

## Research Article

# Extraction of Nanosized Cobalt Sulfide from Spent Hydrocracking Catalyst

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The processes used for the extraction of metals (Co, Mo, and Al) from spent hydrotreating catalysts were investigated in this study. A detailed mechanism of the metal extraction process is described. Additionally, a simulation study was performed to understand the sulfidizing mechanism. The suggested separation procedure was effective and achieved an extraction of approximately 80–90%. In addition, the sulfidization mechanism was identified. This sulfidizing process for Co was found to involve an intermediate, the structure of which was proposed. This proposed intermediate was confirmed through simulations. Moreover, the activities of the spent and the regenerated catalyst were examined in the cracking of toluene. The modification of the spent catalyst through the use of different iron oxide loadings improved the catalytic activity.

## 1. Introduction

In the past, oil refining companies used to dispose of spent catalysts by burning off the entrained carbon, sulfur, and hydrocarbons. The resulting material could then be sold to iron and steel producers as a relatively inexpensive source of cobalt, molybdenum, and nickel. This method started to lose favor in the 1970s, when refiners stopped using the stripping step due to the increasing costs involved. Unfortunately, sulfur is not favored by steel makers because of the problems it causes, and they also do not like carbon in the form in which it is found in spent catalysts. As a result, untreated spent catalysts were no longer of value to smelters; thus, instead of being usable waste, the spent catalysts were encapsulated by the oil refining companies before being sent to landfills.

These techniques were universally banned by the mid-1980s because these catalysts contributed to the environmental pollution of air, soil, and oceans. Thus, the contamination of these environments by these catalysts became a serious global problem. A recent memorandum by the U.S.

Environmental Protection Agency (EPA) stated that spent catalysts are hazardous waste. As a result, the improper classification of such catalysts could become a litigation nightmare for refiners. Therefore, in November 1999, the EPA clarified the referenced memorandum to characterize spent hydroprocessing catalysts as hazardous waste subject to the regulations mandated by the Resource Conservation and Recovery Act (RCRA) subtitle C (2).

As a result, some spent catalysts may soon be classified as hazardous toxic waste, which means that these catalysts will require additional treatment to comply with the required strict controls for their handling and disposal [1]. Moreover, molybdenum and cobalt are in high demand for use in alloy steel, aircraft parts, armor, industrial motors, filaments, and various grades of pigments [2, 3]. Due to the increasing demand for these metals in the industrial market, many approaches, including acid leaching sulfidization, have been suggested for the recovery of these metals from spent catalysts [4, 5]. Additionally, bioleaching processes have been used by many researchers [6–10] for the extraction of metals, such as

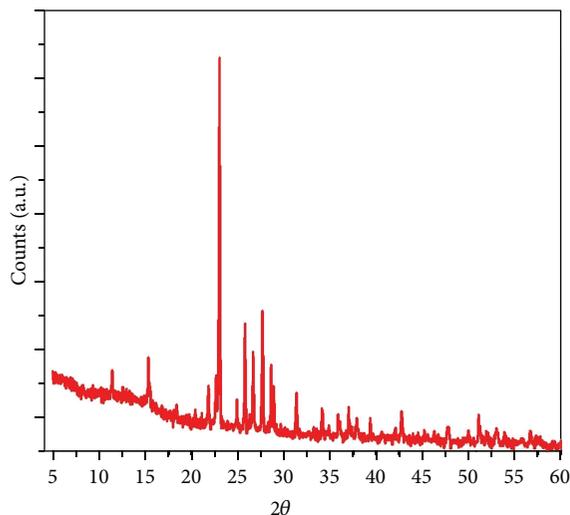


FIGURE 1: XRD of cobalt sulfide sample.

TABLE 1: Concentration of oxalic acid used in the extraction.

Oxalic acid/spent catalyst (mole/g)	% Remaining undissolved solid
0.02	40
0.05	20
0.075	15.5
0.1	0.0

TABLE 2: Extraction analysis of Spent catalyst and Extracted metal oxide.

Sample	Wt%			% Extraction
	Co <sub>3</sub> O <sub>4</sub>	Mo <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	
Spent catalyst	6.5	16.9	76.6	
Co as cobalt sulfide	5.9	—	—	90.7
Mo as molybdenum oxalate	—	13.7	—	81.06
Al as Al <sub>2</sub> O <sub>3</sub>	—	—	74.8	97.65

TABLE 3: EDX analysis of Spent catalyst and Cobalt Sulfide sample.

Sample	Co	Mo	Al	O	C	S
Spent catalyst	2.71	4.15	50	41.4	1.74	0
Cobalt sulfide	16	0	0.42	36.56	29.89	17.13

Mo, Ni, Co, and V, from a variety of spent petroleum catalysts. In these cases, sulfur-oxidizing bacteria play a significant role in the enhancement of the metal leaching efficiencies of the process [11]. However, the main disadvantage of the bioleaching process is that it is very slow compared with other leaching processes.

Cobalt usually forms diverse binary sulfides with the general formula of CoS<sub>x</sub>, for example, Co<sub>9</sub>S<sub>8</sub>, CoS, Co<sub>3</sub>S<sub>4</sub>, Co<sub>1-x</sub>S, Co<sub>2</sub>S<sub>3</sub>, and CoS<sub>2</sub>. These binary sulfides have attracted

attention as a result of their excellent properties and their potential use in the hydrodesulfurization and hydrodearomatization processes that are used in various industrial fields [12]. Of these cobalt sulfides, Co<sub>3</sub>S<sub>4</sub> (linnaeite) has a normal spinel structure (space group *Fd3m*) in which Co atoms occupy both the tetrahedral (A) and the octahedral (B) sites. It has been reported that Co<sub>3</sub>S<sub>4</sub> exhibits an antiferromagnetic (AF) order of less than TN= 58 K [11]. Conventionally, cobalt sulfide powders are prepared using solid-state methods. For instance, cobalt sulfide can be produced by the reaction of cobalt with either sulfur [13, 14] or hydrogen sulfide [15] or by the reaction of cobalt monoxide with hydrogen sulfide [16]. To date, many researchers have attempted to prepare metal sulfide nanocrystallites using a solution-phase method [17–21], which allows the exact modulation (i.e., size, shape, and composition at the nanometer scale) of the resultant nanocrystals. Co<sub>9</sub>S<sub>8</sub> and CoS<sub>2</sub> have been selectively fabricated by the reaction of cobalt chlorides and sodium polysulfide via a toluene thermal process [22], and CoS has been synthesized from the reaction of amorphous cobalt sulfide in a hydrazine solution at 120°C [23].

In this paper, we will examine the mechanisms by which metals, particularly cobalt sulfide, are extracted from spent catalysts using different techniques, including simulation programs.

## 2. Experimental

**2.1. Materials and Methods.** Spent catalysts that had been used in the re-refining of waste lube oil for 10 years (life time) were obtained from a local petroleum company. The following chemicals were used in this study: oxalic acid (molecular weight = 126.07; Min. assay 99.5%), ammonium hydroxide solution (Min. assay 33%), hydrochloric acid (Min. assay 30%), ferrous sulfide, and ammonium chloride (Min. assay 33%).

### 2.2. Pretreatment of the Catalyst

**2.2.1. Catalyst Washing.** The layers of petroleum derivatives contaminating the spent catalyst were washed with different organic solvents (e.g., ethanol and benzene).

The washed catalyst was heat treated in air to eliminate the carbon and sulfur atoms as CO<sub>2</sub> and SO<sub>2</sub>, respectively [24]. The temperature was first raised from 100 to 350°C at a rate of 50°C/h. The product was then maintained at 350°C for 1 h, after which the temperature was increased to 450°C at a rate of 25°C/h. The product was then maintained at this temperature for 24 h.

**2.2.2. Extraction Process.** Five grams of the washed spent catalyst was added to 500 mL of 1M oxalic acid at 100°C. The mixture was then maintained at this temperature and stirred for 3 hours. The dissolved catalyst in the solution contains cobalt oxalate, molybdenum oxalate, and aluminum oxalate. To separate the individual metal salts, an aqueous NH<sub>3</sub> solution containing NH<sub>4</sub>Cl was added to the mixture to precipitate the group (III) metals as hydroxides, that

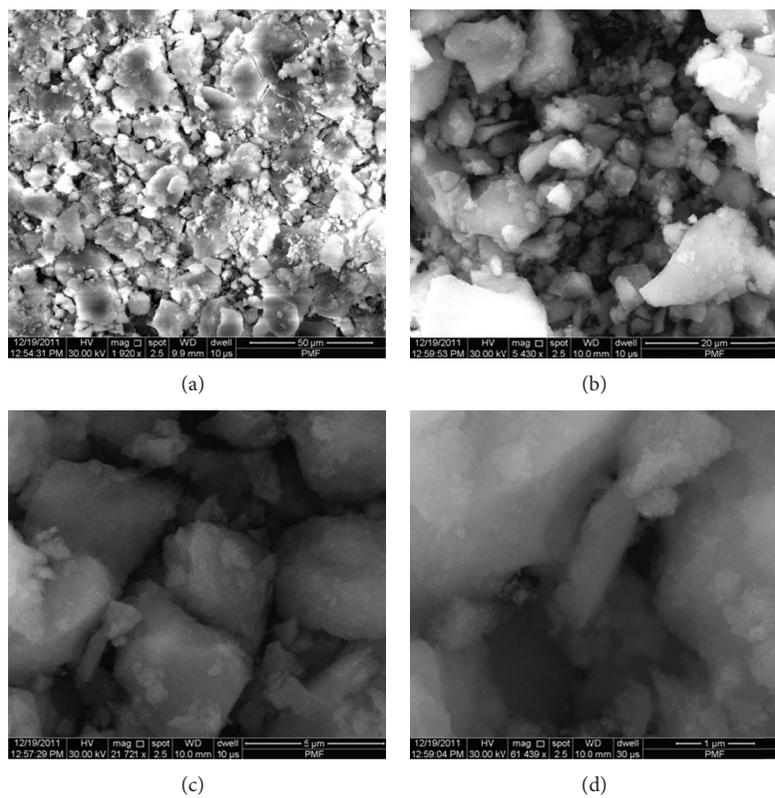


FIGURE 2: SEM images of spent catalyst at different magnifications.

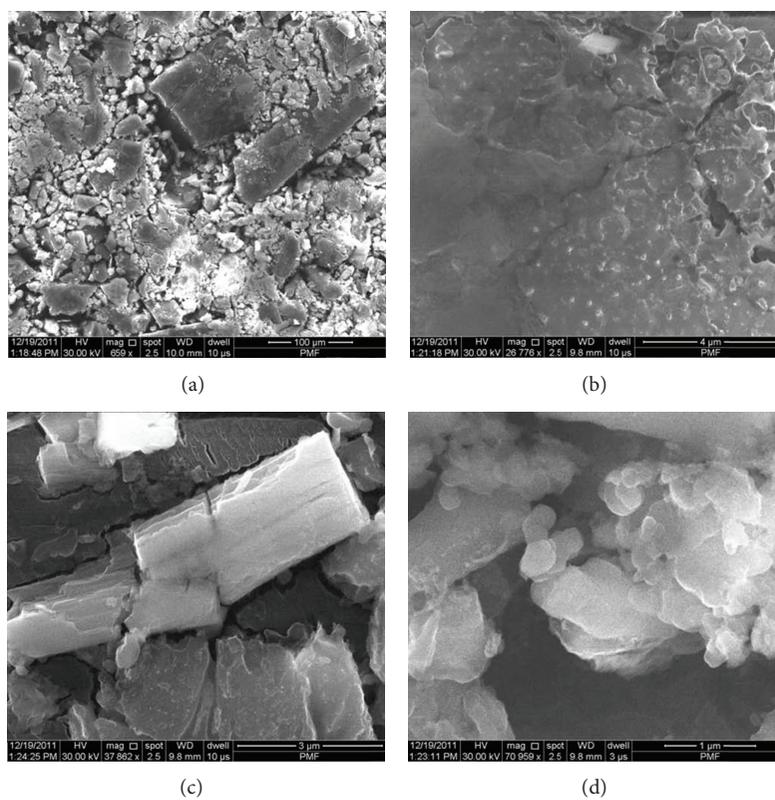


FIGURE 3: SEM image of extracted CoS.

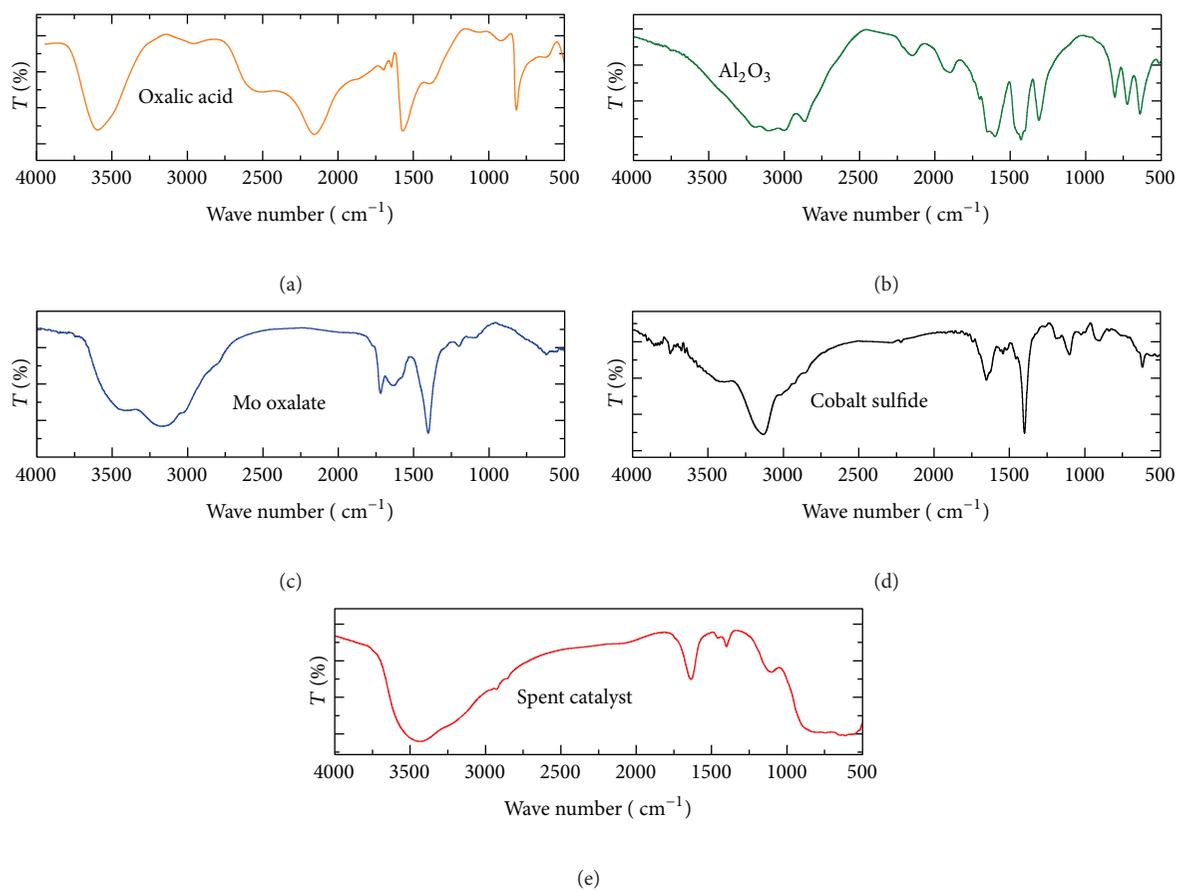
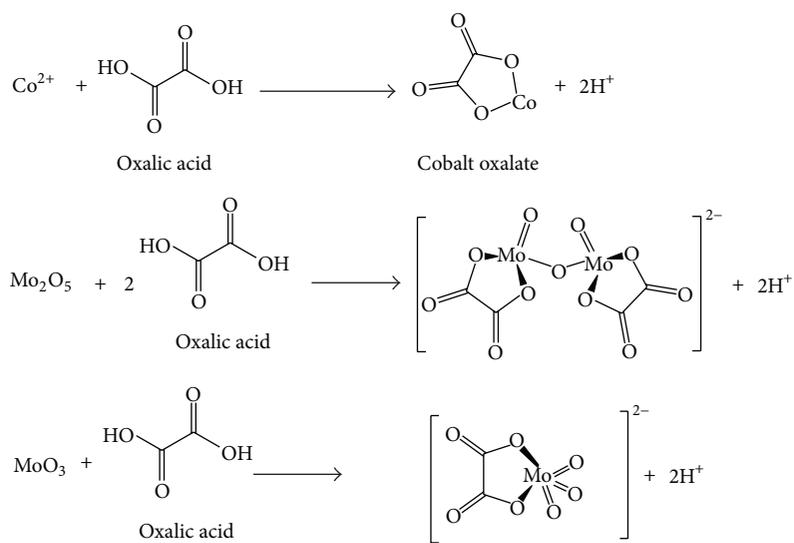
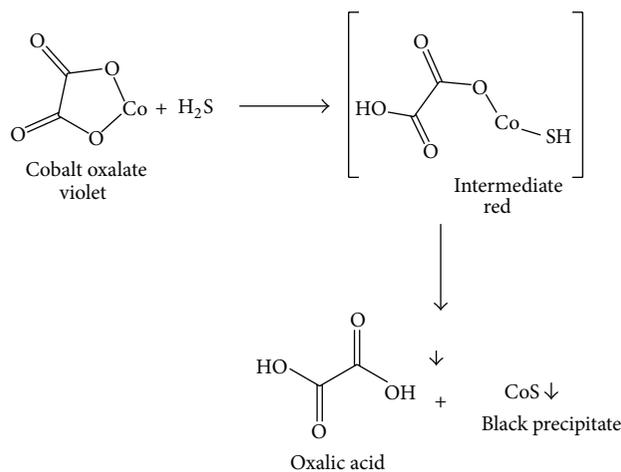


FIGURE 4: Infrared spectra of spent and all extracted metals.



SCHEME 1



SCHEME 2

is,  $\text{Al}(\text{OH})_3$ . The resulting white gelatinous precipitate was calcined at  $1000^\circ\text{C}$  to convert it into  $\text{Al}_2\text{O}_3$ . The separation of Co as CoS was performed by passing  $\text{H}_2\text{S}$  gas through the solution. The residual solution containing Mo oxalate was precipitated as white crystals.

The concentrations used and the corresponding solubility of the metals are shown in Table 1.

### 2.3. Catalyst Characterizations

**2.3.1. XRD (X-Ray Diffraction Analysis).** X-ray diffractograms of the samples under investigation were collected using a Bruker D8 advanced instrument with  $\text{CuK}\alpha 1$  radiation and a secondary monochromator, which was operated at 40 kV and 40 mA. The analyses of the crystal lattice and space group were performed using Philips X'Pert Plus V. 1.0 23.04. 1999.

**2.3.2. SEM and EDX Analysis.** The scanning electron microscopy (SEM) images of the different samples and the EDX analysis were performed using a JXA-840 Electron Probe Microanalyzer (Japan).

**2.3.3. Elemental Analysis.** The elemental analysis was performed using an inductively coupled plasma (ICP) optical emission spectrometer (Model Optima 4100 DV, Perkin Elmer, USA).

**2.3.4. Simulation Study.** The simulations were performed using the HyperChem 8 software. The energy optimization and calculations were performed based on the PM3 method.

## 3. Results and Discussion

**3.1. XRD.** The XRD patterns of the spent catalyst and most of the extracted metal solid samples show that these are amorphous (data not included), likely because most of the samples were not calcined at high temperatures. Only

the cobalt sulfide samples exhibited a detectable crystalline pattern (Figure 1), which belongs to the sulfur metal phase ( $\text{S}_8$ ; PDF card no. P741465). This finding can be explained by the fact that the cobalt present in the sample promotes the formation of  $\text{S}_8$ .

**3.2. SEM and EDX.** SEM images of the spent catalyst at different magnifications are presented in Figure 2, whereas Figure 3 shows an image of CoS at different magnifications.

These images show that the spent catalysts appear as separate aggregates in an amorphous matrix. This finding can be rationalized by the elemental analysis of the spent catalyst, which shows that it is composed of 76.6 wt%  $\text{Al}_2\text{O}_3$  (Table 2).

Moreover, the images of the cobalt sulfide sample (Figure 3) showed unidentified agglomerated shapes of cobalt sulfide. A tetragonal shape could be observed as a single separate phase, which could be assigned to the same  $\text{S}_8$  crystal structure that is shown in the XRD patterns.

In addition, the image analysis revealed that the average particle size of CoS is approximately 90 nm.

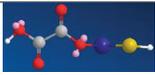
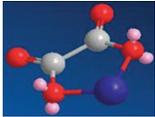
The EDX analyses shown in Tables 2 and 3 reveal that the spent catalyst contains, in addition to Co, Mo, and Al, small amounts of C; this finding was confirmed with the IR spectra.

The EDX analysis of the cobalt sulfide sample showed that, in addition to Co and S, the sample contains very small amounts of Al and the expected amount of C. This result may be due to the adsorption of oxalic acid on the cobalt centers, as will be described in the analysis of the IR spectra.

**3.3. Infrared Spectra.** The infrared spectra of the spent catalyst and all of the extracted metals are shown in Figure 4 and are compared with the IR spectrum of oxalic acid.

The IR spectra of the extracted samples clearly show that some organic matrix was still adsorbed onto the samples. This matrix includes oxalic acid because the characteristic carbonyl peak ( $\text{C}=\text{O}$ ) of oxalic acid at  $1650\text{ cm}^{-1}$  appeared in nearly all of the samples. In addition, the spent catalyst itself

TABLE 4: Data used for the simulation of the cobalt oxalate sulfide intermediate.

Structure	Name	Energy (KJ/mol)	Simulated visible absorption Wavelength
	Carboxy aronyloxy mercapto (cobalt intermediate)	-1188.7	582.49 nm
	Cobalt oxalate	-919.04	382.84 nm
	Cobalt sulfide	-1911.836	—

The red shifted wavelength of the intermediate indicates that it is responsible for the change in color from violet to red.

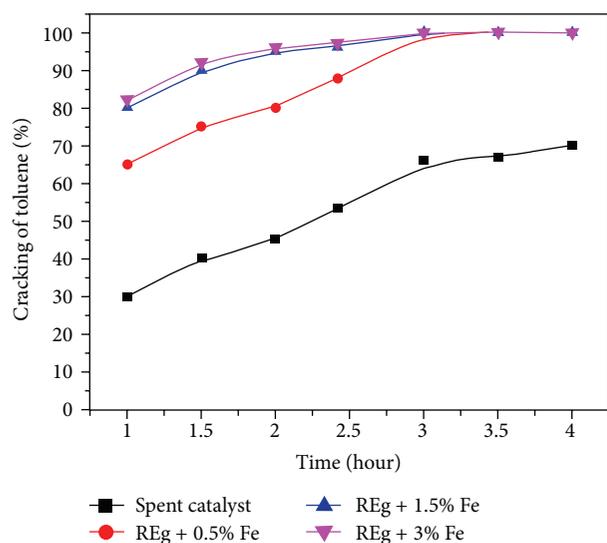


FIGURE 5: Catalytic activity of the spent catalyst with different iron oxide loadings in the cracking of toluene.

contains a trace C=O peak, which may be due to the oxidation of the deposited coke on its surface during calcination.

**3.4. Catalytic Activity.** The effects of the loading of 0.5%, 1.5%, and 3% iron on the regenerated catalyst were tested in the cracking of toluene. To achieve this, 100 mL of toluene and 1 g of the loading catalyst samples were heated at 100°C for 4 h. The reaction product was then subjected to GC.

**3.5. Extraction Mechanism and Sulfidization of Co.** The extraction procedure depends on the formation of soluble oxalate complexes or compounds of all of the metals. The metals under investigation are Al, Co and Mo.

The equations in Scheme 1 represent the compounds and complexes formed by these metals.

Based on these equations, it is clear that oxalic acid forms soluble simple salts with Al and Co and oxocomplexes with Mo. In Scheme 1, we allowed for the possibility that both Mo(V) and Mo(VI) complexes can be formed.

The extraction method described in the experimental section leads to the precipitation of Al as Al(OH)<sub>3</sub> and the separation of Mo as oxalate complexes. In contrast, Co is subjected to sulfidization by H<sub>2</sub>S. During this process, the color change from violet to red is followed by the formation of a black precipitate. The mechanism in Scheme 2 was assumed.

**3.6. Mechanism of the Precipitation of CoS.** The mechanism in Scheme 2 assumes that cobalt oxalate, which exhibits a violet color, is formed first. As a result of the subsequent reaction with H<sub>2</sub>S, a mercapto intermediate with a red color is formed and precipitated as CoS (black precipitate).

A simulation of the energy and electronic spectra of cobalt oxalate, cobalt sulfide, and the proposed intermediate was performed to prove the previous mechanism (Table 4).

Cracking activity toward toluene was shown in Figure 5. Figure 5 compares the catalytic activity of the spent catalyst with different loadings of iron oxide in the cracking of toluene. The curve demonstrates that the addition of iron oxide enhanced the catalytic activity of the spent catalyst. Moreover, the results show that the activity of the spent catalyst does not exceed 70% even after 4 hours. In contrast, the addition of 0.5 wt% iron oxide enhanced the catalytic activity to 100% after 3 hours. An additional increase in the loading of iron resulted in an increase in the catalytic activity of the spent catalyst. However, the addition of 1.5 wt% iron oxide resulted in almost the maximum increase that was observed; the addition of higher amounts of iron oxide resulted in only a slight excess in the catalytic activity of the catalyst.

These results show that the spent catalyst can be used for other purposes. Accordingly, its reuse instead of disposal could be an environmentally friendly alternative. The addition of a small amount of a different metal oxide, such as iron oxide, can enhance its catalytic activity, which maximizes the benefit of the spent catalyst.

## 4. Conclusions

The following conclusions can be drawn from this study.

- (1) Oxalic acid efficiently dissolves the studied spent catalyst at a concentration of 0.1 mol per gram of catalyst.

- (2) A mechanism for the sulfidization of cobalt was proposed, and an intermediate was identified and confirmed.
- (3) All of the metals were able to adsorb oxalic acid.
- (4)  $S_8$  is formed during the precipitation of cobalt sulfide.
- (5) In addition to the economic benefits of the extraction of metals from the spent catalyst, CoS itself can catalyze many reactions.
- (6) The use of the spent catalyst as a catalyst for the removal of an industrial pollutant, such as toluene, was successfully performed.
- (7) The catalytic activity of the spent catalyst in the cracking of toluene was enhanced by the simple impregnation of iron over the spent catalyst. The resulting iron-loaded catalyst exhibited high performance and good catalytic activity (the resulting activity reached almost 100%).

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