

Biodiesel production from waste vegetable oils over MgO/Al₂O₃ catalyst

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Abstract. MgO/Al₂O₃ catalysts with 10 and 20 wt.% MgO loadings have been prepared by incipient wetness impregnation method. A low-surface area alumina with small pore sizes was used as catalyst support to stabilise most of the MgO particles on the external surface area of the support. The prepared catalysts were subsequently tested in the conversion of a waste vegetable oil to biodiesel. The waste vegetable oil conversion was found to increase with the increase in reaction temperature, reaction time and MgO loading in the catalyst.

Introduction

Biodiesel has become very popular as an alternative for fossil fuel over the years because fossil fuel is being exhausted and petroleum prices have increased unbelievably. The use of biodiesel offers many advantages compared to fossil fuel. The main advantage is that biodiesel is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable [1]. Also its properties and performance are similar to conventional diesel fuels [2]. However the production cost of biodiesel is still high compared to fossil fuel and more research and development aiming at improving the biodiesel production process economics is needed. The use of cheap feedstock to the biodiesel production process is one of the possible ways of reducing the production cost. However the use of these cheap materials is usually associated with new challenges: for example, waste vegetable oils are usually characterised by high contents of free fatty acids that lead to soap formation during the transesterification reaction catalysed by homogeneous alkaline catalyst such as potassium hydroxide, potassium methoxide, sodium hydroxide, or sodium methoxide. To avoid this problem, solid base catalysts can be used. The use of a heterogeneous catalyst for biodiesel fuel synthesis has many potential advantages as it is environmentally benign, noncorrosive to the reactor, creates no soap by-products by reacting with free fatty acid (FFAs), and is easily separated from the reaction mixture. Existing solid base catalysts include supported alkaline catalysts [2, 3]. Moreover, solid catalysts permit the application of continuous reaction systems that improve overall process economics [4].

The aim of this study is to design an MgO/Al₂O₃ solid catalyst for biodiesel production from waste vegetable oil and to determine the effect of operating conditions such as reaction temperature, reaction time and MgO loading on the overall conversion of waste vegetable oils to biodiesel.

Experimental details

Catalyst preparation. Alumina (Sigma Aldrich-06285) was first mixed with distilled water in a 1:1 weight ratio, dried in air at 120°C overnight and calcined in air at 500°C for 10 h. The calcined material was subsequently sieved to retain the particles with sizes between 50 and 150 µm for use as catalyst support. The prepared support was impregnated with an aqueous solution of Mg(NO₃)₂.6H₂O (Sigma Aldrich) and dried in air overnight at 120°C followed by calcination in air

at 500°C for 8 h. An appropriate amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used for the support impregnation in order to achieve an MgO loading of 10 and 20 wt.% in the catalyst.

Catalyst characterization. The catalyst was characterised using the following techniques:

- FTIR analysis using a Bruker Tensor 27 with a Pike Golden Gate ATR attachment in the range of 4000-400 cm^{-1} to determine functional groups in the catalyst samples;
- XRF analysis using a MAGIX PRO XRF spectrometer to determine MgO loading on the support;
- BET analysis to determine the surface area and pore size distribution by N_2 adsorption at a temperature of 77 K using a Micromeritics ASAP 2000;
- XRD analysis to determine the structure of the catalyst system using a Philips PW 3040/60 X-ray diffraction apparatus with a $\text{CuK}\alpha$ ($\lambda = 1.54$) radiation. Samples were scanned over a 2θ range of 4–130° with a 0.02° step size and a scan speed of 0.04 s/step.

Catalyst testing. Waste vegetable oil (acid value: 11.1 mg of KOH/g, moisture: 0.12 wt.%) was obtained from local frying houses. It was heated overnight at 120 °C to remove the water before the reaction was performed. The catalyst testing was carried out in a 300 cm^3 stainless steel batch reactor (PARR 4842 series reactor) charged with waste vegetable oil (68 cm^3), methanol (52 cm^3) and varying masses 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. A sample was collected from the reactor after every 15 min up to 1h of reaction. The product was left to cool to room temperature. The catalyst was removed from the products by centrifugation. The remaining product was then heated at 65 °C in a vacuum evaporator to remove any methanol. The products that remained after drying were glycerol, unreacted oil and methyl esters. These products separate into 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 data and the following equation:

$$\% \text{Conversion} = \frac{2A_{\text{ME}}}{3A_{\alpha-\text{CH}_2}} \times 100. \quad (1)$$

Where A_{ME} is the integration value of the protons of the methyl esters; $A_{\alpha-\text{CH}_2}$ is the integration value of the methylene protons.

Results and discussion

Catalyst characterization. The FTIR spectra for the dried and calcined 20% $\text{MgO}/\text{Al}_2\text{O}_3$ catalyst are presented in Fig. 1 below. The NO_3^- group was observed at 1371.35 cm^{-1} in the dried catalyst (spectrum a). This transmittance peak completely disappeared from the FTIR spectrum for the calcined 20% $\text{MgO}/\text{Al}_2\text{O}_3$ suggesting complete decomposition of $\text{Mg}(\text{NO}_3)_2$ during calcination at 500°C. The transmittance peak at ca. 557 cm^{-1} is assigned to the stretching and bending of Al_2O_3 atomic group and $\text{Mg}(\text{OH})_2$ was observed at 819.06 cm^{-1} . O-H bending and stretching vibration modes also disappeared after catalyst calcination due to the removal of the dissociated water.

Fig. 2 shows the XRD pattern of the calcined blank Al_2O_3 (pattern c), the dried catalyst sample (pattern b) and the calcined 20% $\text{MgO}/\text{Al}_2\text{O}_3$ catalyst sample (pattern a). $\text{Mg}(\text{NO}_3)_2$ diffraction peaks were observed in the dried catalyst at $2\theta = 20.7, 28.9$ and 43.3° . These peaks completely disappeared from the XRD pattern for the calcined 20% $\text{MgO}/\text{Al}_2\text{O}_3$ catalyst sample suggesting complete decomposition of $\text{Mg}(\text{NO}_3)_2$ during catalyst decomposition, in agreement with the FTIR data discussed earlier. MgO diffraction peaks were observed at $2\theta = 37$ and 42° . The crystallite size

of MgO in 10% and 20% MgO/Al₂O₃ was calculated and found to be 56.4 and 58.1 nm respectively.

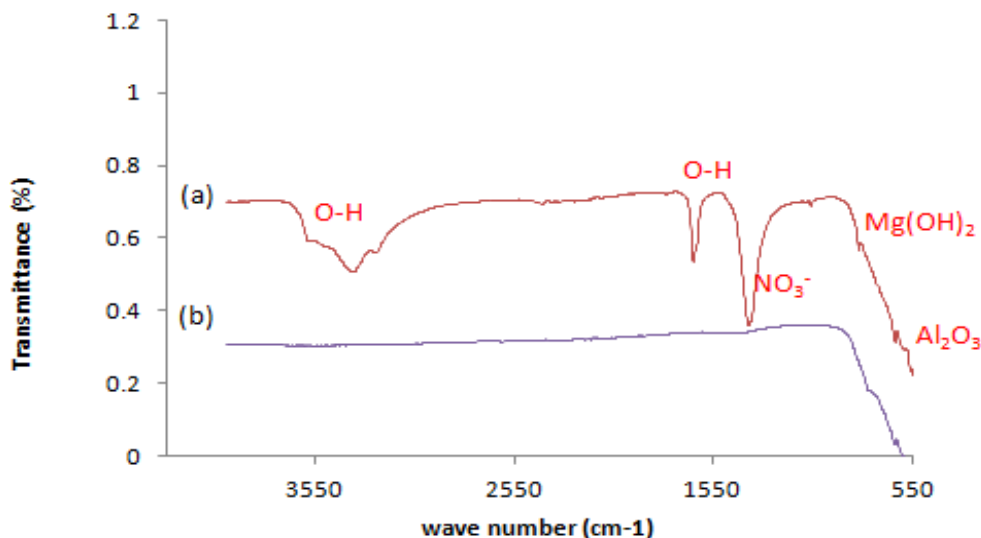


Fig. 1. FTIR spectrum of (a) dried catalyst and (b) calcined 20% MgO/Al₂O₃.

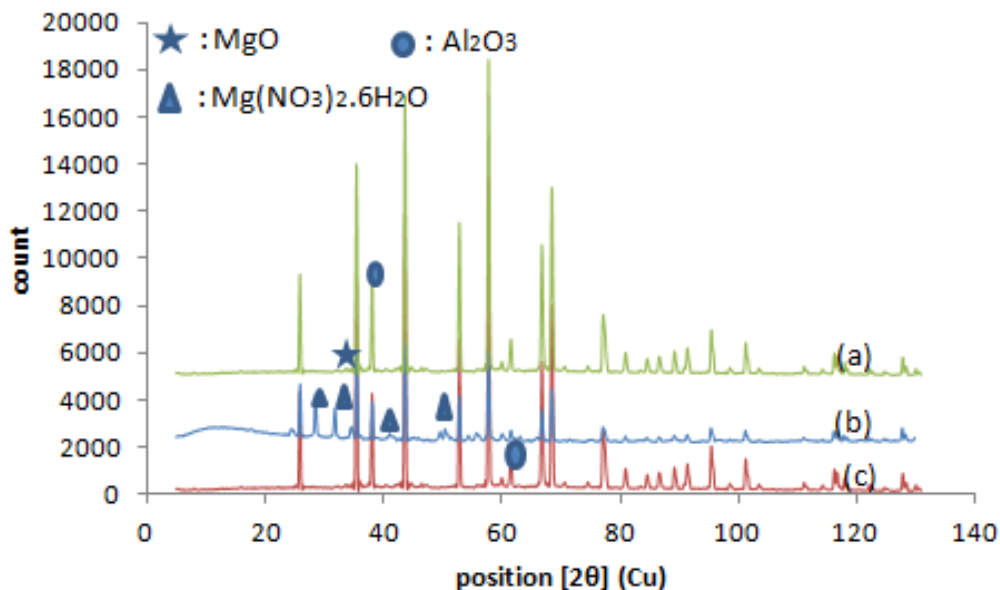


Fig. 2. XRD pattern of (a) 20% calcined MgO/Al₂O₃, (b) dried catalyst and (c) calcined blank Al₂O₃

Fig. 3 shows the XRD pattern of the calcined MgO/Al₂O₃ before and after the transesterification reaction. The three curves on the graph gave the same XRD pattern with the same peaks intensity which can suggest that the catalyst did not undergo significant structural change during reaction.

The XRF analysis results for the synthesized 10 and 20% MgO/Al₂O₃ catalyst samples are summarized in table 1. The measured and target MgO loading in the two samples were within 10% closer and were considered satisfactory.

The surface area for the calcined blank Al₂O₃ support, 10% MgO/Al₂O₃ and 20% MgO/Al₂O₃ catalyst samples are summarized in table 2. The blank alumina support had a very low surface area of ca. 0.13 m²/g and a pore size of ca.10.5 nm. At 10% and 20% MgO loadings, an increase in surface area to ca. 0.17 and 0.19 m²/g was respectively observed. The particles sizes for MgO (in the range of 56 -58 nm) as determined by XRD were significantly larger than the blank alumina

pore size of ca. 10.5 nm and suggested that most of the MgO deposited on the external surface of the support and hence increased the catalyst surface area. This satisfied the initial purpose of using a very low surface area support in order to have most of the MgO active sites stabilized on the outer surface of the support for easy access by the reactants with a result of reducing mass transfer resistances.

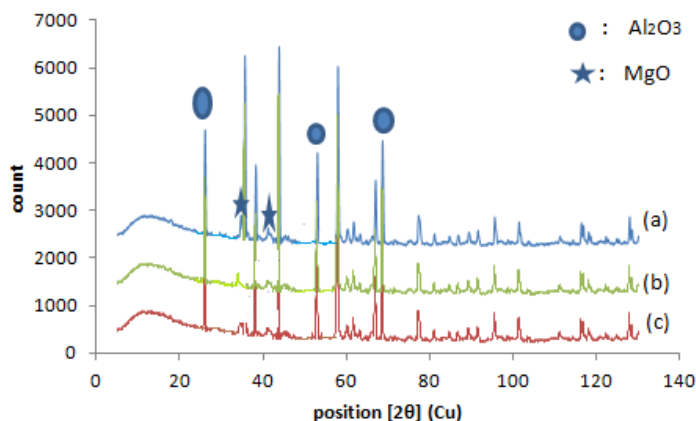


Fig. 3. XRD pattern of calcined 20%MgO/Al₂O₃ (a) before reaction, (b) after transesterification reaction at 150°C (c) after transesterification reaction at 225 °C.

Table 1. XRF analysis results for the prepared catalysts

Target % MgO	Obtained %MgO
10	9.8
20	18.0

Table 2. Summary of BET data

	Calcined blank Al ₂ O ₃	10% MgO/ Al ₂ O ₃	20% MgO/ Al ₂ O ₃
Surface area (m ² /g)	0.13	0.17	0.19

Catalyst testing. Fig. 4 and 5 show the waste oil conversion to biodiesel as a function of temperature, reaction time and MgO loading on Al₂O₃.

Waste vegetable oil conversion was found to increase with temperature. For example oil conversions of ca. 20, 30, 80 and 95% were measured at 60, 150, 175 and 225°C respectively for 20% MgO loading after 60 min of reaction (Fig. 4 a, b, c and Fig. 5). A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate and a shortened reaction time [5].

It was observed that increasing the reaction time also increased the waste oil conversion to biodiesel yield. For example, the catalyst with 10wt.% MgO loading at 200°C led to waste oil conversions of

40, 45 and 70% at 15, 30 and 45 min respectively (Fig. 4 d).

The waste oil conversion at 60 (Fig. 4a) and 150°C (Fig. 4b) was not significantly affected by the MgO loading in the catalyst suggesting that at these conditions the reaction was more controlled by mass transfer limitations. However, the maximum difference in the waste oil conversion over 10%MgO/Al₂O₃ and 20%MgO/Al₂O₃ was measured for the reactions performed at 175°C (Fig. 4c).

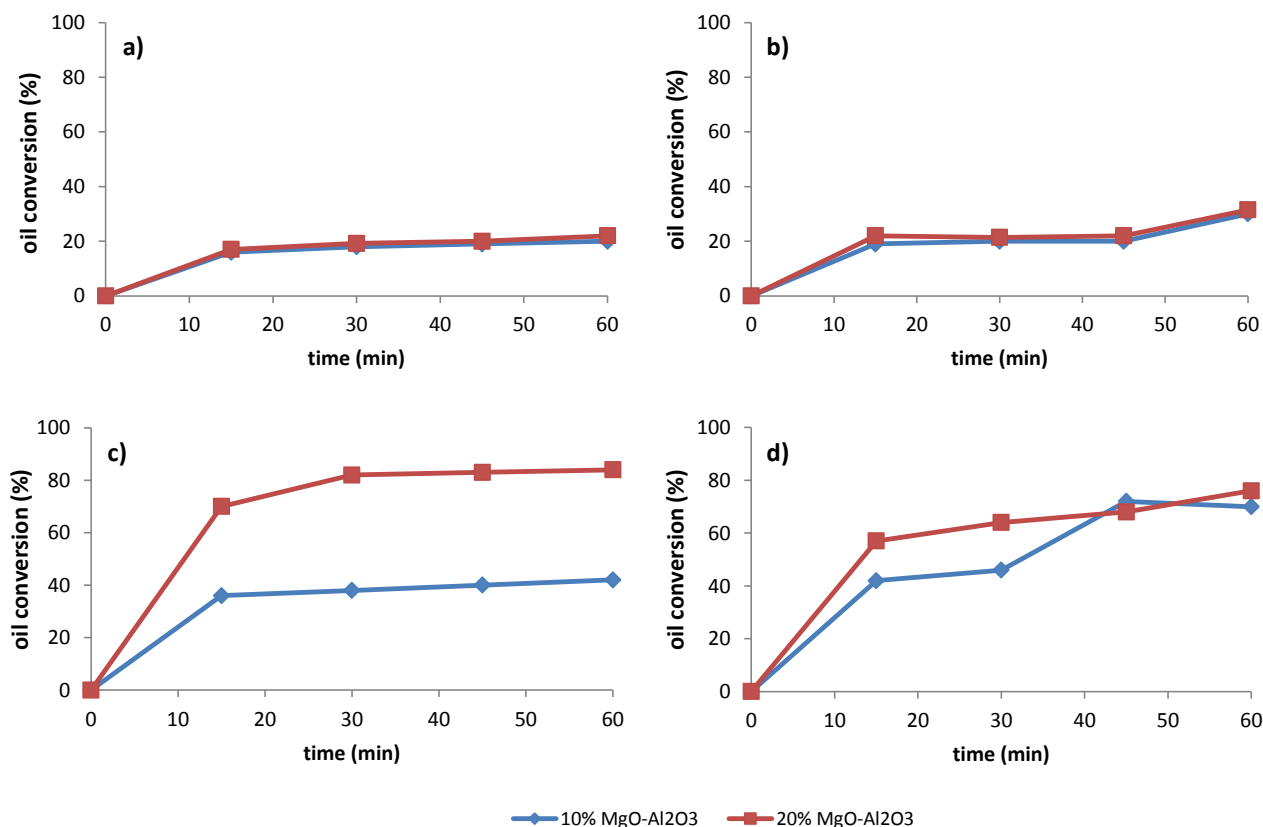


Fig. 4. Waste oil conversion at a) 60°C; b) 150°C; c) 175°C and d) 200°C as function of reaction time and MgO loading (alcohol to oil molar ratio 18:1, catalyst amount 3wt.% with respect to oil)

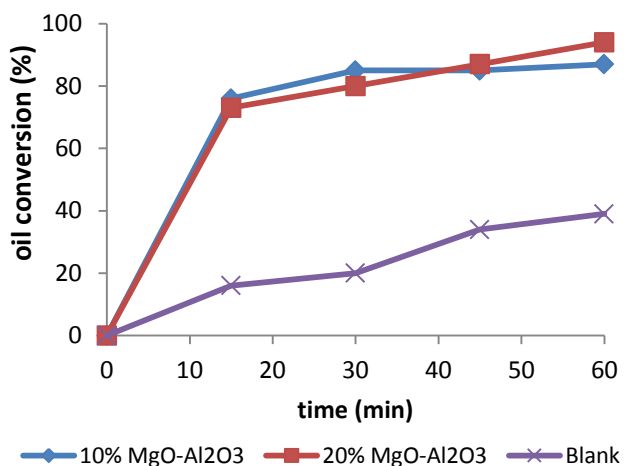


Fig. 5. Waste oil conversion to biodiesel at 225°C as function of time over blank Al₂O₃ support, 10%MgO/Al₂O₃ and 20%MgO/Al₂O₃ respectively (alcohol to oil molar ratio 18:1, catalyst amount 3wt.%) at 225°C.

At this temperature the oil conversion measured over the 20%MgO/Al₂O₃ was approximately the double of that measured on the 10%MgO/Al₂O₃ catalyst indicating that at these conditions the reaction was more controlled by the active sites density. At the highest temperature of 225°C, the effect of MgO loading on biodiesel yield over 10 and 20% MgO loaded catalysts became less significant (Fig. 5). This could be due to the fact that the contribution of the blank alumina support to the waste oil conversion became significant and made it difficult to determine the net effect of MgO loading.

Conclusion

Low-surface area alumina supported MgO catalysts have been prepared and tested for the conversion of waste vegetable oil to biodiesel. The effects of reaction temperature, reaction time and MgO loading in the catalyst on the oil conversion were investigated. It has been found that the waste oil conversion increases with the increase in reaction temperature, reaction time and MgO loading in the catalyst.

References

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