Biodiesel Production over nano-MgO Supported on Titania

Liberty L Mguni, Reinout Meijboom, Kalala Jalama

Abstract—Nano-MgO was successfully deposited on titania using deposition-precipitation method. The catalyst produced was characterised using FTIR, XRD, BET and XRF and its activity was tested on the transesterification reaction of soybean oil to biodiesel. The catalyst activity improved when the reaction temperature was increasedfrom 150 and 225 ^{O}C. It was also observed that increasing the reaction time above 1h had no significant benefit on conversion. The stability fixed MgO on TiO_2 was investigated using XRF and ICP-OES. It was observed that MgO loss during the reaction was between 0.5-2.3 percent and that there was no correlation between the reaction temperature and the MgO loss.

Keywords—Nano-MgO, TiO_2, transesterification

I. INTRODUCTION

SINCE Walton [1] recommended in 1939 that "to get utmost value from vegetable oil as fuel it is academically necessary to split off the triglycerides and run on the residual fatty acid", there has been a number of methods employed to achieve this. These methods include pyrolysis, cracking, micro-emulsification and transesterification [2, 3]. Among the many methods available, transesterification has been found to be the most viable process [4]. Base homogenous catalysts are the most commonly used in commercial plants because of shorter reaction time compared to acid homogenous catalysts and heterogeneous catalysts. Despite this, they present a number of challenges as they cannot be reused; they produce large amounts of waste water and low grade glycerol as a by-product. In contrast, heterogeneous catalysts offer a simplified production and purification process [5] but still face the challenge of slower reaction rates that need to be overcome to make the process more attractive; this can be done by improved catalyst design.

Various metal oxides such as MgO [4, 6-8], ZnO [9], SnO_2[10], CaO[11-13], *etc.* have been reported to be active for the transesterification reaction of triglycerides. Verziu et al. [8] demonstrated that nanostructured MgO can be used effectively as a heterogeneous catalyst system for biodiesel transesterification and that the facet of MgO exposed has an important influence regarding activity and selectivity. For industrial applications nano-MgO would pose serious filtration problems and catalyst separation would be troublesome. In order to exploit the benefit of high catalytic activities for nano-MgO and avoid potential catalyst separation problems for industrial applications, we have dispersed nano-MgO on TiO_2 support.

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Mixed oxides of TiO_2 and MgO have been used for the production of biodiesel from waste oil by Wen et al. [14] who reported that titanium improved the stability of the catalyst because of the defects induced by the substitution of Ti ions for Mg ions in the magnesia lattice. These mixed oxides were prepared by sol-gel synthesis. To the best of our knowledge no other study using nano-MgO precipitated and deposited on TiO_2support for use in biodiesel transesterification has been reported to date. In this study the catalytic behaviour for TiO_2 supported nano-MgO, prepared by deposition precipitation method, for the soybean oil transesterification reaction will be investigated. In particular the effect of reaction temperature, reaction time, MgO loading on TiO_2 and the catalyst quantity will be studied.

II. EXPERIMENTAL PROCEDURE

A. Materials

Magnesium ethoxide [$Mg(OCH_2CH_3)_2$] (98%), soybean oil (99%) and methanol (99%) were obtained from Sigma-Aldrich whereas ethanol (>98%) was obtained from Prolabo and ammonia hydroxide solution (25% NH_3) from Acechem. All reagents were used as received.

1. Support preparation

TiO_2 (Degussa P25 containing 17% rutile) was mixed with deionised water in a mass ratio of 1:1 and dried in air at 120 ^{O}C for 16h [15]. The dried support was then calcined in air at 650 ^{O}C for 2 hours to achieve 78% rutile [16]. After calcinations the support was crushed and sieved. Particles between 50 and 100 microns were used as catalyst support.

2. Catalyst Preparation

The catalyst was prepared by deposition-precipitation. The precursor $Mg(OCH_3CH_3)_2$ was dispersed in ethanol and subsequently TiO_2 was added. A solution of water and ammonia was added drop wise to the mixture. After stirring for 3h, the catalyst was dried at 100 ^{O}C in air for 16 h and then calcined at 500 ^{O}C for 2h. The reactants were added to achieve 10-30 wt.% loading of nano-MgO on TiO_2.

B. Catalyst Characterisation

FTIR spetra were recorded using a Bruker Tensor 27 in the range of 4000-400cm^{-1}to determine functional groups in catalyst samples. XRF was used to determine MgO loading on the support. The BET analysis was performed to determine the surface area (SA) and pores distribution by N_2 adsorption at the temperature of 77 K using a Micromeritics ASAP 2000.

To investigate the leaching of metal content (Ti and Mg) into products, the catalyst was centrifuged and filtered from the liquid reaction mixture after reaction completion, and then the liquid mixture was analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) after acid digestion. The structure of the catalyst system were analysed using a Philips PW 3040/60 X-ray diffraction apparatus with a

CuK_{α} ($\lambda = 1.54$) radiation. Samples were scanned over a 2θ range of 4–130° with a 0.02^{O} step size and a scan speed of 0.04 s/step. The mean crystallite size of MgO in catalyst samples was estimated from the full width at half maxima of the diffraction peak by the Scherrer equation and the rutile to anatase ratios were determined using equation (1) below.

$$\% \, Rutile = \frac{1}{[(\frac{A}{R})0.884 + 1]} * 100 \qquad (1)$$

Where, A and R are the peak areas for major anatase ($2\theta = 25^{O}$) and rutile phase ($2\theta = 28^{O}$), respectively [17].

C. Catalyst Testing

A 300 cm^3 stainless steel batch reactor (PARR 4842 series reactor) was charged with soybean oil (68 cm^3), methanol (52 cm^3) and varying mass of catalyst. The reactor temperature was maintained at a desired value by a temperature control loop consisting of a K-type thermocouple in contact with the reacting medium, a PID temperature controller and a cylindrical heating mantle around the reactor vessel. The stirring rate was set at 1100 rpm. After 30 min – 10 h of reaction, the products were left to cool to room temperature.

The catalyst was removed from the products by centrifugation. The remaining product was heated at $65\,^{O}$C in a vacuum evaporator to remove methanol. The products that remained after drying were glycerol, unreacted oil and the methyl esters. These products separate to two phases: glycerol as the bottom phase and oil and methyl esters as the top phase. The top phase was used to determine the oil conversion to methyl esters using NMR analysis on a Bruker 400 MHz NMR apparatus. The following formula (2) was used to determine the oil conversion from NMR data:

$$\% Conversion = \frac{2A_{ME}}{3A_{\propto - CH_2}} \times 100 \qquad (2)$$

Where A_{ME} is the integration value of the protons of the methyl esters

$A_{\alpha-CH2}$ is the integration value of the methylene protons [18].

III. RESULTS AND DISCUSSION

A. Catalyst characterisation

1. FTIR analysis

The FTIR results for the dried and the calcined supported catalyst samples are presented in fig. 1 below. Drying at $100\,^{O}$C removed most of the adsorbed water, with the gel remaining as $Mg(OH)_2$ shown by the sharp absorption at 3693 cm^{-1} with an absorption at 1394 cm^{-1} attributed to O-H bonded to Mg. After calcining at $500\,^{O}$C and above, these absorptions were no longer observed suggesting complete conversion of $Mg(OH)_2$ to MgO.

The broad absorbance attributable to the ν(O-H) between 2953 and 3512 cm^{-1}, with the concomitant δ(O-H) at 1401 and 1637 cm^{-1} persisted in both solids $Mg(OH)_2/TiO_2$ and MgO/TiO_2. These absorptions were attributed to surface hydroxyl species resulting from a fast reaction between the atmospheric moisture and the solids researchers [6, 19].
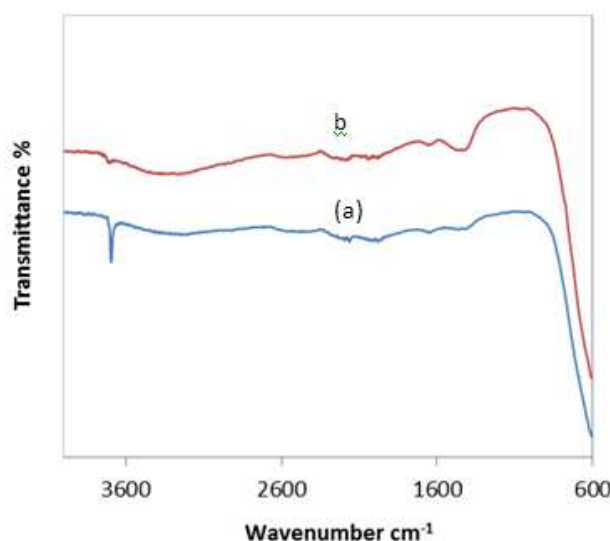

Fig. 1 FTIR spectra for (a) dried catalyst and (b) catalyst calcined at 500°C

2. XRF analysis

The MgO loadings in the catalyst as determined by XRF analysis are summarized in table 1 below. These results suggest that the TiO_2 did provide a surface for nucleation of nano-MgO during the deposition-precipitation process since there is little difference between the target (10, 20 and 30 wt.% MgO) and the achieved (8.7, 20.7 and 31.2 wt.% MgO) loadings. XRF analyses after the reaction gave 8.1, 20.3 and 30.2 wt.% MgO and further suggest that the nano-MgO/TiO_2 catalyst system is stable with insignificant catalyst loss through leaching or any other means under the reaction conditions used. This was further confirmed by ICP-AES results discussed in section A4.

TABLE I
XRF RESULTS FOR FRESH AND USED CATALYSTS

	Nano-MgO loading [wt.%]		
Target loading	10.0	20.0	30
Achieved loading	8.7	20.7	31.2
After reaction ($225\,^{O}$C)	8.1	20.3	30.2

3. BET analysis

Surface area and pore sizes for the blank TiO_2 support and TiO_2 supported nano-MgO catalyst samples with 10 and 30 wt.% MgO loadings are reported in table II below.

TABLE II
BET ANALYSIS RESULTS FOR SAMPLES CALCINED AT $500\,^{O}$C

	Support	10 wt.%	30 wt.%
Surface area (m^2/g)	21.7	14.6	20.3
Pore size (nm)	30.2	27.5	24.7

The deposition of ca. 10% of MgO decreased the surface area from 21.7 (for the blank support) to 14.6 m^2/g. This surface area was further increased for MgO loadings of ca.

30%. A possible explanation is that the resulting accessible surface area on MgO loaded catalyst was determined by the proportion of MgO obstructing the pores of the support and that deposited on the outer surface of the support. It appears that for the 10% loaded catalyst; the loss of accessible surface area due to pores obstruction was significant compared to the gain in surface area due to additional particles on the outer surface of the support. More MgO particles possibly deposited on the outer surface of the support in the case of 30% loading were leading to a higher measured surface area compared to 10% loaded catalyst.

4. ICP-AES analysis

The amounts of catalyst lost during the transesterification reaction at various reaction temperatures were determined by ICP-AES and the results are presented in table 3. No trend showing the loss of catalyst as function of the reaction temperature was evident. The Mg loss only varied between 0.5 and 2.3%. The titania loss at this temperature range was insignificant.

TABLE III
ICP-AES RESULTS ON EFFECT OF REACTION TEMPERATURE ON TI AND MG LOSS

Reaction temperature	Ti		Mg	
		*loss		*loss
[oC]	Conc.[ppm]	[%]	Conc.[ppm]	[%]
150	0.7	trace	17.9	0.5
175	2.0	trace	38.8	1.0
200	0.8	trace	89.9	2.3
225	0.3	trace	17.2	0.5

* amount lost is calculated from ICP-AES results divided by amount of nano-MgO or titania charged into the reactor

5. XRD analysis

XRD analysis for the TiO_2 supported nano-MgO was performed and the data are reported in fig. 2 below. To facilitate the identification of peaks at different diffraction angles, XRD data for the blank TiO_2 support and for nano-MgO were also generated and reported.
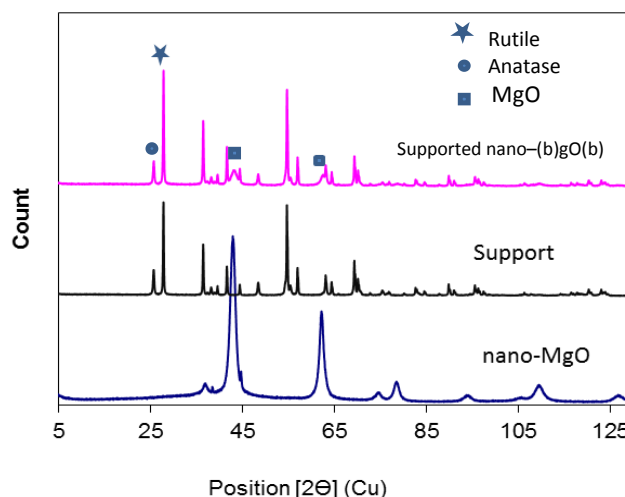

Fig. 2 XRD data for nano-MgO, TiO_2 support and TiO_2-supported nano-MgO

After calcination at 650 ^{o}C the TiO_2 support was found to contain 78% rutile. This rutile proportion did not change in the TiO_2 supported catalyst calcined at 500°C suggesting good thermal stability of the support at this calcination temperature. The diffraction peaks for the TiO_2 supported nano-MgO system were a combination of the blank TiO_2 and nano-MgO diffractions and no new peaks in addition to these were observed. The absence of new peaks on the supported nano-MgO suggests that the interaction between nano-MgO and the support was purely physical [14].

B. Catalyst testing

1. Effect of reaction temperature and MgO loading

Fig. 3 below shows the conversion of soybean oil to methyl esters for various nano-MgO loadings on TiO_2 and different reaction temperatures for a fixed reaction time of 1h. It was observed that, for the same MgO loading, increasing the reaction temperature had a favourable influence on the conversion. For example 15% oil conversion was measured at 150°C for the catalyst containing 10 wt.% MgO and reached ca. 84% at 225°C. To avoid reaching the critical temperature for methanol (239 ^{O}C) the reaction temperatures were limited to a maximum of 225 ^{O}C. This increase of conversion with temperature is consistent with previous studies [4, 7] and might be due to the following factors: i) a decrease in viscosity of reactants with temperature thus reducing mass transfer limitations and ii) an increase in the energy supplied to the system at high temperatures causing more particles to collide and have energy greater than the activation energy and react.
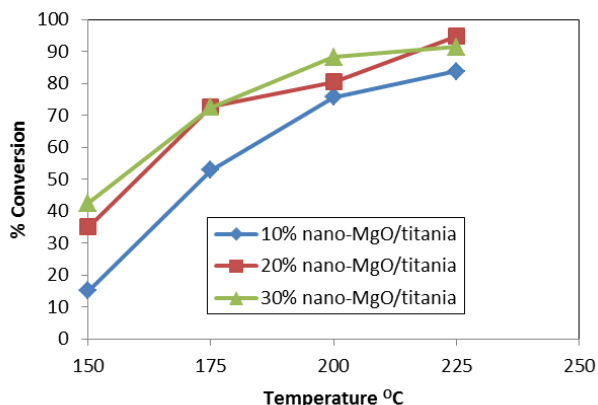
Fig. 3 Effect of MgO loading and reaction temperature (oil to methanol molar ratio 1:6; catalyst amount: 5wt.% with respect to oil, 1h)

When compared at the same reaction temperature, the catalyst activity was found to increase with the MgO loading. For example conversions of 15, 35 and 42 were measured at 150°C for 10, 20 and 30 wt.% MgO loadings respectively. Within an experimental error, these conversions were increasing almost by the same factor as the increase in MgO loading. However, as the reaction temperature was increased, the effect of MgO loading on the catalyst activity decreased.

Conversions of 84, 91 and 95% were measured at 225°C compared 15, 35 and 42% at 150°C respectively for 10, 20 and 30 wt.% MgO catalyst. This could suggest that the measured rate of reaction was more determined by the rate of material transfer to and from the catalyst than the reaction on catalyst surface. A 20 wt.% MgO loading showed the highest activity at 225°C.

2. Effect of reaction time

The effect of reaction time was investigated and the results are summarised in fig. 4. Reactions have been conducted at 225°C for 15, 30, 45, 60 and 600 minutes. The results show that increasing the reaction time above 1 h had no significant benefit. This might be because the equilibrium conditions were almost achieved within 1 h of reaction. It can also be noted that the increase in conversions with time did not significantly change with the MgO loading of the catalyst. This was because of the high reaction temperature where material transfer to and from the catalyst has been improved as discussed in section B1 above. 20% nano-MgO/TiO$_2$ again resulted in a slightly higher conversion as compared to the other catalysts. 20 wt.% MgO loading and maximum reaction time of 1 h were selected for the rest of the investigation.
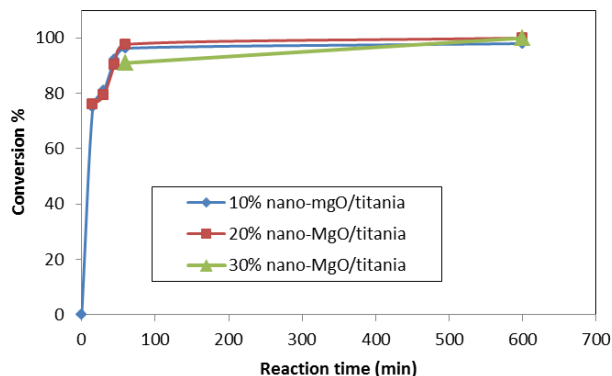

Fig. 4 Effect of reaction time on soybean conversion over catalyst with various MgO loadings (oil to methanol molar ratio: 1:18; temperature: 225°C catalyst amount: 5wt.% with respect to oil)

3. Effect of catalyst amount

The effect of the catalyst amount on the soybean conversion has been studied by running the reaction with 0, 0.1, 1, 3, 5 and 7% catalyst loaded in the reactor. Fig. 5 shows the effect of the amount of catalyst in the reactor on soybean conversion with time. No significant effects of catalysts amounts from 1 to 7% were noted under the conditions used for these runs. Some conversion was still measured for the catalyst-free run and a value of ca. 68% soybean conversion was achieved after 60 minutes of reaction. A 0.10% catalyst loading also resulted in a lower conversion of 15% after 20 minutes of reaction as compared to ca. 76-82% for the 1 - 7% catalyst amounts. The effect of catalyst amounts in the reactor decreased with reaction time. After 60 minutes of reaction almost no difference in conversion could be noted for the various amounts (0.1 to 7%) of catalyst used. For a reaction time of 60 minutes, an amount of ca. 0.1% catalyst in the reactor would be optimum as it would not significantly affect the reactants viscosity and will still lead to good conversion levels resulting in a more economical process.
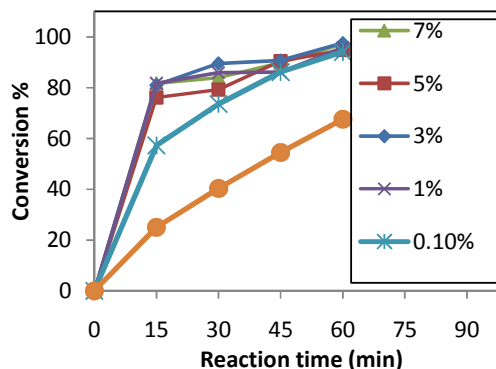

Fig. 5 Effect of catalyst amount in the reactor on soybean oil conversion (oil: methanol molar ratio: 1:18, 225 ^{O}C) selected

IV. CONCLUSION

The nano-MgO/TiO$_2$ system has shown good activity and stability in the transesterification reaction under the conditions

investigated. There was an increase in conversion with increasing reaction temperature. The effect of catalyst loading diminished with long reaction time at high reaction temperature of 225 ^{O}C. The determination of MgO contents in the used catalyst revealed that nano-MgO losses were between 0.5-2.3wt.% and had no correlation with the reaction temperature.

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