

Effect of Calcination Temperature and MgO Crystallite Size on MgO/TiO₂ Catalyst System for Soybean Transesterification

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Abstract—The effect of calcination temperature and MgO crystallite sizes on the structure and catalytic performance of TiO₂ supported nano-MgO catalyst for the *trans*-esterification of soybean oil has been studied. The catalyst has been prepared by deposition precipitation method, characterised by XRD and FTIR and tested in an autoclave at 225°C. The soybean oil conversion after 15 minutes of the *trans*-esterification reaction increased when the calcination temperature was increased from 500 to 600°C and decreased with further increase in calcination temperature. Some glycerolysis activity was also detected on catalysts calcined at 600 and 700°C after 45 minutes of reaction. The *trans*-esterification reaction rate increased with the decrease in MgO crystallite size for the first 30 min.

Keywords—Calcination temperature, crystallite size, MgO/TiO₂, transesterification

I. INTRODUCTION

THE dwindling of oil reserves, as confirmed by the World Energy Forum prediction, suggests that in less than 10 decades all current energy supplies will be exhausted [1]. Coupled with an industrial shift towards processes which are more environmental friendly, the rapid increase in oil demand and the instability in the Middle East, the largest oil producer, have lead to a resurgence in the interest in bio fuels.

Not surprisingly, biodiesel has received most of the interest because 95% of the energy generated from petroleum is consumed by the transport sector [2]. The technology of biodiesel production has been around for almost a century and transesterification has mainly been utilizing base homogenous catalyst [3]. However, there has been a growing interest in heterogeneous catalysis because of the well know advantages it presents. These advantages include: elimination of corrosion problems, fewer disposal problems and much easier separation of products [4]. However, currently there is only one commercial plant utilizing heterogeneous catalyst [3]. This is probably due to the low activity of solid catalyst compared with homogenous catalysts which necessitates the use of extreme reaction conditions [5]. Most of the current work in heterogeneous catalysis is aimed at improving catalyst activity. Previous reports [1, 6-8] have shown that the method of catalyst activation can profoundly affect the reactivity and surface properties of the catalyst. Calcination of MgO has been reported to result in the restructuring of the metal oxide thus leading to an increase in defects which are electron-donating O²⁻ centers, postulated as superbasic sites in solid base catalysis [8].

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Calcination not only affects defect production but also increases the crystallite size [7-9]. This increase in crystallite size makes it difficult to understand the effect of crystallite size alone on the transesterification reaction. In this study we have investigated the effect of calcination temperature and also the effect of different crystallite sizes of nano-MgO supported on TiO₂ and produced using modified Stober synthesis [10]. The latter catalysts were calcined at the same calcination temperature in order to decouple the effect of calcination temperature from the effect of MgO crystallite sizes.

To the best of our knowledge no other study on the effect of calcination temperatures on the structure and catalytic performance of the nano MgO/TiO₂ system prepared by deposit-precipitation for the soybean oil transesterification has been reported to date.

II. EXPERIMENTAL PROCEDURE

A. Materials

Magnesium ethoxide [Mg(OCH₂CH₃)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% NH₃) from Acechem. All reagents were used as received.

B. Catalyst Synthesis

1. Support Preparation

TiO₂ (Degussa P25 containing 17% rutile) was mixed with deionised water in a mass ratio of 1:1 and dried in air at 120 °C for 16h [11]. The dried support was then calcined in air at 650 °C for 2 hours to achieve 78% rutile [12]. 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 using modified Stober synthesis method [10]. A solution of ammonia (12.90 cm³, 25% NH₃ in water) was slowly added to a stirred solution of magnesium ethoxide (0-1.6020 g) and titania in ethanol (25 cm³). The quantity of magnesium ethoxide was varied to achieve different crystallite sizes while titania was varied to achieve 20 wt.% metal oxide loading on the support. The resulting mixture was stirred for 3 h at 0°C. The formed solids were recovered through centrifugation, washed several times with water, dried in air at 100°C for 16 hours and subsequently calcined in air at temperatures ranging from 500 to 800 °C for 2 hours.

C. Catalyst Characterisation

The catalyst was prepared by deposition-precipitation FTIR spectra were recorded using a Bruker Tensor 27 in the range

of 4000-400 cm^{-1} to determine functional groups in catalyst samples. XRF was used to determine MgO loading on the support. The structure of the catalyst system was determined using a Philips PW 3040/60 X-ray diffraction apparatus with $\text{CuK}\alpha$ ($\lambda = 1.54$) radiation. Samples were scanned over a 2θ range of 4–130 $^\circ$ with a 0.02 $^\circ$ 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 most intense diffraction peak by the Scherrer equation and the rutile to anatase ratios were determined using equation (1) below

$$\% \text{ Rutile} = \frac{1}{\left[\left(\frac{A}{R}\right) 0.884 + 1\right]} * 100 \quad (1)$$

Where, A and R are the peak areas for major anatase ($2\theta = 25^\circ$) and rutile phase ($2\theta = 28^\circ$), respectively [13].

D. Catalyst Testing

A 300 cm^3 stainless steel batch reactor (PARR 4842 series reactor) was charged with soybean oil (68-96 cm^3), methanol (52-24 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 and the products were sampled from the reactor between 15 to 60 minutes of reaction. The catalyst was removed from the products by centrifugation. The remaining product was heated at 65 $^\circ\text{C}$ in a vacuum evaporator to remove methanol. The products that remained after evaporating methanol were glycerol, unreacted oil and the methyl esters. These products separated 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 using the method reported by Gelbard *et al.* [14].

III. RESULTS AND DISCUSSION

A. Catalyst characterization

1. FTIR analysis

The FTIR results for the dried and the calcined supported catalyst samples are presented in fig. 1 below. A sharp absorption due to $\text{Mg}(\text{OH})_2$ at 3693 cm^{-1} was observed in the dried catalyst sample (figure 1a) and almost disappeared in the calcined catalyst (figure 1b-e) suggesting that the conversion of $\text{Mg}(\text{OH})_2$ to MgO during calcination was almost complete. The broad absorbance attributable to the $\nu(\text{O-H})$ between 2953 and 3512 cm^{-1} , with the concomitant $\delta(\text{O-H})$ absorption at 1637 cm^{-1} persisted in both the dried and the calcined samples. These absorptions were attributed to surface hydroxyl species, resulting from a fast reaction between the atmospheric moisture and the solids. These absorptions were also previously reported in several studies [1, 15, 16]. An

absorbance between 400 and 1000 cm^{-1} was present before and after calcination and was attributed to the $\nu(\text{Ti-O})$ vibration [15, 17].

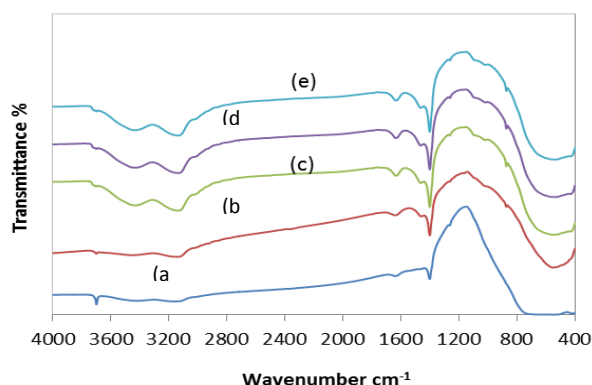


Fig. 1 FTIR spectra for (a) dried catalyst; (b) catalyst calcined at 500 $^\circ\text{C}$; (c) catalyst calcined at 600 $^\circ\text{C}$; (d) catalyst calcined at 700 $^\circ\text{C}$ and (e) catalyst calcined at 800 $^\circ\text{C}$

1. XRD analysis

XRD data for catalyst samples calcined at 500, 600, 700 and 800 $^\circ\text{C}$ are shown in fig. 2 below. The diffraction peaks at 25.3, 48.1, 54.0, 55.1 and 62.8 $^\circ$ were due to the anatase phase of TiO_2 and those at 27.4, 36.1, 41.3, 54.3 and 69.9 $^\circ$ to rutile. MgO was detected at diffraction angles of 42.9, 62.2 and 78.7 $^\circ$. The ratio of rutile to anatase did not significantly change and no new diffraction peaks were observed for catalysts calcined at 500 and 600 $^\circ\text{C}$. However, some of the rutile phase (TiO_2) began to transform to give $\text{Ti}_{0.992}\text{O}_2$ in the sample calcined at 600 $^\circ\text{C}$ and above as that was indicated by slight shift of some rutile peaks i.e 35.84, 41.028 and 54.153 to 36.1, 41.26 and 54.341 respectively. This could indicate an initial loss of titania to the magnesia structure as also suggested by previous studies [18, 19] that indicated that Ti^{4+} transfers to the magnesia structure at this temperature range 400-600 $^\circ\text{C}$ and above. When the calcination temperature was increased to 700 $^\circ\text{C}$ a new phase MgTiO_3 at a diffraction angle of 33.05 $^\circ$ became evident. On further increase of the calcination temperature to 800 $^\circ\text{C}$ the intensity of the peaks due to MgTiO_3 intensified. It can also be observed that as the calcination temperature was raised to 700 $^\circ\text{C}$ the anatase phase peaks reduced and finally disappeared at 800 $^\circ\text{C}$. The change in titania phase from anatase to rutile has been reported by a number of researchers [20-22] but the temperature causing all the anatase to disappear in this study was lower than those reported. This might be due to the presence of MgO.

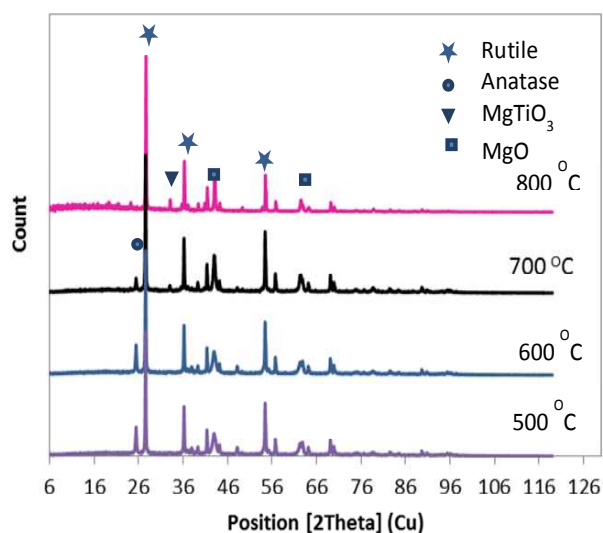


Fig. 2 Effect of calcination temperature on supported MgO catalyst calcined at 500 °C, 600 °C, 700 °C and 800 °C

Fig. 3 shows the nano-MgO crystallite sizes as a function of calcination temperature. These sizes did not significantly change for calcination temperatures from 500 and 700 °C. A significant increase in size from ca. 35 nm to 80 nm was observed in the catalyst calcined at 800 °C. This could be due to sintering of nano-MgO at this high temperature.

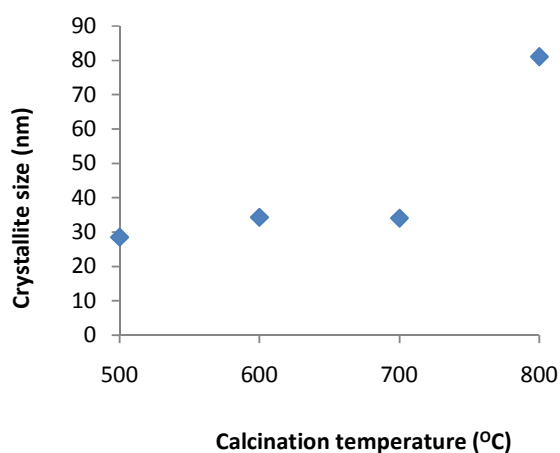
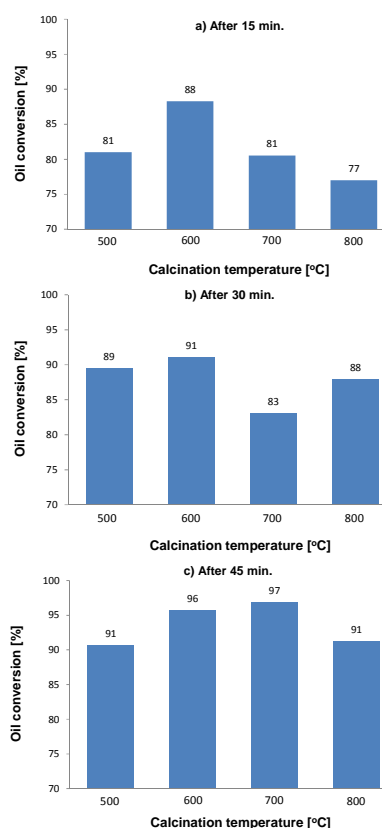


Fig. 3 Effect of calcination temperature on nano-MgO crystallite size

B. Catalyst testing

The soybean oil conversion to methyl esters as function of catalyst calcination temperature are reported in fig. 4 a - d. The effect of the calcination temperature has been assessed at different reaction times, i.e. after 15, 30, 45 and 60 minutes of reaction. The data after 15 minutes of reaction (fig 4a) show a clear trend where the oil conversion first increases with the calcination temperature, passes by a maximum conversion of 88% for the catalyst calcined at 600 °C and then decreases for the catalysts samples calcined at temperatures above 600 °C. This trend cannot be explained by the nano-MgO crystallite sizes resulting from different calcination temperatures presented in fig. 3 above. Catalyst samples calcined at 500, 600 and 700 °C had comparable MgO crystallite sizes but

different yields. No correlation could be established between the yields and the MgO particles sizes. The increase in yield with the calcination temperature from 500 to 600 °C could be related to the Ti⁴⁺ transfer to the magnesia structure as discussed in section A2 leading to more defects in the catalyst [17]. On the other hand the decrease in yield for the catalysts calcined at 700 and 800 °C could be explained by the formation of MgTiO₃ detected in these samples. The lowest oil conversion was measured on the catalyst calcined at 800 °C which had the most intense MgTiO₃ peak (fig. 2). The catalyst calcined at 600 °C still showed higher yield after 30 min of reaction (fig. 4b), however no trend could be obtained after 45 and 60 minutes of reaction as shown in figure 4c and 4d respectively. This could be due to a possible side reaction that took place as the reaction time was increased. The measured conversions for the catalysts calcined at 600 and 700 °C after 45 minutes of reaction were respectively 96 and 97% (fig 4c) and were respectively decreased to 94 and 92 after 60 minutes of reaction (fig. 4d). This finding suggests that part of the formed methyl esters were consumed in a glycerolysis reaction reported to take place during extended transesterification reaction times [23-26]. This has introduced significant errors on the measurement of oil conversion to methyl esters at extended transesterification reaction times. However the data at extended reaction times were useful as they revealed that only the catalysts samples calcined at 600 and 700 °C were also active for the glycerolysis reaction.



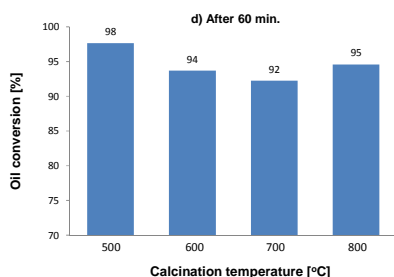


Fig. 4 Effect of calcination temperature of catalyst on soybean oil conversion (methanol to oil molar ratio 1:18, temperature: 225 °C)

The effects of MgO crystallite size on the soybean transesterification reaction are presented in figure 5 a and b. It was observed that the rate of reaction after 15 minutes (fig. 5a) and 30 minutes (fig. 5b) increased with the decrease in MgO crystallite size produced by varying the precursor quantity. These catalysts were calcined at the same temperature of 600 °C. This increase in the rate of reaction can be attributed to an increase in surface area of active metal oxide and/or to the increase in low coordination atoms (defects).

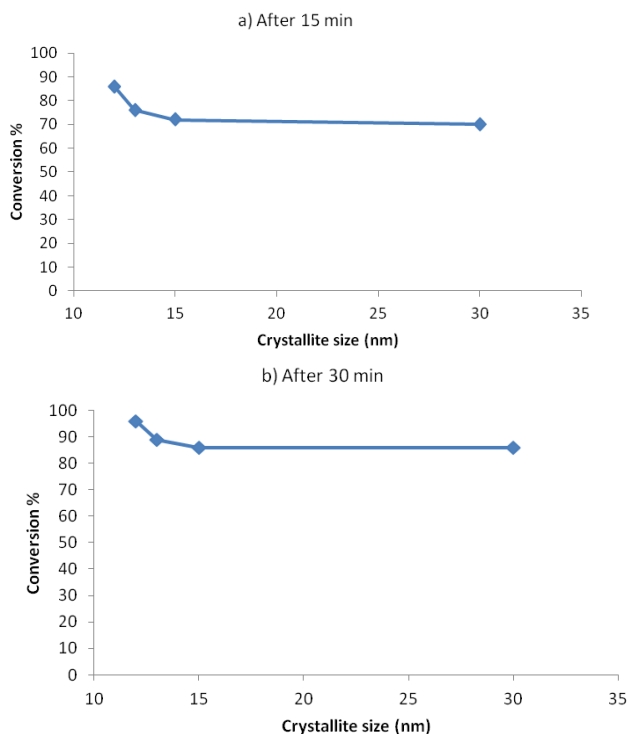


Fig. 5 Effect of crystallite size on soybean oil conversion (methanol to oil molar ratio 1:18, reaction temperature: 225 °C, calcination temperature of catalyst: 600 °C)

C. Carbon deposition on spent catalyst

XRD was used to analyse the used catalyst after the transesterification reaction. The data for the catalysts calcined at 500, 600, 700 and 800 °C are presented in fig 6. Carbon deposition was only observed in the catalyst calcined at 500 °C as shown by the diffraction peak at 26.7° detected for this catalyst. This suggests that the interaction between the support

and the MgO at calcination temperatures above 500 °C was beneficial in eliminating carbon deposition during the transesterification reaction.

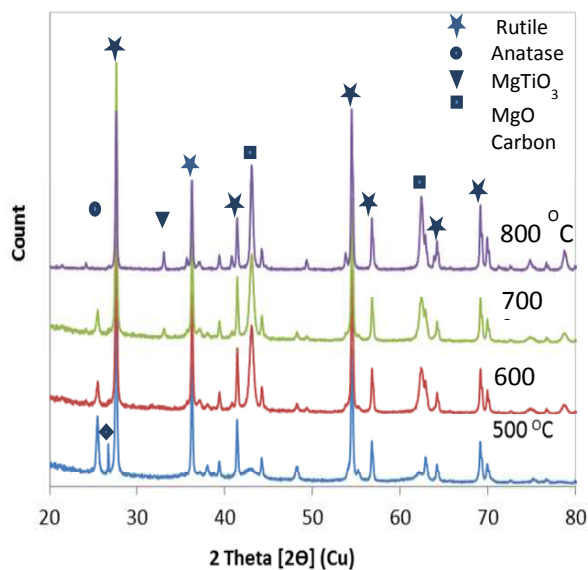


Fig. 6 Effect of calcination temperature (500- 800 °C) on carbon deposition

IV. CONCLUSION

The calcination temperature of MgO/TiO₂ catalyst system had an effect on its structure and catalytic performance for the soybean oil transesterification reaction. No significant effect of calcination temperature on the resulting nano-MgO crystallites was detected in the range from 500 to 700 °C. However a significant increase in nano-MgO crystallite sizes was observed for the catalyst sample calcined at 800 °C. This was explained by possible MgO particles sintering at this higher temperature. The soybean oil conversion after 15 minutes of the transesterification reaction increased when the calcination temperature was increased from 500 to 600 °C and decreased with further increase in calcination temperature. This was explained in terms of changes in the catalyst structure. The catalysts calcined at 600 and 700 °C also showed some glycerolysis activities at extended reaction times. Finally, the MgO crystallite size obtained by a modified Stober method showed an effect on the transesterification reaction rate. When calcined at the same temperature, the catalyst with small MgO particle size showed the highest activity.

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