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Synthesis of $MgO/CoFe_2O_4$ Nanoparticles with Coprecipitation Method and Its Characterization

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Abstract. This research discusses the development of magnetic materials as an effort to produce renewable catalysts in overcoming the energy crisis. The purpose of this study was to synthesize and characterize $MgO/CoFe_2O_4$ nanoparticles using the coprecipitation method. The synergy between substances that are catalysts, namely MgO and $CoFe_2O_4$ to $MgO/CoFe_2O_4$ was expected to produce a superior catalyst for biodiesel production. The stages of this research were to synthesize MgO nanoparticles and $CoFe_2O_4$ nanoparticles by coprecipitation and continued with MgO impregnation on the $CoFe_2O_4$ surface to become $MgO/CoFe_2O_4$ with a mole ratio of 5: 1, then characterize them using X-Ray Diffraction and Scanning Electron Microscopy. The results of XRD analysis showed that $MgO/CoFe_2O_4$ nanoparticles were successfully synthesized according to the standard curves of MgO and $CoFe_2O_4$ (JCPDS Cards No. 89-7746 and 22-1086). SEM analysis results show that impregnated particles have spherical morphology and are larger in size than the two constituent components. The mean particle sizes of MgO, $CoFe_2O_4$, and $MgO/CoFe_2O_4$ were 29.588 nm, 42.282 nm and 65.953 nm, respectively. EDX analysis shows the appropriate atomic percentage and mass of each of the constituents of $MgO/CoFe_2O_4$ namely Magnesium, Iron, Cobalt, Oxygen.

INTRODUCTION

The world's fossil energy reserves are getting depleted in line with the increasing need for fuel every year. Based on OPEC data, the world's petroleum reserves in 2019 amounted to 1189.8 billion barrels, while the demand was 83.8 million barrels per day, so that fossil fuels are expected to run out in the next 40 years. Based on this, various innovations have developed to create alternative energy to replace fossil fuels that are more environmentally friendly, one of that is biodiesel. Biodiesel which has another name fatty acid methyl ester (FAME) is a diesel engine fuel consisting of alkyl ester that can be produced through transesterification reactions of vegetable and animal oils (1).

Parameters that influence the transesterification reaction include reaction temperature, mole ratio of reactants, reaction duration and catalyst (2). In a transesterification reaction without using a catalyst, supercritical conditions are needed to get maximum results, namely at temperatures above 240 °C and pressures above 80 bar (1). In this case, the oxides and hydroxides of alkali metals have the potential to act as heterogeneous base catalysts in the transesterification reaction (3). Related to the need for a catalyst for biodiesel production to overcome the energy crisis, Magnesium Oxide (MgO) nanoparticles are used as heterogeneous catalysts. Compared to homogeneous catalysts, heterogeneous catalysts are easier to separate and can be used repeatedly. In previous research, MgO was successfully used as a transesterification catalyst for soybean oil with methanol (4). Tahvildari, et al. (2) found that magnesium oxide (MgO) nanoparticles gave better results in transesterification reactions when used together with calcium oxide (CaO) nanoparticles. The use of a 5% MgO catalyst gave a yield of 90% while the use of a 3%

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MgO/CaO catalyst resulted in a yield of 98.95%. It seems that the synergy of the two catalysts gives better results. However, the problem that remains here is related to the ease with which catalysts can be recovered to be recycled. It is necessary to explore the catalyst that will synergize with MgO in the transesterification reaction.

Magnetic catalyst, in this case cobalt ferrite ($CoFe_2O_4$) nanoparticles is the main choice as a co-catalyst from MgO as a renewable catalyst. $CoFe_2O_4$ nanoparticles themselves have high magnetic saturation, coercivity and anisotropy of magnetocrystalline at room temperature (5). $CoFe_2O_4$ has been used as a catalyst, including in the Knoevenagel reaction (6), alkene oxidation (7), and transesterification reactions (8). The results of research by Gohain, et al. (8) showed that the $CoFe_2O_4$ catalyst produced a yield of 92% in the transesterification of methyl acetoacetate and benzyl alcohol with a duration of 8 hours. For this reason, in this study, the synthesis of $CoFe_2O_4$ composites with MgO as $MgO/CoFe_2O_4$ nanoparticles will be carried out. The synergy between MgO and $CoFe_2O_4$ as $MgO/CoFe_2O_4$ is expected to produce a catalyst with superior characteristics for biodiesel production.

METHOD

Synthesis of MgO Nanoparticles

Magnesium Oxide (MgO) was obtained from calcination of magnesium carbonate ($MgCO_3$). Meanwhile $MgCO_3$ itself was synthesized by mixing 50 mL of 1 M $(NH_4)_2CO_3$ solution with 50 mL of $MgCl_2$ 1 M solution. The mixture was stirred for 1 hour at 80 °C. The white powder formed, namely $MgCO_3$, was washed with aquademineralized until a neutral pH was obtained, then was washed with ethanol 96% and dried at 100 °C for 24 hours. Then $MgCO_3$ was calcined at a temperature of 550 °C for 4 hours to convert to MgO.

Synthesis of $CoFe_2O_4$ Nanoparticles

The magnetite Cobalt Ferrite ($CoFe_2O_4$) nanoparticles were synthesized by the coprecipitation method. A total of 10 mL of 1.65 M $FeCl_3$ solution was mixed with 10 mL of 0.8 M $CoCl_2$ solution. Then the mixture was added with 500 mL of 0.7 M NaOH solution while stirring for 120 minutes at a temperature of 75 °C. The formed black precipitate was filtered, and then washed with aquademin until a neutral pH was obtained, then was washed further with ethano 96% and dried for 6 hours at a temperature of 120 °C. The precipited was then calcined at 800 °C for 4 hours.

Synthesis of $MgO/CoFe_2O_4$

$MgO/CoFe_2O_4$ nanoparticles were prepared by impregnation method. MgO and $CoFe_2O_4$ were mixed with a mole ratio of 5: 1. The mixture was stirred constantly at 80 °C for 8 hours with a reflux system. Methanol (p.a) was used as a dispersant in this impregnation process. Then the precipited is filtered and washed according to the solvent used, then dried at a temperature of 120 °C for 6 hours. The $MgO/CoFe_2O_4$ nanoparticles was ready to be used as a catalyst in the transesterification processynthesis of $MgO/CoFe_2O_4$.

Characterization

Characterization of the particles was consisting of several tests. X-ray diffraction (XRD) patterns were recorded in the 2θ range of 10°–90° with Cu Kα radiation source (λ = 0.1542 nm, 40 mA, 45 kV) by using Panalytical Xpert Pro Diffractometer. Crystallinity size of the material can be calculated from XRD result using Debye-Scherrer Equation

$$D = \frac{K\lambda}{\beta cos\theta} \quad \text{Equation 1}$$

where λ is the wavelength of X-ray beam, β is full width at half maximum (FWHM) and θ is Bragg scattering angle and K (=0.89) is shape factor. The morphology of the particles was determined by Scanning Electron Microscopy (SEM) images with Type Inspect S50, FEI. Then imageJ® software was used to measure the average of particle size.

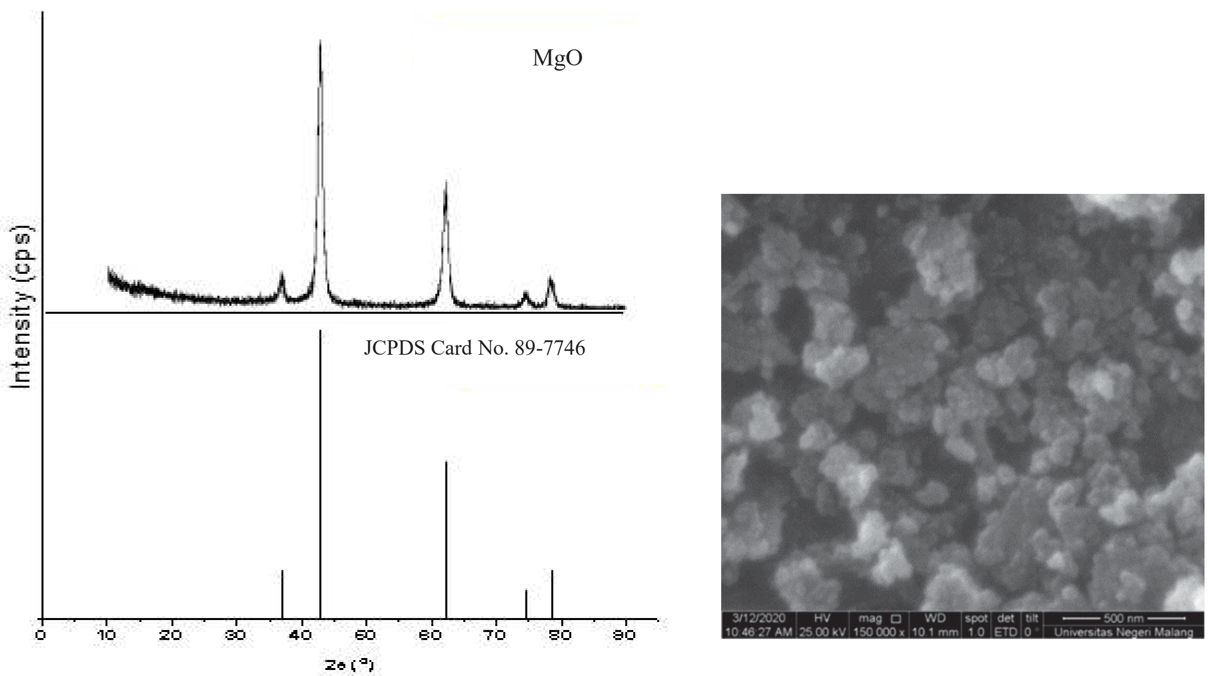
RESULTS AND DISCUSSION

MgO and Its Characterization

Magnesium Oxide (MgO) nanoparticles were successfully synthesized from a solution of Magnesium (II) Chloride and Ammonium Carbonate $(NH_4)_2CO_3$) with a mole ratio of 1: 1. Then the MgO particles were characterisized by X-Ray Diffraction (XRD) and Scanning Electron Mycroscopy (SEM). XRD analysis was performed to confirm the formation of MgO compared to standard diffractogram data in JCPDS Card No. 89-7746.

Fig. 1 (a) shows the correspondence between the diffractogram peaks of the MgO nanoparticles and the standard XRD curve of MgO (JCPDS Card No. 89-7746), i.e at 2θ 36.8º; 42.78º; 62.20º; 74.54º; 78.42º. The curve also shows that the MgO that has been synthesized is of high purity. The calculations using the Debye-Scherrer equation from the results of XRD analysis show that MgO nanoparticles have an average crystallyte size of 24.09 nm. Using MAUD® software knowing that MgO have a cubic structure (fcc) with the lattice parameter 4.2204204 Å.

The SEM images of synthesized MgO in magnification of 150,000 was presented in Fig. 1(b). The image shows that there are no significant morphological differences between the particles, this shows that the resulting uniformity of the MgO particles is spherical. The morphology is in accordance with previous research [9] [10]. The presence of clots indicates agglomeration during the synthesis process. From the results of measuring 100 particles using imageJ® software, it was obtained that the average MgO particle size was 50.903 nm with a size distribution ranging from 24.069 nm to 73.971 nm.



(a) (b)

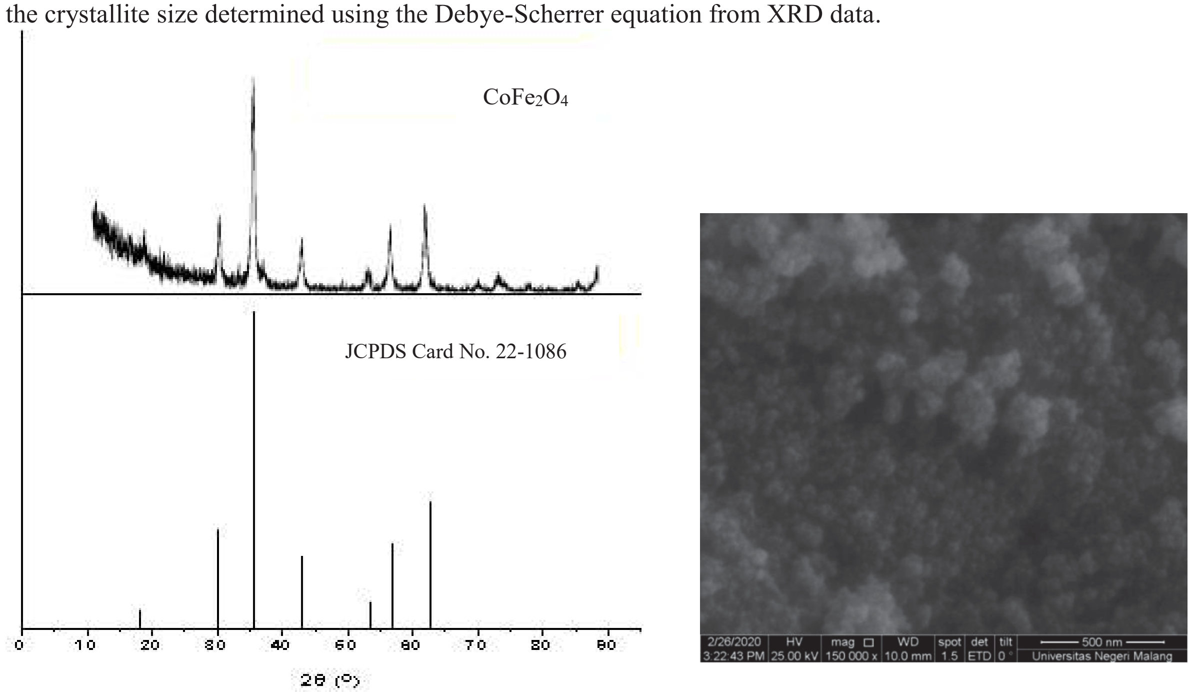
FIGURE 1. (a) Diffractogram of MgO (b) The SEM Image of MgO

$CoFe_2O_4$ and Its Characterization

Cobalt Ferrite ($CoFe_2O_4$) nanoparticles were successfully synthesized by coprecipitation from a solution of Cobalt (II) Chloride and Iron (III) Chloride solution with sodium hydroxide (NaOH) as precipitating agent.

The XRD analysis results of the $CoFe_2O_4$ nanoparticles as shown in Fig. 2 (a) show that the diffractogram peaks are at 2θ 18.28°; 30.14°; 35.52°; 43.16°; 53.44°; 56.97°; and 62.58°, is in accordance with the standard curve of cobalt ferrite nanoparticles namely JCPDS Card No. 22-1086. The absence of other peaks on the curve also indicates that the purity of the synthesized $CoFe_2O_4$ is high. The average crystal size of $CoFe_2O_4$ calculated by the Debye-Scherrer equation is 21.19 nm. Using MAUD® software knowing that $CoFe_2O_4$ also have a cubic structure (fcc) with the lattice parameter 8.380354 Å.

Based on the results of the analysis of $CoFe_2O_4$ results synthesized using SEM at a magnification of 150,000 times shown in Fig. 1(b), it is known that there are no significant morphological differences between particles. The presence of clots indicates agglomeration during the synthesis process. From the results of measuring the diameter of 100 particles that appear in the SEM image using imageJ® software, it is obtained that the average particle size of CoFe2O4 is 31.958 nm with a size distribution ranging from 20.269 nm to 45.066 nm. This particle size differs from the crystallite size determined using the Debye-Scherrer equation from XRD data.



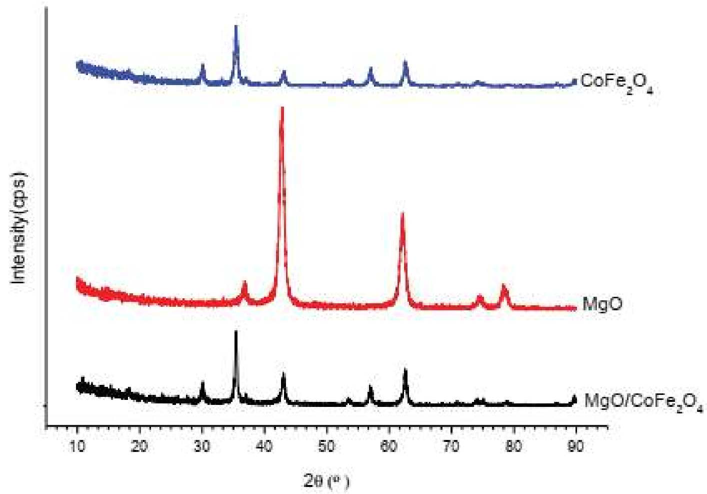
(a) (b)

FIGURE 2. (a) Diffractogram of $CoFe_2O_4$ (b) The SEM Image of $CoFe_2O_4$

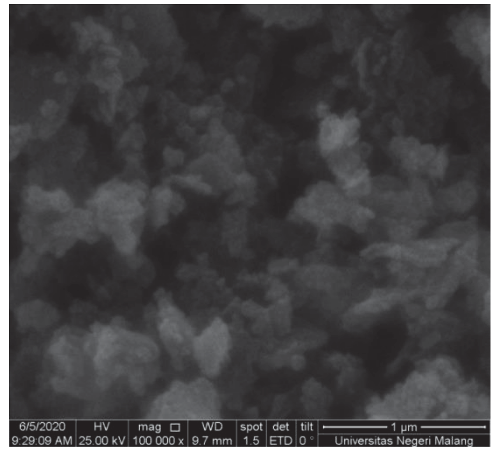
MgO/$CoFe_2O_4$ and Its Characterization

MgO/$CoFe_2O_4$ nanoparticles were prepared by impregnation method from MgO and $CoFe_2O_4$ with a mole ratio of 5: 1. The success indicator for impregnation can be seen in Fig. 3 (a). XRD peaks of MgO/$CoFe_2O_4$ nanoparticles at 2θ 18.03°; 30.09°; 35.45°; 43.08°; 53.52°; 57.02°; 62.57°; 71.02°; 74.14°; 79.08° and 86.82° show a combination of the XRD peaks of MgO and $CoFe_2O_4$. This pattern only decreased in intensity without any significant peak shift. This shows that there is no chemical interaction between the constituent components.

The SEM images of MgO/$CoFe_2O_4$ with magnification of 100,000 are presented in Fig. 3 (b). This shows that MgO/$CoFe_2O_4$ has been successfully synthesized. The proof of that success is by increasing the particle size after impregnation. Unlike the crystallite size that was determined by the Scherrer equation, the mean particle size was determined from the size distribution of 100 randomly selected particles that appear on SEM images using imageJ® software. It was found that the average particle size of MgO/$CoFe_2O_4$ was 88.228 nm with a size distribution ranging from 44.448 nm to 137.920 nm. The particle size of MgO/$CoFe_2O_4$ is bigger than that of MgO or $CoFe_2O_4$.



(a)



(b)

FIGURE 3. (a) Diffractogram of MgO/CoFe$_2$O$_4$ (b) The SEM Image of MgO/CoFe$_2$O$_4$

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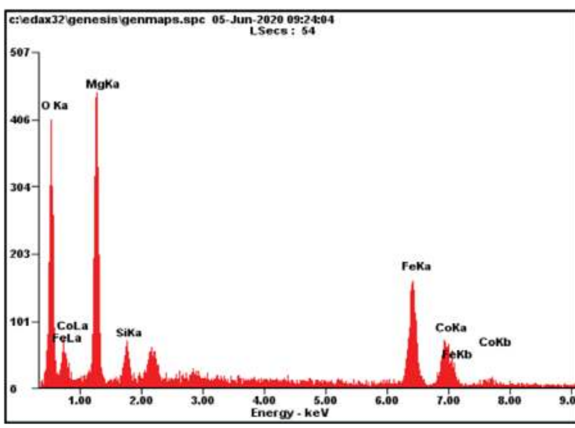
The atomic and mass percentages of each element from the EDX analysis is presented in Fig. 4. Based on these data it is evident that the material consists of Magnesium, Cobalt, Iron and Oxygen in appropriate ratios, that is, in accordance with theoretical calculations. In addition, it appears that Si is the impurity.



Element	*Wt%*	*At%*
OK	28.11	46.73
MgK	29.07	31.80
SiK	03.00	02.84
FeK	26.24	12.50
CoK	13.59	06.13
Matrix	Correction	ZAF

FIGURE 4. The EDX Results of MgO/CoFe$_2$O$_4$

CONCLUSION

MgO/CoFe$_2$O$_4$ nanoparticles were successfully synthesized by the coprecipitation method with a mole ratio of MgO and CoFe$_2$O$_4$ 5: 1. The XRD analysis results showed that the peaks of the diffractogram of nanoparticles MgO/CoFe$_2$O$_4$ in matched with the standard curve of constituent MgO/CoFe$_2$O$_4$, namely the JCPDS Card No. 89-7746 for MgO. and the JCPDS Card No. 22-1086 for CoFe$_2$O$_4$. The SEM analysis results show that the particles size of the impregnated substance is greater than the size of the constituents. The EDX analysis results show that MgO/CoFe$_2$O$_4$ is composed of the elements of Mg, Co, Fe and O with the appropriate ratio. The success of synthesis MgO/CoFe$_2$O$_4$ in this study contributed to the ways of synthesizing heterogeneous catalysts. MgO/CoFe$_2$O$_4$ is expected to be a renewable superior catalyst, particularly in biodiesel production.

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