Biodiesel Production from Soybean Oil over TiO$_2$ Supported nano-ZnO

Mbala Mukenga, Edison Muzenda, Kalala Jalama, Reinout Meijboom

Abstract—TiO$_2$ supported nano-ZnO catalyst was prepared by deposition-precipitation and tested for the trans-esterification reaction of soybean oil to biodiesel. The TiO$_2$ support stabilized the nano-ZnO in a dispersed form with limited crystallite size compared to the unsupported ZnO. The final ZnO dispersion and crystallite size and the material transfer resistance in the catalyst significantly influenced the supported nano-ZnO catalyst performance.

Keywords—nano-ZnO, soybean oil, TiO$_2$, *trans*-esterification

I. INTRODUCTION

BIODIESEL can be synthesized by trans-esterification of vegetable oils with alcohol using both homogeneous and heterogeneous catalysts [1]. Homogeneous basic catalysts provide much faster reaction rates than heterogeneous catalysts but lead to a costly process of separating the catalysts from the reaction mixture [2, 3]. Heterogeneous catalysts are more economical and ecologically friendly. They have many advantages as they are noncorrosive, environmentally benign and present fewer disposal problems. They are also easier to separate from liquid products and can be designed to give higher activity, selectivity and longer lifetimes [4, 5]. Because of these advantages, research on chemical reaction using solid bases as catalysts has increased over the past decade [6].

One of the ways to minimize the mass transfer resistance on heterogeneous catalysts in liquid phase reactions is the use of catalyst supports. Supports can provide higher surface area through the existence of pores where metal particles can be anchored [7]. In this study, the performance of TiO2 supported nano-ZnO for the trans-esterification reaction of soybean oil has been assessed. In particular, the effects of reaction temperature, ZnO loading in the catalyst, reaction time and catalyst to oil ratio on the soybean oil conversion have been evaluated.

II. EXPERIMENTAL

A. Reagents

Sodium metal, soybean oil (99%), methanol (99%) and titania (P25 Degussa) were obtained from Sigma-Aldrich. Zinc chloride (98%) was obtained from Associated Chemical Enterprises, ethanol (>98%) from Prolabo and ammonia hydroxide solution (25% NH$_3$) from Acechem. All reagents were used as received. Zinc methoxide was synthesized by reacting sodium metal with methanol, followed by reaction with zinc chloride.

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B. Catalyst preparation and characterization

The catalyst support was prepared by mixing TiO$_2$ powder with distilled water in a mass ratio of 1:1 followed by drying at 120°C overnight [8] and calcination at 650°C for 2 hours [9]. The calcined support was crushed and screened to get particles with sizes between 50 and 100 µm to be used to support the nano-ZnO. A procedure similar to the one reported by Razo *et al.* [10] was followed in order to precipitate and deposit zinc methoxide on the TiO$_2$ support.

A solution of ammonia (12.90 cm3, 25% NH$_3$ in water) in water (2.12 cm^3) was added to a stirred solution of zinc methoxide (0-1.6020 g in 25 cm^3 ethanol) simultaneously with a particular amount of the TiO$_2$ support in order to achieve 5, 10 and 20 wt.% loading of ZnO in the catalyst after calcination. The resulting mixture was stirred at 0°C for 3 h. The formed solid was recovered through centrifugation, washed with water (3 x 40 cm^3), dried in air at 100°C for 16 hours and calcined at 500°C for 4 hours.

The calcined TiO$_2$ support and the prepared TiO$_2$ supported ZnO were characterized by X-ray diffraction (XRD) on a Philips PW 3040/60 diffractometer equipped with a CuKα (λ = 1.54 Å). Samples were scanned over a 2θ range of 4 - 80 degrees at a scan speed of 0.2 s/step. The mean crystallite size for ZnO was estimated from the full width at half maxima of the diffraction peak by the Scherrer equation. BET analysis was performed on a Micromeritics ASAP 2000 apparatus to determine the surface area and the pore size for the TiO$_2$ support.

C. Catalyst testing

The prepared TiO$_2$ supported ZnO catalyst was tested for the *trans*-esterification of soybean oil in a 300 cm^3 Parr batch reactor under a nitrogen pressure that was selected to keep all the reactants in liquid phase at different reaction temperatures. The reactor was fitted with a stirrer that was operated at a constant stirring speed 1100 rpm for all the runs. A K-type thermocouple in contact with the reacting medium was connected to a PID controller which controlled the reaction temperature to the desired set-point by regulating the current to the heating mantle around the reactor. After the reaction, methanol was removed by evaporation and two phases remained and were separated by centrifugation into glycerol as one phase and methyl esters and unreacted soybean oil as the second phase.

The conversion of soybean oil was determined by measuring the area of the ^{1}H-NMR signal relative to the methoxy and α-carbon CH$_2$ groups respectively [11].

III. RESULTS AND DISCUSSION

A. Catalyst characterization

XRD data for the blank calcined TiO$_2$ support, the unsupported ZnO and the TiO$_2$ supported ZnO (20 wt.%

ZnO/TiO$_2$) are reported in figure 1 below. After calcination the proportion of rutile and anatase were respectively 86% and 14% which can be explained by the fact that rutile is stable at higher temperatures compared to anatase. The major peaks for the unsupported ZnO (Fig. 1a) were detected at diffraction angles of ca. 32, 35, 37, 46, 48, 57, 63 and 68° consistent with data reported in literature [12-14]. The crystallite size of the unsupported ZnO was ca. 50 nm. The XRD pattern for the TiO2 supported ZnO (Fig. 1b) was a combination of the XRD patterns for the unsupported ZnO (Fig. 1a) and the blank TiO$_2$ (Fig. 1c). No new peak indicating the formation of new compounds in addition to TiO$_2$ and ZnO was detected in the supported ZnO. This could suggest that there were no significant ZnO-TiO$_2$ compounds formation and that the ZnO-TiO$_2$ interactions were purely physical. The crystallite size for the supported ZnO was ca. 17 nm, about a third of the crystallite size for the unsupported ZnO. These findings indicate that the TiO$_2$ support limited the growth of ZnO crystallite size. The BET analysis for the blank TiO$_2$ support gave a surface area of 21.7 m^2/ g and a pore size of 30.2 nm. It is possible that more ZnO was growing in the TiO$_2$ pores and therefore the resulting crystallite size was less than the pore size. Thus the TiO$_2$ stabilized ZnO particles in a more dispersed form.
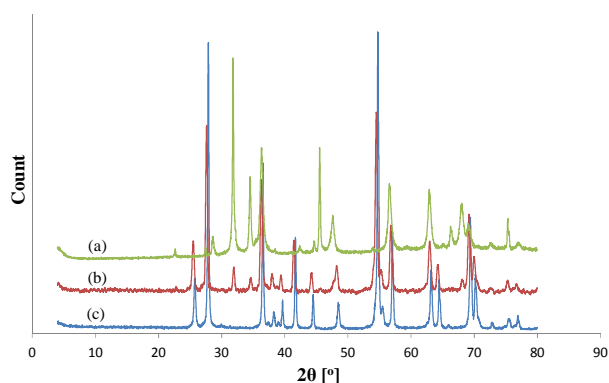

Fig. 1 XRD data for calcined (a) unsupported ZnO, (b) TiO$_2$ supported ZnO and (c) blank TiO$_2$

B. Catalyst testing

1. Effect of reaction temperature and ZnO loading

The data showing the effect of temperature and ZnO loading in the catalyst on the soybean trans-esterification with methanol are reported in Fig. 2. The general trend of the data shows that when catalysts with the same ZnO loading are used, the oil conversion increases with reaction temperature. For example soybean oil conversions of ca. 16, 55, 82 and 96% were respectively measured at 150, 175, 200 and 225°C when a catalyst containing 5% ZnO was used. The effect of ZnO loading on the oil conversion depends on the range of reaction temperature used. The lowest conversions were measured on catalysts with the highest ZnO loading, i.e. 20% ZnO for the reactions performed at 150 and 175°C. However, the oil conversion passes through a minimum on catalyst with 10%

ZnO and increases on the catalyst containing 20% ZnO for reactions performed at 200 and 225°C. These findings can be explained by the ZnO dispersion on the support and the mass transfer limitations. The crystallite size, determine by XRD analysis, for the catalyst containing 5% ZnO was ca. 31 nm compared to ca. 17 nm for the catalyst containing 20% ZnO. The ZnO crystallite size for the 5% ZnO catalyst was slightly larger than the pore size of the TiO$_2$ support suggesting that most of the ZnO particles were stabilized on the outer surface of the support. The mass transfer resistance on these particles was lower compared to the case of 20% ZnO catalyst where most of the particles were most likely stabilised inside the pores of the TiO$_2$ support as discussed in section A. As the temperature increased to 200 and 225°C the viscosity of the reacting medium decreased and improved the mass transfer on particles inside the pores of a 20% ZnO catalyst resulting in a significant increase in oil conversion. The highest conversion has been achieved in the reaction performed over a 20% ZnO catalyst at 225°C. A temperature of 225°C was selected as the reaction temperature for the rest of the study.
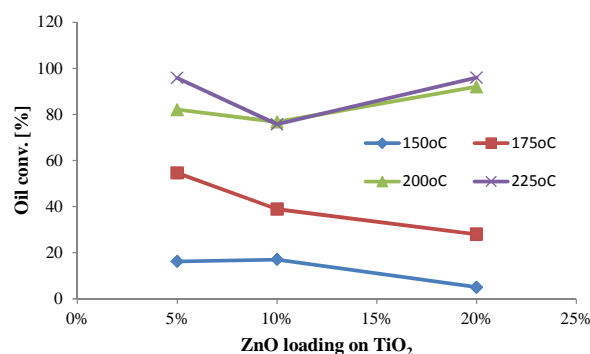

Fig. 2 Effect of oxide loading on biodiesel conversion: alcohol to oil molar ratio 18 to 1, catalyst amount 3 wt.%, 1 hour reaction time

2. Effect of reaction time on biodiesel conversion

The oil conversion after 1, 6 and 10 hours of the soybean transterification reaction over 5, 10 and 20% ZnO catalysts are reported in Fig. 3. Oil conversions of ca. 96% were achieved over 5 and 20% ZnO catalyst after 1 hour of reaction. No significant change in the oil conversion was observed when the reaction time was extended to 6 and 10 hours on a 5% ZnO catalyst. An almost total oil conversion was measured on a 20% ZnO catalyst when the reaction time was extended to 6 hours but a decrease in conversion to ca. 90% was observed after 10 hours of reaction. This could be due to glycerolysis reaction reported to take place at extended trans-esterification reaction time [15]. The lowest oil conversion (ca. 75%) was measured over 10% ZnO catalyst after one hour of reaction followed by an increase to 85% after 6 hours of reaction. No significant change in conversion was measured on 10% ZnO catalyst after 10 hours of reaction. These findings revealed that a reaction time of ca. 1 hour over a 5 or 20% ZnO catalyst was enough to achieve satisfactory levels of oil conversion.
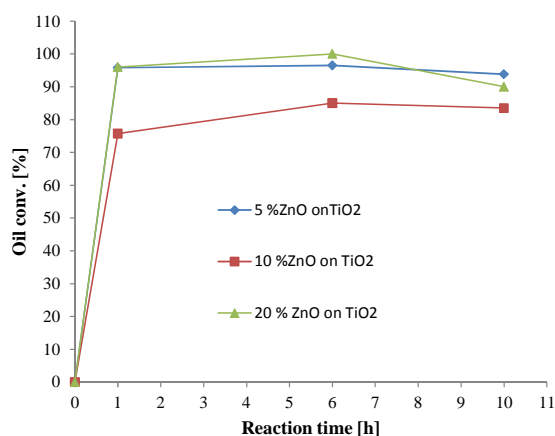
Fig. 3 Effect of reaction time on soybean conversion (alcohol to oil molar ratio: 18 to 1, catalyst amount 3 wt.% with respect to oil and reaction temperature of 225°C)

3. Effect of catalyst amount on soybean oil conversion

The effect of catalyst amount on the oil conversion has been evaluated by running the trans-esterification reaction at 225°C without catalyst and subsequently with 0.5, 1.5, 3 and 6 wt.% catalyst (20% ZnO/TiO$_2$) with respect to the amount of oil loaded in the reactor. The results summarized in Fig. 4 show that after 15 minutes (Fig. 4a) of reaction the oil conversion for the run without catalyst reached ca. 25% compared to 81, 87, 88, 89% respectively for the runs with catalyst amounts equal to 0.5, 1.5, 3 and 6 % catalyst loaded in the reactor. Oil conversions in excess of 90% were measured for the reactions with 0.5-6 wt.% catalyst after 30 minutes of reaction (Fig. 4b). Within an experimental error, no difference in oil conversions were noted after 45 minutes of reaction (Fig. 4c) with 1.5-6 wt.% catalyst in the reactor. These conversions were at their maximum values of ca. 100% compared to 54 and 95% respectively for 0 and 0.5 wt.% catalyst in the reactor. Further increase in reaction time to 60 minutes (Fig. 4d) led to a decrease in conversion to ca. 99% for the run with 1.5% catalyst and 96% for the reaction run with 3 and 6% catalyst respectively. This decrease in oil conversions is suggestive of a glycerolysis reaction at extended reaction times as discussed in section B2. The activity of the glycerolysis reaction, as indicated by a drop in measured oil conversion, was high for the reaction with the highest amount of catalyst (6 wt.%). No indication of glycerolysis reaction activity was observed for the reaction with 0 and 0,5 wt.% catalyst which showed monotone increases in oil conversion with time up to 68 and 98% respectively after 60 minutes of reaction.
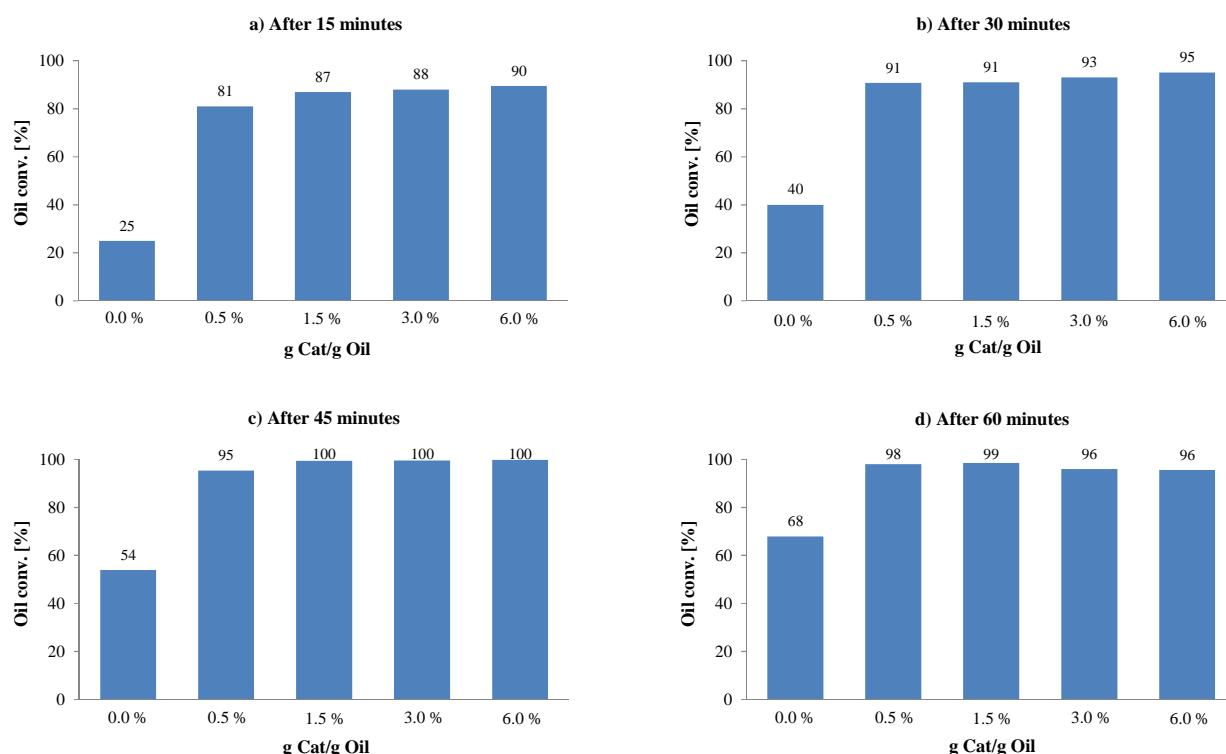
Fig. 4 Effect of catalyst amount in the reactor on biodiesel conversion (alcohol to oil molar ratio 18 to 1, 20% ZnO/TiO$_2$, 225°C)

4. Effect of alcohol to oil molar ratio on biodiesel conversion

Methanol to oil ratios of 6:1, 12:1 and 18:1 were used to evaluate the effect of methanol to oil ratio on the soybean oil conversion during the transesterification reaction. The results are presented in Fig. 5 and show that up to 60 minutes of reaction, the measured conversion was higher for the reaction that was performed with the highest methanol to oil ratio (18:1 in this study) as also reported in other studies [16, 17]. However, it can be observed that the reaction with a methanol to oil ratio of 18:1 showed some decline in measured oil conversion from ca. 30 minutes of reaction where the oil conversion was almost complete to ca. 96% after 60 minutes. Although a high methanol to oil ratio increases the rate of oil *trans*-esterification, it appears that the glycerolysis reaction is also favoured when the reaction time is extended.
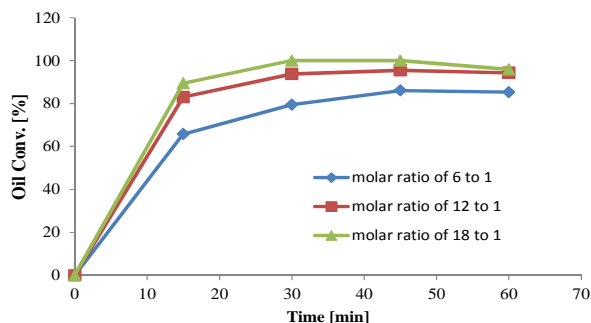

Fig. 5 Effect of alcohol to oil molar ratio on biodiesel conversion: 3 wt.% of ZnO/TiO$_2$ at 20% and reaction temperature of 225°C

IV. CONCLUSION

Nano ZnO were prepared and supported on a TiO$_2$ support and tested for the trans-esterification of soybean oil to biodiesel. The TiO$_2$ support stabilized the nano-ZnO in a dispersed form with limited crystallite size compared to the unsupported ZnO. For the same ZnO loading in the catalyst, the oil conversion improved at high reaction temperatures. The effect of ZnO loading on the oil conversion was significantly dependent on the reaction temperature selected. Indications of some glycerolysis activity were observed during reactions with catalyst to oil ratios of 1.5 to 6% at extended reaction times.

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