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Characterization of Cobalt Oxalate Dihydrate Obtained from Spent Co-Mo/Al_2O_3 Hydrodesulfurization Catalyst

Ahmet Orkun KALPAKLI*[1]

Abstract

In this study, roasted spent Co-Mo/Al_2O_3 hydrodesulfurization (HDS) catalyst was dissolved in oxalic acid ($H_2C_2O_4$) solution and optimum conditions were determined for obtaining cobalt oxalate dihydrate ($CoC_2O_4 \cdot 2H_2O$). The thermal decomposition behavior of the obtained $CoC_2O_4 \cdot 2H_2O$ was investigated by TG/DTG-DTA analysis. The characterization of $CoC_2O_4 \cdot 2H_2O$ was carried out by XRD, FT-IR and SEM-EDS analytical techniques. Optimum conditions for the production of $CoC_2O_4 \cdot 2H_2O$ were determined as 25 ^{o}C temperature, 0.25 M $H_2C_2O_4$ concentration, 1/20 g mL^{-1} solid/liquid ratio and 300 rpm stirring speed. $CoC_2O_4 \cdot 2H_2O$ was obtained with a reaction yield of 90.9 %. TG/DTG-DTA analysis carried out in dry air atmosphere showed that $CoC_2O_4 \cdot 2H_2O$ decomposed in two steps. In the first step that occurs between 118-196 ^{o}C temperatures, $CoC_2O_4 \cdot 2H_2O$ is dehydrated. In the second step, which occurs between 248-279 ^{o}C temperatures, it was determined that metallic cobalt was formed first, and then metallic cobalt was oxidized and converted into Co_3O_4 compound because it was performed in the air atmosphere.

Keywords: Hydrodesulfurization catalyst, cobalt oxalate dihydrate, cobalt oxide, characterization.

1. INTRODUCTION

Hydrodesulfurization (HDS) is a catalytic chemical process applied to remove sulfur from natural gas and refined petroleum products (petroleum, jet fuel, fuel oil, gasoline). The purpose of removing sulfur is to reduce the SO_2 emissions that are released during the use of natural gas and petroleum products. In the HDS process, catalysts containing Mo, Co, Ni and V are used on γ-Al_2O_3 substrate. The catalysts used in the process can be regenerated and reused, but after a certain number of regenerations, they become waste [1, 2]. The disposal or storage of spent catalysts requires compliance with strict environmental regulations. Spent HDS catalysts are classified as hazardous waste by the US Environmental Protection Agency (EPA) [3].

HDS catalysts account for one-third of the world’s catalyst consumption. The generation of spent HDS catalyst is estimated to be 1-1.2x10^{5} tons per year around the world [4, 5]. Recovery of metals from spent catalysts has become more important in recent years. Metal recycling is crucial not only for metal recovery, but also for making waste catalysts

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harmless to the environment [3]. Spent HDS catalysts are an important secondary source in the production of molybdenum, nickel and cobalt [6, 7]. Alkali or acidic leaching is generally used for metal recovery from spent catalysts [8- 10]. Precious metals dissolved by leaching are recovered by solvent extraction or precipitation processes [11- 14]. Before the leaching process, oxidative roasting is applied to remove the volatile components and sulfur in the spent catalyst in order to increase the leaching efficiency and prevent possible secondary reactions [15- 17].

Spent Co-Mo/Al_2O_3 HDS catalysts contain 10-15 % Mo, 2-4 % Co, 25-30 % Al and very low amounts of P, Si, Fe and Ca. The remaining part consists of volatile components and sulfur [18, 19].

In the literature, there are many studies on the leaching of spent Co-Mo/Al_2O_3 HDS catalysts with acidic and basic solutions. By using H_2SO_4 [18, 20, 21], HNO_3 [19], HCl [12], H_2SO_4-HNO_3 mixture [6], first Na_2CO_3, then H_2SO_4 solutions (two stage alkali-acid leaching) [22, 23] and NaOH [21], Co and Mo in Co-Mo/Al_2O_3 HDS catalyst can be dissolved with high efficiency. However, these leaching agents are more expensive and require more safety precautions compared to organic acids. Therefore, the use of organic acids as a leaching agent provides advantages. Oxalic acid is a strong organic acid and oxidizer, cheaper and has good chelating properties [24].

Cobalt oxalate has two hydrated crystal forms, $CoC_2O_4{\cdot}4H_2O$ and $CoC_2O_4{\cdot}2H_2O$. $CoC_2O_4{\cdot}4H_2O$ dehydrates to $CoC_2O_4{\cdot}2H_2O$ at low temperatures such as 7-8 ^oC. $CoC_2O_4{\cdot}2H_2O$ crystallizes in β-form orthorhombic crystal structure and then recrystallizes into α-form monoclinic crystal structure which thermodynamically stable [25].

No study has been found in the literature on the production of $CoC_2O_4{\cdot}2H_2O$ from Co-Mo/Al_2O_3 HDS catalyst. Therefore, this study was the first study in which $CoC_2O_4{\cdot}2H_2O$ was obtained from Co-Mo/Al_2O_3 HDS catalyst. Ilhan obtained nickel oxalate dihydrate ($NiC_2O_4{\cdot}2H_2O$) from the spent Ni-Mo HDS catalyst and carried out its characterization [26].

In this study, roasted spent Co-Mo/Al_2O_3 HDS catalyst was dissolved in 0.25 M $H_2C_2O_4$ solution at 4 different temperatures (25, 40, 55 and 70 ^oC) and optimum conditions were determined for obtaining $CoC_2O_4{\cdot}2H_2O$. The characterization of the obtained $CoC_2O_4{\cdot}2H_2O$ was carried out using XRD, FT-IR, SEM-EDS and TG/DTG-DTA analysis techniques and its thermal decomposition behavior was investigated.

2. EXPERIMENTAL

Spent Co-Mo/Al_2O_3 HDS catalyst was obtained from a refinery. Co-Mo/Al_2O_3 HDS catalyst is cylindrical in shape, 1.2 mm in diameter and 1.3 mm in length. The CHNS analysis (Thermo Finnigan Flash EA 1112) of the catalyst was carried out to determine the amount of volatile compounds. Catalyst was heated to 500 °C with a heating rate of 5 °C min^{-1} and roasted for 4 h in a dynamic air atmosphere in a tube furnace (Lenton) in order to convert sulfur compounds into oxidized compounds and to remove volatile compounds. Air was passed through the system during the roasting process. XRF analysis (PANalytical Axios Minerals) was carried out to quantitatively determine the chemical composition of the roasted catalyst. XRD analysis (Rigaku D/Max-2200, Cu-Kα monochromatic X-Ray) was performed to determine the phases in the samples. Experiments for the production of $CoC_2O_4{\cdot}2H_2O$ from spent Co-Mo/Al_2O_3 HDS catalyst were carried out in a water–heated, jacketed borosilicate glass reactor system (HWS) having a volume of 500 mL. 25 g of spent Co-Mo/Al_2O_3 HDS catalyst (solid/liquid ratio: 1/20 g mL^{-1}) sample were dissolved using 300 rpm stirring speed in 0.25 M, 500 mL of oxalic acid ($H_2C_2O_4$) solution at 25, 40, 55 and 70°C temperatures. $H_2C_2O_4$ solutions used in the experiments were prepared using anhydrous $H_2C_2O_4$ (Fluka). The acid solution in the reactor was heated to the experimental temperature and the sample was added to the reactor when isothermal conditions were obtained. Solutions were taken from the reactor at certain time intervals and dissolved elements were analyzed quantitatively by inductively coupled plasma–optic emission spectroscope (ICP-OES) (Spectro Ciros Vision). After the experiments were completed, the reactor contents were taken into a beaker. Solid/liquid separation was carried out by filtering the contents of the beaker through a G-4 Gooch crucible. It was observed that the solid material contained a different material in light pink color with a very fine particle size in addition to the granular leach residue. This solid material was collected from the bottom of the Gooch crucible with a spatula, dried in an oven at 105 °C for 3 h. The characterization of the obtained solid was carried out using XRD, TG/DTG-DTA (TA SDT Q600), FT-IR (Perkin Elmer Spectrum 100), SEM (Jeol JSM 5600), EDS (iXRF 500) and ICP-OES analytical techniques.

3. RESULTS AND DISCUSSION

a.Spent Co-Mo/Al_2O_3 HDS Catalyst

CHNS analysis of the spent Co-Mo/Al_2O_3 HDS catalyst sample is shown in Table 1. Quantitative analysis results show that the catalyst contains high sulfur content. It is seen that the total amount of volatile material in the catalyst is 19.43 %.

The results of XRF analysis of Co-Mo/Al_2O_3 HDS catalyst applied oxidative roasting at 500 °C for 4 h are given in Table 2. The catalyst contains 35.13 % Al, 16.66 % Mo and 3.71 % Co. The fact that the amount of S was determined as 0.004 % indicates that the roasting process was carried out successfully. The XRD diagram of the spent Co-Mo/Al_2O_3 HDS catalyst (Figure 1) applied to the oxidative roasting process includes the peaks of the Al_2O_3 (ICDD No: 050-0741), MoO_3 (ICDD No: 005-0508), Co_3O_4 (ICDD No: 009-0418) and $AlPO_4$ (ICDD No: 003-0447) phases.

Table 1 CHNS analysis of spent Co-Mo/Al_2O_3 HDS catalyst

Element	C	H	N	S
Wt. (%)	5.92	1.12	0.59	11.80

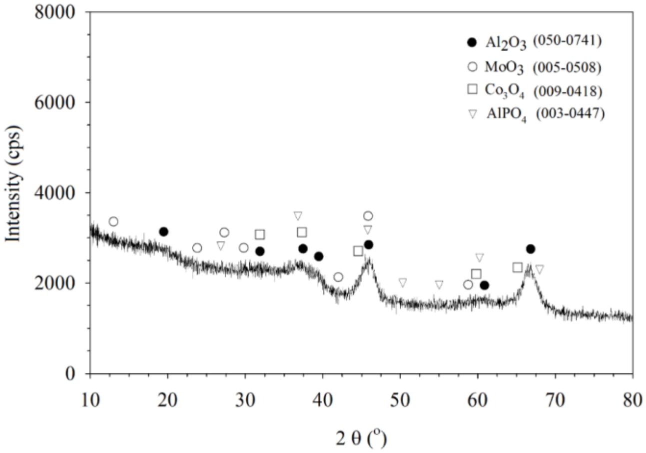

Figure 1 XRD diagram of Co-Mo/Al_2O_3 HDS catalyst oxidative roasted

Table 2 Elemental analysis of oxidative roasted Co-Mo/Al_2O_3 HDS catalyst

Element	Al	Mo	Co	P	Si	Fe	Ca	S
Wt. (%)	35.131	16.656	3.706	1.170	0.312	0.104	0.041	0.004

b.Characterization of Cobalt Oxalate Dihydrate Produced from Spent Co-Mo/Al_2O_3 HDS Catalyst

In order to determine optimum conditions for the production of cobalt oxalate dihydrate from spent Co-Mo/Al_2O_3 HDS catalyst, dissolution experiments were carried out in 0.25 M $H_2C_2O_4$ solution at 300 rpm stirring speed at different temperatures. In these experiments, the results obtained from the % Co extraction - time diagrams drawn by using the ICP-OES analysis results of the solutions taken from the reactor at different times (Figure 2), showed that the optimum conditions for the production of cobalt oxalate dihydrate ($CoC_2O_4{\cdot}2H_2O$) were 25 ^oC temperature, 0.25 M $H_2C_2O_4$ concentration, 1/20 g mL^{-1} solid/liquid ratio and 300 rpm stirring speed. Therefore, solid material obtained from the experiment performed under these conditions was used in the characterization analyses.

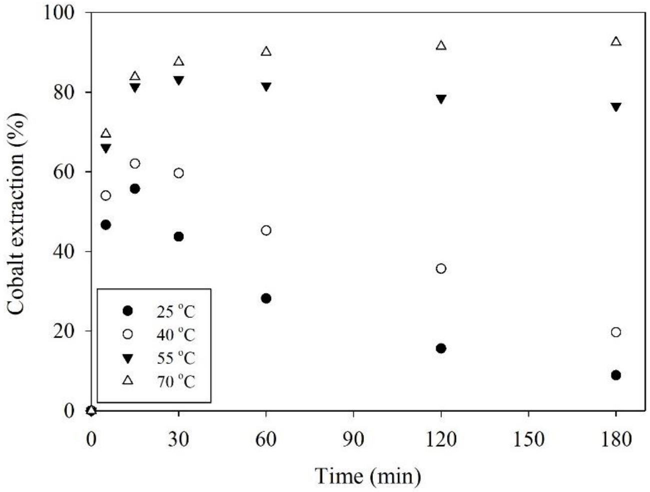

Figure 2 Cobalt extraction (%) – time diagram obtained by dissolving oxidative roasted Co-Mo/Al_2O_3 HDS catalyst in oxalic acid (Sample: 25 g, $H_2C_2O_4$ solution: 0.25 M, 500 mL, stirring speed: 300 rpm)

When the cobalt extraction (%) - time diagrams are examined, it is seen that the amount of cobalt in the solution increases rapidly at the beginning of the experiment for all experimental temperatures (Figure 2). The results obtained from the experiment carried out at 70 ^oC show that the dissolves at a rate of 70 % in the first 5 minutes of the experiment. It is seen that the amount of cobalt in the solution reached 90 % at the 60th minute of the experiment, and then remained constant and took the value of 92.5 % at the end of the 180 minutes experiment period. In the experiment carried out at 55 ^oC, the value of the cobalt amount in the solution, which took its highest value with 83 % at the 30th minute, decreased slowly in the following experiment periods and decreased to 76 % at the end of the 180 minutes experiment period. The results of the experiments carried out at 25 and 40 ^oC differ greatly from the results of the experiments carried out at 55 and 70 ^oC. The amount of cobalt in the solution, which reaches its maximum value at the end of 30 minutes in both experiments (25 ^oC: 56 %, 40 ^oC: 62 %), decreases rapidly in the following reaction times and takes its lowest value at the end of the 180 minutes experiment period. While the amount of cobalt in the solution was 19.7 % at the end of 180 minutes in the experiment carried out at 40 ^oC, this amount was 8.86 % in the same test period in the experiment carried out at 25 ^oC. Cobalt is present as Co_3O_4 in the spent Co-Mo/Al_2O_3 HDS catalyst after oxidizing roasting (Figure 1). $CoC_2O_4{\cdot}2H_2O$ is formed as a result of the reaction of Co_3O_4 with $H_2C_2O_4$ (Reaction 1).

$$Co_3O_{4\,(s)} + 3\,H_2C_2O_{4\,(aq)} + 3\,H_2O_{(aq)} \rightarrow 3\,CoC_2O_4{\cdot}2H_2O_{(s)} + 1/2\,O_{2\,(g)} \qquad (1)$$

$CoC_2O_4{\cdot}2H_2O$, which is formed according to Reaction 1, has a high solubility in acidic medium at high temperatures. $CoC_2O_4{\cdot}2H_2O$ precipitates at low temperatures and increasing pH values. The ICP-OES quantitative analysis showed that 8.86 % cobalt was present in the solution after 3 h of reaction time in the experiment using 0.25 M $H_2C_2O_4$ solution (Figure 2). Since other components (MoO_3, Al_2O_3, $AlPO_4$) in the spent Co-Mo/Al_2O_3 HDS catalyst also react with $H_2C_2O_4$ during the experiment, $H_2C_2O_4$ is consumed and the pH value of the solution is constantly increasing. According to these findings, the optimum concentration of $H_2C_2O_4$ for precipitation of $CoC_2O_4 \cdot 2H_2O$ was determined as 0.25 M.

The ICP-OES quantitative analysis results showed that MoO_3, Al_2O_3 and $AlPO_4$ compounds in the spent Co-Mo/Al_2O_3 HDS catalyst were also dissolved under experimental conditions. As a result of the dissolution of these compounds, Mo, Al and P also pass into solution. The % extraction values calculated using the ICP-OES analysis results of the solutions taken from the reactor at the end of the 3 hours experiment period are given in Table 3. When Table 3 is examined, it is seen that the % extraction values of Mo, Al and P increase with increasing temperature. While the temperature dependence of the Mo and P amounts in the solution is relatively low, the temperature dependence of Al is quite high. 97.9 % of Mo, 56.2 % of Al and 63 % of P in spent Co-Mo/Al_2O_3 HDS catalyst can be taken into solution at 70 ^oC (Table 3).

Table 3 Extraction (%) values of Mo, Al and P obtained by dissolving oxidative roasted Co-Mo/Al_2O_3 HDS catalyst in oxalic acid (Sample: 25 g, $H_2C_2O_4$ solution: 0.25 M, 500 mL, stirring speed: 300 rpm, reaction time: 3 h)

Temperature	25 ^oC	40 ^oC	55 ^oC	70 ^oC
Mo extraction (%)	84.8	89.7	95.7	97.9
Al extraction (%)	8.2	13.9	32.7	56.2
P extraction (%)	32.1	40.5	56.3	63.0

Cobalt can be found as a result of the dissolution of $CoC_2O_4 \cdot 2H_2O$ in the $H_2C_2O_4$ solution during the dissolution experiment, as well as in the form of cobalt oxalato ($Co(C_2O_4)_2^{2-}$), cobalt biokzalato ($(Co(HC_2O_4)^+$ components and $Co(HC_2O_4)_2$) [27, 28].

The XRD diagram of the light pink solid material obtained after dissolution experiment performed at 25 ^oC temperature, 0.25 M $H_2C_2O_4$ concentration and 300 rpm stirring speed is given in Figure 3. In the XRD diagram, the peaks of $CoC_2O_4 \cdot 2H_2O$ (ICDD No: 025-0250) are seen. SEM-EDS analysis of solid material is given in Figure 4. From the SEM micrograph, acicular (needle-like) crystals of $CoC_2O_4 \cdot 2H_2O$ are seen. The acicular morphological structure of $CoC_2O_4 \cdot 2H_2O$ is compatible with the morphological structure in Romero et al.'s study [29]. The EDS analysis of the solid material includes the peaks of cobalt and oxygen. SEM-EDS analysis also shows that the solid is $CoC_2O_4 \cdot 2H_2O$.

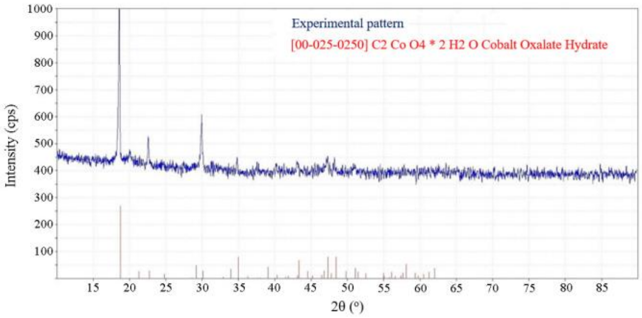

Figure 3 XRD analysis of light pink solid obtained by dissolving spent Co-Mo/Al_2O_3 HDS catalyst in oxalic acid

In order to determine the thermal decomposition behavior and decomposition reactions of the light pink solid material obtained as result of the dissolution experiment performed at 25 ^oC temperature, 0.25 M $H_2C_2O_4$ concentration and 300 rpm stirring speed, TG-DTA analysis was carried out in dry air atmosphere with a linear heating rate of 5 C min^{-1} and gas flow rate of 100 mL min^{-1} (Figure 5-a). In order to clearly determine the number of decomposition steps, DTG diagram is also given in Figure 5-b. Decomposition start and finish temperatures and DTG_{max} values are indicated on the DTG diagram.

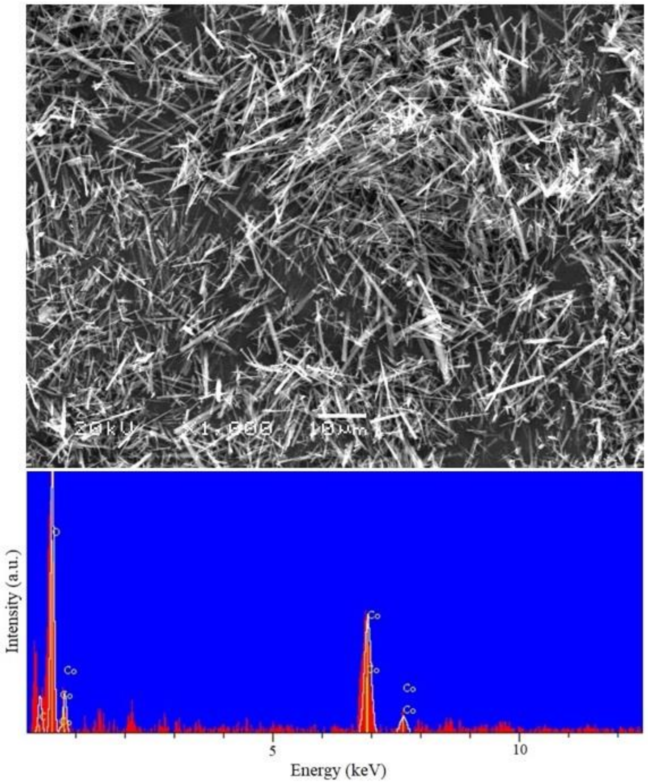

Figure 4 SEM-EDS analysis of solid obtained by dissolving spent Co-Mo/Al_2O_3 HDS catalyst in oxalic acid

When the TG and DTG diagrams is examined, no significant weight loss is observed up to 118 ^oC. Weight loss occurs from 118 ^oC and the material loses H_2O rapidly up to 196 ^oC. The substance loses 17.42 % weight up to 196 ^oC and continues to lose water slowly from this temperature up to 248 ^oC. At 248 ^oC, the weight loss is 18.40 %. According to Reaction 2, when the material is completely dehydrated and converted to CoC_2O_4, the theoretically calculated weight loss is 19.68 %. This decomposition step causes the endothermic peak to be observed in the DTA diagram.

In the second decomposition step occurring between 248-279 ^oC temperatures, the weight loss was determined as 42.73 %. In this step, two successive reactions occur. First, CoC_2O_4 converted to Co (Reaction 3), and then the Co formed is oxidized to Co_3O_4 (Reaction 4) due to performing in air atmosphere. The theoretically calculated weight loss during the conversion of CoC_2O_4 to Co_3O_4 is 45.38 %. Reaction 3 is an endothermic reaction. However, a sharp exothermic peak occurs because the highly exothermic reaction heat formed during the oxidation of Co to Co_3O_4 dominates the endothermic heat of Reaction 3.

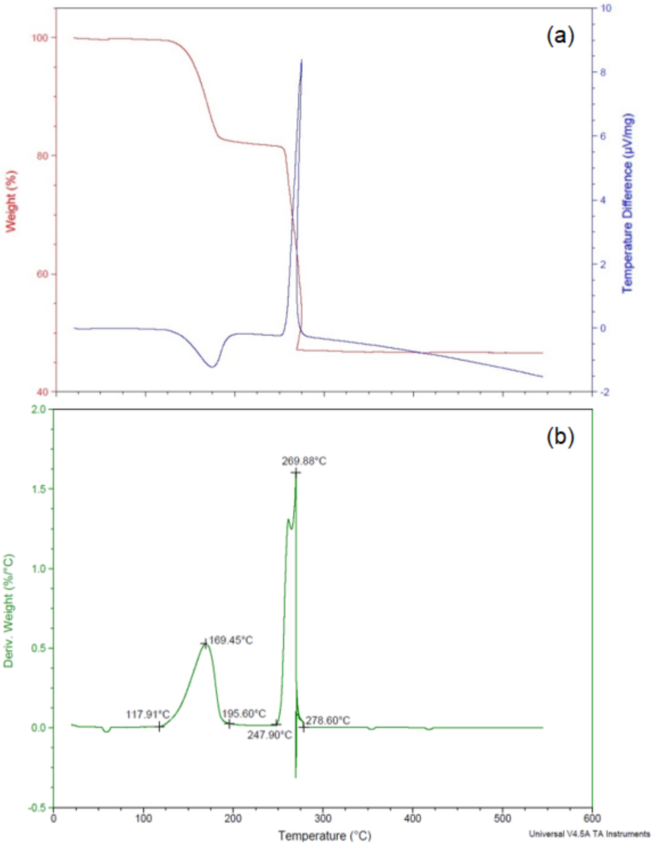

Figure 5 TG-DTA (a) and DTG (b) diagrams of the solid obtained by dissolving the spent Co-Mo/Al_2O_3 HDS catalyst in oxalic acid in dry air atmosphere (heating rate: 5 ^oC min^{-1}, air flow rate: 100 mL min^{-1})

$$CoC_2O_4{\cdot}2H_2O \rightarrow CoC_2O_4 + 2\,H_2O \tag{2}$$
$$CoC_2O_4 \rightarrow Co + 2\,CO_2 \tag{3}$$
$$3\,Co + 2\,O_2 \rightarrow Co_3O_4 \tag{4}$$

Decomposition start-finish temperatures, derivative thermogravimetric curve (DTG_{max}) temperatures, % weight loss and % total weight loss values were determined using the data obtained from TG-DTA and DTG diagrams and are given in Table 4.

Table 4 Details of decomposition steps of solid obtained by dissolving the spent Co-Mo/Al_2O_3 HDS catalyst in oxalic acid in dry air atmosphere

	Start temperature (°C)	Finish temperature (°C)	DTG_{max} (°C)	% Weight loss	% Total weight loss
First step (Reaction 2)	118	196	169.5	17.42*	17.42
Second step (Reaction 3 and 4)	248	279	269.9	42.73	53.27

Molecular weight of $CoC_2O_4 \cdot 2H_2O$ = 182.98 g mol^{-1}

(*) After 196 °C, the substance continues to lose water slowly up to 248 °C. At 248 °C, the weight loss is 18.40 %.

Majumdar et al. [30] studied the thermal decomposition behavior of $CoC_2O_4 \cdot 2H_2O$ in an inert gas atmosphere. In Majumdar et al.'s study [30], Reaction 4 does not occur because it is performed in an inert gas atmosphere. The results obtained in this study are in agreement with the findings of Majumdar et al. [30]. Maciejewski et al. [31] determined that metallic Co formed as a result of the decomposition of CoC_2O_4 is highly active and converts to Co_3O_4 by oxidizing with O_2 when performing in air atmosphere.

Co_3O_4, obtained by thermal decomposition of $CoC_2O_4 \cdot 2H_2O$ in the air atmosphere, is in the form of nanorods or nanoparticles [32]. Co_3O_4 nanoparticles can be produced by thermal decomposition of $CoC_2O_4 \cdot 2H_2O$ in air atmosphere, as well as by methods such as microwave-assisted method, hydrothermal method, sol-gel technique, vapor deposition method, solution combustion method and chemical spray pyrolysis [32- 40].

Co_3O_4 in nanorod or nanoparticle form has many applications due to its optical, magnetic and electronic properties as well as its biological properties (antibacterial, antiviral, antifungal, antileishmanial, therapeutic agents, anticancer, and drug delivery). These nanostructures are used as anode material in lithium-ion rechargeable batteries as well as catalyst, phosphate ion sensors, electrochromic sensors, supercapacitor. Co_3O_4 nanoparticles are also used in electronics and electrooptic fields due to its p-type semiconductor properties [34- 42].

FT-IR diagram of the light pink solid material obtained after leaching experiment performed at 25 °C temperature, 0.25 M $H_2C_2O_4$ concentration and 300 rpm stirring speed is given in Figure 6-a. FT-IR spectrum includes vibration bands of ν(Co-O) at 486 cm^{-1}, ν(CC) + δ(CO_2) at 740 and 821 cm^{-1}, ν_{sym}(CO) at 1315 cm^{-1}, ν_{asym}(CO) at 1361 cm^{-1}, ν(CO) at 1612 cm^{-1} and ν(OH)(H_2O) at 3350 cm^{-1} (Figure 6-a). These results are in good agreement with the FT-IR spectral analysis findings of Prananto et al. [32] and support that the light pink solid material obtained is $CoC_2O_4 \cdot 2H_2O$.

FT-IR diagram of the final product obtained by decomposition of light pink solid material in air atmosphere is given in Fig 6-b. FT-IR spectrum includes broad absorption band of ν(Co-O) at 488 cm^{-1} and narrow sharp absorption band of O-Co-O at 655 cm^{-1}. Patel et al. [43] stated that the strong absorption band determined at 662 cm^{-1} belongs to the stretching vibrations of the octahedrally coordinated Co^{3+} metal ions in the metal oxide. Prabaharan et al. [33] stated that the absorption band determined at 661 cm^{-1} is the stretching vibration of the O-Co-O bond. The findings obtained in this study are in good agreement with the findings of Patel et al. [43] and Prabaharan et al. [33] and it shows that the final product obtained by the decomposition of the light pink solid material in the air atmosphere is Co_3O_4.

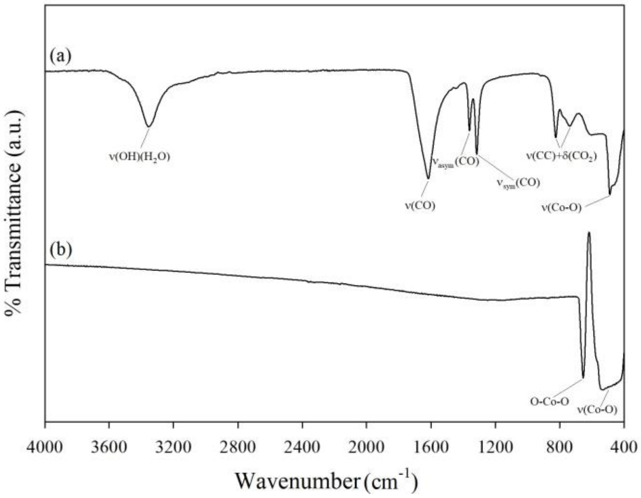

Figure 6 FT-IR diagrams of solid obtained by dissolving spent Co-Mo/Al_2O_3 HDS catalyst in oxalic acid (a) and the final product obtained by decomposition of this solid in air atmosphere (b)

In addition to XRD, SEM-EDS and TG/DTG-DTA analyses, FT-IR analysis also shows that the light pink colored material obtained is $CoC_2O_4{\cdot}2H_2O$. The decomposition steps and the decomposition start and finish temperatures in the TG-DTA and DTG diagrams given in Figure 5 are in good agreement with the literature [30]. On the other hand, it is seen that the weight loss values obtained from the TG diagram are slightly lower than the theoretically calculated weight loss values.

In order to determine the Co content of the light pink solid material ($CoC_2O_4{\cdot}2H_2O$) obtained, 100 mg of solid was completely dissolved in 1 M NH_3 (ammonia) solution. As a result of the ICP-OES quantitative analysis of the obtained solution, the Co content of $CoC_2O_4{\cdot}2H_2O$ solid was determined as 31.45 %.

By using the ICP-OES quantitative analysis results of the solution obtained at the end of the experiment carried out at 25 ^{o}C temperature, 0.25 M $H_2C_2O_4$ concentration, 300 rpm stirring speed and by weighing the light pink solid obtained from dissolving the spent Co-Mo/Al_2O_3 HDS catalyst in oxalic acid solution, the reaction yield of obtaining $CoC_2O_4{\cdot}2H_2O$ solid was calculated as 90.9 %.

4. CONCLUSION

In this study, roasted spent Co-Mo/Al_2O_3 HDS catalyst was dissolved in $H_2C_2O_4$ solution and optimum conditions were determined for obtaining $CoC_2O_4{\cdot}2H_2O$. The characterization of the obtained $CoC_2O_4{\cdot}2H_2O$ was carried out and its thermal decomposition behavior was investigated. The conclusions can be summarized as follows;

- It is determined that $CoC_2O_4{\cdot}2H_2O$ can be obtained by dissolving the spent Co-Mo/Al_2O_3 HDS catalyst in $H_2C_2O_4$ solution. Optimum conditions for $CoC_2O_4{\cdot}2H_2O$ production were determined as 25 ^{o}C temperature, 0.25 M $H_2C_2O_4$ concentration, 1/20 g mL^{-1} solid/liquid ratio and 300 rpm stirring speed. $CoC_2O_4{\cdot}2H_2O$ was obtained with a reaction yield of 90.9 %.

- $CoC_2O_4{\cdot}2H_2O$ is formed in accordance with the following reaction of Co_3O_4, in Co-Mo/Al_2O_3 HDS catalyst after oxidizing roasting, with $H_2C_2O_4$.

$$Co_3O_{4\,(s)} + 3\,H_2C_2O_{4\,(aq)} + 3\,H_2O_{(aq)} \rightarrow$$
$$3\,CoC_2O_4{\cdot}2H_2O_{(s)} + 1/2\,O_{2\,(g)}$$

- The light pink solid material obtained from dissolving of spent Co-Mo/Al_2O_3 HDS catalyst in solution containing $H_2C_2O_4$ was characterized by XRD, SEM-EDS, TG/DTG-DTA and FT-IR analyzes and it was determined as $CoC_2O_4{\cdot}2H_2O$.

- Co_3O_4 is obtained by decomposition of $CoC_2O_4{\cdot}2H_2O$ in air at temperatures above 280 ^{o}C.

- Co_3O_4 is a multifunctional material and has many applications such as biomedical applications, catalysts, phosphate ion sensors, electrochromic sensors, supercapacitor, as anode material in lithium ion rechargeable batteries. The fact that Co_3O_4 is produced by thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ obtained from spent Co-Mo/Al_2O_3 HDS catalyst, which is a waste, in the air atmosphere is important for the studies to be carried out on this subject.

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The Declaration of Conflict of Interest/Common Interest

No conflict of interest or common interest has been declared by the author.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The author of the paper declare that he comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that he do not make any falsification on the data collected. In addition, he declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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