

Preparation of bimetallic catalyst (Ni –Co)for deep oxidative desulfurization

تحضير عامل مساعد ثنائي المعدن (Ni –Co) لاستخدامه في ازالة الكبريت بطريقة الأوكسدة

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Abstract

A bimetallic catalyst Ni-Co / γ -Al₂O₃ was prepared by impregnation method . Characterized by atomic absorption (AA) technique and XRD diffraction. The surface area and pore volume was measured according to the BET method.

This catalyst was used in the oxidative desulfurization of gasoil in the presence of hydrogen peroxide H₂O₂ 30% as an oxidizing agent.

The results indicated that the catalyst was efficient to remove sulfur from gas oil depending on temperature, hydrogen peroxide H₂O₂ 30 % , solvent used for extraction.

The maximum observed sulfur removal reached 70.44%.

Keywords: Bimetallic Catalyst, Ni-Co / γ -Al₂O₃, Desulfurization, Gasoil.

الخلاصة

تم خلال البحث تحضير عامل مساعد ثنائي المعدن من نوع Ni-Co/ γ -Al₂O₃ بطريقة التشبييع وشخص بواسطة تقنيات الامتصاص الذري (AA) وحيود الاشعة السينية وقياس المساحة السطحية والحجم الحبيبي .

استخدم هذا العامل المساعد في عمليات الأوكسدة لإزالة الكبريت من زيت الغاز بوجود بيروكسيد الهيدروجين كعامل مؤكسد.

دلنت النتائج على أن العامل المساعد كان كفوءاً في ازالة الكبريت وتعتمد كفاءته على درجة الحرارة, وكمية بيروكسيد الهيدروجين وكمية المذيب المستخدم لأغراض الاستخلاص وانافضل ازالة للكبريت بلغت 70.44%.

الكلمات الدالة: العوامل المساعدة ثنائية المعدن , Ni-Co/ γ -Al₂O₃, نزع الكبريت، زيت الغاز.

Introduction:-

A catalyst is a substance that increases the rate of reactions , but is not itself consumed^[1].

A catalyst provides an alternative reaction pathway in which the activation barriers of a reaction are lowered and the reaction rate is increased. Generally, catalysts are classified into three main categories, namely: heterogeneous, homogeneous, and enzymatic (or biocatalysts). Catalysts are widely used in nature, in industry, and in the laboratory. It is estimated that more than 20 % of the gross national product of industrial countries depend on catalytic processes; thus catalysts play a major technological role in society covering a wide range of processes from biological reactions to large-scale production of bulk chemicals. Traditionally, a significant number of catalytic processes involve the use of transition-metal catalysts, particularly precious noble metals which are not prone to oxidation. Some of the most

common metals used for catalysis are Pd, Pt, Ru, Rh, Ni, and Cu. Thus, optimizing the usage of active materials has been a major aspect of catalyst optimization and thus many scientists have studied catalysis in order to take advantage of the higher surface areas exposed to the reactants^[1,2].

Sulfur enters our atmosphere as gaseous sulfur dioxide through the burning of fossil fuels such as diesel. Sulfur is also converted to sulfur trioxide (SO₃) and hydrogen sulfide (H₂S). Oxidative desulfurization of fuels is a matter of major interest not only because of increasing environmental concern. Sulfur dioxide SO₂ affects the environment, man-made structures, our health, and even the industries that generate the toxic gas. 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^[3].

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^[4].

Experimental Work:

Materials:

All reagents and solvents used were available commercially, nickel nitrate Ni(NO₃)₂.6H₂O, cobalt nitrate Co(NO₃)₂.6H₂O, activated alumina γ -Al₂O₃, 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 in table 1.

Table (1). 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:

Catalysts were prepared in various proportions and diagnosed by means of analysis. Catalyst Ni-Co / γ -Al₂O₃ was prepared according to impregnation methods, the wanted weight of activated alumina γ -Al₂O₃ was dried at 120 °C for 24 hours.

Prior to the impregnation process, individual standard solutions of Co (NO₃)₂ .6H₂O and Ni (NO₃)₂ .6H₂O were prepared, with concentration of 0.2 g metal ml⁻¹.

The 2nd Scientific Conference of the College of Science 2014

In the first impregnation step, 16 g of alumina was accurately weighted and wetted with 15 ml of distilled water. 5 ml of standard $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was then added to the wetted alumina, 15 ml of standard $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and more water added so that the total liquid added during the process was 60 ml, which was necessary for efficient and uniform stirring. Subsequently, the precipitation of metals was made through adjusting the pH value of the solution to (8-9) by adding a precipitating reagent solution using sodium

bicarbonate NaHCO_3 (1.0 M), the contents were continuously stirred during precipitation and the resulting slurry was stirred for 3 hours at 60°C , and then dried in an oven at 120°C for 24 hours. In the first 6 hours of drying, the catalyst was manually stirred every hour until most of the water was removed to maintain relative homogeneity of the slurry.

The catalyst was calcined at 400°C for 2 hours in air. Thermally unstable compounds in the catalyst are decomposed to oxides^[5-8].

Catalyst characterization:

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

Experimental Procedure and Analysis :

Catalyst activity was studied through its application in the process of oxidative desulfurization of gasoil which involves the following step :

Oxidative desulfurization procedure:

- 1- A sample 100 ml of gasoil (Al-Dura Refinery) was put in a round bottom flask with three-neck in water bath. The sample content of sulfur was of 1.407% .
- 2- The wanted weight (3) g of catalyst was previously added to the flask.
- 3- 10ml of 30% H_2O_2 as an oxidizing agent was added to the flask followed by 5ml of CH_3COOH as a co-catalyst.
- 4- The mixture was refluxed for 3 hours at 40°C temperature using a mechanical stirrer at moderate speed (700 rpm/minute), while stirring, 2g of Na_2CO_3 was dissolved in 20ml of distilled water and added to the mixture. At the end of reaction, the mixture was left at room temperature for 0.5 hour to attain phase separation .
- 5- The biphasic mixture was separated by extraction with acetonitrile and barium

chloride three times. Obviously a precipitate formed in the aqueous layer when BaCl_2 was added. This phenomenon suggests that the gasoil sulfur compounds are converted to SO_4^{2-} during the oxidation^[10,11].

- 6- The Gasoil phase was withdrawn and the concentration of the remaining sulfur compounds was determined by X-ray Fluorescence (XRF).

Results and Discussion:

Characterization of catalysts :

Catalysts were characterized by X-ray diffraction (XRD) using diffractometer with $\text{Cu K}\alpha$ radiation (1.5406 \AA ; 40 kv; 30 mA) and step scan technique was in 2θ range of 20 to 60° . The results of the X-ray diffraction of catalyst samples are shown in Table 2.

Table(2) Results of the X-ray diffraction:

sample	2 θ (deg.)	d(A ^o)	I/I ₀
Cat- B 1 Ni : Co : γ-Al₂O₃ 15: 5 : 80	37.5107	2.3957	100
	45.7428	1.9819	75
	48.9038	1.8609	38
	36.3867	2.4671	33
Cat- B 2 Ni : Co : γ-Al₂O₃ 14 : 6 : 80	37.5961	2.3905	100
	48.8693	1.8621	92
	45.0807	2.0094	77
	36.6614	2.4492	25

The results are in a good agreement with those reported in literature^[5]. The values of NiO /Al₂O₃ at (2 θ = 37° and 44.8°) and CoO/Al₂O₃ at (2 θ = 36.7°). The simple reason for the difference in the values is due to the different calcining temperature where it was at 400 °C in our research compared to 600 °C. The different values in literature^[9].

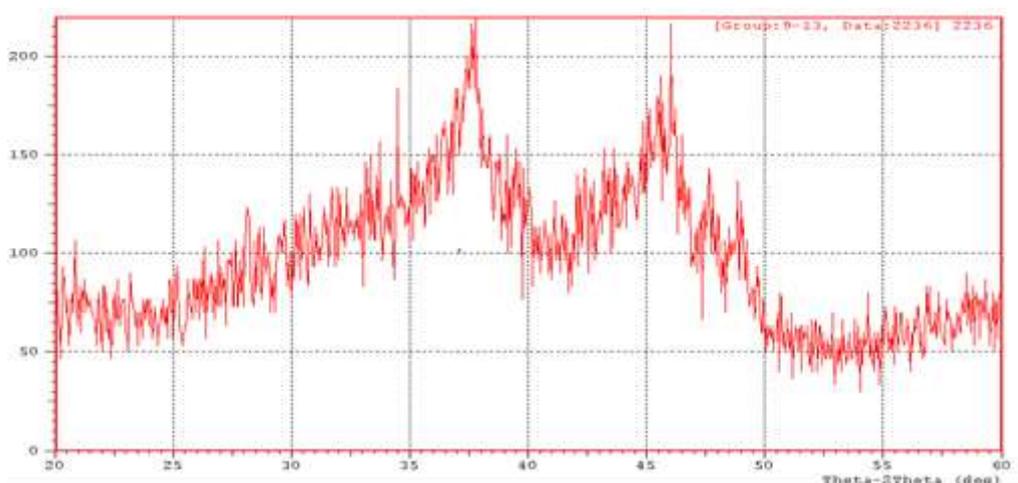


Figure 1 X-ray diffraction patterns of the Cat- B 1 Ni : Co : γ -Al₂O₃ (15: 5 : 80)

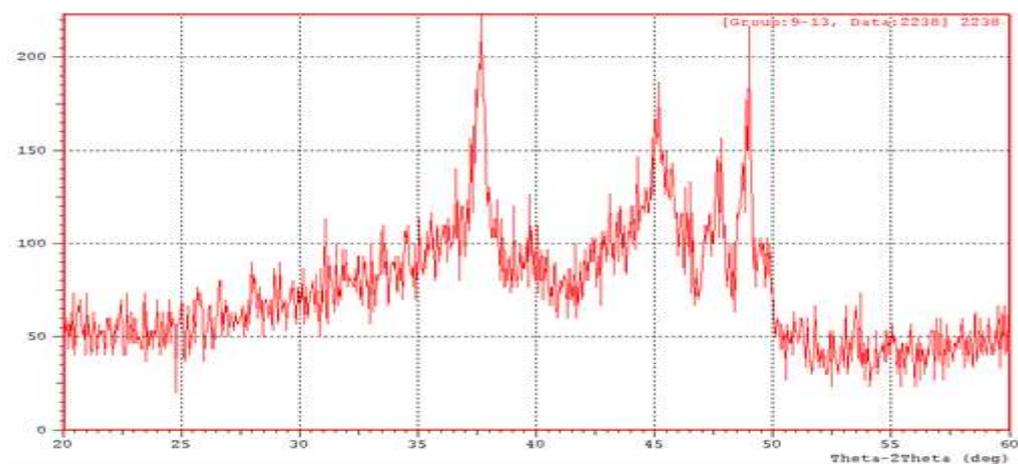


Figure 2 X-ray diffraction patterns of the Cat- B 2 Ni : Co : γ -Al₂O₃ (16: 4 : 80)

The specific surface area and pore volume were measured according to the BET method. The results of the pore volume and surface area of catalyst samples are shown in Table 3.

Table(3).Surface area and pore volumeresults:

Catalyst	Ratio Ni : Co : γ -Al ₂ O ₃	Surface area m ² /g	Pore volume cm ³ /gm.
Cat- B 1	15: 5 : 80	219.697	0.512
Cat- B 2	14 : 6 : 80	215.108	0.171

Chemical analysis was conducted to catalysts Ni-Co / γ -Al₂O₃ to determine the percentages of the elements nickel and cobalt components of these catalysts Ni-Co / γ -Al₂O₃ depending on the atomic absorption technique. The results are listed in Table4

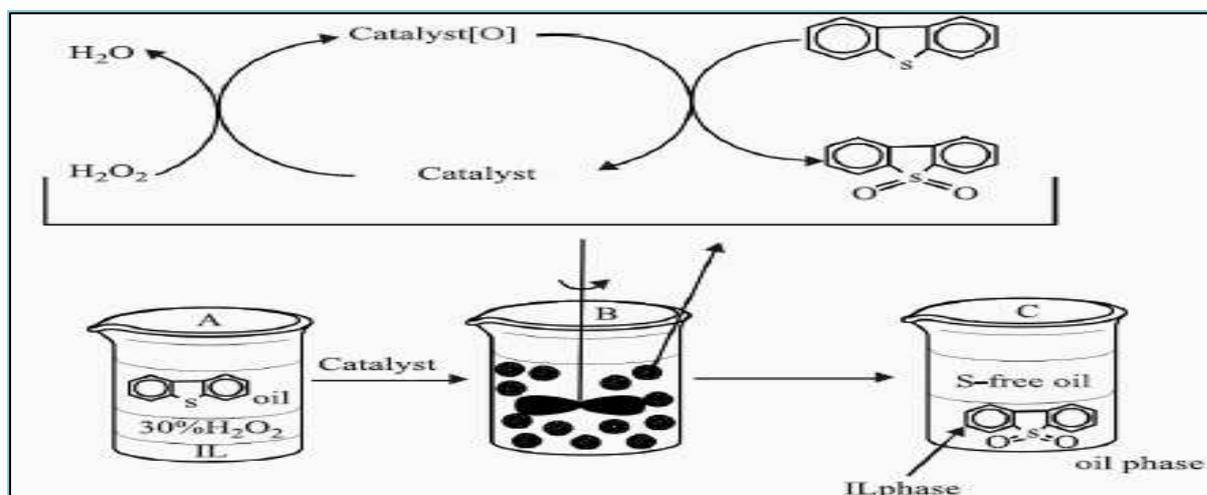
Table (4) Percentages of nickel and cobalt elements and oxides composing the catalyst Ni-Co / γ -Al₂O₃.

Catalyst	Ni%	NiO%	Co%	CoO%	γ Al ₂ O ₃ 80% Weight taken (g)	Total ratio of NiO%+CoO%
Cat- B 1 Ni : Co : γ -Al ₂ O ₃ 15: 5 : 80	2.612	3.32	0.318	0.40	16	3.72
Cat- B 2 Ni : Co : γ -Al ₂ O ₃ 14 : 6 : 80	0.916	1.166	0.583	0.741	16	1.907

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 .



Scheme 1. Mechanism of the oxidation of dibenzothiophene.

Also the mechanism can be represented as in the following scheme, which shows the effect of catalyst that takes (O) from the oxidizing agent (H₂O₂) giving this (O) to oxidize the sulfur compounds into SO₂.

This (ODS) method, showing more energy efficient, cost effective and environment friendly in comparison with other (ODS) methods reported in literature^[4] and 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 was calculated as the ratio of sulfur concentration that was oxidized in presence of catalyst and extracted (with acetonitrile and barium chloride) to the initial sulfur concentration in the gasoil that used.

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

Where S₀ was the initial S-content and S₁ was the final S-content after (ODS). The results indicate that the catalyst was efficient to remove sulfur from gas oil with the catalyst and they are listed in Table 5.

Table (5) Results of the removal efficiency of sulfur compounds:

Catalyst	Efficiency %
Cat- B 1 (Ni : Co : γ -Al ₂ O ₃) (15: 5 : 80)	70.44
Cat- B 2 (Ni : Co : γ -Al ₂ O ₃) (14: 6 : 80)	54.51

Conclusions:

The present study describes the preparation of Ni-Co / γ -Al₂O₃ catalysts by impregnation using different Ni-Co loadings. The catalysts were tested for the oxidative desulfurization reaction of gas oil at selected parameters of oxidation temperature: 40⁰C, oxidation time: 3 hours. The oxidized sulfur compounds were extracted with acetonitrile. Ni-Co / γ -Al₂O₃ catalysts prepared by the impregnation technique showed high activity towards sulfur removal. The high surface area, sufficient pore volume are the reasons for this activity which reached 70.44%.

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