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Research Article

A Novel Synthetic Nano-Catalyst (Ag_2O_3/Zeolite) for High Quality of Light Naphtha by Batch Oxidative Desulfurization Reactor

Amer T. Nawaf[1], Shymaa Ali Hameed[2], Layth T. Abdulateef[3], Aysar T. Jarullah[2,*],
Mohammed S. Kadhim[4], Iqbal M. Mujtaba[5]

[1]Petroleum & Gas Refinery Engineering, College of Petroleum Process Engineering, Tikrit University, Iraq.
[2]Chemical Engineering Department, College of Engineering, Tikrit University, Iraq.
[3]Chemical Engineering, Middle Technical University, Iraq.
[4]Nanotechnology and Advance Material Research Center, University of Technology, Iraq.
[5]Chemical & Process Engineering Division, University of Bradford, Bradford BD7 1DP, UK.

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Abstract

Oxidative desulfurization process (ODS), enhanced with a novel metal oxide (Ag ions) as an active component over nano-zeolite that has not been reported in the literature, is used here to improve the fuel quality by removing mercaptan (as a model sulfur compound in the light naphtha). Nano-crystalline (nano-support (Nano-zeolite)) composite is prepared by Incipient Wetness Impregnation method loaded with a metal salt to obtain 0.5, 1 and 1.5% of Ag_2O_3 over Nano-zeolite. The new homemade nano-catalysts (Ag_2O_3/Nano-zeolite) prepared are characterized by Brunauer–Emmett–Teller (BET) (surface area, pore volume and pore size), X-ray Diffraction (XRD), Fourier Transform Infra Red (FTIR), and Scanning Electron Microscopy (SEM) analysis. The ODS process is then used to evaluate the performance of the catalysts for the removal of sulfur at different reaction temperatures (80–140 °C) and reaction times (30–50 min) in a batch reactor using the air as oxidant. 87.4% of sulfur removal has been achieved using 1% silver oxide loaded on Nano zeolite (1% of Ag_2O_3/Nano-zeolite) giving a clear indication that our newly designed catalyst is highly efficient catalyst in the removal of sulfur compound (mercaptan) from naphtha. A new mechanism of chemical reaction for sulfur removal by oxygen using the new homemade catalyst (Ag_2O_3/Nano-zeolite) prepared has been suggested in this study. The best kinetic model parameters of the relevant reactions are also estimated in this study using pseudo first order technique based on the experimental results.

Keywords: Nano-Catalyst; Oxidative desulfurization; Silver Oxide; Kinetic Model

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1. Introduction

The main and important source of future's energy in the world is the crude oil owing to the transportation fuels such as light naphtha (gasoline), kerosene (jet fuel), and diesel (light gas oil, heavy gas oil) founded in crude oil. But, the major issue for such fuels is the sulfur compounds presented in these fuels affecting the quality of oils and as a result on the price of fuels [1,2]. Light naphtha is regarded a promising fuel candidate for fuel cell vehicles having

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Corresponding Author.
* Email: a.t.jarullah@tu.edu.iq (A.T. Jarullah);
Email: amer.talal@tu.edu.iq (A.T. Nawaf);
Email: i.m.mujtaba@bradford.ac.uk (I.M. Mujtaba)

significant amounts of organo-sulfur compounds mainly thiols (mercaptans) that must be removed [3]. Sulfur compounds are undesirable impurities in oil feed stocks and petroleum distillates and removing them is necessary for both industrial and environmental legislations [4,5]. Sulfur compound in feedstock (fuel) is regarded a major source of air pollution and the environmental regulations have recently reported that the sulfur content of transportation fuels should be under ultralow levels (10–15 ppm) [6,7]. Although the regulations are beneficial from the environmental point of view, meeting the required stringent specifications represent a major operation and economic challenges for the petroleum refining industry (mainly light naphtha, kerosene and diesel fuel) [8].

To achieve deep desulfurization, it is necessary to remove refractory aromatic sulfur compounds (ASCs), such as mercaptan, benzothiophene (BT), dibenzothiophene (DBT) and their alkylated derivatives. Organo-sulfur compounds in petroleum refining industries are usually removed by the conventional process, which is called hydrodesulfurization (HDS) process, but such process can not economically be produced ultra-clean fuels with extremely low sulfur content, especially for fuel cell vehicles. Such process requires modified catalyst, higher operating conditions (temperature, pressure and liquid hourly space velocity, *etc.*) and toxic emissions generated due to the combustion of the fuels producing gases [9]. Therefore, many investigators have focused their studies to find an alternative environmentally friendly process under low cost, high efficiency for sulfur removal, safe and moderate conditions. Among these technologies, oxidative desulfurization process (ODS) has attracted a great of attention in such area due to its advantages mentioned above [10–12].

The oxidative desulfurization process (ODS) is aimed to oxidize sulfur compounds in fuels their corresponding components (for instance, mercaptan compound will be oxidized to disulfide directly, then sulphide to sulfone and finally sulfone is oxidized to sulfoxide) giving a polar form and becoming as non-active compounds that can be removed by extraction or desorption process. ODS processes have received considerable attention by many Authors owing to its mild reaction conditions used without needing hydrogen, low-cost and an environmental friendly oxidizing reagent is applied [13]. A number of oxidants are used in the ODS that have been employed for the selective oxidation of sulfur compounds in oil feedstock [14–17]. In order to improve the efficiency of sulfur removal in the ODS via using air as an oxidant, various catalysts have been evaluated including Al_2O_3-zeolite [18], Nano-Fe_3O_4 [19], α-MnO_2 (Nano sheets) [20], alumina [21], carbon Nano tube [20] and silica gel [19] found to enhance the desulfurization efficiency of the ODS process.

Many studies related to the oxidative desulphurization (ODS) have been reported in the public domain and such studies can be summarized in Table 1. From this Table, a number of gas oxidants are employed in ODS including air, oxygen, ozone, and hydrogen dioxide (H_2O_2) applied alone or along with other oxidizing agents - catalysts. It is noteworthy that utilization of hydrogen peroxide via batch reactor led to a low value of sulfur removal (approximate 44% process conversion) in 15 ml H_2O_2 [30]. However, the application of ODS process in the gas-liquid systems has not been reported yet. Therefore, desulfurization improvement can be achieved via application of batch reactor in the gas-liquid ODS process with new nano-catalyst.

A large quantity of sulfur compound are enhanced by the use of an oxidizing agent compared with traditional agent (hydrogen peroxide) [21]. The oxidative desulfurization process has been applied by [4] for sulfur compounds presented in naphtha feedstock using 0.1 wt% of palladium/functionalized MWNTs prepared by impregnation method. The catalyst prepared has been tested for sulfur removal in oxidation reaction using hydrogen peroxide (H_2O_2) as oxidant in batch reactor under the operating conditions of 25 °C, reaction temperature, 30 min reaction time at 2 ml from H_2O_2 at atmospheric pressure. Sulfur was removed from naphtha by 90% under these conditions.

Shi *et al.* [31] found that the lower electron density upon sulfur atom led to lower activity in removing of sulfur related to the electron density of thiophene, BT, DBT and the oxidation reactivity of the model sulfur compounds has been conducted based on the oxygen as an oxidant and complex solid as a catalyst. Abdulateef *et al.* [22] have used the ODS of sulfur compounds found in kerosene using several different reactor temperatures, different reaction time and different catalyst weight in a batch reactor based on a prepared nano catalyst of manganese oxide (ZnO-MgO/γ-Al_2O_3), and high sulfur removal was observed. Nawaf *et al.* [21] have examined the ODS process of kerosene based on composite nano catalyst (18%ZnO/γ-Al_2O_3) prepared by thermal coprecipitation method in a batch system. The highest conversion of sulfur is about 70.52% at a temperature of 190 °C, time 50 min and catalyst weight of 1 g at optimum operating conditions using air as oxidant. Transition active materials (metal oxides) having high reactivity for enhancement of fuel via removing sulfur compound because it have unique physiochemical properties and can directly convert to sulfoxide and sulfone during ODS reactions. But, owing to the difficult separation of such compounds from the reaction media, the materials (supports) that have high surface area (BET) is very important to disperse such metals on it [24]. Oxidative desulfurization process is widely studied in the public domain, but using nano-zeolite as a support over silver oxide as active component, which is used in this study is rare has not been reported in the literature.

Silver oxide is considered the most active metal compared with other metals toward ODS reactions and having high selectivity and adsorption toward sulfur removal from fuel oil or oil fractions [25]. Also, silver oxide having the ability to convert or removal sulfur compound without any changing in the main hydrocarbon (fuel) structure with keeping the fuel oil with the same physical and chemical properties[26]. Thus, this work is aimed to prepare a new—nano-catalyst (0.5, 1, and 1.5% silver oxide loaded on zeolite Nano- particles) for the purpose of testing the possibility of sulfur removal from model light naphtha under safe and moderate operating conditions utilizing the oxidative desulfurization process (ODS) in a batch system by air as an oxidant and finding the best metal oxide loaded for removal. Estimation the best kinetic parameters of the relevant reactions have also been studied in this studied.

It is necessary to remove sulfur compounds from oil fractions to get fuels with high quality. The use of HDS process requires high operating conditions (high pressure, high temperature) and the size of the reactor should be large

Table 1. A review on the research for the ODS of liquid fuels oxidation systems.

Ref.	Feedstock (Fuel)	Reactor type	Catalyst type	Oxidizing agent and operating conditions	Sulfur removal (%)
[16]	Naphtha	Magnetic stirrer	Formic acid /H_2O_2/pyrolysis	Temperature: 60 °C Time: 60 min and H_2O_2	70
[21]	Kerosene (sulfur)	Batch reactor	ZnO /γ-Al_2O_3 (Nano-Catalyst)	Temperature: 190 °C time: 50 min and air catalyst weight: 1 g and air	70.52
[22]	Kerosene (sulfur)	Batch reactor	ZnO-MgO /γ-Al_2O_3 (Nano-Catalyst)	Temperature: 190 °C time: 45 min and air catalyst weight: 1 g and air	84.6
[23]	Heavy Naphtha (H.N.)	Batch reactor	Granulated Activated carbon-GAC and White egg-shell-WES	Temperature: 25-80 °C Time: 10-180 min and H_2O_2	86, 65
[24]	Light Naphtha (L.N.)	Magnetic stirring	NiMo/γ-Al_2O_3	Temperature: 35 °C Time: 1 h and O_2	76.25
[25]	Heavy Naphtha	ultrasound waves	Activated carbon (AC-Catalyst)	Temperature: 25 °C time: 5-40 min and acetic acid, H_2O_2	89
[26]	Naphtha	Batch reactor	Acetic acid/H_2SO_4	Temperature: 70 °C Time: 2 h and H_2O_2	99
[27]	Model light gas oil	Trickle bed reactor	MnO_2/γ-Al_2O_3	Temperature: 200 °C LHSV: 1 h^{-1} and air	81
[28]	Naphtha	Magnetic stirring	WES and GAC (Catalyst)	Temperature: 80, 85 °C Reaction time: 150 min agitation speed of 400 rpm: 2.5 and H_2O_2	56.87, 81.37
[29]	Naphtha	Glass-batch reactor	Pd/FMWNT	Temperature: 25 °C Time: 30 min and H_2O_2	90

and the catalyst should have high activity in addition to the high cost and hydrogen amounts. There are some problems related to the catalyst using HDS process such as low surface area, activity loss, coke deposition and rapid deactivation of the catalyst used leading to more regeneration processes due to high operating conditions applied. Therefore, it is significant to develop a method that can work under mild conditions and having high efficiency in removing all types of sulfur compounds to get clean light naphtha (clean fuel) without sulfur content to achieve an environmentally friendly fuel.

Several studies upon oxidative desulphurization have been reported and claimed in the literatures. These include the use of different catalysts and oxidants such as TBHP/air, oxygen–aldehyde, air/CuO/Al_2O_3 and H_2O_2 for oxidation of sulfur compounds. Silver oxide is a strong active component (Ag_2O_3) with excellent metals. Silver has the ability to increase the pore volume and pore size of the catalyst and more hardness can be generated providing enough active sites for the reaction. In this study, a new catalyst (Ag_2O_3/nano-zeolite) loaded with different percent of metal oxide (0.5, 1, and 1.5% of Ag_2O_3) as an active component over nano-zeolite (that has not been reported in the public domain for sulfur removal) from light naphtha by air (as oxidant) for ODS reactions, will be prepared and studied. Ag_2O_3/nano-zeolite is expected to have a high performance toward oxidation desulfurization process. Silver oxide has an excellent high activity and reusability owing to its useful effects upon the surface area and the acidic-site strength of the appropriate heat treatment temperature at moderate operating condition giving high conversion of sulfur compounds.

It has also been observed based on the literature that the zeolite used as a support for

Table 2. Light naphtha properties.

No.	Test Description	Unit	Test Method	Results
1	Specific gravity @15.5 °C	…….	ASTM D4052	0.7477
2	Octane number, Research	…….	FTIR	86
3	Octane number, Motor	…….		77
4	Total sulfur content	wt. ppm	ASTM D7039	650
5	Color (Say bolt)	……	ASTM D6045	> +30
6	Vapor Pressure at 37.8 °C	kPa	ASTM D5191	6
7	Total aromatic components	Vol.%	ASTM D6277 By (FTIR)	18.2
8	Olefins	Vol.%		4.3
9	Saturates compound	Vol.%		77.5
10	Oxygen content	Mass%		0
11	Water content, KF	Vol. ppm	ASTM D6304	78
12	Doctor test	…….	IP 30	Negative
13	Corrosion, Copper strip (30 hours at 50 °C)	…….	ASTM D130	1a
	Distillation			
1	Initial boiling point, IBP	°C	ASTM D86	103
2	10% Recovered, Vol%	°C		115
3	50% Recovered, Vol%	°C		132
4	90% Recovered, Vol%	°C		162
5	Final boiling point, FBP	°C		178
6	Recovered	Vol.%		98
7	Evaporated	Vol.%		1.5
8	Residue	Vol.%		0.5
	Aromatic Components			
1	Benzene, C_6H_6	Vol.%	ASTM D6277 by (FTIR)	0
2	Toluene, $C_6H_5(CH_3)_2$	Vol.%		2.88
3	Total Xylene, $C_6H_5(CH_3)_2$	Vol.%		4.08
4	Ethylbenzene	Vol.%		1.48
5	Pseudocumene, C_9H_{12}	Vol.%		0.95
6	Hemellitol, $C_6H_3(CH_3)_3$	Vol.%		1.57
7	Naphthalene	Vol.%		0.14

HDS catalysts showed excellent promoter of such catalysts. Therefore, such new active component with a new nano-support (nano-zeolite) is met together here achieving new nano-catalyst (Ag_2O_3/nano-zeolite). Such new catalyst (which is a new challenge that has not been reported in the literature) will be evaluated toward ODS reaction at moderate conditions using air as oxidant. Also, a new mechanism of the chemical reaction for sulfur removal by oxygen using the new nano-catalyst prepared in this study was suggested.

2. Materials and Method

2.1 Reagents Used

Treated light naphtha (L.N) obtained from the Ministry of Oil (with sulfur concentration of 650 ppm), Iraq (*Kar-Company-Erbil),* was mixed with model sulfur compounds mercaptan to and was used as model fuel in this work. The initial sulfur concentration of this model fuel was 650 ppm (which is same as untreated light naphtha found in refineries). The physical properties of the light naphtha used in this study are illustrated in Table 2. Material (silver nitrate ($AgNO_3$)) utilized for preparation of active component was supplied by *Alpha chemika* with a purity of 99% and deionized water supplied by *Samarra Company* employed for nano-catalyst preparation. Active component dissolved in ethylene glycol ($C_2H_4(OH)_2$) has supplied from *Laboratories of North Refineries Company*. The nano-support (*NaY*-zeolite) was supplied by *Merck Company*.

2.2 Preparation of Nano Materials

2.2.1 Preparation of (0.5, 1, and 1.5%) Ag_2O_3/Nano-Catalyst

The Impregnation Wetness Incipient (IWI) method was used to prepare the new nano-catalyst. The procedure steps have been conducted in *Middle Technical University*, *Iraq*. Metal salt (silver nitrate) was loaded as an active component in different proportions on nano-zeolite particles. Different ratios of metal oxides were loaded for testing the best percent for sulfur removal by ODS process. Nano-zeolite particles were dried in a furnace for 2 h at 200 °C to remove any moisture out in the pore of the support for nano zeolite. The nano-materials (nano-zeolite) have high mechanical strength, high purities, high porosity, more stable density, high chemical and thermal stability and environmentally friendly material [32,33]. The amount of the metal salt used as active component for nano-catalyst prepared is 0.5% Ag_2O_3, 1% Ag_2O_3 and 1.5% Ag_2O_3. The silver nitrate was dissolved in 50, 75, and 100 mL of deionized water supplied by *Middle Technical University*, *Iraq* and mixed for 2.5 h to obtain a good solubility from salt and getting the saturated solution then it was filtered and the residue was collected. The metal salt (silver nitrate) solution prepared was slowly added onto nano-zeolite particles under continuous mixing to get high distribution of the active material with a little heating to increase the dispersion process of the particles then ethylene glycol was added to increase the metal oxide attached upon the support.

The precipitation of nano-zeolite was dried then calcinated in the oven by the following four steps. In the first step the prepared mixture was heated for 2.5 h in the oven at 150 ˚C with laminar air flow to easily convert the metal salt to metal oxide. In the second step, the mixture was heated at 300 ºC for 2 h and the temperature was then increased to 400 ºC for 1 h to get a well drying of the mixture. Thirdly, the mixture was heated up to 600 ºC for 2 h where the metal oxides were loaded on the supported nano-zeolite then finally followed gradually by a cooling process. The prepared synthesized nano catalysts (0.5 Ag_2O_3%, 1 Ag_2O_3% and 1.5 Ag_2O_3%/Nano zeolite) were characterized by elemental analysis through BET surface (surface area, pore volume and pore size) analysis, XRD, SEM and FTIR. Figure 1 shows the enhancement of the Nano-Zeolite support via silver oxide. Procedure includes the percentage from metal oxide (for example 5% Ag_2O_3/Nano-Zeolite) and amount of deionized water used in the preparation process have applied based on the literature [34]:

$$\left(\frac{metal\ oxide\%}{100}\right)\times Amount\ of\ Nano-support(g)=Ag(g) \tag{1}$$

$$Percentage\ metal\ oxide=5\%Ag \tag{2}$$

$$Amount\ of\ Supported\ (gm)=5Nano-zeolite \tag{3}$$

$$\left(\frac{5}{100}\right)\times 5=0.25Ag(g) \tag{4}$$

$$\left(\frac{Ag}{AgNO_3}\right)=\left(\frac{107.868\ {}^{g}\!/\!_{gmol}}{169.873\ {}^{g}\!/\!_{gmol}}\right)=\left(\frac{0.25gm}{x}\right) \tag{5}$$

$$x=0.3937gm, the\ amounts\ of\ metal\ in\ metal\ salt$$

Distill water required to prepare a solution containing metal salt (silver nitrite $AgNO_3$) for 0.1 M in vol. (mL) was:

$$Volum\ in\ ml=\left(\frac{mass\ of\ salt(g)\times 1000}{Molar\ mass\left({}^{g}\!/\!_{gmol}\right)\times Concentration\left({}^{mol}\!/\!_{dm^3}\right)}\right) \tag{6}$$

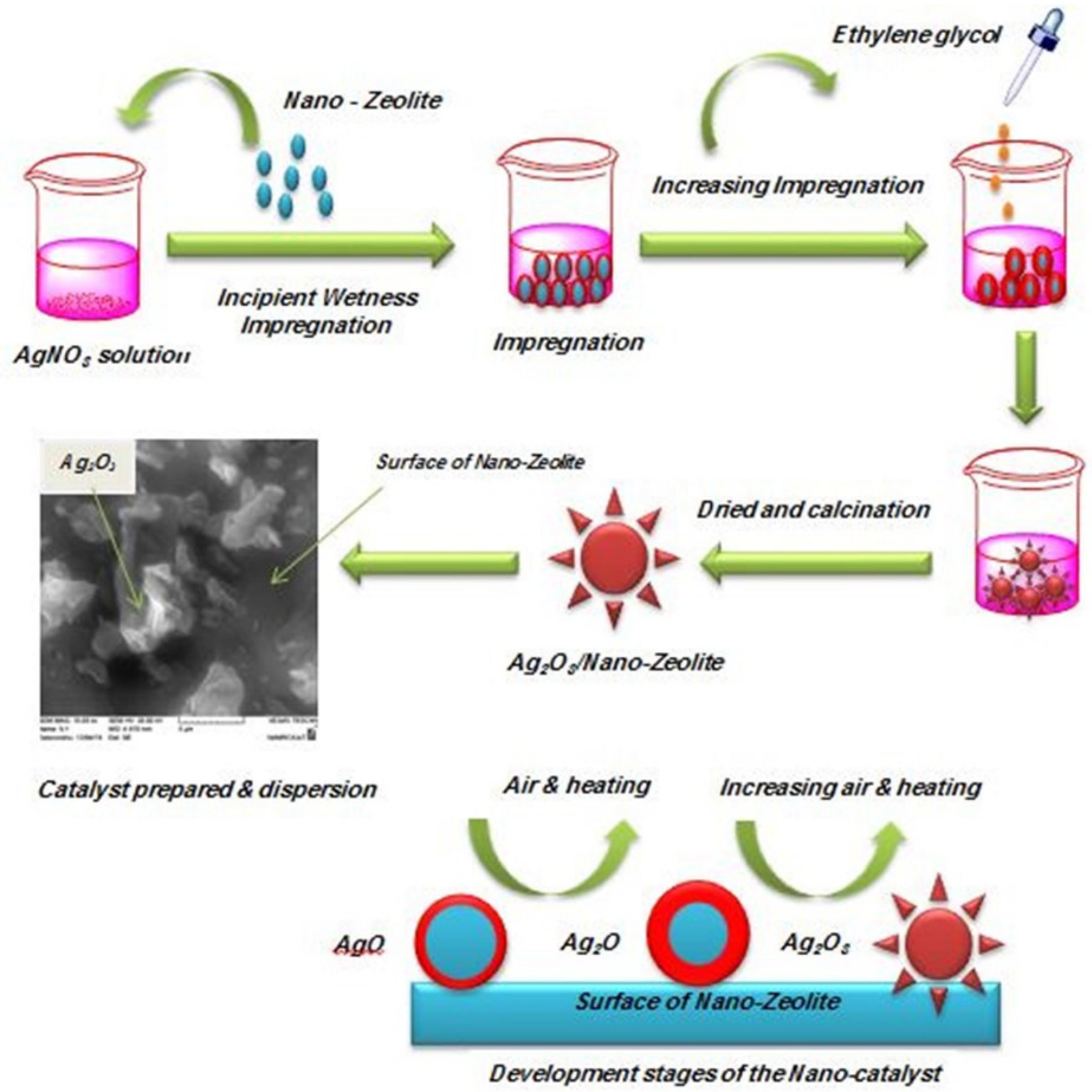

Figure 1. Enhancement of Nano-zeolite with metal oxide (Ag_2O_3/Nano-Zeolite).

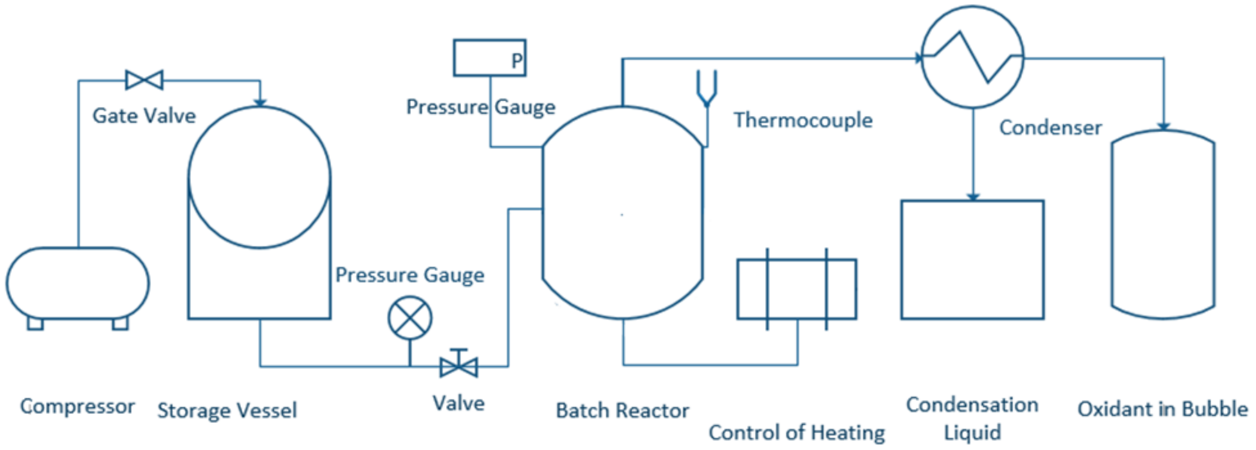

Figure 2. Schematic of batch reactor ODS process.

$$Volum\ in\ ml = \left(\frac{0.3937 \times 1000}{169.873 \times 0.1}\right) = 23.176\,ml \quad (7)$$

2.3 Oxidative Desulfurization of Model Light Naphtha

Batch reactor was employed for oxidative desulfurization of sulfur compound inform model light naphtha. Experimental design having three-neck round bottom flask of 100 mL was used for ODS process. The middle neck was connected to a vertical condenser to condensate the vapor (light naphtha) with leaving behind the oxidant (air) without any loss. The second neck was used for the oxidant (air) to pass at constant inlet pressure (0.5 bar) which was connected to compressor. The air reaches to the bottom of the flask by glass tube leading to increasing contact among the gas, liquid and solid particles. The third neck was used to measure the temperature of the reaction in the flask by inserting a thermometer to the solution inside the flask and to withdraw the sample when the reaction time is achieved. The percent of the catalyst Ag_2O_3/Nano-zeolite prepared is charged to the batch reactor containing the model light naphtha, where the oxidative desulfurization process is carried out. The experimental design diagram of the batch reactor system is illustrated in Figure 2. In this study, the experimental work includes different experiments of oxidative desulfurization process by using the moderate operating conditions and different metal oxide composition (0.5 Ag_2O_3%, 1 Ag_2O_3%, and 1.5 Ag_2O_3%): the reaction temperatures (80, 110, and 140 °C) and reaction time (30, 40, and 50 min).

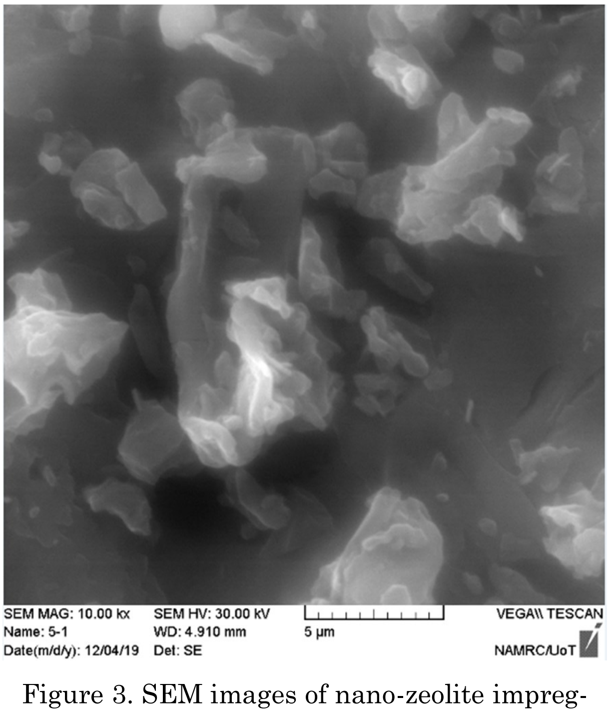

Figure 3. SEM images of nano-zeolite impregnated with silver oxide.

2.4 Sample Analysis

The inlet and outlet sulfur compound found in model light naphtha was determined in *Baiji North Refinery Company, Iraq*. In model light naphtha samples, the concentration of total sulfur was determined through sulfur analyzer via X-Ray diffraction instrument using the ASTM D7039 [35,36].

3. Results and Discussions

3.1 Characterization of Nano-catalyst

3.1.1 Morphology and elemental analysis of the as-synthesized Ag_2O_3/Nano-Zeolite

Figure 3 presents the SEM image of the catalyst prepared (Ag_2O_3/Nano-zeolite). An excellent distribution of silver oxide over surface of support in which metal is represented by white regions while Nano zeolite support can be observed from this Figure by dark regions. The characteristic different pore of silver oxide are marked in the triangular and the SEM picture clearly shows randomly distributed grains with smaller size. From the SEM analysis, it can be concluded that the formation of nanoparticles have a homogeneous shape structure and it is grown in very high-density with almost uniform spherical shapes. High performance catalysts usually consist of high surface area material and such properties with respect to particle size, shape and porosity of the catalyst contribute to the reaction activity greatly. Therefore, very small particles of highly-ordered porous support would provide a high surface area and large active site for the catalysts offering a beneficial effect towards the reaction activity.

3.1.2 FTIR for Ag_2O_3/Nano-Zeolite

FTIR spectroscopy analysis of the nano-catalyst (Ag_2O_3/Nano-Zeolite) was carried out to study the features of their structure by the chemical bonds (functional group) between molecules. This test was determined using a Shimadzu FTIR 8400S (Japan) with wave number ranged between 400 to 4000 cm^{-1}. Samples were prepared by mixing 1 wt% of the nano-catalyst zeolite and 99% of KBr pressed as disk. As shown in Figure 4, the band at around 3450 cm^{-1} could be assigned to O−H stretching vibration of hydroxyl groups. The bands at about 1850 cm^{-1} and 1350 cm^{-1} were attributed to the carboxyl group and carbonyl group. The absorption band at 1112 cm^{-1} remarked the O−H bending vibration while the bands in the proximity of 850 cm^{-1} and 525 cm^{-1} are attributed to the Ag−O and Ag−O−Ag stretching vibrations based on the likely presence of silver oxide on the surface nano-zeolite. The peak observed about 1609.23 cm^{-1} corresponds to the bending vibration of water molecules in the zeolite structure.

3.1.3 X-Ray Diffraction (XRD) for Ag_2O_3/nano-zeolite

The XRD patterns of the nano-zeolite prepared (illustrated in Figure 5) showed that the disorderly peaks of 2θ between 6.33–23.778 and 40–50 indicate to amorphous zeolite [37–39]. For 1% Ag_2O_3/nano-zeolite, the clear peaks (shown in this Figure 5) at 2θ of 23.5, 31.5,

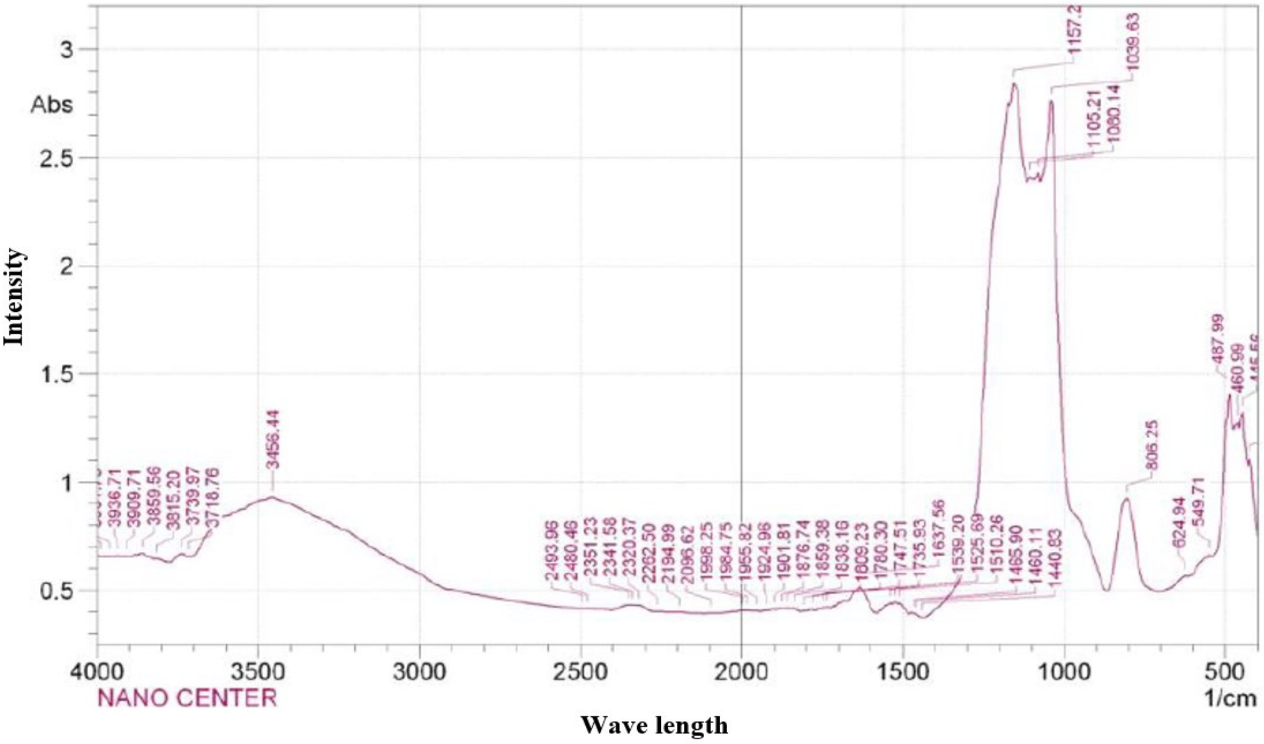

Figure 4. FTIR for nano-catalyst (Ag_2O_3/Nano-Zeolite).

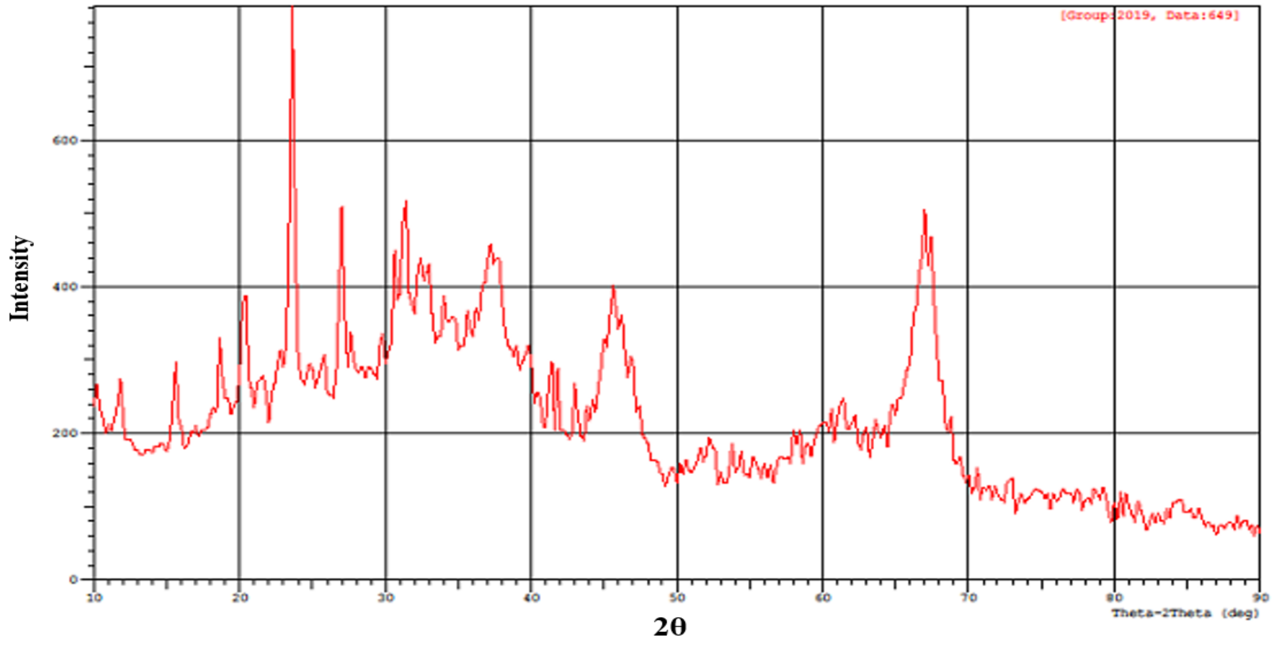

Figure 5. The XRD patterns of the Ag_2O_3/nano-zeolite.

26.2, 45.5, and 68.1 gave a crystalline Ag_2O_3, while the background patterns refer to amorphous support.

3.1.4 Surface area and pore volume Ag_2O_3/nano-zeolite

The chemical and physical properties of the nano–zeolite–supported and the specific surface area are considered important factors affecting the process with respect to the activity of the catalyst. The BET of nano catalyst is found to decrease after loading the metal oxide on the catalyst support for all catalysts concentrations (0.5%, 1%, 1.5% Ag_2O_3/nano–zeolite). The surface area of the catalyst prepared is still high but such decreases could be attributed to the deposition of silver oxide powder in the pores of zeolite [32]. However, these values (298.1 m^2/g, 293 m^2/g and 287 m^2/g for 0.5%, 1 % and 1.5% of Ag_2O_3/nano-zeolite, respectively) are still acceptable for adsorption compared to the surface area of metal oxides. The pore volume of the catalysts is found to increase and the number of effective active site, which are expected to increase the reaction rate of the ODS process. The values of the surface area, pore volume and pore size are reported in Table 3. These specifications have clearly showed that the zeolite nanoparticle size is within nanoscale size.

3.2 Performance of the Catalyst Prepared with Process Conditions on the Sulfur Removal

3.2.1 Effect of metal oxide percent on sulfur removal

The influence of metal oxide over nano zeolite having a significant effect on the sulfur removal during oxidative desulfurization reactions of model light naphtha is presented in Figures 6–8. Increasing the percent of metal oxide from 0.5% to 1 % over nano support (nano-zeolite) leads to increase in the sulfur conversion from 56.8% to 87.4 % at 50 min and 140 °C. While at 1.5 g of the metal oxide for the prepared nano-catalyst (1.5%Ag_2O_3) at different reaction time and temperature, the sulfur removal has decreased indicating that the best distribution of the metal oxide is at 1% (i.e. 1% Ag_2O_3). Such behavior is probably attributed to the blocking of the catalyst support through the surface at this composition of the catalyst. High sulfur conversion were obtained due to the high surface area available whenever the nano-catalyst (Ag_2O_3/Nano-Zeolite) metal oxide was increased from (0.5–1 wt%) giving high

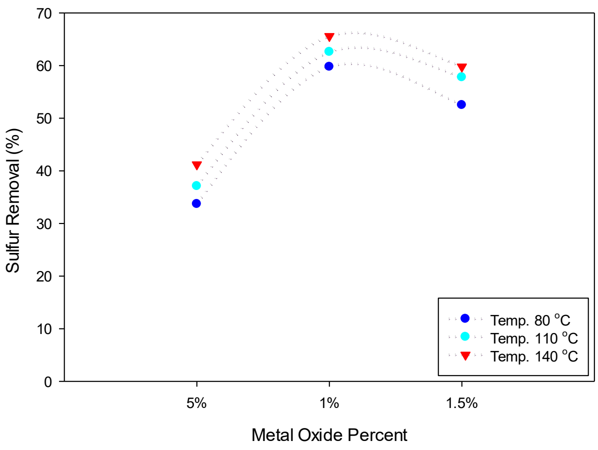

Figure 6. Metal oxide impact on sulfur removal at reaction time of 30 min and several temperatures.

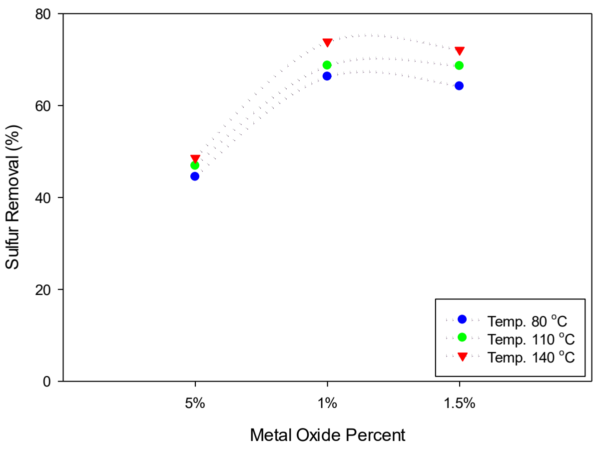

Figure 7. Metal oxide impact on sulfur removal at reaction time of 40 min and several temperatures.

Table 3. The BET of different percent for metal oxide on nano support.

Catalyst prepared	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Nano-Zeolite-Supported	300	0.205	0.275
0.5% Ag_2O_3/Nano-Zeolite-Supported	298.1	0.20	0.255
1% Ag_2O_3/Nano-Zeolite-Supported	293	0.36	0.245
1.5% Ag_2O_3/Nano-Zeolite-Supported	287	0.33	0.246

sulfur removal. Also resulting increase in the vacuum size of the pore sites contributes to enhanced chemical reaction rate leading to increased interaction of the sulfur molecules and oxygen.

3.2.2 Effect of reaction time on sulfur removal

The effect of reaction batch time on sulfur removal at different metal oxide is illustrated in Figure 9 and 10. It can be noticed from these Figures that the effect of reaction time has also played an important part in sulfur removal process [40], where an increases in the reaction time cause increasing the sulfur conversion. The contact time among the reactants within the designed nano-catalyst increases allowing longer contact with the active sites of catalyst (Ag_2O_3/Nano-Zeolite). It has also been shown from Figure 9 that the conversion of sulfur compound during the ODS process based on the new catalyst prepared has increased from 65.6% to 87.4% when the reaction time increased from 30 min to 50 min at 140 °C and 1% Ag_2O_3. Same behavior was noted in Figure 10 at different reaction temperature and metal oxide of 1% Ag_2O_3/Nano-Zeolite. It has also been observed that the highest removal of sulfur compound was obtained at the following operating conditions based on experiments (reaction time = 50 min, percent of active materials (metal oxide) = 1%Ag_2O_3, reaction temperature = 140 °C), where reaction batch time of oxidative desulfurization process are considered to be the biggest factor affecting the ODS reaction.

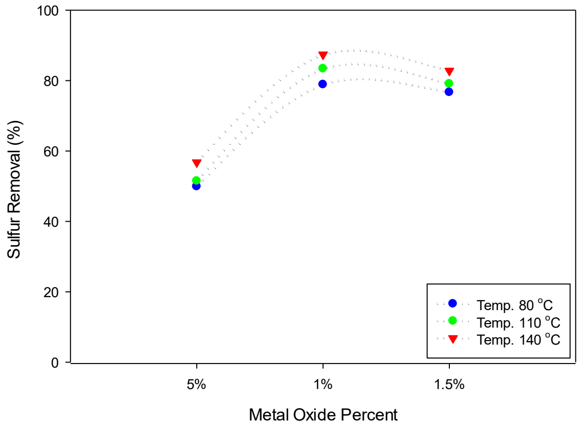

Figure 8. Metal oxide impact on sulfur removal at reaction time of 50 min and several temperature.

3.2.3 Effect of reaction temperature on sulfur removal

The influence of temperature reaction on the conversion of oxidation desulfurization of sulfur compound is studied at 80, 110 and 140 °C. The experimental data are plotted in Figures 10–13 at different temperatures. It noticed that an increasing in the reaction temperature through ODS leads to increasing removal of sulfur compound [41,42]. This behavior is due to the fact that increasing temperature increases the number of molecules involving in the oxidation reaction and increases the activation energy. Effect of temperature on the sulfur molecules increases the diffusion and osmoses inside the pores of the catalyst and increasing the temperature will have high impact on physical properties. Thus, raising the temperature promotes the absorption rate of molecular air into light naphtha and the diffusion rate of sulfur compound. Also, the rate of dissolving

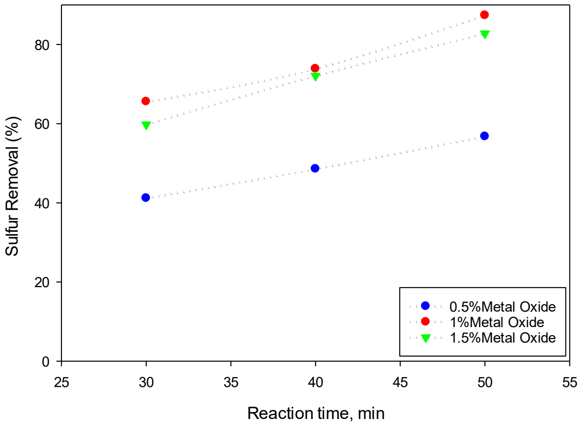

Figure 9. Effect of reaction time on sulfur removal at different metal oxide and reaction temperature of 140 °C.

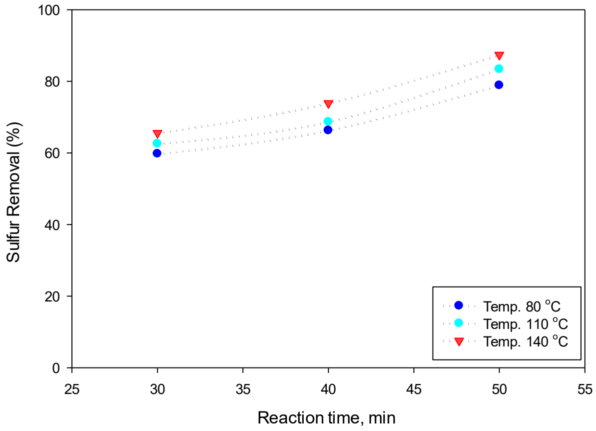

Figure 10. Effect of reaction time on sulfur removal at different reaction temperature and metal oxide of 1% Ag_2O_3/Nano-Zeolite.

air inside the catalyst pores to reach the active sites is increased resulting more oxidation reactions [31].

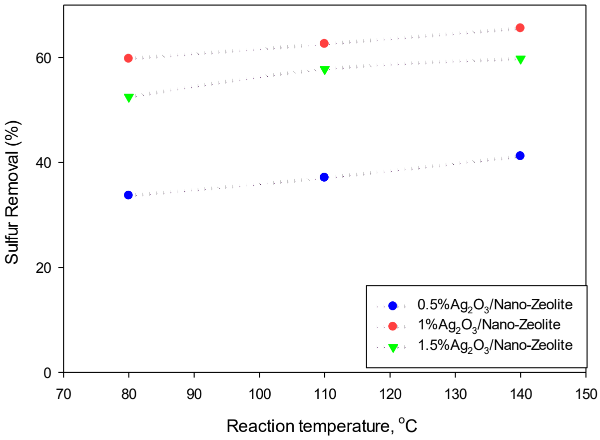

Figure 11. Effect reaction temperature on sulfur removal at different metal oxide with a reaction time of 30 min.

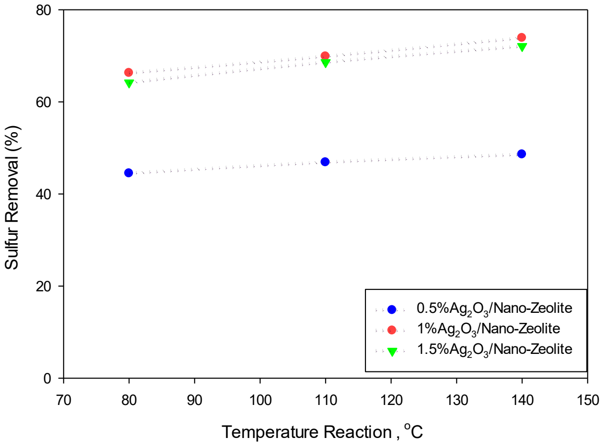

Figure 12. Effect reaction temperature on sulfur removal at different metal oxide with a reaction time of 40 min.

3.2.4 Activity of nano-zeolite for sulfur removal

The oxidation performance of the silver oxide/Nano-zeolite catalyst at different concentrations of metal oxide (0.5%, 1%, and 1.5%) prepared in this work has been compared with some other published results related to zeolite-based catalysts under mild operating conditions for sulfur removal. As shown in the Table 4, Nano-catalyst and air oxidant that extensively have investigated here for ODS reaction indicated that the new nano-catalysts prepared showed high selectivity toward sulfur removal and the highest conversion has observed in comparison with last studies.

3.3 Mechanism of Chemical Reaction for Sulfur Removal by Oxygen

Mechanism of oxidation process of thiols and other sulfur compounds is based on changing the oxidation state of sulfur rather than carbon. For instance thiols, in such case, mild

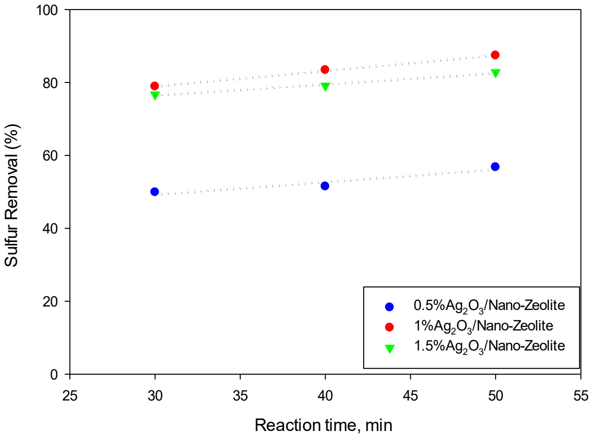

Figure 13. Effect reaction temperature on sulfur removal at different metal oxide with a reaction time of 50 min.

Table 4. Comparison results obtained by this study and last studies.

Catalyst	Oxidant	Operating conditions	Solvent	Conversion	Ref.
ZnO/ɣ-nano-Al_2O_3	air	Temperature: 190 °C Time: 50 min	Without solvent	70.52%	[21]
NiMo/γ-Al_2O_3	O_2	Temperature: 35 °C Time: 60 min	Without solvent	76.25%	[27]
MnO_2/ɣ-Al_2O_3	O_2	Temperature: 200 °C LHSV: 1 h^{-1}	Without solvent	81%	[34]
MO/Al_2O_3	TBHP	Temperature: 60 °C Time: 30 min	DMF/Oil	83%	[43]
Ti/MM	H_2O_2	Temperature: 60 °C Time: 120 min	Acetonitrile	64%	[44]
Ag_2O_3/Nano-Zeolite	air	Temperature: 140 °C Time: 50 min	Without solvent	87.4%	This work

oxidation converts thiols to disulfides. The S−S single bond is nearly twice as strong as the O−O bond in air (oxygen). Thus, thermodynamics favors disulfide formation over oxygen. Finally, oxidation of sulfides with oxygen is first led to sulfoxides and then to sulfones as shown in the Figure 14.

3.4 Effect of Operating Conditions on the Properties of Light Naphtha (LN)

In laboratory of *Petroleum Process Engineering at Tikrit University*/Iraq and laboratory of *Baiji North Refineries Company*/Iraq, a complete measurement of the physical properties of model light naphtha before and after oxidation process is conducted to ensure that there is no change in the physical properties using the new nono-catalyst. The main physical properties of light naphtha before and after ODS process is reported in Table 5. The distillation process for both cuts (before and after ODS reactions) of LN is represented in Figure 15 at the best operating conditions (reaction time, 50 min, reaction temperature, 140 °C and metal percent 1% Ag_2O_3/Nano-zeolite). Chemical re-

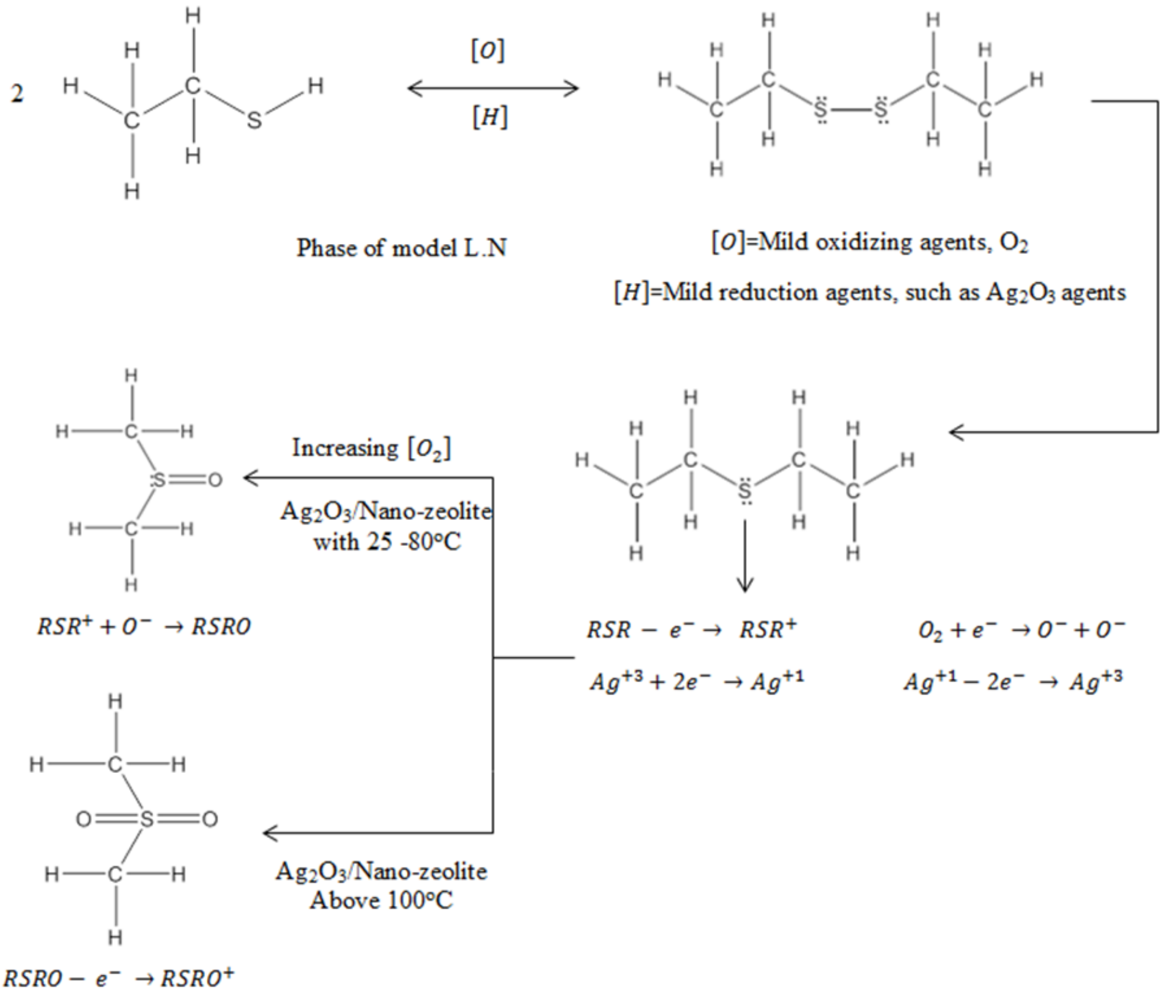

Figure 14. Mechanism of chemical reaction suggested for sulfur removal by oxygen using the new homemade catalyst prepared.

Table 5. The main physical properties of light naphtha before and after ODS process.

No.	Test Description	Unit	Test Method	L.N before ODS	L.N after ODS
1	Specific gravity @15.5 °C	…	ASTM D4052	0.7477	0.7469
2	Octane number, Research	…	FTIR	86	88
3	Octane number, Motor	…		77	78
4	Vapor pressure at 37.8 °C	kPa	ASTM D5191	6	5.7
5	Viscosity cSt (20 °C)	…	ASTM D6045	3.8	3.7

action was conducted at low and moderate operating condition and it has been clearly noticed that there is no effect on the physical properties. Oxidation reactions tested at the best operating conditions indicated zero effect on the hydrocarbon chains meaning that there will be no broken hydrocarbon chains based on physical properties of light naphtha obtained before and after oxidation particularly viscosity, boiling range and density. Also, some volatile compounds in light naphtha feedstock will transfer to the environment at high temperature leading to decrease in the Read vapor pressure [45]. It is clearly seen from the results presented in Table 5 that the physical properties of light naphtha before and after ODS reactions were very close to each other and no significant differences were observed. Hence, the ODS process based on the new nano-catalyst prepared here is regarded an efficient process and aimed to remove harmful sulfur compounds without causing a detrimental on the other physical properties of the treated light naphtha. The octane number before and after ODS has given a great indication that the aromatic compounds have not been involved in the oxidation reactions indicating that the new nano-catalyst prepared here can be applied with high confidence.

3.5. Mathematical Modeling of Oxidative Desulfurization (ODS) Process

3.5.1 Kinetic model of ODS reaction

The kinetic model of oxidation of sulfur removal is studied under moderate operating condition in batch reactor at different reaction temperatures varied from 80–140 °C. The chemical reaction is a three phase heterogeneous kind and the organic phase contains the reactant sulfur, while the aqueous phase contains the oxidant air and the nano-catalyst (Ag_2O_3/Nano-Zeolite) makes the solid phase. The interfacial mass transfer effect between three phases is eliminated by fixing the optimum stirrer speed at 560 rpm. The reaction may be written as [21]:

$$\text{Sulfur} + \text{Oxidant} \rightarrow \text{Disulfide} \tag{8}$$

$$RSH + O_2 \rightarrow RSSR \tag{9}$$

An empirical kinetic model has been assumed to predict the reaction rate in the absence of mass transfer for its simplicity:

$$-\frac{dC_S}{dt} = K\left(C_S\right)^n \left(C_{O_2}\right)^m \tag{10}$$

The amount of air is taken in excess amount of air (excess oxygen content) neglecting the concentration change of O_2 to sulfur concentration thus the term dependent on O_2 concentration has been neglected. Hence, the reaction may be considered as a pseudo first order plotted in Figures 16-18. The rate of the reaction may be expressed as:

$$-\frac{dC_S}{dt} = K'\left(C_S\right)^n \tag{11}$$

where:

$$K' = K\left(C_{O_2}\right)^m \tag{12}$$

K' is termed as apparent rate constant. Equation (11) has been integrated for $n = 1$, with limit $t = 0$, $C_s = C_0$ and $t = t$, $C_s = C_t$ and the following equation is obtained:

$$\ln\left(\frac{C_0}{C_t}\right) = K't \tag{13}$$

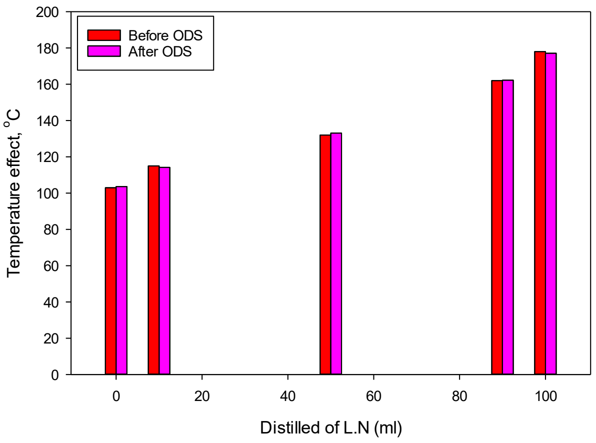

Figure 15. ASTM distillation scheme of light naphtha before and after oxidation process.

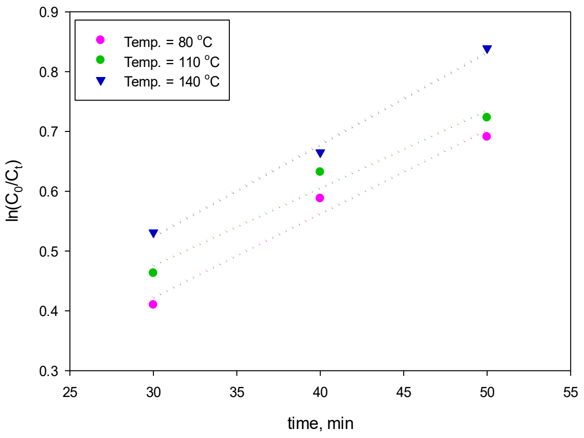

Figure 16. Plot ln(C_0/C_t) versus time for different temperature at 0.5% Ag_2O_3/Nano-Zeolite.

3.5.2 Activation energy for oxidative desulfurization process

The plot of ln(C_0/C_t) versus time gives a linear plot depending on Arrhenius equation as shown in Equations (10) and (11).

$$K = K_0 \exp\left(\frac{EA}{RT}\right) \tag{10}$$

$$\ln K = \ln K_0 - \frac{EA}{RT} \tag{11}$$

Figure 19 shows the straight line observed to pass through the origin reactions confirming that the kinetics of pseudo having first order reaction. The apparent rate constant *K'* can be calculated from the slope of the straight line. The plot of ln *K'* as function of 1/T gives the value of the activation energies of 60.455, 90.525, and 60.484 kJ/mol, for 0.5%, 1%, and 1.5 Ag_2O_3/Nano-Zeolite, respectively.

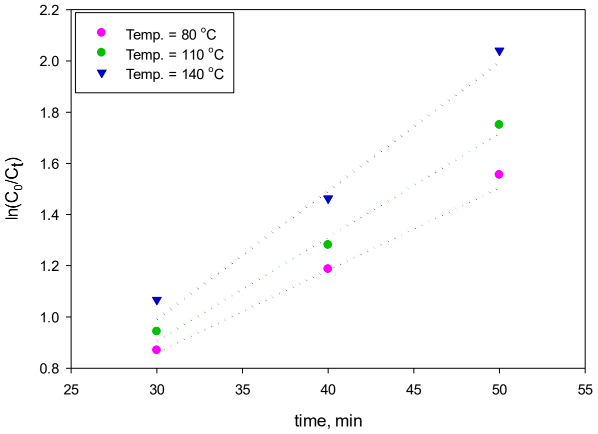

Figure 17. Plot ln(C_0/C_t) versus time for different temperature at 1% Ag_2O_3/Nano-Zeolite.

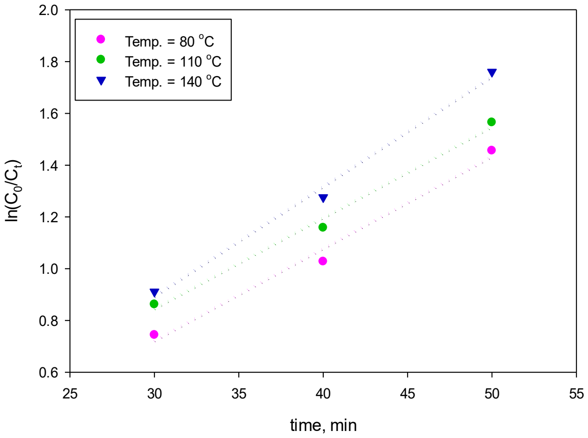

Figure 18. Plot ln(C_0/C_t) versus time for different temperature at 1.5% Ag_2O_3/Nano-Zeolite.

6. Conclusions

A novel synthetic homemade nano-catalyst (silver oxide) has been designed to remove sulfur compounds from light naphtha (car fuel) and such new nano catalyst has successfully been prepared using IWI method. Results showed a well-defined by morphology, uniform distribution, high surface area, and stable structure tests. Sulfur removal by air from light naphtha has been conducted in a batch reactor based on the new Nano-catalyst using different mental oxides (0.5, 1, 1.5% Ag_2O_3/Nano-Zeolite) prepared for sulfur removal utilizing air as an oxidant. Oxidative desulfurization process (ODS) appears to be technically and economically feasible for processing ultra-low sulfur fuel. So, the new homemade nano-catalyst has been tested to evaluate its performance with respect to sulfur compound and showed a very high effective toward sulfur removal by air with silver oxide with keeping the main physical properties without changing during the ODS reactions. The best operating condition is found to be 140 °C (reaction temperature), 50 min (reaction time) and 1% Ag_2O_3/Nano-Zeolite (the metal oxide loaded). Also, new mechanism for sulfur removal using the new catalyst with ODS reactions has been reported. The ODS reactions has followed first order reactions giving a clear indication that such new catalyst can easily be applied for sulfur removal.

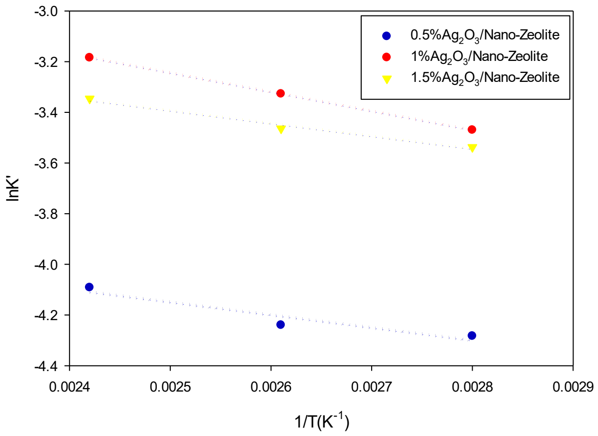

Figure 19. Arrhenius scheme of ODS a reaction.

Nomenclatures

g : Gramm (-)
S_o : Concentration of sulfur in light naphtha untreated (ppm)
S_t : Concentration of sulfur in light naphtha treated (ppm)
C_o : Initial concentration (ppm)
C_t : Final concentration (ppm)
K : Rate constant (min^{-1}.(concen.)$^{1-n}$)
n : Order of sulfur (-)
m : Order of oxygen (-)
C_{RSH} : Concentration of mercaptan (ppm)
C_{O2} : Concentration of oxygen in chemical reaction (ppm)
K' : Apparent constant (min^{-1}.(concen.)$^{1-n}$)
EA : Activation energy (kJ/mol)
R : Gas constant (J/mol.K)

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