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## Preparation and Characterization of Bimetallic Catalyst (NiO – CoO) for Desulfurization of Gas Oil

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### Abstract:

In this study NiO - CoO bimetallic catalysts are prepared with two Ni/Co ratios (70:30 and 80: 20) using the precipitation method of nitrate salts. The effects of Ni /Co ratio and preparation methods on the catalyst are analyzed by using different characterization techniques, i.e. atomic absorption (AA) , XRD, surface area and pore volume measurements according to the BET method .

The results indicate that the best catalyst is the one containing the percentage of Ni :Co ( 70 : 30 ). Experiments indicate that the optimal conditions to prepare catalyst are stirring for three hours at a temperature of 60°C of the preparation , pH= (8-9) , calcination temperature at 400°C for two hours using the impregnation method.

The catalyst activity is studied through the application in the process of oxidative desulfurization of gas oil fuel . The optimal conditions for deep oxidative desulfurization processes are : catalysts 3% , 2 gm. Na<sub>2</sub> CO<sub>3</sub> , reflux time 3 hours at 40<sup>0</sup> C , using a mechanical stirrer at moderate speed (700 rpm), the volume ratio of gas oil : H<sub>2</sub>O<sub>2</sub> : acetic acid is 10: 1: 0.5 and extracted with 1:1 ratio of acetonitrile to the gas oil for three times .

The results indicate that the catalysts are efficient to remove sulfur from gas oil depending on temperature, time, concentration of hydrogen peroxide H<sub>2</sub>O<sub>2</sub> 30 % and solvent used for extraction.

The efficiency of the best catalyst gives a maximum sulfur removal reaching 68.97%.

**Key words:** Bimetallic Catalyst, Ni- Co, Desulfurization, Gas Oil.

### Introduction:

A catalyzed reaction is faster than an unanalyzed version of the same reaction because the catalyst provides a different reaction pathway with lower activation energy [1]. Generally, catalysts can be classified into

heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate or not . Biocatalysts (enzymes) are often seen as a separate group [1, 2].

Catalysts are widely used in nature, in industry, and in the laboratory. It is estimated that they contribute to one-sixth of the value of all manufactured goods in industrialized countries [1].

The suitability of a catalyst for an industrial process depends mainly on the following three properties [3]:

- 1- Activity.
- 2- Selectivity.
- 3- Stability.

The major advantages/disadvantages of heterogeneous vs. homogeneous catalysts are summarized in Table (1) [4].

**Table (1): Comparison of Main Advantages / Disadvantage of Heterogeneous vs. Homogeneous Catalysts**

Property	Homogeneous	Heterogeneous
Catalysts activity	difficult and expensive	easy and cheap
Stability	poor	good
Selectivity	excellent /good–single active site	good/poor–multiple active site

The term green catalytic processes have been used frequently in recent years, implying that chemical processes may be made environmentally benign by taking advantage of the possible high yields and selectivities for the target products, with little or no unwanted side products and also often high energy efficiency and implying the catalysts to play a steadily increasing role in achieving a cleaner environment. An example is the reduction of hydrocarbons from automobile exhaust gases [5].

Sulfur enters our atmosphere as gaseous sulfur dioxide through the burning of fossil fuels such as diesel. Sulfur is also converted to sulfur trioxide (SO<sub>3</sub>) and hydrogen sulfide (H<sub>2</sub>S). Oxidative desulfurization of fuels is a matter of major interest not only because of increasing environmental

concern. Sulfur dioxide SO<sub>2</sub> affects the environment, man-made structures, our health, and even the industries that generate the toxic gases. It combines with water vapor in the air to form sulfurous and sulfuric acid. These acids fall back to earth in water vapor and slowly devour away stone. The gas easily corrodes steel and iron structures as well. More importantly, sulfur emissions affect our health and environment and have been correlated with higher incidences of asthma, lung disease, heart disease, and bronchitis. Finally, sulfur poisons the catalysts used in oil and gas refineries and in the catalytic diesel particulate filters of vehicles that are designed to eliminate the very problem of pollution [6].

The oxidative desulfurization (ODS) technology has been widely recognized as one of the most effective methods for the sulfur removal of fuel oils; due to the very mild operation conditions it requires [7].

## Materials and Methods:

All reagents and solvents used are available commercially, which are nickel nitrate Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, cobalt nitrate Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, sodium bicarbonate, barium chloride, hydrogen peroxide, acetic acid, sodium carbonate and acetonitrile.

Some physical and chemical properties for the gas oil from Al-Dura Refinery are listed on Table 2.

**Table (2): Some Physical and Chemical Properties for the Gas Oil Sample Used**

Properties	Value	Standard
Sp.gr at 15.6 (°C)	0.85	0.85
Flash Point (°C)	54	54
API – Gravity	31.9	31.9
Total sulfur content wt. %	1.477	1.0

API = American Petroleum Institute.

**Catalyst Preparation:**

Catalyst (NiO- CoO) is prepared according to precipitation methods. The six basic preparation steps are used in the synthesis of the catalysts in our laboratory. The preparation methods are described as follows [8]:

**1) Solution Preparation :** The solution containing various metal salts (Ni – Co) is prepared through dissolving metal precursors using distilled water according to the desired ratio as ( 70:30 and 80: 20 ).

**2) Precipitation:** The precipitation of metals is made through adjusting the pH value of the solution to be 8-9 by adding precipitating reagent . In this research , mild basic compounds are sodium bicarbonate  $\text{NaHCO}_3$  (1.0 M) ,the contents are continuously stirred during precipitation and agitation at 60 °C for 3 hours.

**3) Filtration and Washing:** Filtration is used to remove most of water and unwanted ions through a Buchner funnel in vacuum. The cake remaining after filtration is washed using distilled water at room temperature until the pH value of washing flow is close to 7, with being sure that the filtrate is free from sodium ions as well as drops of barium chloride (0.1M) are added to the filtrate as filtrate turbidity means the presence of sodium ions and continue panning with water until it is free.

**4) Drying:** After removing most of unwanted ions by washing, the precipitated cake contains a significant portion of water. The precipitate is then dried in an oven at 120 °C for 24 hours to remove the water.

**5) Calcination:** The catalyst calcination is one of the most important pretreatment procedures. Calcination temperature is at 400 °C for 2 hours in a muffle furnace. Thermally unstable compounds in the catalyst are decomposed to oxides. High temperature process can generate strong

interaction between metals and oxide support, resulting in the formation of stable catalysts.

**6)Forming Operation:** After calcination, the catalyst is grinded and formed as pellets .

**Catalyst Characterization:**

The prepared catalysts are characterized by using different techniques. The metal contents of the catalysts are determined by the atomic absorption (AA) technique. The specific surface area and pore volume are measured according to the Brunauer – Emmett - Teller (BET) method. The crystal structure and determination of crystallographic parameters of the metal oxides forming the catalysts are performed by XRD analysis .

**Experimental Procedure and Analysis:**

The catalyst activity is studied through its application in the process of oxidative desulfurization of gas oil which involves the following steps :

**Oxidative Desulfurization Procedure:**

1- A sample 100 ml of gas oil from Al-Dura Refinery is put in a round bottom flask with three-necks in water bath . The sample content of sulfur is of 1.407%.

2- The wanted weight (3) g of the catalyst is previously added to the flask .

3- 10 ml of 30%  $\text{H}_2\text{O}_2$  as an oxidizing agent is added to the flask followed by 5 ml of  $\text{CH}_3\text{COOH}$  as a co-catalyst.

4- The mixture is refluxed for 3 hours at 40 °C temperature using a mechanical stirrer at moderate speed (700 rpm/minute) , while stirring , 2 g of  $\text{Na}_2\text{CO}_3$  is dissolved in 20 ml of distilled water and added to the mixture . At the end of reaction, the mixture is left at room temperature for 30 minutes to attain phase separation .

5- The biphasic mixture is separated by extraction with acetonitrile and barium chloride three times. Obviously a precipitate formed in the aqueous layer when  $\text{BaCl}_2$  is added. This phenomenon suggests that the gas oil sulfur compounds are converted to  $\text{SO}_4^{2-}$  during the oxidation [9,10].

6 – The gas oil phase is withdrawn and the concentration of the remaining sulfur compounds is determined by X-ray Fluorescence (XRF).

## Results and Discussion:

### Characterization of Catalysts:

Catalysts are characterized by X-ray diffraction (XRD) using diffractometer with  $\text{Cu K}\alpha$  radiation

( $1.5406 \text{ \AA}$ ; 40 kv; 30 mA) and step scan technique is in  $2\theta$  range of 20 to  $60^\circ$ .

The results of the X-ray diffraction of catalyst samples are shown in Table 3.

**Table (3): Results of the X-ray Diffraction:**

Sample	$2\theta(\text{deg.})$	$d(\text{\AA}^\circ)$	$I/I_0$
CoO standard	36.500	2.244	85%
	42.650	2.026	100%
	61.500	1.470	35%
NiO standard	37.248	2.411	60%
	43.286	2.088	100%
	62.852	1.477	30%
Cat- A Ni : Co 70 : 30	43.436	2.082	100%
	37.011	2.427	90%
	59.125	1.561	14%
Cat-B Ni : Co 80 : 20	43.201	2.093	100%
	37.136	2.419	66%
	36.087	2.487	6%

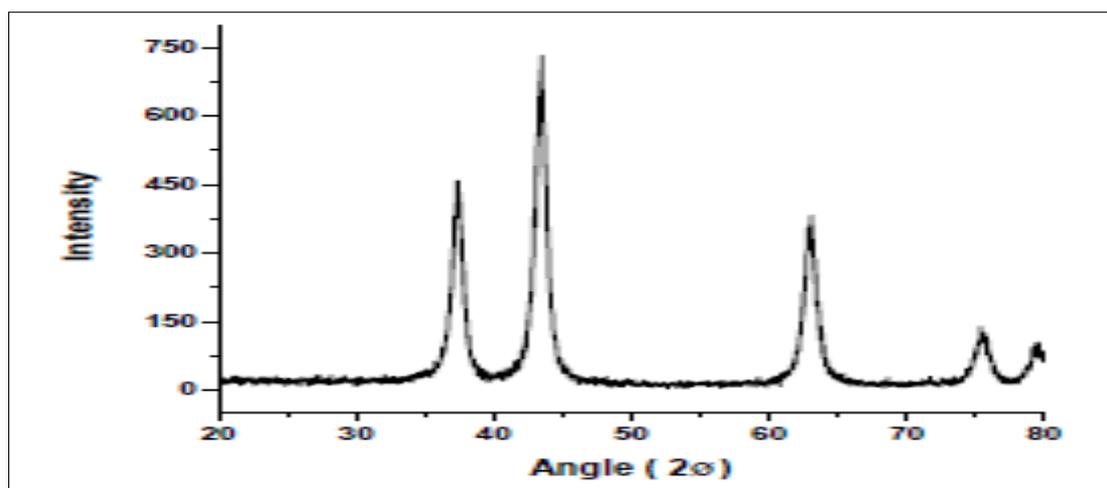


Fig (1): The X-ray Diffraction of Nickel Oxide (NiO)[11].

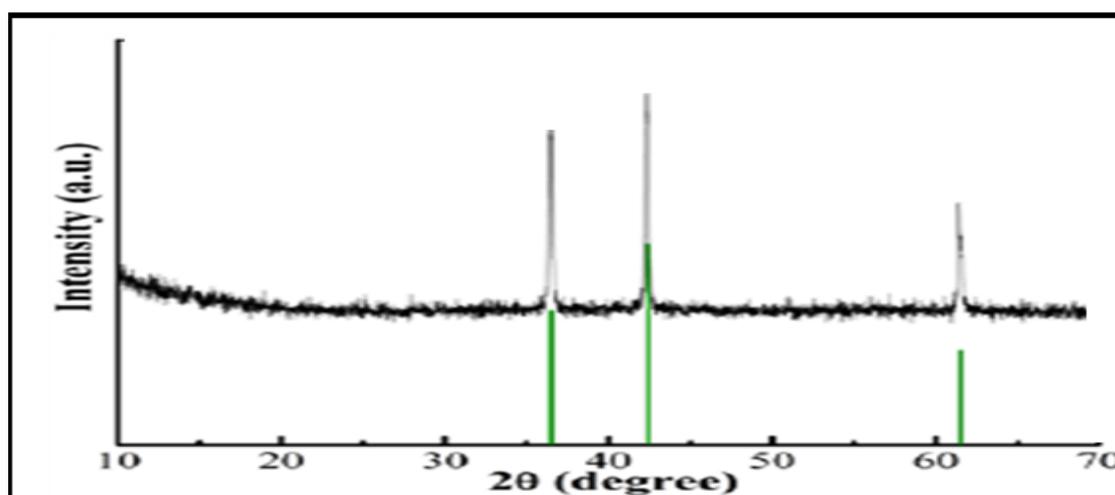


Fig (2): The X-ray Diffraction of Cobalt Oxide (CoO)[12].

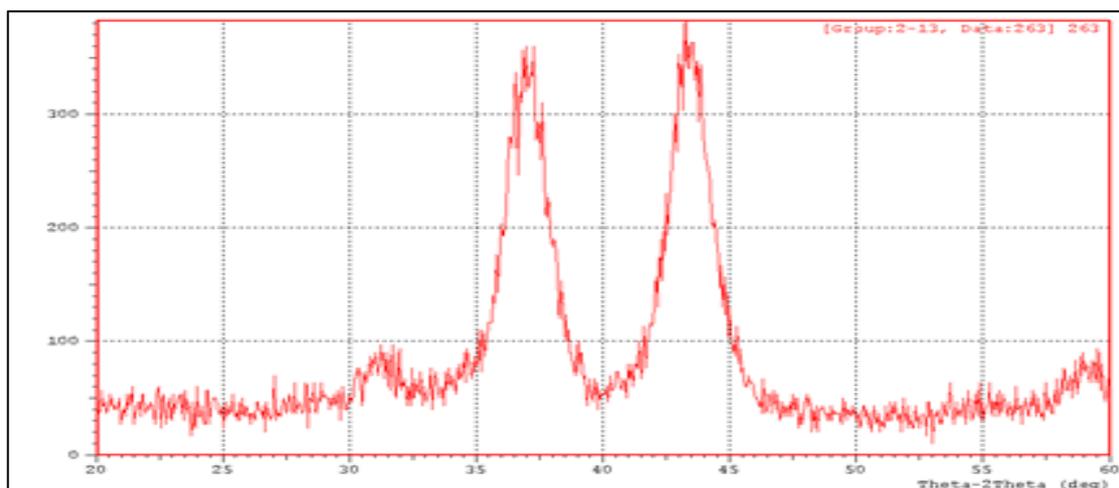


Fig (3) : The X-ray Diffraction of Cat - A .

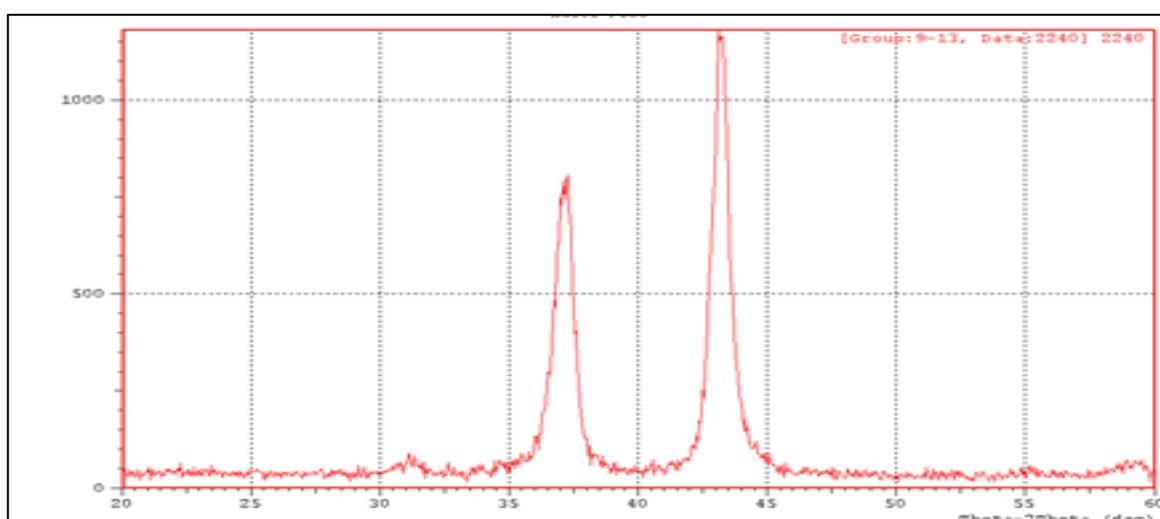


Fig (4): The X-ray Diffraction of Cat - B.

As shown in Table (3), the values of the diffraction are presented for NiO at  $2\theta$  (37.248, 43.286 and 62.852) and for CoO at  $2\theta$  (36.5, 42.65 and 61.5), the catalysts nickel-cobalt oxides display similar diffraction patterns compared to the standard diffraction NiO and CoO[11,12].

Furthermore from Table (3) and Figures (1 - 4) no apparent differences are observed in all catalysts nickel-cobalt oxides, reveal between the XRD patterns of Ni-Co bimetallic catalyst and NiO or CoO monometallic catalyst because  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  have similar lattice in the Ni-Co composite catalysts. The  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  spinel-type solid solution and  $\text{NiCoO}_2$  spinel can be

formed at high calcination temperatures, this is in good agreement with those reported in literature<sup>[13,14]</sup>. The values of diffraction peaks at  $2\theta$  (36.7, 37.1, 43.4 and 44.6) are observed in the catalysts with different Ni-Co content. The reason for the difference in the values is related to the different calcining temperature where it is at 400 °C in this work compared with the (500 – 900) °C in other studies [15,16]. The specific surface area and pore volume are measured according to the BET method. The results of the pore volume and surface area of catalyst samples are shown on Table 4.

**Table (4): Surface Area and Pore Volume Results :**

Catalyst	Ratio Ni : Co	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /gm.
Cat- A	70 : 30	72.971	0.200
Cat- B	80 : 20	44.060	0.204

A chemical analysis is conducted to catalysts NiO - CoO to determine the percentages of the elements nickel and cobalt components in the NiO - CoO catalysts by the atomic absorption technique . The results are listed on Table 5.

**Table ( 5 ): Percentages of Nickel and Cobalt Elements and Oxides ( Found , Calculated ) Composing the Catalysts NiO - CoO .**

Catalyst Code	Ni %		NiO %		Co%		CoO %		Total ratio of (F) NiO%+CoO%
	C	F	C	F	C	F	C	F	
Cat- A 70 : 30	54.92	54.12	69.89	68.87	23.63	22.96	30.05	29.19	98.06
Cat- B 80 : 20	62.76	61.99	79.87	78.89	15.75	15.06	20.03	19.15	98.04

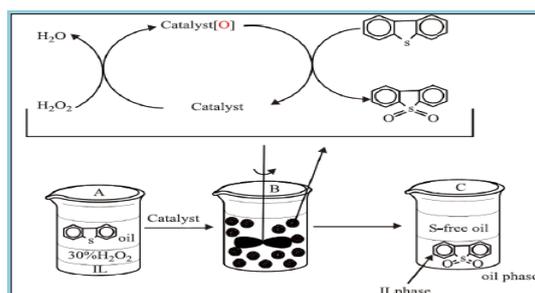
C = Calculated , F = Found .

### Mechanism of Sulfur Removal:

The removal of sulfur from gas oil is a very important global issue in order to decrease atmospheric pollution caused.

The (ODS) process has been studied in various systems , including oxidation (Hydrogen Peroxide) with organic acids. The catalytic oxidation of the sulfur compounds existing in the liquid hydrocarbons to form the corresponding sulfones and/ or sulfoxides improves significantly the extraction liquid-liquid separation process and the two liquid phases must be immiscible [17].

Also the mechanism can be represented as in the following scheme (1) ,which shows the effect of catalyst that takes (O) from the oxidizing agent (H<sub>2</sub>O<sub>2</sub>) giving this (O) to oxidize the sulfur compounds into SO<sub>2</sub> .



### Liquid Phase

### Scheme(1): Mechanism Of The Oxidation Of Dibenzothiophene.

This (ODS) method, showing more energy efficient, cost effective and environment friendly, thus it could be a more promising process for deep desulfurization of the liquid hydrocarbon fuels.

### Determination of the Removal Efficiency of Sulfur Compounds

The removal efficiency of sulfur compounds is calculated as the ratio of sulfur concentration that is oxidized in presence of catalyst and extracted (with acetonitrile and barium chloride) to the initial sulfur concentration in the gas oil used:

$$\text{Desulfurization efficiency (\%)} \\ = \frac{S_0 - S_1}{S_0} \times 100$$

Where  $S_0$  is the initial S-content and  $S_1$  is the final S-content after (ODS). The results indicate that the catalyst is efficient to remove sulfur from gas oil with the catalyst., they are listed on Table (6).

**Table (6): Results of The Removal Efficiency of Sulfur Compounds :**

Catalyst	Surface Area	Efficiency (%)
Cat- A	72.971	68.97
Cat- B	44.060	62.89

The results indicate that the increase in the removal efficiency of sulfur compounds is due to the increase in the surface area , and more active sites.

The effect of temperature on the removal efficiency of sulfur compounds is determined at temperature (30, 40 and 50) °C .The ODS reaction efficiency results versus the three different temperatures at a constant time using catalyst (Cat- A) are shown on Table (7). A rise of temperature from 30 to 40 °C leads to a large increase in the removal efficiency of sulfur , however, the increase in temperature from 40 to 50 °C is less effective . This means that the increase in the temperature above 50 °C is not effective in such reaction as reported in literature [10, 18] .

**Table (7) Results of the Desulfurization Process in Different Temperature Using Catalyst (Cat- A ) at 2 Hours.**

Experiment (no)	Temperature ( °C )	Efficiency (%)
1	30	16.14
2	40	51.78
3	50	56.39

Time is an important technical parameter for oxidation reactions, which reflects the oxidation reaction efficiency and determines the experimental time. As a whole , Table (8) shows that S-content in the gas oil decreases with the increase of reaction time ,while the efficiency of oxidative desulfurization (ODS) increases with the increase in reaction time.

**Table (8): Results of the Desulfurization Process in Different Times at 40 °C .**

Experiment (no)	Catalyst	Reaction Time (h)	Efficiency (%)
1	Cat- A	2	51.78
2	Cat- A	3	68.97

## Conclusions:

The present study describes the preparation of NiO - CoO catalysts by precipitation using different Ni – Co percentages. The catalysts are tested for the oxidative desulfurization of gas oil at selected parameters of oxidation temperature: 40 °C, oxidation time: 3 hours. The oxidized sulfur compounds are extracted by acetonitrile. NiO - CoO catalysts prepared by the precipitation technique show high activity towards sulfur removal. The high surface area , sufficient pore volume are the reasons for this activity which reached 68.97% .

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## تحضير وتمييز عامل مساعد ثنائي المعدن ( NiO –CoO ) لازالة الكبريت من زيت الغاز

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### الخلاصة:

تم تحضير عوامل مساعدة ثنائية المعدن من نوع NiO – CoO وبنسب مختلفة من الكوبلت والنيكل (70:30 و80:20) بطريقة الترسيب باستخدام نترات المعادن وشخصت العوامل المساعدة المحضرة بواسطة تقنيات الامتصاص الذري (AA) وحيود الاشعة السينية وقياس المساحة السطحية والحجم الحبيبي . اشارت النتائج الى ان أفضل العوامل المساعدة هي التي تحتوي على نسبة النيكل : كوبلت (70:30) . دللت التجارب ان أفضل الظروف لتحضير العامل المساعد هي الترسيب بدرجة حرارة 60 م<sup>0</sup> و pH تتراوح بين (8-9) ويتم التحميص عند درجة حرارة 400 م<sup>0</sup> لمدة ساعتين.

استخدمت هذه العوامل المساعدة المحضرة في عمليات الاكسدة لازالة الكبريت من زيت الغاز gas oil بوجود بيروكسيد الهيدروجين كعامل مؤكسد و حامض الخليك (co-catalyst) . دللت النتائج على أن العامل المساعد كان كفوءاً في ازالة الكبريت وتعتمد كفاءته على درجة الحرارة ، كمية بيروكسيد الهيدروجين وكمية المذيب المستخدم لأغراض الاستخلاص وأن الظروف المثلى لعملية الاكسدة هي : 3% من العامل المساعد و2 غرام من كربونات الصوديوم ، واستخدام محرك ميكانيكي سرعته 700 دورة بالدقيقة وبنسب زيت الغاز : بيروكسيد الهيدروجين 30% : حامض الخليك (10:1:5:0) اضافة الى استخدام استيونتريل للاستخلاص بنسبة (1:1) ثلاث مرات وكان زمن التصعيد ثلاث ساعات وبدرجة حرارة 40 م<sup>0</sup> . ولقد بلغت افضل ازالة للكبريت 68.97% .

**الكلمات المفتاحية:** العوامل المساعدة ثنائية المعدن ، Ni-Co ، نزع الكبريت، زيت الغاز.