Thermal Stability Analysis using Iron Oxide Nanoparticle Coated with SDS

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ABSTRACT

The unique characteristic of iron oxide nanoparticles (IONPs) such as low toxicity, high coercivity, superparamagnetic, high magnetic susceptibility and high surface-to-volume ratio have created much attention in various field especially in the oil and gas sector. However, bare IONPs are easily to oxidize in air and tends to agglomerate due to the high surface energies between the nanoparticles. Therefore, surface coating is an essential step to maintain the stability of IONPs. In this research, IONPs were synthesized using facile co-precipitation method and surface coated with Sodium Dodecyl Sulphate (SDS) as ionic surfactant by the dip-coating method. Molar ratio of the coating agent was varied from 0.1 to 0.5 M and the calcination temperature after coating process was varied from 60^{o}C to 606^{o}C to study the effect on the crystallite size, degree of crystallinity and magnetite content of the coated IONPs. The coated IONPs were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction device (XRD), and Thermogravimetric Analysis (TGA). The result has shown that at greater SDS to IONPs molar ratios, the crystalline size and crystallinity increased, while the magnetite content dropped. Higher calcination temperatures, however, resulted in larger sized crystals with less crystallinity and magnetite concentration. The TGA plot showed that more stable nanoparticles will be produced at higher calcination temperatures. Therefore, the ideal coating condition obtained is at molar ratio of 0.1 and calcination temperature of 154 °C as it produces smallest crystallite size (8.56nm) and highest magnetite content (56.8%).

Keywords: iron oxide nanoparticles; sodium dodecyl sulphate; thermal stability

1 Introduction

Recently, the prospective of iron oxide nanoparticles (IONPs) has immensely increased in the subsurface application due to its intrinsic physicochemical properties. The high magnetic susceptibility has enable the IONPs to be quickly recovered and reused for the next EOR operation [1]. Magnetite, which is one type of IONPs, is most desired due to its superparamagnetic properties, low cost, low toxicity, and simplicity of production.

However, during the synthesis level, IONPs is exposed to structural transformation causing the IONPs to have different magnetic properties hence, having different application potential[2]. One of the common factor that could lead to phase transformation is exposure to oxidation during heating process[2]. Under high temperature, oxidation of magnetite can form hematite. Previous study showed that magnetite can phase change to maghemite at calcination temperature 200 ^{o}C and to hematite under temperature above 800 ^{o}C[3]. Up until today, there is little published literature on the phase change occurring between 300-600 ^{o}C. It is expected that during the temperature, the magnetite is slowly transformed to hematite phase.

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Coating of iron oxides is considered a vital step to avoid further oxidation and aggregation of nanoparticles. Surface coating by various materials such as polymer, silica, surfactant, or carbon coating can overcome this problem. As a surface coating agent, sodium dodecyl sulphate (SDS) is suitable because of its ability to alter wettability of the reservoir rock by reducing the contact angle and its low adsorption capacity on the reservoir rock[4-5].Recent study by Shalbafan et al. [6] showed that IONPs coated SDS have strong wettability alteration from oil-wet to water-wet. However, there are not enough literatures that study on the effect of SDS concentration and also the ability of the IONPs coated SDS to withstand high temperatures of the reservoir condition

Calcination temperature not only causes phase change in IONPs but also affects the crystallography properties and grain size of crystals of IONPs. Therefore, this study will carry out the thermal stability of IONPs coated SDS. Here, IONPs was synthesized via co-precipitation method and surface coated with SDS by simple dip-coating method at varying molar ratio and calcination temperatures. Then, the synthesized nanoparticles were characterized to study the crystallographic properties and the thermal stability of the nanoparticles.

2 Materials and Methods

The present study introduced the thermal stability study of IONP coated with SDS. The effect of molar ratio of the coating agent and calcination temperature after coating process were investigated. Characterization studies before and after coating process were conducted in this research.

2.1 Materials

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), sodium dodecyl sulphate ($NaC_{12}H_{25}SO_4$) and ammonium hydroxide solution (NH_4OH) were purchased from Sigma Aldrich. All the chemicals and reagents are analytical grade and directly in this work without further purification. Nitrogen (N_2) gas were used throughout the experiment.

2.2 Synthesis of bare IONPs

Bare IONPs was synthesized through a simple co-precipitation method. First, 400 mL of distilled water was heated using a hotplate magnetic stirrer until it reaches 75 ºC. Then, 12.2 g of $FeCl_3 \bullet 6H_2O$ equivalent to 0.451 M and 4.49 g of $FeCl_2 \cdot 4H_2O$ corresponding to 0.226 M were added to the round bottomed flask containing the distilled water [7]. The molar ratio of $FeCl_2 \cdot 4H_2O$ to $FeCl_3 \cdot 6H_2O$ were always kept at a ratio of 1:2. The homogenous solution was stirred vigorously for 30 minutes under nitrogen atmosphere until the colour of the solution changed to dark orange. Next, ammonia solution was added dropwise into the aqueous solution for 2 hours until the pH reached at 10. The colour of the mixture has changed to dark black. The solution was stirred for another 30 minutes to let the reaction to be completed. The solution was let to cool to room temperature. The solid black magnetic product in the mixture was separated by magnetic decantation. The remaining mixture was filtered using Smith filter paper (125 mm) and washed three times to remove impurities. Lastly, the black precipitate was dried in an oven for 12 hours at 60 ºC.

2.3 Synthesis of IONPs coated SDS

The surface coating was adapted from Shalbafan et.al [4] with some modification. 4.63 g of bare IONPs was added to 20 mL of distilled water. The aqueous IONPs solution was sonicated for 30 minutes using ultrasonic bath to fully disperse the IONPs. At the same time, 0.1 M of SDS was dissolved in 20 mL of distilled water and mixed at 400 rpm for 1 hour at room temperature. Both of IONPs and SDS solution

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were mixed and stirred at 300 rpm for 20 hours to allow complete coating process. The colour of the mixture has changed to brownish-black. The mixture was centrifuged at 1000 rpm for 15 minutes to separate product from the solution and washed three time to eliminate impurities. The product was then dried in a furnace at various calcination temperature ranging from 60 ^{o}C, 154 ^{o}C, 380^{o}C and 606 ^{o}C. The dried IONPs coated SDS was obtained. The same step was repeated for different molar ratio of SDS at 0.2 M and 0.5 M.

2.4 Characterization of the synthesized nanoparticles

The phase and crystallographic properties of the synthesized nanoparticles were determined by XRD (Ultima IV, Rigaku) at room temperature with angle range (2θ) of 20-80^{o}. The functional groups in organic molecules before and after the surface coating process was confirmed using a FTIR (Spectrum One, Perkin Elmer) at wavelengths between 400 and 4000 cm^{-1}. TGA (Mettler Toledo) was used to measure the weight changes in the synthesized nanoparticles as a function of temperature under a pure nitrogen atmosphere between 25 ^{o}C and 800 ^{o}C at a rate of 10 ^{o}C/min.

3 Theory and Calculation

Magnetite behaves differently at various temperature condition. The effect of temperature and molar ratio of SDS towards the crystallite size, degree of crystallinity and content of magnetite was obtained and calculated from the XRD patterns.

The crystallite size of bare IONPs and IONPs coated SDS can be estimated by Scherrer's equation as follows:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

Where D is the average crystallite size in nm, K is the Scherrer constant equal to 0.9, λ is the wavelength of X-rays Cu-Kα radiation (λ = 0.154 nm), β is FWHM (in radian) and θ is the diffraction peak angle (in radian).

The crystallinity and magnetic content are calculated through the peak area ratio as shown in equations as follows:

$$Crystallinity\ (\%) = \frac{Area\ of\ crystalline\ peaks}{Area\ of\ all\ peaks\ (Crystalline+Amorphous)} \quad (2)$$

$$Magnetite\ content(\%) = \frac{Total\ area\ of\ magnetite\ peaks}{(Total\ area\ of\ magnetite\ peaks+\ Total\ area\ of\ hematite\ peaks)} \quad (3)$$

The area of peaks that are magnetite and hematite were distinguished by referring to Inorganic Crystal Structure Database (ICSD) reference number 01-079-0007 for hematite and 01-076-1849 for magnetite diffraction peaks [8].

4 Results and Discussion

The result of the study consists of 1) characterization of IONPs coated SDS, 2) effect of molar ratio and calcination temperature on crystallite size, crystallinity and magnetite content, 3) thermal stability of IONPs

coated SDS.

4.1 Characterization of IONPs coated SDS

In the FTIR spectrum, Figure 1 (a), the band observed at 599 and 625 cm^{-1} for bare IONPs and IONPs coated SDS, respectively, was ascribed to the strong Fe-O absorption band [9]. The band at 3391 and 3410 cm^{-1} corresponds to the stretching vibrations of –OH groups. The band at 1613 cm^{-1} was assigned to bending vibrations of H-O-H due to adsorbed water on surface[9]. After the surface coating process, Figure 1 (b) was obtained. The characteristic bands at 2916 and 2845 cm^{-1} are attributed to the stretching vibrations of C-H group of SDS, and the absorption band at 1215 cm^{-1} is allocated to the stretching mode of S=O of SDS[6]. Thus, these finding confirm that surface coating process of IONPS coated SDS was successful.

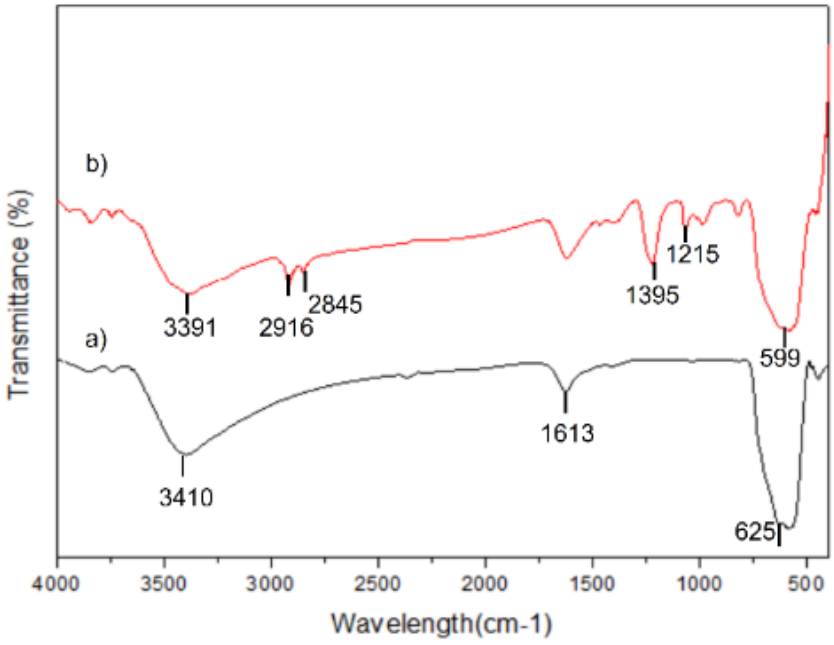

Figure 1: *The FTIR spectra of a) bare IONPs and b) IONPs coated SDS*

The XRD patterns for bare IONPs, IONPs coated SDS at different molar ratio and calcination temperature were given in Figure 2. The diffraction peaks at Braggs angle 2θ = 30.81°, 36.20°, 38.38°, 44.64°, 53.95°, 57.55°, 63.17°, 71.89° and 74.80° can be assigned to the (220), (311), (222), (400), (422), (511), (440), (620) and (533) planes respectively. These peaks represent the cubic spinel crystal structure of bare IONPs (magnetite). On the other hand, the diffraction peak at Braggs angle 2θ = 36.20° and 43.61° corresponding to the Miller indices [110] and [113]. These peaks indicate the crystal structure of α-Fe_2O_3 (hematite). No characteristics for impurities were found in the XRD patterns. The XRD pattern of Figure 2 (a), was taken at 154 ºC with varying molar ratio. According to Figure 2 (a), as the molar ratio increased, the diffraction peaks are becoming stronger in intensity and narrower. The narrowing of peaks showed that higher crystallinity can be obtained when molar ratio increased. Also, at higher molar ratio, the appearance of new hematite peak can be clearly seen. In Figure 2 (b), the molar ratio was kept constant at 0.5 M to study the effect of temperature on the XRD peaks. The diffraction peaks are becoming sharper and narrower as the calcination temperature increases. The appearance of hematite peaks is stronger at higher calcination temperature.

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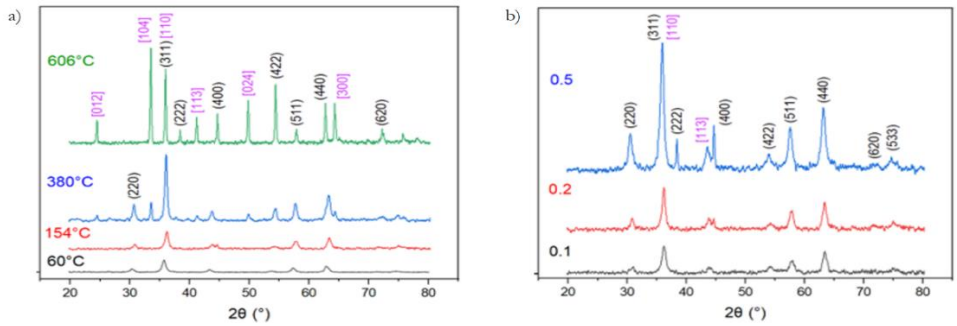

Figure 2: *XRD patterns of IONPs with a) varying calcination temperature at molar ratio of 0.5 and b) varying molar ratio at calcination temperature of 154 ºC*

4.2 Effect of molar ratio and calcination temperature on crystallite size, crystallinity, and magnetic content

Based on the XRD patterns obtained, crystallite size, crystallinity and magnetite content were calculated. Figure 3 (a) in general, showed that increasing molar ratio led to high crystallite size of IONPs coated SDS. This is due to the high molar ratio consisting of high amount of SDS. Hence, more SDS can be coated and forming larger micelles and crystallite size[10]. The increased in crystallite size was also contributed by the Ostwald ripening mechanism which involve growth of larger nanoparticles from the smaller ones[11]. On the other hand, the crystallite size showed a constant increase when the calcination temperature increased as shown on Figure 3 (a). For IONPs coated SDS at 60 ºC, the crystallite size was observed to be 11.81 nm, 10.26 nm, 12.27 nm for 0.1, 0.2 and 0.5 M of SDS, respectively. When the calcination was increased to 606 ºC, the crystallite size increased by 50%, 67%, and 65% for 0.1, 0.2 and 0.5 M of SDS, respectively. The higher crystallite size values showed that the nanoparticles are susceptible to agglomerating and form big clusters when dispersed in solvent. High calcination temperature can lead to growth of crystals hence higher particle size[12]. Thermal decomposition of SDS that might occurred after the temperature reached 380 ºC potentially caused the growth of polycrystalline particles. The void in between the crystallites of each particles can be contributing to faster oxidation process causing the presence of grain boundaries[2]. Other than that, polycrystalline particles have less compact structure. Therefore, oxygen can penetrate easily into the particles' void and through the edges of the structural discontinuation[2].

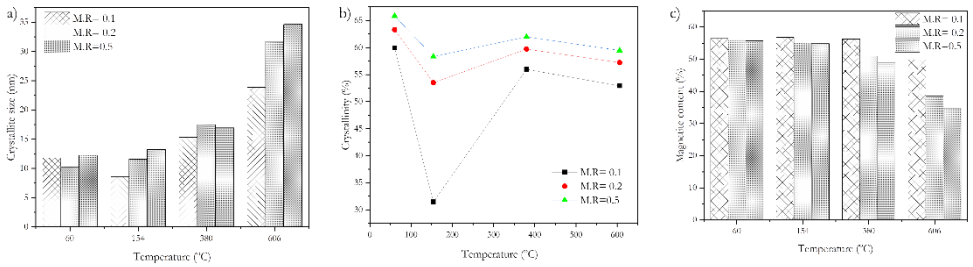

Figure 3: *Effect of molar ratio and calcination temperature on the a) crystallite size, b) degree of crystallinity and c) percentage of magnetite content of IONPs coated SDS*

According to Figure 3 (b), increasing the molar ratio from 0.1 to 0.5 M, has led to increase in crystallinity. These finding were consistent with the XRD spectra obtained in Figure 3 (b) previously where at higher molar ratio, the peaks are becoming higher and narrower. The strengthening in intensity of XRD peaks contributed to the crystallinity of IONPs coated SDS. Temperature has a clear effect on the growth of

crystal. According to Figure 3 (b), when the temperature increases from 60 ºC to 154 ºC, the crystallinity dropped by half from 60% to 31% for 0.1 M of SDS. The reduction in crystallinity could be due to evaporation of moisture in the nanoparticles and the shielding effect of SDS on the high crystalline nanoparticles[13]. As the temperature rises to 380 ºC, the crystallinity started increased due to the growth of the crystal. Only small reduction in crystallinity by less than 1% when the temperature reached 606 ºC owing to the transformation of hematite phase at high temperature.

The magnetite content of IONPs coated SDS decreased as the molar ratio increased (Figure 3 c). This could be ascribed by the presence of new and stronger hematite peak in the XRD patterns at higher molar ratio. There is no direct evidence of molar ratio affecting the magnetite content. However, calcination temperature has a significant effect on the magnetite content. The decrease trend of calcination temperature towards the magnetite content is attributed by the formation of hematite at high temperatures. At low temperature of 60 ºC, the magnetite content was at the highest for all range of molar ratios used. As the temperature started increased to 606 ºC, magnetite content reduced significantly for 0.2 M (31% reduction) and 0.5 M (37% reduction) of SDS. The coating molecules may bind with the surface atoms of the magnetic core to form a non-magnetic layer, reducing amount magnetite phase in the nanoparticles[14].

4.3 Thermal stability of IONPs coated SDS

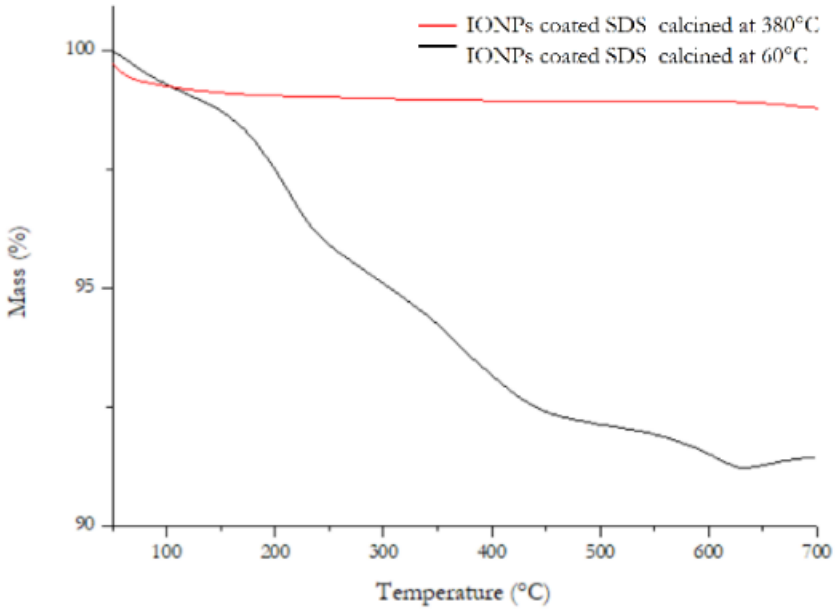

Figure 4: *TGA curves of IONPs coated SDS at 0.5M*

The percentage weight loss of IONPs coated SDS as a function of temperature, was studied by TGA analysis. Figure 4 shows TGA plot of IONPs coated SDS synthesized at fixed molar ratio of 0.5 M and calcination temperature of 60 ºC and 380 ºC. The TGA plot of IONPs coated SDS calcined at 380 ºC showed a very small amount or negligible amount of weight loss of 0.97% up to 700 ºC. On the other hand, TGA plot for IONPs coated SDS calcined at 60 ºC experienced series of weight loss that contributed to the overall weight loss of 8.68% up to 700 ºC. The weight loss was due to the loss of adsorbed water from the surface of the IONPs[9]. Further weight loss as the temperature increased was then ascribed to the presence of multiple layers of water attached to the IONPs that is negatively charged due to high pH during preparation. Other than that, the underlying SDS layer also contributed to the overall weight loss[15].

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5 Conclusions

The current study showed the thermal evaluation of IONPs coated SDS. The average crystallite size obtained after the surface coating were in the range of 8-30 nm. The FTIR confirmed that SDS was successfully coated on the surface IONPs. The XRD pattern also showed that crystallinity and magnetite content are more affected by the calcination temperature compared to the molar ratio. However, crystallite size is affected by both molar ratio and calcination temperature. The results displayed that as the molar ratio of SDS to IONPs increased, the crystallite size and crystallinity increased but the magnetite content decreased. On the other hand, when the calcination temperature of SDS coated IONPs increased, the crystallite size increased but the crystallinity and magnetite content decreased. Thermogravimetric studies proved that IONPs coated SDS consists of multilayered coating between water and SDS. The ideal coating condition that can produce the smallest crystallite size and highest magnetite content is at molar ratio of 0.1 and calcination temperature of 154 ^{o}C as the integrity of SDS-IONPs is still intact, no presence of hematite found and produced more stable IONPs.

6 Declarations

6.1 Acknowledgements

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6.3 Competing Interests

There is no conflict of interest.

6.4 Publisher's Note

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