The Effect of SrO Impregnation on The Characteristics of Cobalt Ferrite (CoFe₂O₄) Nanoparticles Synthesized by Coprecipitation

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Abstract. Cobalt Ferrite (CoFe₂O₄) nanoparticles are magnetic materials that have greater hardness than Fe₃O₄. CoFe₂O₄ is widely applied in many fields, including as a heterogeneous catalyst in various chemical reactions such as photocatalysis, phenol degradation, and transesterification reactions. This is supported by the thermal and chemical stability possessed by CoFe₂O₄. Coating or impregnation of non-magnetic material on the surface of the ferrite, on one side will reduce its magnetism and possibly its surface area. But on the other hand, the positive impact of coating or impregnation is the increase in particle monodispersity. Weakening the magnetism of the particles will reduce the interaction of attraction between particles, so that the particles are getting more monodisperse. This will optimize its potential as a heterogeneous catalyst. In this research impregnation of strontium oxide (SrO) would be carried out on the surface of CoFe₂O₄. After that, the characters were compared with CoFe₂O₄ before being impregnated. The CoFe₂O₄ synthesis was carried out through the coprecipitation method, followed by wet impregnation with SrO. The results showed that the impregnation of SrO on CoFe₂O₄ increased the zeta potential of the particles which indicated the stability of the particles in the dispersion.

1. Introduction
Cobalt Ferrite (CoFe₂O₄) is a spinel ferrite crystal classified AB₂O₄ type. Element A is a divalent metal which occupies a tetrahedral position, while B is a trivalent metal that occupies an octahedral position [1]. CoFe₂O₄ is a magnetic compound with a magnetic value slightly lower than Fe₃O₄. CoFe₂O₄ is a hard metal while Fe₃O₄ is a soft metal [2]. This causes CoFe₂O₄ have good thermal and chemical stability [3]. Based on this stability makes CoFe₂O₄ to be useful material with wide applications, such as material for electronic, sensor, drug delivery, and catalyst [4]. This material is often used as a heterogeneous catalyst in several chemical reactions, including photocatalysis, phenol degradation of acetylene decomposition in carbon nanotube production (CNT), biomedical applications [5].

The homogeneous catalyst usually makes reactions going quickly and efficient, but the catalyst cannot be recovered for reuse and also corrosive for environment. That is different from heterogeneous catalyst which is easy to separate, recoverable, and environment-friendly [6]. Catalyst properties will be maximized if the size of material is very small (especially in nanometers orders). Because of the smaller the particle, the wider the specific surface area. The wider the surface area of the catalyst, the wider the active side which is in contact with substrate [7].
The factor that must be avoided in order to obtain uniform particle distribution and small particle size is material agglomeration. For this reason, it is necessary to add materials that can reduce or prevent particle agglomeration in the synthesis process. One of the metal oxides that can be used as a deterrent for agglomeration in ferrite is Strontium Oxide (SrO). SrO also has a dual function to assist the catalytic process, especially the transesterification reaction [5] [8].

In this research, we intend to synthesize and characterize material of SrO/CoFe$_2$O$_4$ nanocomposite. The stages of this research include: (1) synthesis of SrO by precipitation; (2) synthesis of CoFe$_2$O$_4$ by coprecipitation; (3) Impregnation of SrO into CoFe$_2$O$_4$ by wet-impregnation; (4) Characterization of the synthesized material by XRD, BET, SEM, EDX, Zeta Potential, and VSM.

2. Materials and Method

Materials used are Strontium Chloride hexahydrate (SrCl$_2$.6H$_2$O) Merck, Ammonium Carbonate (NH$_4$CO$_3$) Merck, Iron (III) Chloride hexahydrate (FeCl$_3$.6H$_2$O) Merck, and Cobalt Chloride hexahydrate (CoCl$_2$.6H$_2$O) SAP, and Sodium Hydroxide (NaOH) Merck.

2.1. Synthesis of Strontium Oxide (SrO)

Strontium Oxide (SrO) was synthesized by precipitation method from Strontium Chloride (SrCl$_2$) solution and Ammonium carbonate (NH$_4$CO$_3$) solution. This process was going on stirring at 80 °C for 2 hours. The result of this process was smooth white powder; it’s Strontium Carbonate (SrCO$_3$). The powder was then washed to remove the impurities with demineralized water until pH of filtrate became neutral and free from chloride ions. After that washing process, the powder was continued washed using ethanol and acetone. SrO was formed by calcination of SrCO$_3$ at 1000 °C for 4 hours. The product was brittle white powder, which is the specific characterization of SrO. Then this material was cooled at room temperature and stored in a desiccator.

2.2. Synthesis of Cobalt Ferrite (CoFe$_2$O$_4$)

Nano-magnetic Cobalt Ferrite (CoFe$_2$O$_4$) was synthesized by co-precipitation reaction of an aqueous solution of Iron (III) Chloride and Cobalt Chloride by an alkaline solution. A mixture of aqueous solution of CoCl$_2$ and FeCl$_3$ in mole ratio of 1:2 was mixed with solution of Chloride Acid. An alkaline solution is added drop by drop to this solution. In this research, using Sodium Hydroxide (NaOH) as an alkaline solution.

This Co-precipitation process was carried out in a reflux system equipped with a magnetic stirrer. The set of equipment used is presented in Figure 1. This process took place at 70 °C for about 4 hours. The result was black sediment at the bottom of the flask. Then the black sediment was separated from the solution by filtering. The material was washed with demineralized water until pH of the filtrate is neutral and free from chloride ions. After that, the material was dried at 150 °C for 5 hours and calcined at 850 °C for 4 hours. The end result was black Cobalt Ferrite (CoFe$_2$O$_4$).

2.3. Impregnation SrO on CoFe$_2$O$_4$

The impregnation process was conducted by using wet-impregnation method. Strontium Oxide (SrO) and Cobalt Ferrite (CoFe$_2$O$_4$) were mixed with a weight ratio of 5:1. This mixture was dispersed in pure methanol and stirred in a reflux system at 80 °C for about 8 hours. The resulting deposit was filtered and dried at 120 °C for 6 hours. The end result was a composite of SrO/CoFe$_2$O$_4$.

2.4. Characterization of SrO/CoFe$_2$O$_4$

Characterization of the particles was consisting of several tests for material characteristics. 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.

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)
where $\lambda$ is the wavelength of X-ray beam, $\beta$ is full width at half maximum (FWHM) and $\theta$ is Bragg scattering angle and $K (=0.89)$ is shape factor.

The specific surface area was determined by N$_2$ adsorption at $-196 \degree C$ using Nova 1200 Quantchrome by the BET methods. The morphology of the prepared nanocomposites was determined by scanning electron microscopy (SEM) images with Type Inspect S50, FEI. Zeta Potential was done by Malvern Zetasizer using methanol as dispersant at room temperature. Analysis with Vibrating sample magnetometer (VSM) was done by using Oxford VSM 1,2 H with magnetic fields in the range – 8000 to 8000 Oe at room temperature.

![Figure 1. Co-precipitation method.](image)

### 3. Result and Discussion

#### 3.1. XRD Result

The synthesized SrO was started through SrCO$_3$ synthesis by coprecipitation method through reaction:

\[
\text{SrCl}_2(\text{aq}) + (\text{NH}_4)_2\text{CO}_3(\text{aq}) \rightarrow \text{SrCO}_3(s) + \text{NH}_4\text{Cl}(s)
\]

Then SrO formed by calcination of SrCO$_3$ at 1000 °C following this reaction:

\[
\text{SrCO}_3(s) \rightarrow \text{SrO}(s) + \text{CO}_2(g)
\]

Meanwhile, the synthesis process of cobalt ferrite (CoFe$_2$O$_4$) was through co-precipitation method using an alkaline (NaOH) solution as precipitant. The XRD results shown in Figure 2. The diffraction peaks of CoFe$_2$O$_4$ suitable with JCPDS Card No. 96-591-0064 for CoFe$_2$O$_4$ indicated by the crystal planes of (220), (311), (222), (400), (422), (333), (440), (531), (620), (553), and (444). Furthermore, through the refining method using Rietvield for CoFe$_2$O$_4$ diffractogram as shown in Figure 3, there is a Good of Fitness (GOF) value of 3.213, and obtained data that the synthesis material has molecular weight of 235.73 g/mol with density of 66.324 g/cm$^3$ that suitable for CoFe$_2$O$_4$.

Another curve in Figure 2 show XRD spectrum of SrO/CoFe$_2$O$_4$ which was the result of SrO impregnation on the surface of CoFe$_2$O$_4$ by wet impregnation using methanol as solvent. The successful indicator of the impregnation can be seen in Figure 4, the XRD spectrum appears to be a combination of typical peaks of SrO corresponding to JCPDS Card no. 96-152-9601 at $2\theta$ 25.3° and typical peaks of CoFe$_2$O$_4$ with JCPDS Card No. 96-591-0064. This result is similar with result of Falcao [9].

Crystallite size calculated by the Debye-Scherrer equation of the material before and after impregnation is 24 nm and 44 nm. This result showed that SrO covers CoFe$_2$O$_4$ nanoparticle. Based on this size, this composite still can be classified as nanoparticle because its lower than 100 nm. So it can be concluded that co-precipitation method is an effective preparation method of nanomaterial.

#### 3.2. BET Result

BET characterization gave a specific surface area of CoFe$_2$O$_4$ and SrO/CoFe$_2$O$_4$ of about 24.317 m$^2$/g and 9.223 m$^2$/g, respectively. This indicated that surface of CoFe$_2$O$_4$ has been covered with large
amounts of SrO powder. This result is match with crystallinity size analysis using Debye-Scherrer Equation, i.e. the nanomaterial became bigger after impregnation, so the specific area of nanomaterial became tighter than before impregnation. But the composite with specific surface area of 9.223 m²/g is still potential as nanocatalyst.

3.3. SEM and EDX Result
Based on SEM photographs as shown in Figure 5, the surface morphology of CoFe₂O₄ is similar to a boulder polydisperse (Figure 5a). This is different from the photo of SrO/CoFe₂O₄ (Figure 5b) which looks much smaller and monodisperse, although taken with the same magnification.

![Figure 2. XRD Diffractograms.](image)

![Figure 3. Rietveld of CoFe₂O₄ Diffractogram.](image)
Figure 4. Match of SrO/CoFe$_2$O$_4$ Diffractogram.

Figure 5. SEM of CoFe$_2$O$_4$ (a) before impregnation and (b) after impregnation using SrO.

From the CoFe$_2$O$_4$ EDX result shown in Figure 6 that it is proven that material consists of Cobalt, Iron, and Oxygen with correct atom and weight ratio. In Figure 7 we can see the presence of SrO in composite, but we can’t find a correct number result. It's very difficult to get the correct number in composite material, because it was very difficult to get homogenous impregnation material.
3.4. Results of Zeta Potential Analysis
Zeta potential analysis is potentially useful for checking the stability component in disperse condition and to know the surface charge of material. If the zeta potential value of a material in a dispersion outside the range of -30 mV to 30 mV, the dispersion is stable. But if zeta potential value in a range between -30 mV and 30 mV, the dispersion of the material is not stable and tend to aggregate and then flocculate [10]. In relation with biodiesel catalytic reaction, zeta potential parameter of a catalyst affects the conversion value of biodiesel. the more positive the zeta potential of a material, the more potential it is as a Lewis acid which is the more potential for starting the formation of free radicals needed in the transesterification reaction to produce biodiesel.

The zeta potential result value show in Table 1, the average value for CoFe$_2$O$_4$ is -18.5 mV. After impregnation process using SrO, the value becomes 30.3 mV. This shows that the presence of SrO makes the material more stable in dispersion and has the potential as a transesterification catalyst.

| Element | Wt%  | At%  |
|---------|------|------|
| OK      | 26.27| 55.91|
| FeK     | 46.89| 28.59|
| CoK     | 26.84| 15.51|
| Matrix  | Correction | ZAF  |

| Element | Wt%  | At%  |
|---------|------|------|
| OK      | 35.64| 73.52|
| FeK     | 07.39| 04.37|
| CoK     | 03.57| 02.00|
| SrK     | 53.41| 20.12|
| Matrix  | Correction | ZAF  |
Table 1. Zeta Potential Results.

| No. | Experiment | Zeta Potential Value (mV) | CoFe$_2$O$_4$ | SrO/CoFe$_2$O$_4$ |
|-----|------------|---------------------------|---------------|------------------|
| 1   |            | -12.8                     | 30.9          |                  |
| 2   |            | -16.6                     | 29.8          |                  |
| 3   |            | -18.4                     | 30.4          |                  |
| 4   |            | -23.6                     | 30.8          |                  |
| 5   |            | -21.0                     | 29.6          |                  |
|     | **Average**| **-18.5**                 | **30.3**      |                  |

3.5. Results of VSM Analysis

Figure 8 shows the magnetic moment of CoFe$_2$O$_4$ is relatively very high, which is around 76 emu/g. This value is almost same with magnetization value of Fe$_3$O$_4$ (magnetite). This result also shows that CoFe$_2$O$_4$ can be classified as ferro-paramagnetic material. After impregnation using SrO, magnetization value goes down until 12 emu/g. But it still be concluded that the material can be easily to separate from the system using an external magnetic field.

![VSM Result of CoFe$_2$O$_4$ and SrO/CoFe$_2$O$_4$.](image)

4. Conclusion

Based on the results of this study, it can be concluded that the SrO/CoFe$_2$O$_4$ nanocomposite has been synthesized by the coprecipitation method and followed by the impregnation of SrO on the surface of CoFe$_2$O$_4$. Based on XRD analysis results that provide information on crystal size, BET analysis results that show large surface area, SEM results that inform particle morphology, zeta potential analysis results that show the dispersion of synthesized particles in reaction media is stable, and VSM results that show magnetism material, it can be concluded that SrO/CoFe$_2$O$_4$ material has the potential as a catalyst in biodiesel synthesis.

References

[1] Houshiar M, Zebhi F, Razi Z J, Alidoust A and Askari Z 2014 J. Magn. Magn. Mater. 371 43–8
[2] Horng L, Chern G, Chen M C, Kang P C and Lee D S 2004 J. Magn. Magn. Mater. 270 389–96
[3] Chitu L, Jergel M, Majkova E, Luby S, Capek I, Satka A, Ivan J, Kovac J and Timko M 2007 Mater. Sci. Eng. C 27 1415–7

[4] Amiri S and Shokrollahi H 2013 Mater. Sci. Eng. C 33 1–8

[5] Semwal S, Arora A K, Badoni R P and Tuli D K 2011 Bioresour. Technol. 102 2151–61

[6] Yan S, DiMaggio C, Mohan S, Kim M, Salley S O and Ng K Y S 2010 Top. Catal. 53 721–36

[7] Ross J R H 2012 Catalyst Preparation Heterogeneous Catalysis (Elsevier) pp 65–96

[8] Gryglewicz S 1999 Bioresour. Technol. 70 249–53

[9] Falcão M, Garcia M, de Moura C, Nicolodi S and de Moura E 2017 J. Brazil. Chem. Soc.

[10] Joseph E and Singhvi G 2019 Multifunctional nanocrystals for cancer therapy: a potential nanocarrier Nanomaterials for Drug Delivery and Therapy (Elsevier) pp 91–116