Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

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Abstract

In this study, a nanocomposite cobalt ferrite / graphene, CoFe2O4-G was prepared by sol-gel method, and was identified by (XRD, AFM, and SEM) techniques. The composite was used to remove sulfur from the Iraqi kerosene (Al-Doura refinery) with a concentration of 500 ppm of sulfur. Oxidative desulfurization was used in the sulfur removal from kerosene and the composite appeared to have good effectiveness in the removal of sulfur from this kerosene under various conditions (Time, temperature, O/S ratio, and catalyst weight) as it showed a high removal activity of sulfur at optimum conditions which exceed 90 %.

Keywords: Oxidative desulfurization, Kerosene, Cobalt ferrite, Sulfur removal.

تحضير وتشخيص متراكب الكوبلت فيرايت / الكرافين لازالة الكبريت من الكيروسين في عملية ازالة الكبريت بالاكسدة

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الخلاصة

في هذه الدراسة، تم تحضير الكوبلت فيرايت/ الكرافين بواسطة طريقة sol-gel، وتم تشخيص المركبات المحضرة بتقنيات مختلفة (XRD,AFM,SEM)، و استخدام المتراكب المحضر لإزالة الكبريت من الكيروسين العراقي الذي تم الحصول عليه من مصفى الدورة حيث اجريت ازالة الكبريت بواسطة عملية الإزالة المؤكسدة من الكيروسين واظهر المركب فعالية جيدة تحت ظروف مختلفة (الزمن ، درجة الحرارة ، نسبة S / O ، ووزن المحفز)، أظهر المتراكب المحضر في الظروف المثلى فعالية جيدة لسحب الكبريت تصل الى 90 %.

الكلمات المفتاحية: ازالة الكبريت بالاكسدة، الكيروسين، كوبلت فيرايت، أزالة الكبريت.

Introduction

The organosulfur / containing components in petroleum fuels output poisonous sulfur oxide gases through its oxidation, which can cause adverse effects on the environment [1]. Mercaptans as a type of sulfur materials is undesirable due to its unpleasant odours and corrosive properties [2]. Therefore, desulphurization of fuels is very important to environmental safety and has become a major challenge of the world [3]. The usual hydrodesulfurization (HDS) method displays high efficiency in the removal of sulfides, thiols, and mercaptans from fuels at industrial scale [4]. However, it is less effective in treating refractory alkylated organic sulfur compounds such as dibenzothiophene (DBT) and its derivatives due to the steric hindrance of these compounds [5,6]. Mentioned technology needs too high temperatures, high pressure, and high hydrogen exhaustion. Therefore, HDS is not appropriate for affordable reduction of the sulfur content from fuel [7,8]. It has economic damages due to requirement of severe operation conditions like high hydrogen pressure and high temperature to catalytically decompose the more refractory organo-sulphur compounds [9]. Moreover, high active HDS catalysts are being required by the industry [10]. Therefore, alternated operations are needed to achieve low cost targets and can be operated in moderate conditions. Among the alternate operations to the conventional hydrodesufurization, desufurization through adsorption [11], bio-desulfurization [12,13], ionic liquid extraction [14], electrochemical oxidation [15] and oxidative desulphurization [16]. One of these is the oxidative desulfurization (ODS) in which, the refractory organo-sulphur compounds such as dibenzothiophene (DBT) can be oxidized to

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

their corresponding sulfones or/and sulfoxides, and subsequently are removed by adsorption or/and extraction with polar solvents [17,18]. For ODS process, a suitable oxidant, an active catalyst, the efficiency of some organic and inorganic oxidants is required. The H2O2 is the most widely used, because of its environmentally friendly properties [19-21].

In the present work, we selected $CoFe_2O_4$-Graphene to be active in removing sulfur compounds from kerosene in ODS processes. The catalytic activities were evaluated for oxidative removal of dibenzothiophene in kerosene using H_2O_2 as oxidant.

Experimental

Material used

Graphite Powder (99% purity) was purchased from applechim company, potassium permanganate, sodium nitrate, sulfuric acid (98%), hydrogen peroxide (30%), hydrazine hydrate, cobalt nitrate hexahydrate, iron nitrate nonahydrate, dibezothiophene, kerosene, ethanol and distilled water, were analytical point and were used without any purification.

The kerosene used were obtained from Dora refinery in Baghdad with specifications given in table 1.

Table 1: Properties of used kerosene

Test	Result
Density 15 oC	0.7906 g/cm3
Flash point (Adel) oC	47.4
Final Boiling point oC	245
Doctor Test	Neg.
Distilled 185 oC Vol %	25
Sulfur Content Wt. %	0.0020
Smoke point (mm)	28
Aromatics Content Vol. %	13
Calorific Value Kcal/Kg (gross)	11087

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

Preparation of nanomaterials

Preparation of graphene oxide and Graphene

Hummer method [22] was used to oxidize the graphite's for the preparation of GO and follows:

2 gm of graphite, 1.3gm of sodium nitrate (NaNO3) and 50 ml of sulfuric acid (H2SO4) were placed in 500 ml reaction flask and then immersed in ice bath. It is then mixed and stirred at 0° C for 15 minutes. Then 6gm of potassium permanganate (KMnO4) was added slowly to the above solution and cooled for 30 minutes. The suspended solution was stirred continuously for 1 hour at 35˚C, and 92 ml water was added drop wise to the suspension for 10 minutes. The solution was left with stirring for 1hr. Subsequently, the suspension was diluted by 280 ml of warm water and stirred for 4 hours and maintained at room temperature, treated with 15 ml (30%) H2O2 to reduce superfluity permanganate to soluble manganese ions. Finally, the resulting suspension was filtered, washed with distilled water, and dried in a vacuum oven at 70°C for 24 hours to obtain GO. Graphene was synthesized in a typical procedure as follows, GO (100 mg) was loaded in a 250 ml round bottomed flask and (50 ml) water was then added, yielding a homogeneous yellow-brown dispersion solution. This was sonicated until it became clear with no visible particulate matter. Hydrazine hydrate (1.00 ml) was then added and the solution heated in an oil bath at 100°C using a water-cooled condenser for 24h.The reduced black solid GO gradually precipitated out. This product was isolated by filtration, and then washed continuously five times with 100 ml of distilled water and finally dried in an oven at 70°C for 24 hours.

Preparation of cobalt ferrite and cobalt ferrite / Graphene

For preparation of CoFe2O4 nanoparticle compound, the sol-gel method was implemented in which (1:2) molar ratios of Co(NO3)2.6H2O, and Fe(NO3)3.9H2O were used, a typical reaction of cobalt nitrate hexahydrate [Co(NO3)2.6H2O], (1.164 g, 4 mmol) was dissolved in distilled water (25 ml) and separately, ferric nitrate nonahydrate Fe(NO3)3.9H2O (3.232 g,8mmol) was dissolved in distilled water (50 ml). The two solutions were mixed together and

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

added slowly to an aqueous solution of citric acid (2.304 g), then, ammonia solution (NH4OH) was added to the above solution to adjust the pH value to 7, and stabilize the nitrate-citrate solution. During this process, the solution was continuously stirred using a magnetic stirrer with keeping the temperature at 50ºC, then the mixture was poured into beaker (250 ml), and heated slowly to 90-95ºC with stirring until it became viscous and the color changed and turned into a green porous dry gel. The dried gel was completely burn out to produce a loose powder and then submitted to calcinations at 600ºC for 2 hours [23]. Finally, the CoFe2O4 nanoparticles was obtained, as displayed in scheme 1. To disperse CoFe2O4 nanoparticles on G, an amount of CoFe2O4 and G were dispersed into absolute ethanol and ultrasonically treated for 10 min. The gained mixture was dried at 60oC for 10 hr. in oven, and then ethanol was vaporized, leaving behind CoFe2O4 nanoparticles well anchored on G. By changing the amount of CoFe2O4, several samples with G content of 5%,10% and 15% were prepared.
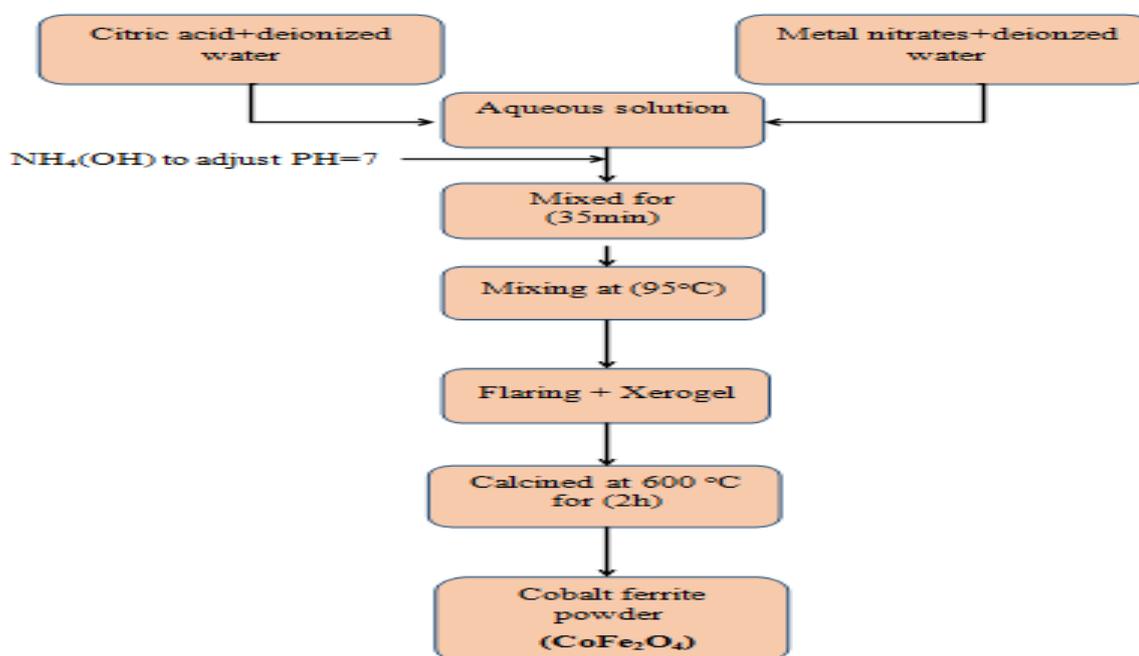
Scheme 1: The synthesis $CoFe_2O_4$ nanoparticles by sol-gel method

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

Oxidative desulfurization process

The kerosene sample with a sulfur concentration of 500 ppm was prepared from hydrotreated kerosene which contain 20 ppm of sulfur and DBT by mixed the required amount, then the oil bath was first heated up and set at 60oC. 20 cm3 of thus prepared kerosene, H2O2 oxidant (O/S = 5) and composite (0.4g) were put into the round-bottom flask and refluxed at 1 atm pressure with strong stirring (900 rpm) for 0.75 hour. After that, the oxidized kerosene was extracted by DMF, (DMF to Kerosene ratio of1:6), followed by separation of kerosene from DMF in a separating funnel [24] and then the sulfur content of separated kerosene was measured by MultiTek instrument.

The percentage removal of sulfur compounds was calculated by applying the following equation:

$$Sulfur\ Removal\ \% = \frac{(C_o - C_t)}{C_o} * 100$$

Where Co is initial concentration of total sulfur in the Kerosene, Ct is total sulfur concentration in the treated Kerosene after reaction for (t) minutes.

Result and Discussion

Characterization of nanocomposites:

X-ray Diffraction Characterization (XRD):

The structure of the various modified samples is investigated by X-ray diffraction.

X-ray diffraction of Graphene Oxide:

Figure 1a explains the X-ray diffraction pattern (XRD) of GO powder. The disappearance of a sharp peak near (2θ = 26.49o) (002) shows the changing in the crystalline structure of the graphite and indicated the destroying of the crystalline form of graphite. A large interlayer

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

spacing created equal to 8.803A° at the position (2θ =10.0392o) (001) and other two bands at (2θ = 25.9346°) is attributed to the intermediate, beside the peak at (2θ =54.3°).

3.1.1.2. X-ray Diffraction of graphene:

From the XRD pattern of graphene, in figure (1b) one observed the major broad peak at about (2θ =26.49o) (002). This gives an interlayer spacing of approximately 3.54A°. This interlayer spacing is much smaller than the 8.803A° for GO, and is closer to the graphite peak. Moreover, it has a broad shoulder at approximately (2 θ = 43°) (100). The disappearing of the major strong peak at (2θ = 10.0392o) in graphene indicated that the graphene oxide is converted to graphene.
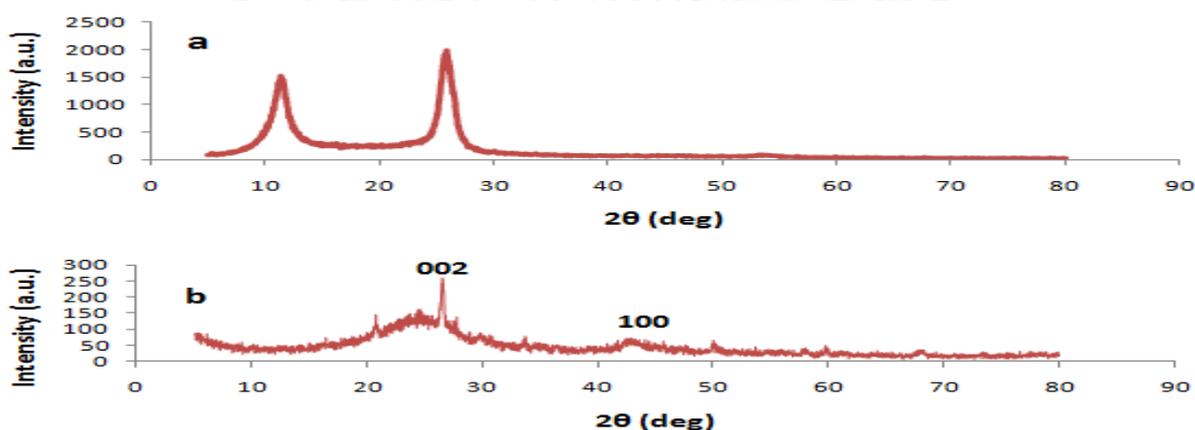
Figure 1: XRD of (a) GO, (b) G.

X-ray Diffraction of cobalt ferrite

The XRD structural properties of the synthesized CoFe2O4 pattern in figure (2a) shows the characteristic peaks of the following reflection planes (111), (220), (311), (400), (422), (511), (440), and (533). These planes prove the presence of a spinel cubic structure. The average crystalline size was studied using the Debye–Scherrer's formula, and was found to be 31.18 nm.

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

X-ray Diffraction of cobalt ferrite-graphene nanocomposite

The phase structures of as-synthesized samples were firstly determined by XRD shown in Figure 2b. The XRD for CoFe2O4-G shows a sharp peak at 2θ of 26.58o corresponding to the (002) reflection of G. By contrast, the main diffraction peaks at 2θ=30.79o, 35.40o, 42.49o, 56.91o and 62.52o are well matching with the spinel structure of cobalt ferrite (JCPDS card no.22-1086), which agree to crystal indexes of (220), (311), (400), (511) and (440), respectively [25].
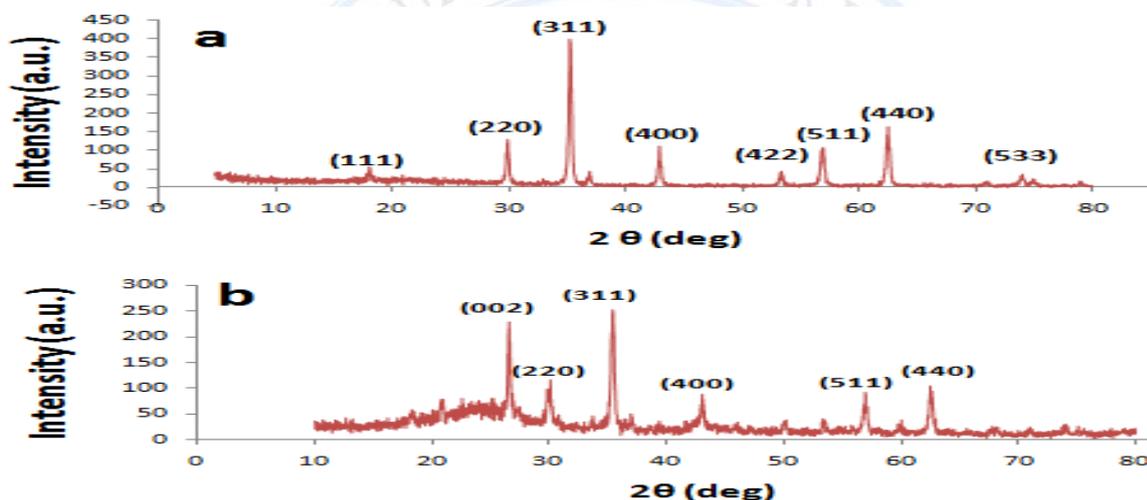
Figure 2: XRD of (a) $CoFe_2O_4$, and (b) $CoFe_2O_4$-G

AFM of characterization studies

AFM of graphene oxide

The AFM image shown in figure 3a is for graphene oxide produced by Hydro thermal method. It was clear that this method produces GO sheets exfoliated from graphite, overlapping each other despite the separation between them. Measurements of AFM indicated that the highest thickness of the sheets was 21.03 nm in the three-dimensional form of the sample. The length of the sheet was 2361.55 nm. The height of the sheet was (13.10 nm), such sheet thickness value was suggested to demonstrated presence of oxidized functional groups on edges of single GO sheets. So, the graphene oxide was synthesized in nano size.

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

AFM of graphene

The AFM measurement showed that the graphene sheets is of thickness about 8.88nm, with the exception of the sheets which doped with $CoMoO_4$, and the image measurement indicated that the graphene sheets was produced by reducing the functional groups on edges of single GO sheets. Figure 3b illustrates it.
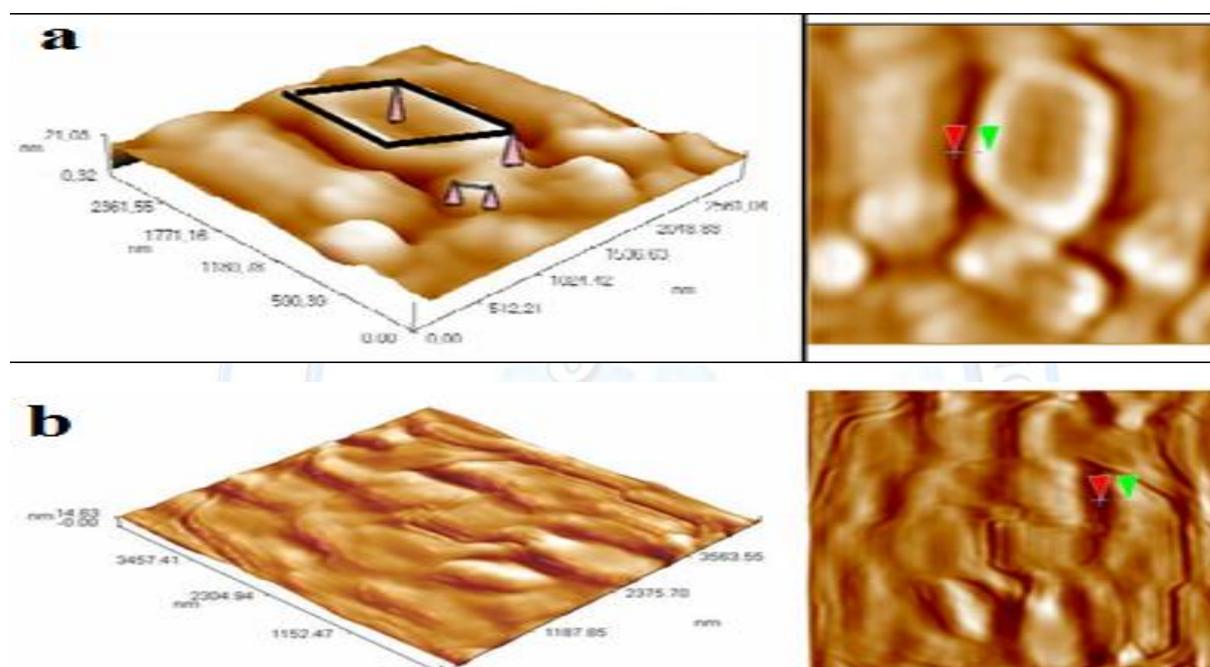
Figure 3: AFM images of (a) GO, (b) G

AFM of Cobalt Ferrite

Figure 4a is the AFM image of $CoFe_2O_4$. it indicates that 10 % of the prepared sample has <65 nm particle size and 50% has a particle size of < 85 nm and 90% has a particle size of 105nm and the average particle size 85 nm, and the height of detected place was 11.99 nm.

AFM of Cobalt Ferrite- graphene

The AFM image shown in figure 4b points to the thickness of $CoFe_2O_4$-G sheets is about 5.75nm and the height and length of it are 14.34 nm,106 nm respectively.

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan
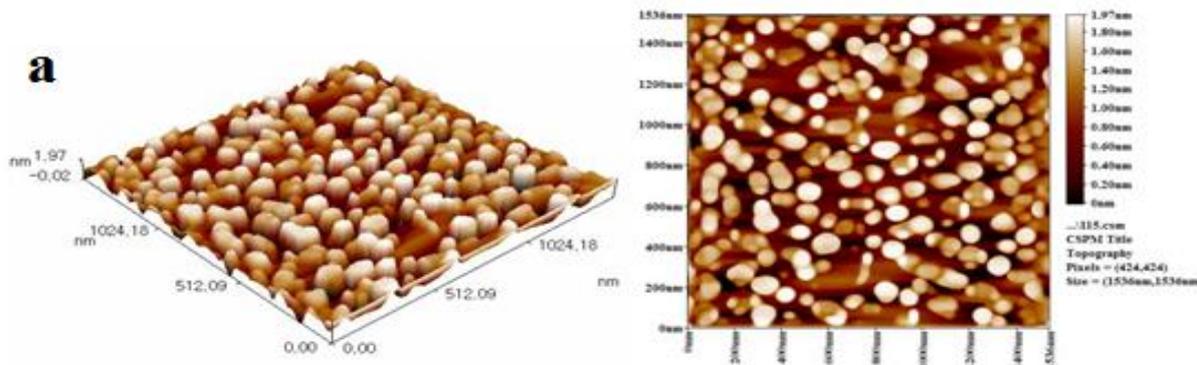
Avg. Diameter: 85.55 nm   **<= 10% Diameter: 65.00 nm**

<= 50% Diameter: 85.00nm   **<= 90% Diameter 105.00 nm**
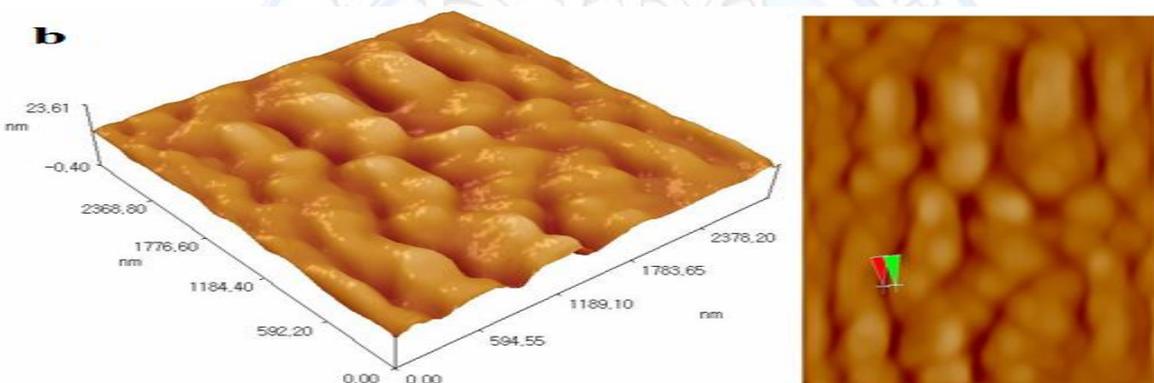
Figure 4: AFM images of (a) $CoFe_2O_4$, and (b) $CoFe_2O_4$- G

Scanning Electron Microscope

SEM of graphene

The scanning electron microscopy (SEM) of the graphene showed that the G is in the form of sheets, but there are some abnormalities in this sheet due to the oxidation and reduction of the graphite and this is fully consistent with atomic force microscopy assays, seen in figure 5 (a1 and a2).

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

SEM of cobalt ferrite

The scanning electron microscopy of cobalt ferrite CoFe2O4 is shown in Figure 5 (b1 and b2) with magnification strength 500 nm and 1μm. The prepared cobalt ferrite is in nanoparticle scale and this is in full consistent with atomic force microscopy data.

SEM of cobalt ferrite- graphene
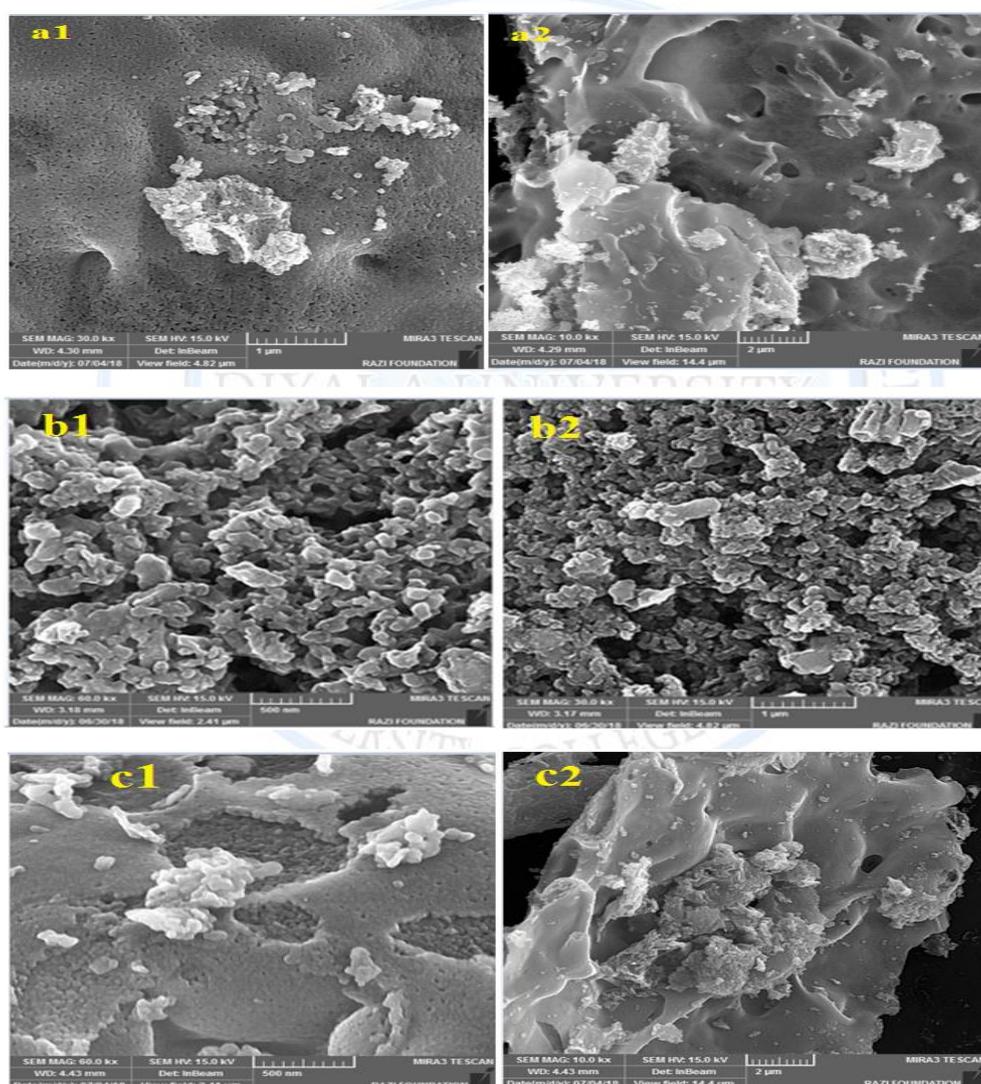
Figure 5: SEM of (a) G, (b) $CoFe_2O_4$, and (c) $CoFe_2O_4$-G

The $CoFe_2O_4$-G nanocomposite in figure 5 (c1 and c2) explains the distribution of $CoFe_2O_4$ particles in between G sheets. In addition, the figure also depicts the aggregation of $CoFe_2O_4$ particles because of the magnetic dipolar interaction between them.

Oxidative desulfurization of kerosine

The oxidative desulfurization was studied using different reaction conditions and as fallow:

Effect of loading percentage

Different loading percent of nanoparticles (5%,10% and 15%) were examined to limit the optimum quantity of catalyst for oxidation reaction and as in figure 6. The sulfur removal efficiency seems to increase by raising the loading percent and reach the maximum percentage removal of 58% with the loading of the nanoparticle on the graphene sheet of 15%.
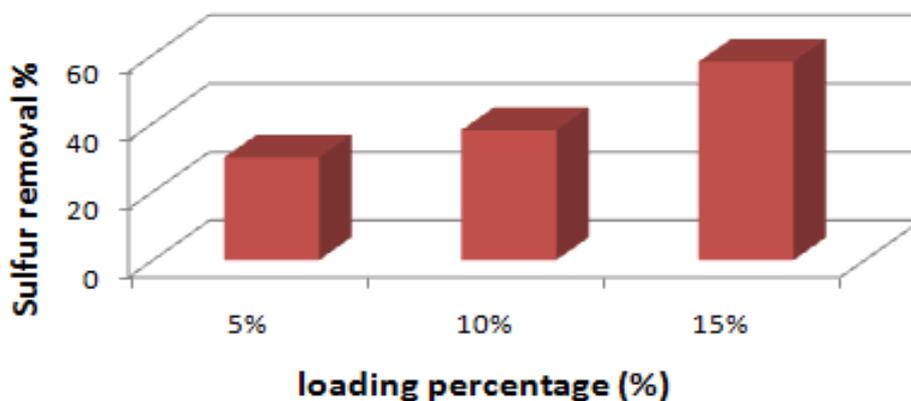
Figure 6: Effect of loading percentage on total sulfur removal %

Effect of reaction time

In figure 7, 0.25-2 hours reaction times were examined for the catalytic sulfur removal efficiency. However, there is insignificant sulfur removal observed after 1-hour reaction time and for prolong reaction time of more than 1.5 hour, no much influence of time on the percentage of desulfurizations due to the degradation of most H_2O_2 oxidant.

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan
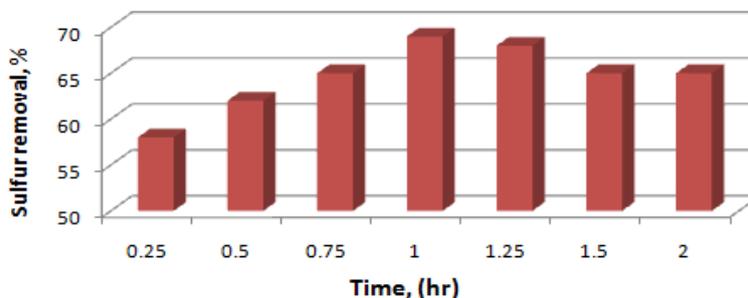
Figure 7: Effect of contact time on sulfur removal

Effect of reaction temperature

The effect of reaction temperature was studied with reaction conditions:

Reaction conditions

kerosene containing (DBT), 0.5 g, O/S 5 mol ratio, 0.75 hour and 900 rpm at different temperature (35, 40, 50, 60, 70 and 80º C), and the results are shown in figure 8. The increase of reaction temperature from 30 to 60º C will improve activity of sulfur from kerosene to a value of 75.3% at 60º C. The highest selected temperature was 60º C because it had the highest removal of sulfur. On the other hand, higher temperature will initiate decomposition of H2O2, and destroy the oxidation ability [26,27]. The reason is indicated that increasing of the temperatures lead to increase the internal energy between the reacted compounds and hence will promote the rapid molecular movement, which will cause more efficiency desulfurization.
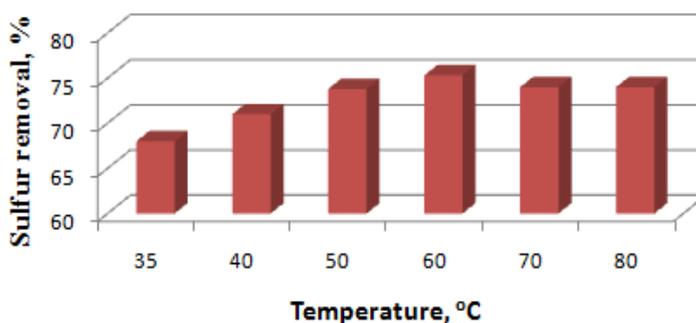
Figure 8: Effect of temperature on sulfur removal

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

Effect of O/S ratio

The effect of the oxidizing agent (H2O2) to sulfur content ratio oxygen/sulfur (O/S) on the desulfurization efficiency is shown in figure 9. The results disply that the sulfur removal efficiency increases with increasing of oxygen/sulfur (O/S) ratio. When O/S equal 5 molar ratios, which is higher than the reaction stoichiometry, the sulfur removal was 81.1 %. On the otherhand, when O/S molar ratio increased more than 5, the oxidant content lead to decrease the sulfur removal efficiency, due to unproductive decomposition of H2O2 to O2 and water which is then reduce the oxidation efficiency.
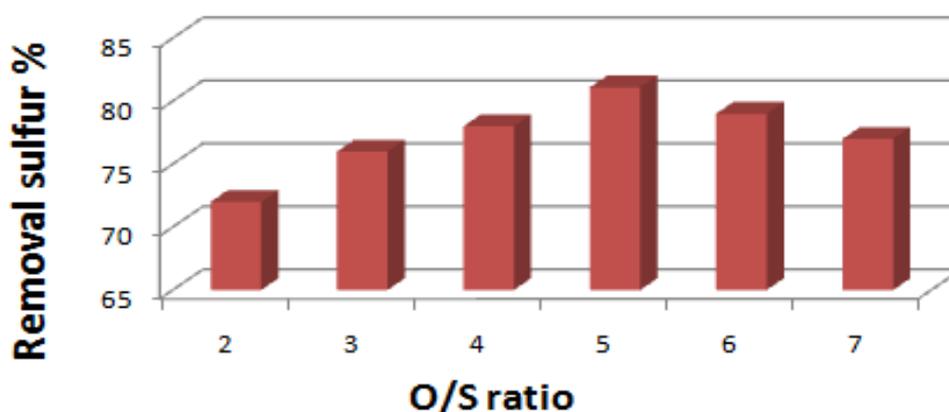
Figure 9: Effect of O/S molar ratio on sulfur removal

Effect of catalyst quantity

Different catalyst weight of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6g were examined to limit the optimum weight of catalyst required for oxidation reaction and as in Figure 10. The efficiency of sulfur removal is rose by increasing the catalyst mass and becoming maximum sulfur removal percentage of 90% when the weight of the catalyst is 0.5 g. Extra increase in the catalyst weight caused a decrease of the sulfur removal efficiency; less than 86 % sulfur removal at a catalyst weight of 0.6 g. This decrease in efficiency could be referred to an agglomeration and aggregation effects, which minimized the number of active sites on catalyst surface which then reduce the effective surface area [27].

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan
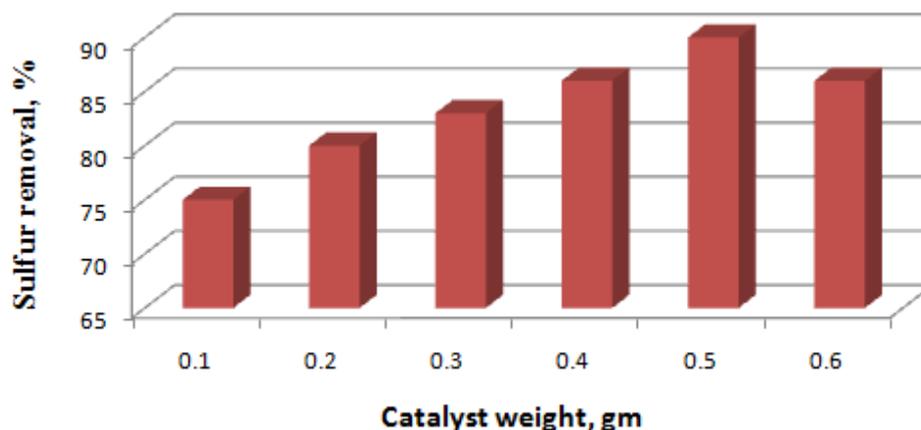
Figure 10: Effect of catalyst weight used on sulfur removal

Conclusions

CoFe2O4-G samples were selected for the study of the removal of sulfur by oxidative desulfurization from kerosene, where the results showed that the removal of sulfur the higher the loading rate (doping) of the reduced graphene oxides increased the rate of sulfur removal where the highest percentage of removal of sulfur is with loading rate of (15%).

In addition, different conditions were experimented for the removal of sulfur reaction (time, temperature, O / S ratio, catalytic weight), and the results exhibited that the increase in time and temperature increased the removal of sulfur. The results showed also that increasing the ratio of O / S and the weight of the catalyst increases the rate the removal of sulfur and reaching a stable removal rate.

Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

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Synthesis and Characterization of Cobalt Ferrite / Graphene for The Removal of Sulfur from Kerosene by Oxidative Desulfurization

Omar G. Hammoodi, Emaad T. Bakir Al-Tikrity and Karim H. Hassan

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