

Oxidative Desulfurization of Simulated Diesel Fuel by Synthesized Tin Oxide Nano-Catalysts Support on Reduced Graphene Oxide

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Abstract

The modified Hummers method was applied to prepare graphene oxide (GO) from the graphite powder. Tin oxide nanoparticles with different loading (10-20 wt.%) supported on reduced graphene oxide were synthesized to evaluate the oxidative desulfurization efficiency. The catalyst was synthesized by the incipient wetness impregnation (IWI) technique. Different analysis methods like FT-IR, XRD, FESEM, AFM, and Brunauer-Emmett-Teller (BET) were utilized to characterize graphene oxide and catalysts. The XRD analysis showed that the average crystal size of graphene oxide was 6.05 nm. In addition, the FESEM results showed high metal oxide dispersions on the rGO. The EDX analysis shows the weight ratio of Sn is close to its theoretical weight. The reduction of metal oxide and (GO) has occurred in one step at temperatures of 400 °C for 2 hours. The performance of the catalysts for dibenzothiophene (DBT) removal using H₂O₂ as an oxidizing agent was determined under a range of different operating conditions. The results showed that the maximum desulfurization was 71.68% in the best conditions (DBT concentration = 385 ppm, time = 90 min, temperature = 60 °C, catalyst dosage = 0.04g, and amount of oxidant = 0.375 ml).

Keywords: Graphene Oxide, Tin Oxide, Oxidative Desulfurization.

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1- Introduction

Petroleum is the world's largest and most economically used source of energy. Gasoline, kerosene, and diesel oil are the main products of crude oil used for automobiles [1]. Sulfur compounds in fuels are mainly present in the form of organic sulfur compounds (OSCs) [2]. The presence of sulfur compounds in fuels causes environmental problems (air or water pollution, and acid rain), and global warming due to the release of toxic SO_x during the combustion of the fuel used in automotive engines [3, 4]. Conventional hydrodesulfurization (HDS) is a major process applied for stripping sulfur compounds from fuels by converting them into hydrogen sulfide (H₂S) [5]. Recently, alternative technologies have been employed in desulfurization processes, such as oxidative desulfurization (ODS) [6]. The ODS process produces sulfur-free fuels at moderate conditions, for example, low temperature and atmospheric pressure, and with the absence of hydrogen. In addition, it is a low-cost process compared to HDS which has high costs associated with severe operating conditions. Various types of oxidants, like H₂O₂, molecular oxygen, formic acid, tert-butyl hydroperoxide, ozone are widely used in the ODS process [7].

Graphene is a monoatomic layer two-dimensional (2D) honeycomb lattice of sp²-bonded carbon atoms.

Since its discovery in 2004 by Geim and Novoselov [8], graphene has received increasing interest in numerous applications such as catalyst support. Such material has many properties, like high surface area [8], high electron mobility [9], and high thermal conductivity [10].

A. Liu et al. [11] synthesized SnO₂ nanoparticle catalyst by precipitation method and then calcined at different temperatures. The catalyst activity for removing DBT from model diesel fuel was examined in the (ODS) process using H₂O₂ as an oxidant. The effect of different reaction conditions, for example, temperature, O/S mole ratio, time of reaction, and catalyst dosage on the efficiency of the ODS process was studied. The results showed that the high removal rate of sulfur was 99.8% at the conditions (333 K, O/S = 10, 2 h, and 0.08 g). A study was done by W. Piao et al. [12] to prepare (WO_x/meso-SnO₂) with different WO_x loads (10-30 wt.%) by conventional wet impregnation. The effectiveness of the ODS process in the system (n-heptane as model oil with sulfur content = 2000 ppm, H₂O₂ as oxidant, and acetonitrile as an extract) was examined at different operating conditions. The results indicated that dibenzothiophene (DBT) was completely removed within 60 min at 50 °C, H₂O₂/DBT molar ratio = 5, catalyst = 0.1 g, and using (20 wt. %) of WO_x/meso-SnO₂.



W. Ahmad et al. [13] studied the performance of the oxidative desulfurization process for simulated and fuel oil samples using an $H_2O_2/HCOOH$ oxidation system and catalyst ($MnO_2/MrGO$). They concluded that the desulfurization efficiency from the model oil was attained up to 80% in time of 60 min, the temperature of 40 °C, a catalyst dosage of 0.08 g/10 mL, and 2 mL of H_2O_2 /formic acid. In addition, the removal rate was only 41% for fuel oil. S.S. Otaghsaraei et al. [14] prepared SnO_2/rGO catalysts with different loads of active metal by the incipient wetness impregnation (IWI) method. The activity of the catalyst for the ODS process was evaluated. Several factors, such as reaction time, metal loading, and concentration of the (DBT) were first investigated. After determining optimum factors, the effect of oxidizing/substrate (O/S), catalyst/substrate (Cat/S), and temperatures was examined by using response surface methodology (RSM). They found that under optimal conditions (time = 180 min, DBT concentration = 500 ppm, (O/S) molar ratio = 30, temperature = 60 °C, (Cat/S) molar ratio = 0.06, and 15% SnO_2) removal of sulfur was 96%.

This work focuses on reducing the sulfur (dibenzothiophene) content of diesel fuel by oxidative desulfurization using SnO_2/rGO as a nanocatalyst and hydrogen peroxide as an oxidant in a batch reactor. The support (graphene oxide GO) was prepared from natural graphite powder by the modified hummer method, while the SnO_2/rGO catalyst was synthesized using the incipient wetness impregnation method. Further analyses like FT-IR, XRD, FESEM, AFM, and BET method have been used to characterize graphene oxide and the catalysts. The effectiveness of the catalyst for oxidative desulfurization was investigated under different operating conditions. The kinetics of the ODS process was studied.

2- Experimental Section

2.1. Materials

The properties of all chemical materials used in this work are shown in Table 1.

Table 1. Chemical Materials used in Research

Substance	Chemical Formula	Molecular Weight	Purity wt. %	Company
Graphite powder	C	12.01	99	Glenthams life sciences
Sodium nitrate	$NaNO_3$	84.9947	99	Sigma-Aldrich
potassium permanganate	$KMnO_4$	158.034	99	Sigma-Aldrich
sulfuric acid	H_2SO_4	98.079	98	Sigma-Aldrich
Hydrochloric acid	HCL	36.458	36	Sigma-Aldrich
Ethanol	CH_3CH_2OH	46.07	99	Germany
Hydrogen peroxide	H_2O_2	34	30	Sigma-Aldrich
Stannous chloride dihydrate	$(SnCl_2 \cdot 2H_2O)$	225.64	99	Sigma-Aldrich

2.2. Preparation of Graphene Oxide (GO)

Graphite oxide (GO) was prepared from graphite powder by the modified Hummer's method with the oxidation time set at 12 h [13]. 3 g of graphite powder (40 to 100 micrometers) and 1.5 g of $NaNO_3$ were mixed and then added to (81 mL) of H_2SO_4 with stirring in an ice bath at 10 °C for 30 min. (18 g) of $KMnO_4$ was gradually added to the mixture to keep the temperature lower than 10°C. Then the mixture was settled over the night (12 hr.). (162 mL) of distilled water was added to the solution and heated to 95°C for 15 min. (15 mL) of hydrogen peroxide was added to finish the reaction. The solution was washed with distilled water and then with diluted HCl (10 wt. %) more than once and then dried in an oven at 70 °C for 12 h, which gave a thin sheet of GTO. Finally, ultra-sonication was done for the complete exfoliation of GTO to GO. Reduction of graphene oxide was carried out thermally by heating graphene oxide at a rate of 10 °C/min to the temperature of 400 °C for 2 hr under a flow rate of N_2 .

2.3. Preparation of SnO_2/rGO Catalysts

The incipient wetness impregnation (IWI) method was applied to synthesize SnO_2/rGO according to the following steps[15]. (1.9 g) of Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) was added to 100 ml of deionized water, and the solution was stirred for 60 minutes. Then (10 g) of graphene oxide were added to the solution with stirring for 120 min. The solution prepared was dried in an oven at 70 °C for 24 hr. Finally, the catalyst was calcinated at 400 °C for 2 hr to convert metal salt to metal oxide and reduction of graphene oxide to reduce graphene oxide by one step.

2.4. Oxidative Desulfurization Process

10 ml of simulated diesel fuel was poured into a 100 ml flask with an initial dibenzothiophene concentration of (385-933) ppm. Experiments were performed in a batch reactor under several operating conditions, for instance, temperature (40-70 °C), catalyst dosage range (0.02-0.08 g), amount of oxidant (0.012-0.5 ml), reaction time (45-180 min) and various loading of the active metal (10-20 wt.%). Removal of sulfones and sulfoxides from fuels after ODS has been done by solvent extraction (ethanol) under the following conditions (temperature = 25 °C, stirring rate = 200 rpm, solvent/fuel volume ratio = 1, and time of extraction =30 min).

2.5. Analysis

Sulphur content of diesel fuel was obtained by utilizing the Analytic Jena device located in the Arab Company for Detergent Chemicals, manufactured by (Germany).

3- Results and Discussion

3.1. Catalyst Characterizations

XRD pattern of graphene oxide synthesized from natural graphite powder was shown in Fig. 1a. The result shows that the characteristic diffraction peak of graphene oxide was observed at ($2\theta = 11.16^\circ$), with interlayer spacing ($d = 0.797$ nm) and had average crystal size of 6.05 nm [13]. XRD patterns of SnO₂ nanoparticles deposition on the GO surface are shown in Fig. 1b-d. XRD peaks of SnO₂ appeared at 2θ of (26.8° , 33.9° , 38.16° , 51.9° , and 65.5°). The intensity of the SnO₂ peaks was increased after increasing loading Sn from 10 to 20 wt.% on the GO, which matches well with other references [11].

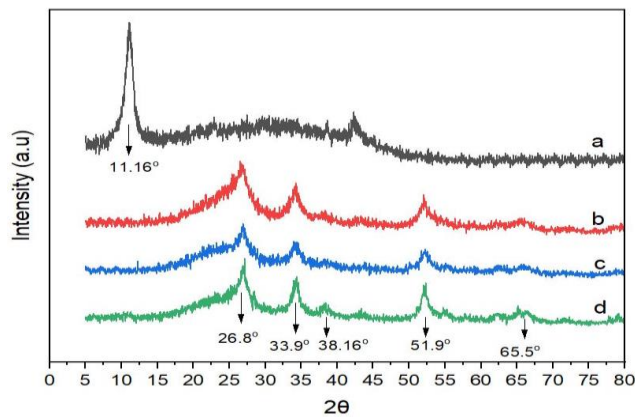


Fig. 1. XRD Patterns of (a) Graphene Oxide, (b) 10%SnO₂/rGO, (c)15%SnO₂/rGO, and (d) 20%SnO₂/rGO

The FT-IR spectra of graphene oxide and catalyst with various loading of SnO₂ are shown in Fig. 2. The results show that the peaks at around (3400 cm^{-1}) are due to hydroxyl O-H stretching. The characteristic peaks at 1726 cm^{-1} , 1624 cm^{-1} , and 1190 cm^{-1} correspond to the carboxyl (C=O), (C=C), and (C–OH) stretching vibration [14,15]. In addition, the (Sn–O) bond vibration peak was observed in the region ($500\text{--}700\text{ cm}^{-1}$) [11].

Fig. 3 shows the FESEM morphologies of graphene oxide and catalyst. From the Figures, it can be observed that graphene oxide had a layered and wrinkled structure. Furthermore, particles of SnO₂ were deposited well on the surface of rGO without any agglomeration [14].

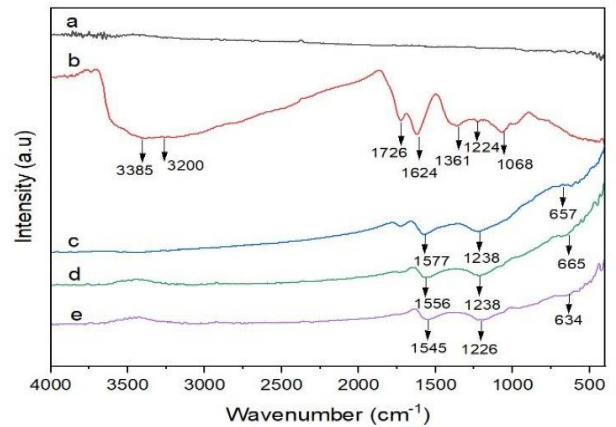


Fig. 2. FT-IR Spectra of (a) Graphite, (b) Graphene Oxide, (c) 10%SnO₂/rGO, (d) 15%SnO₂/rGO and (e) 20%SnO₂/rGO

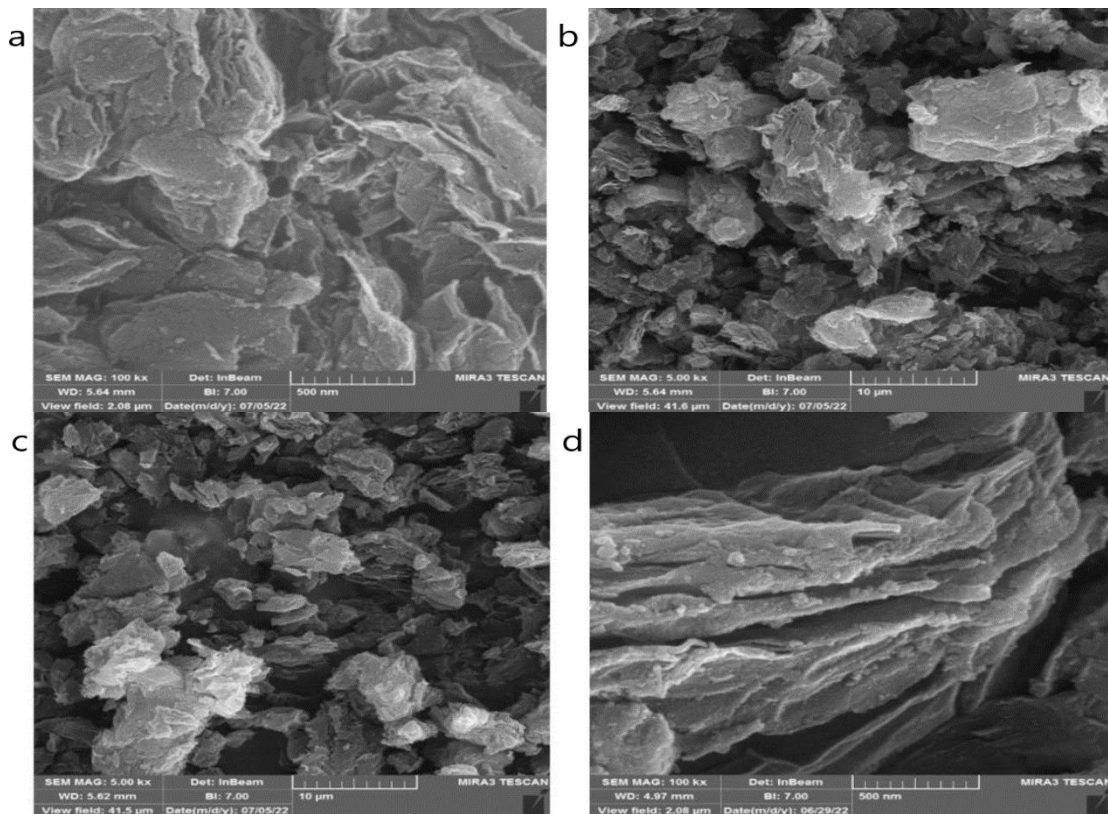


Fig. 3. FESEM of (a) Graphene Oxide, (b) 10%SnO₂/rGO, (c) 15%SnO₂/rGO, and (d) 20%SnO₂/rGO

The EDX spectra of graphene oxide and 20%SnO₂/rGO are shown in Fig. 4. From the data, it is seen that GO is composed of C and O as the two main elements (44.69% and 44.99%, respectively), with some amount of Al and Cl that may be caused by impurities in

the natural graphite [13]. In the case of 20%SnO₂/rGO, the principle elements were C (31.97%), O (31.49%), Cl (7.91%), and Sn (28.63%), where the weight percent of Sn in 20%SnO₂/rGO is close to its theoretical Weight [14].

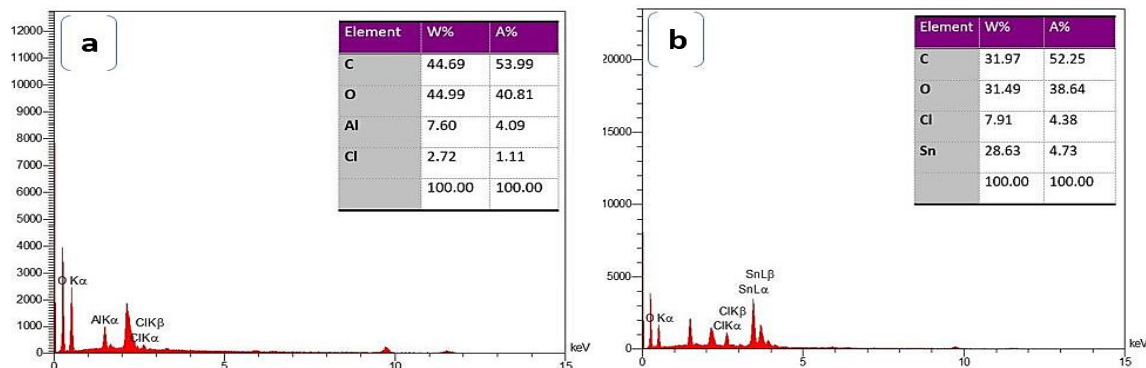


Fig. 4. Energy Dispersive X-ray (EDX) Spectra of (a) Graphene Oxide and (b) 20%SnO₂/rGO

Atomic force microscopic (AFM) analysis was carried out to determine the topography of deposited SnO₂ on rGO. Fig. 5 shows 3D images of catalysts and their height profile. The surface roughness was measured using root

mean square roughness (R_{msr}), defined as the standard deviation of the surface height profile from the mean height. The surface roughness of SnO₂ on rGO was found to be (4.65, 66.45, and 1.46 nm), respectively [18].

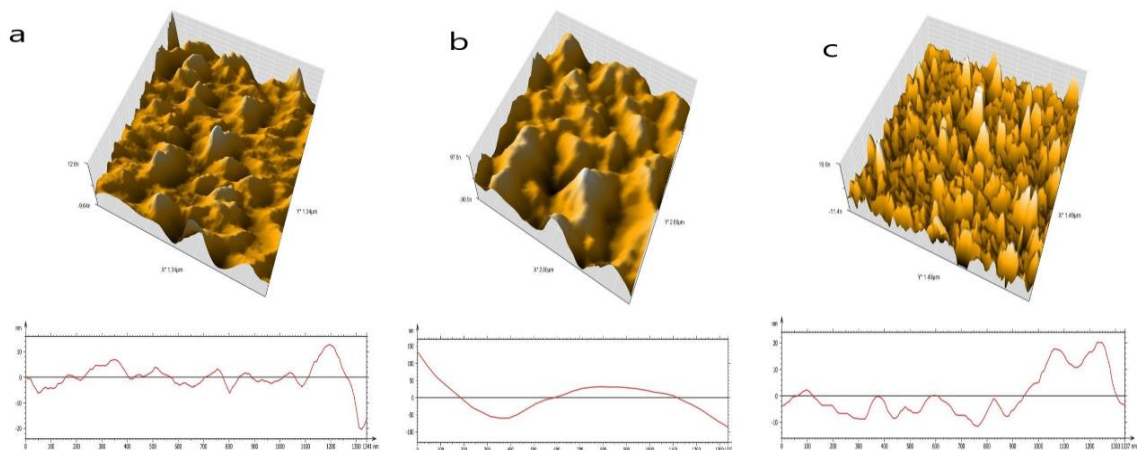


Fig. 5. AFM of (a) 10%SnO₂/rGO, (b) 15%SnO₂/rGO, and (c) 20%SnO₂/rGO

The surface area (S_{BET}) and pore volume (V_P) of the graphite, graphene oxide, and catalyst were tabulated in Table 2.

Table 2. Textural Properties of Graphite, Support-1, and Catalysts

Sample	S_{BET} (m ² /g)	V_P (cm ³ /g)	D (nm)
Graphite (G)	4.40	0.013	11.82
Graphene oxide (GO)	19.88	0.03	6.13
10%SnO ₂ /rGO	154.72	0.339	8.78
15%SnO ₂ /rGO	136.94	0.24	7.09
20%SnO ₂ /rGO	84.80	0.14	6.45

The S_{BET} of the GO was 19.88 m²/g, while the pore volume was 0.03 cm³/g. After calcination at 400 °C, the surface area of the catalyst was increased to 154.72 m²/g

for 10%SnO₂/rGO. This behavior may be due to the rapid degradation of the oxygen groups that occurs during the calcination of catalysts [19]. In addition, with increasing SnO₂ loading, the S_{BET} of the catalyst declined dramatically to 84.80 m²/g for 20%SnO₂/rGO.

3.2. Catalysts test performance

The catalytic effects of a SnO₂/rGO were evaluated in a batch reactor by dissolving DBT in normal heptane as simulated diesel oil and H₂O₂ as an oxidant. Different loading of active metal (10 – 20 wt. %), different concentrations of DBT (385-933 ppm), and times (45-180 min) were studied in the first attempt, at a constant temperature of 50 °C, catalyst dosage 0.02 g, and amount of oxidant 0.25 ml. As appeared in Fig. 6 to Fig. 8, the removal of DBT follows the order of 20% SnO₂/rGO >

15% SnO₂/rGO > 10% SnO₂/rGO at a DBT concentration of 385 ppm and time of 90 min [16, 18].

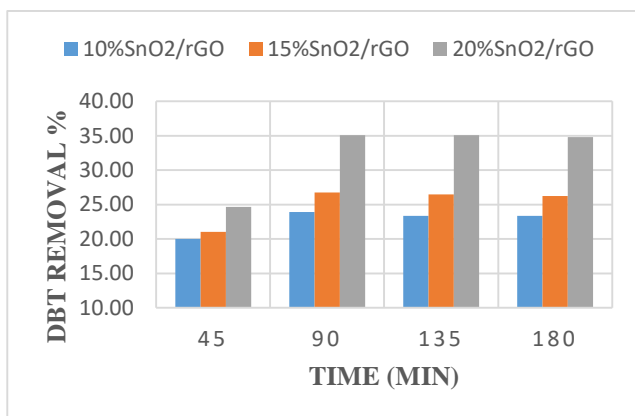


Fig. 6. Comparison of the Catalysts Activities at Dibenzothiophene Concentration of 385 ppm [Reaction conditions: T = 50 °C, Cat. Dos = 0.02 g, and amount of oxidant = 0.25 ml]

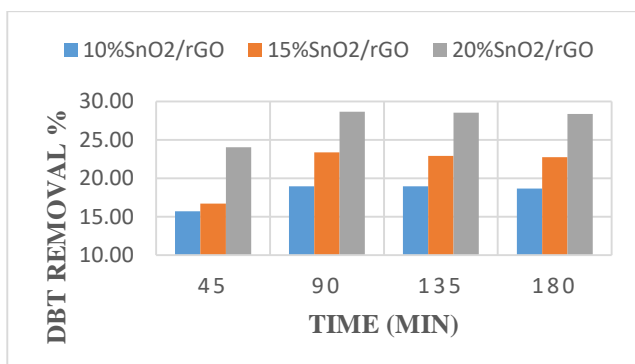


Fig. 7. Comparison of the Activities of the Catalysts at a Concentration of Dibenzothiophene of 659 ppm [Reaction conditions: T = 50 °C, Cat. Dos = 0.02 g, and amount of oxidant = 0.25 ml]

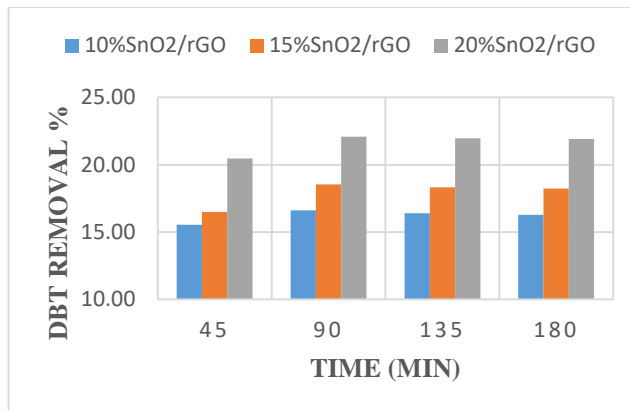


Fig. 8. Comparison of the Activities of the Catalysts at a Concentration of Dibenzothiophene of 933 ppm [Reaction conditions: T = 50 °C, Cat. Dos = 0.02 g, and amount of oxidant = 0.25 ml]

The main reaction conditions are shown in Fig. 9. Fig. 9A shows an increase in desulfurization conversion with increasing reaction temperature. When the temperature was raised to 60 °C, the conversion was a maximum of (71.68%). After the temperature exceeded 70 °C, the conversion declined dramatically due to the decomposition of hydrogen peroxide. Fig. 9B shows the 20% SnO₂/rGO catalyst activity with an oxidation amount ranging from 0.125 to 0.5 ml. The DBT conversion increased significantly with the increasing amount of oxidant. When the amount of oxidant reached 0.375 ml, the DBT conversion was approximately 71.68% and declined above this ratio. The influence of the catalyst dosage is another affecting parameter on the ODS process [11]. As presented in Fig. 9C, by increasing the catalyst dosage from 0.02 to 0.04 g, the DBT conversion was improved. With increasing catalyst dosage after 0.04 g, the DBT removal was decreased due to catalyst aggregation [19, 20].

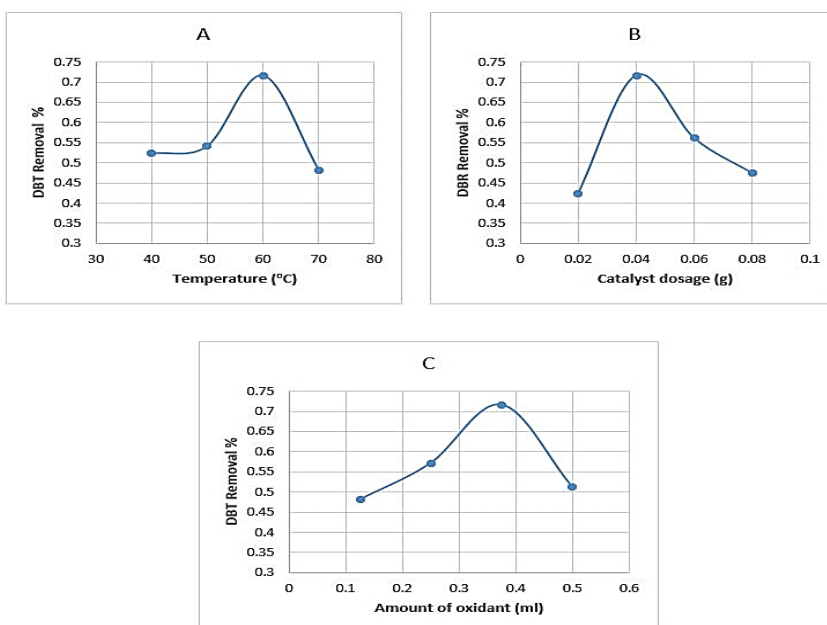


Fig. 9. Effect of the (A) reaction temperature, (B) catalyst dosage, (C) amount of oxidant on the conversion of DBT. T = 60 °C, amount of oxidant = 0.375 ml, catalyst dosage = 0.04 g/10 ml, time = 1.5 h

4- Kinetic Model of Oxidative Desulfurization

A kinetic model of oxidative desulfurization (ODS) using H_2O_2 as an oxidant and SnO_2/rGO nanocatalyst was investigated in a batch reactor with different reaction temperatures for 90 min. The reaction rate constant was estimated by pseudo-first order and pseudo-second order as shown in equations 1 and 2.

$$\ln \frac{c_o}{c_t} = kt \quad (1)$$

$$\frac{1}{c_t} = \frac{1}{c_o} + kt \quad (2)$$

Comparison between reaction rates constant for two kinetic models was tabulated in Table 3. From the results, it can be concluded that pseudo-first order is a good fit than pseudo-second-order kinetics.

The activation energy of the reaction was determined from Arrhenius equation 3 by plotting the relation between $(\ln k)$ and $(1/T)$ Fig. 10, the slope of the relationship gives the value of activation energy 20.51 kJ/mole.

$$\ln k = \ln A - \frac{E}{RT} \quad (3)$$

Table 3. Comparison between Kinetic Models

Order of Reaction	Temperatures							
	30 °C		40 °C		50 °C		60 °C	
	k	R ²	k	R ²	k	R ²	k	R ²
n=1	0.00 41	0.95 3	0.00 49	0.99 37	0.0 06	0.96 64	0.00 87	0.94 52
n=2	3.8E -08	0.60 99	4.4E -08	0.36 6	4.3 E-09	0.00 24	4.8E -07	0.36 46

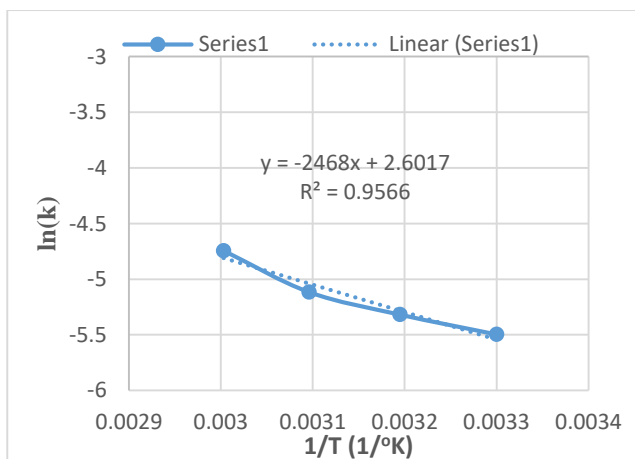


Fig. 10. Reaction Rate Constant versus 1/T

5- Conclusions

Graphene oxide (GO) was prepared from natural graphite powder using the modified Hummers method. The XRD analysis showed that the average crystal size of graphene oxide was 6.05 nm. After calcination, the surface area of the catalyst was decreased from 154.72 m^2/g for (10% SnO_2/rGO) to 84.80 m^2/g for (20% SnO_2/rGO). The EDX analysis shows the weight ratio of

Sn is close to its theoretical weight. The activity of the catalyst was investigated under different operating conditions. The results showed that the maximum desulfurization was 71.68 % in the best conditions were DBT concentration = 385 ppm, time = 90 min, temperature = 60 °C, catalyst dosage = 0.04g, and amount of oxidant = 0.375 ml. By comparing the regression coefficients of the corresponding curves of the two kinetic models, the pseudo-first-order is closest to the unit.

Nomenclature

BET: Brunauer, Emmett, Teller

DBT: dibenzothiophene

EDX: Energy Dispersive X-ray Spectroscopy

FESEM: Field Electron Scanning Electron Microscopy

FTIR: Fourier-Transform Infrared Spectroscopy

GO: Graphene Oxide

(HDS): Conventional hydrodesulfurization

IWI: Incipient Wetness Impregnation

ODS: Oxidative Desulfurization

OSC: Organosulfur Compounds

rGO: Reduced Graphene Oxide

XRD: X-ray Diffraction

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إزالة الكبريت المؤكسدة من وقود الديزل المحاكاة بواسطة محفزات نانو أكسيد القصدير المدعمة على أكسيد الجرافين المختزل

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الخلاصة

تم تطبيق طريقة هامر المعدلة لتحضير أكسيد الجرافين (GO) من مسحوق الجرافيت. تم تصنيع جزيئات أكسيد القصدير النانوية ذات التحميل المختلف (١٠-٢٠ وزن٪) المدعمة بأكسيد الجرافين المختزل لتوصيف كفاءة إزالة الكبريت المؤكسدة. تم تصنيع المحفز بواسطة تقنية التشريب الأولي بالرطوبة (IWI). تم استخدام طرق تحليل مختلفة مثل FT-IR و XRD و FESEM و AFM و Brunauer-Emmett-Teller (BET) لتوصيف أكسيد الجرافين والمحفزات. أظهر تحليل XRD أن متوسط الحجم البلوري لأكسيد الجرافين كان ٦.٠٥ نانومتر. بالإضافة إلى ذلك، أظهرت نتائج FESEM تشتت أكسيد معدني عالي على rGO. يوضح تحليل EDX أن نسبة الوزن لـ Sn قريبة من وزنها النظري. حدث اختزال أكسيد الفلز و (GO) في خطوة واحدة عند درجات حرارة ٤٠٠ درجة مئوية لمدة ساعتين. تم تقييم أداء المحفزات لإزالة ثنائي بنزو ثيوفين (DBT) باستخدام H₂O₂ كعامل مؤكسد تحت مجموعة من ظروف التشغيل المختلفة. أظهرت النتائج أن الحد الأقصى لنزع الكبريت كان ٧١,٦٨٪ في أفضل الظروف (تركيز DBT = 385 جزء في المليون، الوقت = ٩٠ دقيقة، درجة الحرارة = ٦٠ درجة مئوية، جرعة المحفز = ٠,٠٤ جم، كمية المؤكسد = ٠,٣٧٥ مل).

الكلمات الدالة: أكسيد الجرافين، أكسيد القصدير، نزع الكبريت التأكسدي.