SYNTHESIS OF MgFe_2O_4 - MgO NANOCOMPOSITE: INFLUENCE OF MgO ON THE CATALYTIC ACTIVITY OF MAGNESIUM FERRITE IN BIODIESEL PRODUCTION

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ABSTRACT

A novel magnetic solid base catalyst consisting of an MgFe_2O_4 - MgO nanocomposite was successfully prepared by synthesizing magnesium ferrite (MgFe_2O_4) as the catalyst support, and it was employed in an esterification reaction for the production of biodiesel. MgFe_2O_4 was synthesized by a ball-milling mechanochemical method at various furnace temperatures (350°C, 550°C and 750°C), and the best results were obtained at 750°C. The results of TEM revealed an average size of 39 nm. A nanocomposite of MgFe_2O_4 - MgO was successfully synthesized in this study, as confirmed by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy-energy dispersive x-ray (SEM-EDX) and transmission electron microscopy (TEM) characterization. The results of the FTIR characterization revealed peaks with wavenumbers corresponding to Mg-O and Fe-O bonds in the range of 500-900 cm^{-1} , SEM mapping showed that MgO was distributed on the surface of the MgFe_2O_4 catalyst support, and the MgFe_2O_4 - MgO average size was found to be 50 nm by TEM. The influence of MgO on MgFe_2O_4 was determined by varying the molar ratio of MgFe_2O_4 to MgO from 1: 1, 1: 2 and 1: 3 and by studying the catalytic activity in the esterification of oleic acid to biodiesel. The best MgFe_2O_4 - MgO nanocomposite have a molar ratio of 1: 2 and gave a percent conversion of 96.089%. Impregnating MgFe_2O_4 with MgO increased the number of basic active sites, thereby increasing the catalytic activity. This type of nanocomposite is a promising new material for future catalysts.

Keywords: Biodiesel, Catalyst, Magnesium Ferrite, Nanocomposite, Oleic Acid

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INTRODUCTION

Renewable fuels such as biodiesel are one of the alternative energy sources that can overcome the limitations of nonrenewable energy resources.^{1,2,3} Compared to fossil fuels, the use of biodiesel can reduce the hydrocarbons and particulates in exhaust emissions by 70% and 50%, respectively, and CO_2 emissions by 78% due to its renewable nature.⁴ Biodiesel is a mixture consisting of fatty acid methyl esters (FAMEs) generally derived from methyl and ethyl alcohol. Catalysts are currently being developed to improve the efficiency of biodiesel production.⁵

Alkaline catalysts have higher catalytic activities than acid catalysts in transesterification reactions.⁶ Heterogeneous solid base catalysts, such as the metal oxides MgO ⁷, CaO/SiO_2 ¹, $\text{MgO/Li}_2\text{O}$ ⁸, ZrO_2 ⁹, NiO/CNZ ¹⁰, etc., have been widely used in various studies to synthesize biodiesel. Although these heterogeneous catalysts are advantageous in terms of catalyst separation and pollution reduction, most of them have limited catalytic activity and stability.¹¹

Bimetallic catalysts, such as ferrite metal (XFe_2O_4), where X is a divalent metal cation, are of significant interest to many researchers because of their unique magnetic properties, thermal and structural stabilities, and higher catalytic activities than monometallic oxides.^{6,12} Therefore, in this study, a nanocomposite was synthesized by impregnating MgFe_2O_4 , which has acid sites, with MgO, which has basic sites, according to the previous studies⁶, with modifications based on mechanochemical methods.¹³

In particular, ball-milling mechanochemistry was employed in this work as a simple and low-cost methodology. The synthesized products were characterized by FTIR, XRD, SEM-EDX and TEM. The

catalytic activity of the catalyst in the esterification of oleic acid to fatty acid methyl esters (FAMES) was determined according to our previous studies.^{2,14,16} The amount of residual acid remaining after the esterification reaction was then measured to determine the percent conversion to biodiesel.

EXPERIMENTAL

Materials

The chemicals were analytical grade and used without further purification. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, urea, oleic acid and methanol (98%) were all purchased from Merck.

Synthesis of the MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{MgO}$ Nanocomposites

The synthesis of the MgFe_2O_4 nanocomposite in this study was based on previous literature methods⁵ with mechanochemical modifications¹³. In this work, ball-milling mechanochemistry was performed using a hard small ball. The first stage, the synthesis of MgFe_2O_4 , involved mixing a given amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and then adding a urea solution. The mixture was heated at 70°C and stirred by ball milling until a brown gel was obtained. Then, the mixture was calcined at various temperatures (350°C , 550°C and 750°C) in a furnace for 3 hours. The resulting reddish-brown precipitate was MgFe_2O_4 , and it was characterized by FTIR, XRD, SEM-EDX and TEM.

In the second stage, a given amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in a urea solution, and then MgFe_2O_4 was added in various molar ratios (1: 1, 1: 2, 1: 3) at 80°C . The mixture was stirred at a medium speed to give a precipitate, which was subsequently dried in an oven at 110°C for 24 hours. Furthermore, the precipitate was calcined in a furnace at a temperature of 550°C for 4 hours. A reddish brown $\text{MgFe}_2\text{O}_4/\text{MgO}$ nanocomposite was obtained and characterized by FTIR, XRD and SEM mapping.

Catalytic Activity

The catalytic activity of the $\text{MgFe}_2\text{O}_4/\text{MgO}$ nanocomposite in the esterification of oleic acid with methanol to biodiesel was evaluated using a batch method. The esterification reaction was performed at 60°C for 3 hours with a ratio of oleic acid to methanol of 1: 12 and 0.1 g catalyst. In this study, the percent conversion was determined by calculating the acid number, or free fatty acids (FFAs). The acid numbers were determined by an acid-base titration method using 0.1 N KOH. The acid number was calculated using the following equations (1) and (2).^{15,16}

$$FFA = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times Mr_{\text{KOH}}}{\text{sample mass}} \quad (1)$$

$$\text{Conversion (\%)} = \frac{FFA_{\text{initial}} - FFA_{\text{final}}}{FFA_{\text{initial}}} \times 100 \quad (2)$$

Where FFA is the free fatty acid number, FFA initial is the FFA oleic acid number, and FFA final is the FFA number after the esterification reaction.

RESULTS AND DISCUSSION

Composite of MgFe_2O_4

Magnesium ferrite (MgFe_2O_4) is successfully synthesized with a reddish-brown color and is paramagnetic in accordance with the previous studies⁶.

The proposed formation reaction of magnesium ferrite is as follows.

In the first stage, urea is ionized in water and then decomposes into NH_3 and CO_2 gas as shown in equation (3):

Furthermore, the reaction of ammonia with water gives ammonium hydroxide, as shown in equation (4):

Ammonium hydroxide is then ionized into ammonium (NH_4^+) and hydroxide (OH^-) ions, as in equation (5):

The $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursors are ionized to Fe^{3+} and Mg^{2+} ions in water, as shown in equations (6) and (7), respectively:

The hydroxide ions in equation (5) react with the Fe^{3+} and Mg^{2+} ions to give $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ in equations (8) and (9), respectively:

In the last step, $\text{Fe}(\text{OH})_3$ decomposes into $\alpha\text{-Fe}_2\text{O}_3$ at high temperatures, and then $\alpha\text{-Fe}_2\text{O}_3$ reacts with $\text{Mg}(\text{OH})_2$ to form MgFe_2O_4 , as shown in equations (10) and (11):

The resulting MgFe_2O_4 has magnetic properties that are observable using external magnets.

FTIR Analysis of Magnesium Ferrite (MgFe_2O_4)

Figure-1 shows the FTIR spectra of magnesium ferrite (MgFe_2O_4) obtained at furnace temperatures of 350°C (Fig.-1a), 550°C (Fig.-1b), and 750°C (Fig.-1c). In all the spectra, peaks are observed at wavenumbers in the range of 475-700 cm^{-1} , indicating the presence of Mg-O and Fe-O bonds⁵. In Fig.-1c, a sharp peak appears at 1522 cm^{-1} due to NO_3 groups, which reveals that the precursor does not burn completely in the calcination process. The peak at 1642 cm^{-1} is a specific absorption of the C=O group of the remaining urea ($\text{CO}(\text{NH}_2)_2$). The peaks approximately 3000-3800 cm^{-1} are attributed to the O-H stretching of the remaining $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ that do not decompose into MgFe_2O_4 and of water vapor absorbed by the sample. The peak in Fig.-1a is lower than those in Fig.-1b and 1c, indicating that fewer impurities remain after calcination at 750°C than after calcination at 350°C and 550°C.

Fig.-1: FTIR Spectra of MgFe_2O_4 Obtained at Different Temperatures

Fig.-2: XRD Patterns of MgFe_2O_4 Obtained at Different Temperatures

XRD Analysis of MgFe_2O_4

Figure-2 shows the XRD patterns of MgFe_2O_4 at various furnace temperatures (350°C (Fig.-2a), 550°C (Fig.-2b) and 750°C (Fig.-2c). At furnace temperatures of 350°C and 550°C (Fig.-2a and 2b, respectively), peaks due to $\alpha\text{-Fe}_2\text{O}_3$ (sphere shape) are observed because some $\alpha\text{-Fe}_2\text{O}_3$ does not decompose into MgFe_2O_4 , whereas at a furnace temperature of 750°C (Fig.-2c), 2θ peaks are observed at 30.2°, 33.2°, 35.5°, 43.3°, 54.1°, 57.0°, and 62.6°, which is in accordance with JCPDS 01-073-2211 for the crystalline phase of MgFe_2O_4 (square shape). This result shows that MgFe_2O_4 is successfully

synthesized at a furnace temperature of 750°C. The XRD results are consistent with the FTIR data. The peaks observed in the results of this study are also similar to those observed in a previous study⁶.

SEM-EDX Analysis of MgFe_2O_4

Figure-3a shows a micrograph of MgFe_2O_4 with a nanospherical shape and rough surface morphology. The surface morphology and shape of MgFe_2O_4 are similar to those observed in previous studies^{17,18}. SEM-EDX analysis was performed to determine the mass percent of each element in the synthesized compound, as shown in Fig.-3b. The compositions of Mg, Fe and O are 12.1, 47.8 and 40.2 wt.%, respectively. To support the SEM-EDX results, the percentage of mass was calculated using equation (12), and the calculated results for the elemental mass percentages of Mg, Fe and O are interpreted in Fig.-3c.

$$\text{Element Mass Percentage (\%)} = \frac{\text{Ar element}}{\text{Mr Compound}} \times 100\% \quad (12)$$

Figure-3c shows the elemental mass percentages in this study compared with the theoretical mass percentages of MgFe_2O_4 and MgFeO . The experimental elemental mass percentages of Mg, Fe and O are 12.1%, 47.8% and 40.1%, respectively. Using equation 10, the mass percentages of MgFe_2O_4 are theoretically calculated to be 12.15%, 55.85% and 32%, whereas those of MgFeO are 25%, 58.3% and 16.7%. The mass percentages of Fe and O in Fe_3O_4 compounds are 72.4% and 27.6%, respectively. Therefore, the successful synthesis of the MgFe_2O_4 compound is confirmed by the similarities between the mass percentages obtained in this study and the theoretical values for MgFe_2O_4 .

Fig.-3: (a) SEM and (b) SEM-EDX Results and (c) Percent Mass Graph for MgFe_2O_4

TEM Analysis of MgFe_2O_4

Figure-4a shows that the MgFe_2O_4 composite shape is nanospherical, supporting the results of the SEM analysis. In this Fig.-4a, the bright and dark colors indicate single particles and particles that overlap each other, respectively. In addition, the TEM results in Fig.-4b show several MgFe_2O_4 particles (red circle), and the average particle size is determined to be approximately 39 nm.

Fig.-4: (a) TEM Results and (b) Average Diameter for MgFe_2O_4

Nanocomposite of MgFe_2O_4 - MgO

To prepare the MgFe_2O_4 - MgO nanocomposite with various molar ratios of $\text{MgFe}_2\text{O}_4/\text{Mg}(\text{NO}_3)_2$ (1: 1, 1: 2, 1: 3), $\text{Mg}(\text{NO}_3)_2$ was added to the best MgFe_2O_4 particles.

FTIR Analysis of MgFe_2O_4 - MgO

Figure-5 shows the spectra of MgFe_2O_4 - MgO with ratios of 1: 1 (Fig.-5a), 1: 2 (Fig.-5b) and 1: 3 (Fig.-5c). The peak of approximately $475\text{--}700\text{ cm}^{-1}$ corresponds to the wavenumbers of Mg-O and Fe-O inorganic compounds and is observed in all the spectra in Fig.-5. The other peaks are attributed to the precursors remaining after the calcination process in the furnace. The peak at 1450 cm^{-1} is due to NO_3 groups. In the three spectra, the peak at 3707 cm^{-1} is attributed to the OH stretching of the residual $\text{Mg}(\text{OH})_2$ that does not decompose into MgO . This peak is lower in Fig.-5b and 5c, indicating that molar ratios of 1: 2 and 1: 3 are better than a molar ratio of 1: 1.

Fig.-5: FTIR Spectra of MgFe_2O_4 - MgO Fig.-6: XRD Patterns of MgFe_2O_4 - MgO

XRD Analysis of MgFe_2O_4 - MgO

Figure-6 shows the XRD patterns of MgFe_2O_4 - MgO with various molar ratios of MgFe_2O_4 to MgO (1: 1, 1: 2 and 1: 3). As shown in Fig.-6, the MgFe_2O_4 - MgO diffraction patterns for all the molar ratios have 2θ peaks at $30.2, 33.2, 35.5, 43.3, 54.1, 57.0,$ and 62.6 (square shape), similarly to JCPDS 01-073-2211 for the crystalline phase of MgFe_2O_4 . The peaks confirming the formation of MgFe_2O_4 - MgO composites are only observed at ratios of 1: 2 and 1: 3; the 2θ peaks at $37.0, 43.0, 62.4, 74.8$ and 78.7° (sphere shape) are specific to MgO , according to JCPDS 01-077-2364. These results demonstrate the successful formation of

MgFe₂O₄-MgO nanocomposites with ratios of 1: 2 and 1: 3. Meanwhile, MgFe₂O₄-MgO with a ratio of 1: 1 does not exhibit the peaks specific to MgO. The diffraction patterns for all the molar ratios also have a 2θ peak at 33.2° (triangle shape) corresponding to α-Fe₂O₃, according to JCPDS 01-080-2377.

SEM Mapping Analysis of MgFe₂O₄-MgO

To determine the distribution of each element in the synthesized composite, SEM mapping analysis was performed, as shown in Fig.-7. This image shows the distributions of Mg (Fig.-7a), Fe (Fig.-7b), and O (Fig.-7c), and Fig.-7d presents the SEM image of MgFe₂O₄-MgO with no color. Figure-7 shows that Mg, Fe and O are evenly distributed across the entire surface of the sample or mingle with each other. This means that MgO is distributed on the surface of the MgFe₂O₄ catalyst support. This result shows that MgFe₂O₄ and MgO are successfully and well composited.

Fig.-7: SEM Mapping of MgFe₂O₄-MgO Showing the Distributions of (a) Mg, (b) Fe, and (c) O and (d) the Morphology of MgFe₂O₄-MgO

TEM Analysis of MgFe₂O₄-MgO

Figure-8a shows that the shape of the MgFe₂O₄-MgO nanocomposite varies and the average particle size is 50 nm. In Fig.-8, bright and dark colors are observed and are attributed to single particles and particles that overlap each other, respectively. The TEM results in Fig.-8b are obtained from several MgFe₂O₄ particles (red circle), and the average particle size is determined to be approximately 50 nm.

Catalytic Activity of the MgFe₂O₄-MgO Nanocomposite in an Esterification Reaction

In this study, MgFe₂O₄-MgO was synthesized with various molar ratios of MgFe₂O₄ to MgO (1: 1, 1: 2 and 1: 3.) to optimize the amount of MgO used in the nanocomposite synthesis for catalysis. The conversion was determined using equations 1 and 2 and is plotted as a function of the molar ratio of MgFe₂O₄/MgO in Fig.-9.

Figure-9 shows that using MgFe₂O₄/MgO with a molar ratio of 1: 1 results in a percent conversion to biodiesel of 71.557%. When the ratio is 1: 2, the percent conversion to biodiesel increases to 96.089%. This result shows that the addition of MgO to the composite increases the percent conversion of the catalyst, because MgO functions as the basic active site of the catalyst, and the collision of the reactants

with the catalyst is more effective, increasing the activity of the catalyst. However, when the molar ratio is 1: 3, the conversion is 96.160%, and the percent increase in the biodiesel conversion is not significant. Therefore, the optimal percent conversion is obtained at a 1: 2 MgFe_2O_4 to MgO molar ratio. The percent conversion obtained in this study is higher than the results of previous studies^{14,19}.

The best MgFe_2O_4 - MgO nanocomposite, which has a molar ratio of 1: 2, as compared to MgO and MgFe_2O_4 to determine the role of each component. Figure-10 shows the percent conversion to biodiesel for the different catalyst types. The biodiesel percent conversions obtained with MgO and MgFe_2O_4 are 71.031% and 39.68%, respectively. These results show that MgO acts as the basic active site of the catalyst, whereas MgFe_2O_4 functions as an auxiliary catalyst; therefore, combining them in a MgFe_2O_4 - MgO nanocomposite increases the catalytic activity to 96.089%.

Fig-8: TEM results Results and (b) Average Diameter for MgFe_2O_4 - MgO

Fig.-9: Percent Conversion to Biodiesel at Different Molar Ratios

Fig.-10: Percent Conversion to Biodiesel for Different Catalyst Types

CONCLUSION

A nanocomposite of MgFe_2O_4 - MgO was successfully synthesized and used as a catalyst in the esterification of oleic acid to biodiesel. In the first stage, MgFe_2O_4 was synthesized by a ball-milling mechanochemical method with the optimal results obtained at a calcination temperature of 750°C. The results of the FTIR characterization reveal the presence of peaks with wavenumbers corresponding to Mg-O and Fe-O bonds in the range of 500-900 cm^{-1} . The XRD results show that the structure is a crystalline phase, the SEM results reveal nanospherical shapes, and TEM indicates average size of approximately 39 nm. The MgFe_2O_4 - MgO nanocomposite was successfully synthesized, and the average particle size obtained by TEM is approximately 50 nm. The catalytic activity in oleic acid esterification to methyl ester

biodiesel was studied. The best $\text{MgFe}_2\text{O}_4\text{-MgO}$ nanocomposite has a molar ratio of 1:2 and gives a percent conversion of 96.089%.

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