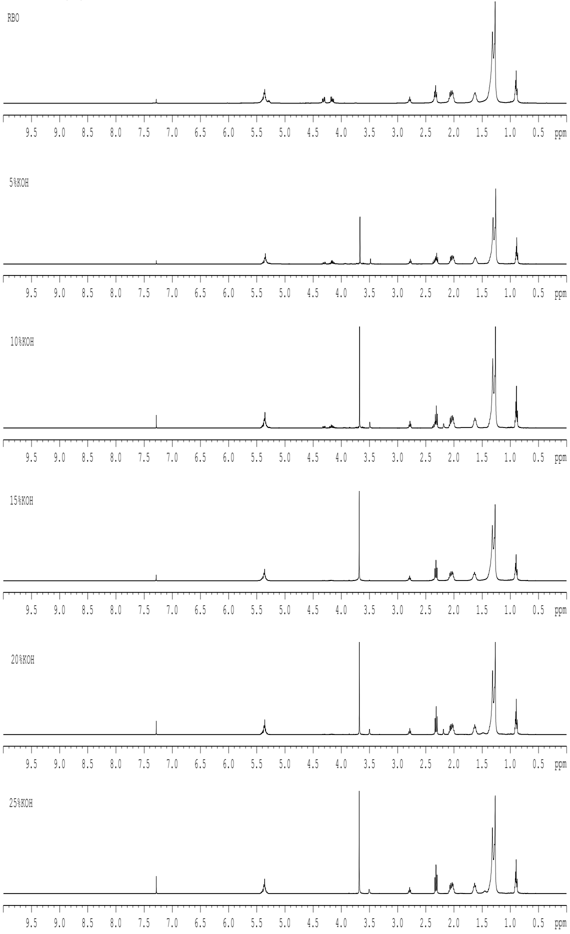

Figure 2: NMR spectra of biodiesel from the KOH modified nano-ZnO

It can be observed that in spectra of biodiesel from 5% and 10% KOH-modified ZnO there is still the presence of glyceride proton at 4.3 ppm indicating an incomplete conversion. This peak disappeared for 15, 20 and 25% modified KOH indicate near or complete conversion of the oil to biodiesel. From the results given in Table 2, it could be observed that 0%KOH ZnO shows no significant peak at 3.7 ppm and is the same with that of the oil. But 5%KOH modified ZnO formed 55.60 % biodiesel, the lower conversion can be seen from the spectra due to the low signal intensity of methyl group ester at 3.7, and the appearance of methylene protons of glyceride signal at 4.2 ppm confirms the presence of unconverted oil. 10%KOH-ZnO produced better yield of 63.31 %, this can be observed from the decreased intensity of the glyceride protons, indicating better yield but not complete conversion. 15%KOH-ZnO produced 96.24 % biodiesel yield, the glyceride peak disappeared, indicating near or complete conversion of the oil to biodiesel. 20%KOH-ZnO produced 96.43 % biodiesel yield and from ZnO.KOH-25% 96.51 % conversion yield was obtained. This indicates very high conversion as obtainable from heterogeneous catalysis. The result also indicates direct relationship between the KOH concentrations used and conversion up to 15%KOH. But there was no significant increase of conversion above 15 % suggesting this as the optimum amount needed in the modification which is further supporting that the active sites created during the modification where largely responsible for the conversion of oil to FAME but not the amount of KOH used. This is also in agreement with BET, XRD and TPD-CO_2 results discussed.

Table 2: Summary of biodiesel yield obtained from different modified catalysts

Catalyst	Conversion (%)	Reference
KOH/ZnO	96.00	This study
$MnCO_3$/ZnO	94.20	(Wan *et al.* 2014)
MgO/ZnO	80.00	(Lee *et al*. 2013)
CaO/ZnO	90.00	(Alba-Rubio *et al.* 2010)
$Sr(NO)_2$/ZnO	94.70	(Yang and Xie 2007)
CaO/SnO_2	89.3	(Xie and Zhao 2013)
Al_2O_3/KI	95.20	(Evangelista *et al.* 2012)

In general, all the results from the analyses done are consistent, indicating improvement in catalytic activity after KOH modification from 0 - 15% and the properties studied either deteriorate or remain constant above that. Summary of the relationship can be seen in Figure 3.

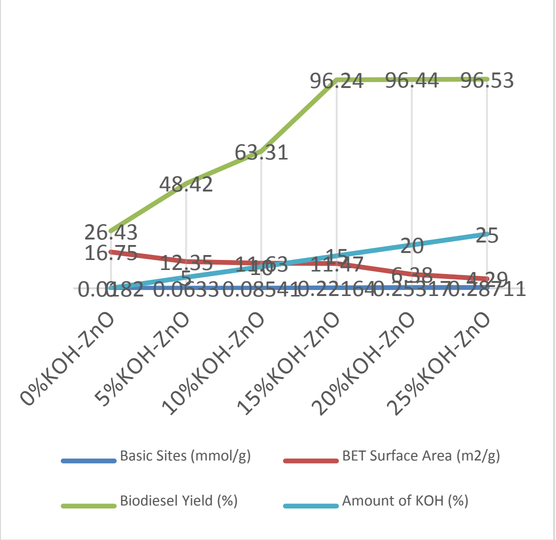

Figure 3: Relationship between basic sites, surface area, yield and amount of KOH used.

CONCLUSION

The results obtained shows direct relationship between the TPD-CO_2 basic sites and the catalyst activity from 0 to 15%, above that the increased amount of KOH does not cause significant increase in the biodiesel yield, indicating that the catalyst activity is due to the active sites created during the modification. The high yield obtained from RBO shows that zinc oxide from hydration-dehydration method and modified with KOH can be used efficient as a heterogeneous catalyst for the simultaneous esterification/transesterification of oils having relatively moderate or high free fatty acid content to biodiesel at very high oil to ester conversion with ease of products separation at relatively lower reaction conditions and moderate oil to methanol molar ratio of 9:1. It also shows that, at optimum amount of needed in the modification is 15% KOH. We can therefore conclude that, through this simple and environment friendly method, a new and efficient heterogeneous catalyst for oil to biodiesel conversion process has been prepared.

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