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## Dissolution behavior of sulfur and some metals from spent petroleum catalysts by alkaline solutions

Minhnhan Le, Manseung Lee

Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Republic of Korea

Corresponding author: [mslee@mokpo.ac.kr](mailto:mslee@mokpo.ac.kr) (Manseung Lee)

**Abstract:** The petroleum refining industry produces a large amount of spent catalysts which contain sulfur and some valuable metals. During the recovery of these valuable metals, sulfur should be processed and removed from the surface of the spent catalyst. Several chemical reagents including NaOH, Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, CS<sub>2</sub>, and decanol were employed to investigate the removal of sulfur from the spent catalysts. NaOH and ultrasound-assisted oxidative treatment with H<sub>2</sub>O<sub>2</sub> showed better performance than the other reagents for the removal of sulfur from spent catalyst. Sulfur and valuable metals dissolved together to the solution by using ultrasound-assisted oxidative treatment with H<sub>2</sub>O<sub>2</sub>, while the covered sulfur was removed from the spent catalyst without affecting the dissolution of valuable metals. The removal of sulfur as well as the leaching of valuable metals was discussed on the basis of oxidation and reduction reaction. The optimum conditions for sulfur removal were chosen as follows: temperature, 60°C; pulp density, 20 g/dm<sup>3</sup>; reaction time, 1.5 h; stirring speed, 800 rpm; and NaOH concentration, 0.5 M. The obtained results can be applied to develop an environment-friendly process to treat sulfur from the spent catalysts.

**Keywords:** sulfur, spent petroleum catalyst, NaOH, H<sub>2</sub>O<sub>2</sub>

### 1. Introduction

Nowadays, solid catalysts play an essential role in the production of clean fuels, gasoline and heavy hydrocarbons in the petroleum distillation and petrochemicals industry. The catalyst materials became contaminated and deactivated after several hydro-treating processes. Since the demand for catalysts increases, large quantities of spent catalyst are generated from chemical and petrochemical processes. It has been reported that the amount of spent catalysts discarded is 170000 tons per year (Kim et al., 2012). These spent catalysts have been considered as hazardous waste and thus should be handled under strict disposal guidelines (Mishra et al., 2010). Conventionally, the spent catalysts are abandoned in the land for their disposal, but it is ineffective due to the dissolution of heavy metals into earth (Marafi and Stanislaus, 2011). Many efforts have been conducted on the regeneration and reuse of the spent catalyst in the light of environmental problems (Marafi and Stanislaus, 2003; Dufresne, 2007).

The spent catalysts generated from petroleum refining typically contain 7-15 wt.% elemental sulfur with some valuable metals like molybdenum, cobalt, nickel, vanadium, and alumina (Marafi and Stanislaus, 2008a; Barik et al., 2012). These metals are extensively used in the steel industry and the manufacture of alloys (Marafi and Stanislaus, 2008b). Thus, the recovery of valuable metals from spent catalysts in recent years has attracted attention by researchers. Unlike valuable metals, the sulfur on the surface of the spent catalysts is combusted in the roasting process and emitted to the atmosphere which is regarded as an environmental pollutant by the US Environmental Protection Agency (U.S. EPA, 2008). Moreover, when catalysts become inactive, the accumulation of sulfur, phosphorus and metal impurities on its surface can prevent the processing or recycling of the catalysts (Park et al., 2006a). Therefore, in order to recover the valuable metals in spent catalysts, the covered sulfur on the surface

of spent catalyst should be handled. The emission of SO<sub>2</sub> gas during the calcination or leaching process can affect the health and environment. In addition, the presence of sulfur layer can hinder the contact of leaching reagents with the components in the spent catalysts, resulting in their low dissolution efficiency from the spent catalyst (Mishra et al., 2010). Instead of combustion of elemental sulfur which consumes a lot of energy, it is necessary to develop an efficient and environmentally friendly process in which sulfur can be removed from the spent catalyst without affecting the valuable metals. Several works have been done for the dissolution of elemental sulfur in the solution from sulfur powder material in the laboratory (Lelieur et al., 1991; Ren et al., 2011; Wang et al., 2018). These works may be useful for studying the removal of sulfur from the spent catalysts.

Since most of the work focuses mainly on the recovery of valuable metals from the spent catalysts, very few studies focus on the removal of elemental sulfur. Therefore, the removal of elemental sulfur from spent catalyst by various chemical reagents was investigated in the present study. Aqueous and non-aqueous solutions were employed in this work. The effect of reaction temperature and reactants concentration on the removal of sulfur was investigated. Structural properties of the spent catalyst material were also analyzed. The current results would provide insight into a promising process to remove sulfur and to facilitate the leaching and recovery of valuable metals from the spent catalysts.

## 2. Materials and methods

The spent petroleum catalysts employed in this work were obtained from a Korean refinery. Preliminarily, the received catalyst from the refinery was first washed with acetone to remove soluble organic matters and then dried overnight in an oven (WiseVen Wids, Daihan Scientific Co., Korea) at 80°C. The obtained material was mixed thoroughly to get a homogenized sample for chemical characterization and subsequent pretreatment experiments. The characteristics of spent catalyst material was analyzed by X-Ray Diffractometer (XRD, Cu K $\alpha$  radiation,  $\lambda = 1.54060 \text{ \AA}$ , PANalytical X'Pert-PRO, The Netherlands) and X-Ray Fluorescence (XRF) Spectrometer (M1MISTRAL, Bruker, Karlsruhe, Germany).

Chemical reagents such as NaOH (98%), Na<sub>2</sub>CO<sub>3</sub> (99%), H<sub>2</sub>O<sub>2</sub> (30%), and CS<sub>2</sub> (99%), were employed in this work and were purchased from Daejung Chemical & Metals Co., while Decanol (99%) was purchased from Acros Organics Co. Kerosene (Daejung Chemical & Metals Co.) was employed as a diluent and all the other chemicals used were of analytical grade and used without any purification.

All experiments were performed with a desired concentration of reagents in a 250 cm<sup>3</sup> three-neck round bottom flask. A magnetic stirrer bar in a heating mantle (WiseStir MSH-20D, Daihan Scientific Co., Korea) was used to control the temperature, time and stirring speed. The solution was separated from the residue on the filter paper using vacuum filtration. The concentrations of the aqueous samples resulted from the pretreatment of the spent catalyst were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Arcos, Kleve, Germany), while elemental compositions of the residue samples after treatment with non-aqueous solvents were analyzed by XRF measurement. The removal/leaching percentage of component X measured by XRF and ICP-OES was calculated by employing Eqs. (1) and (2), respectively:

$$X_{XRF}(\%) = \frac{W_{X,initial} - W_{X,residue}}{W_{X,initial}} \times 100\% \quad (1)$$

$$X_{ICP}(\%) = \frac{C_X \times V}{W_{X,initial}} \times 100\% \quad (2)$$

where  $W_{X,initial}$  and  $W_{X,residue}$  represent the weight of X in the materials before and after the leaching experiments,  $C_X$  and  $V$  refer to the concentration of X in the leaching solution and the volume of leaching solution after filtration, respectively.

## 3. Results and discussion

### 3.1. Characteristics of material

The shape of the original spent catalyst and after acetone washing was black cylindrical as shown in Figs. 1(a) and (b), respectively. Fig. 1(a) shows that the original spent catalyst contained residual oil and was darker in color. After being washed with acetone and dried in the oven, the soluble organic matters

were removed and the color of spent catalyst became brighter (Fig. 1(b)). The XRD patterns of the original spent catalyst are shown in Fig. 2. As can be seen in Fig. 2, the spent catalyst mainly contains valuable metals. Namely, Co, Mo, and Ni exist in the form of their oxides as well as sulfide. Al and V exist as oxide ( $\text{Al}_2\text{O}_3$ ) and sulfide ( $\text{V}_2\text{S}_3$ ), respectively. Besides the existence of metal sulfide, sulfur (S) is also present in the elemental state. Table 1 shows the chemical composition of the original spent catalyst by weight (wt.%) which was analyzed by XRF. The concentration of vanadium was the highest in the spent catalyst. The weight percentage of Fe, Si, and Co was low, while other elements accounted for a moderate proportion. The results obtained from XRF are consistent with XRD data.

Table 1. Chemical compositions of original spent catalyst by weight (wt.%)

Element	Al	S	Fe	Ni	Mo	Si	Co	V
Contents	10.71	19.78	3.53	13.46	14.86	1.60	0.06	36.00

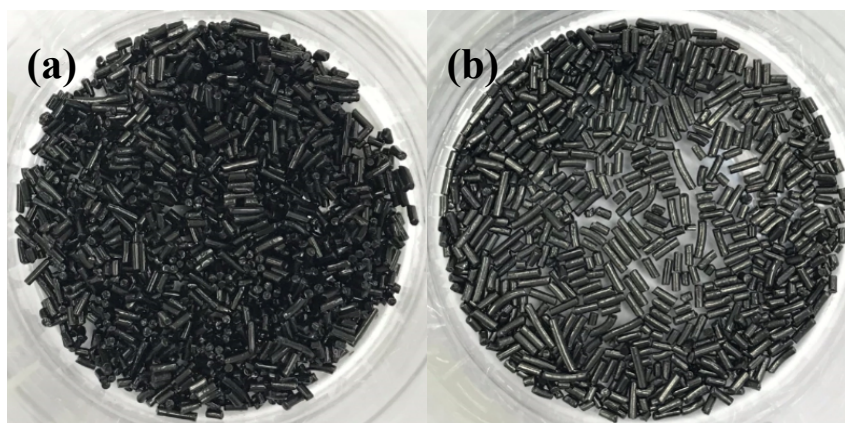


Fig. 1. (a) Original spent catalyst and (b) spent catalyst after acetone washing

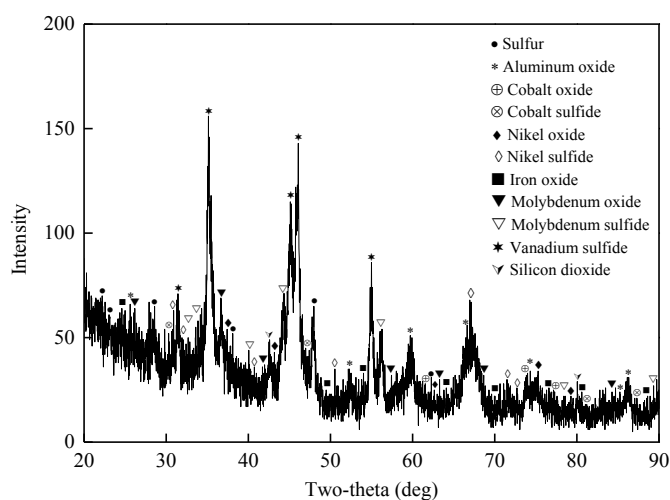


Fig. 2. XRD pattern of the original spent catalyst. Reference from National Bureau of Standards (NBS), Joint Committee on Powder Diffraction Standards (JCPDS), and the American Society for Testing Materials (ASTM)

### 3.2. Removal of sulfur from spent catalyst by various solutions

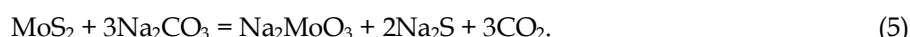
A series of experiments were conducted to investigate the removal of sulfur in various solutions including aqueous and non-aqueous solutions. The obtained results are listed in Table 2. The experimental conditions were employed from our preliminary results on the treatment of sulfur powder material by decanol, NaOH, and  $\text{Na}_2\text{CO}_3$  solution. In the case of  $\text{H}_2\text{O}_2$ , the process parameters were obtained from the reported literature (Park et al., 2006b). The purpose of these tests is to remove sulfur from the spent catalyst. It is important to find an appropriate organic solvent for handling only sulfur

without interacting with metals. It has been reported that elemental sulfur dissolves well in organic solvents like carbon disulphide (Austin et al., 1971). The fact that CS<sub>2</sub> solvent is a health hazard due to its toxicity should be carefully considered before its use. CS<sub>2</sub> was tested to remove sulfur from spent catalyst in this work. However, the removal percentage of sulfur by CS<sub>2</sub> was still low. This may be due to the fact that there was little amount of sulfur on the surface of spent catalyst and most of the sulfur exists as metal sulfide form. Similar results were obtained by Decanol at the temperature of 80°C. The removal percentage of sulfur was lower than 10%. It can be said that non-aqueous solutions such as carbon disulfide and decanol had a little effect in removing sulfur from the spent catalyst.

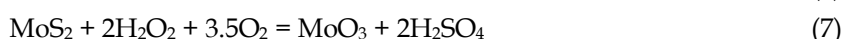
Table 2. Removal percentage of sulfur from spent catalyst (SC) by various solutions

Sample	Conditions	% removal of S
SC + CS <sub>2</sub>	Temperature: 25°C, pulp density: 20 g/dm <sup>3</sup> , reaction time: 5 h, pure CS <sub>2</sub> , stirring speed: 700 rpm	2.53%
SC + decanol	Temperature: 80°C, pulp density: 20 g/dm <sup>3</sup> , reaction time: 0.5 h, 20 vol.% Decanol, stirring speed: 500 rpm	9.60%
SC + NaOH	Temperature: 60°C, pulp density: 20 g/dm <sup>3</sup> , reaction time: 1.5 h, 0.5 M NaOH, stirring speed: 800 rpm	16.4%
SC + Na <sub>2</sub> CO <sub>3</sub>	Temperature: 80°C, pulp density: 20 g/dm <sup>3</sup> , reaction time: 1.5 h, 0.7 M Na <sub>2</sub> CO <sub>3</sub> , stirring speed: 800 rpm	36.4%
SC + H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	Temperature: 25°C, pulp density: 20 g/dm <sup>3</sup> , reaction time: 2 h, 5 vol.% H <sub>2</sub> O <sub>2</sub> , stirring speed: 500 rpm	52.8%
SC + H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> with ultrasound	Temperature: 25°C, pulp density: 20 g/dm <sup>3</sup> , reaction time: 2 h, 5 vol.% H <sub>2</sub> O <sub>2</sub> , stirring speed: 500 rpm	58.1%

In alkaline medium, the removal percentage of sulfur from spent catalyst by NaOH and Na<sub>2</sub>CO<sub>3</sub> was 16.4 and 36.4%, respectively. Elemental sulfur can be dissolved in alkaline solutions according to the following Eqs. (3) and (4). The change in the oxidation state of sulfur from S(0) to S(2-) and S(2+) in Eqs. (3) and (4) indicates that elemental sulfur undergo disproportionation reaction according to the oxidation state diagram of sulfur in alkaline solution (Rayner-Canham and Overton, 2013). Table 2 also indicates that the removal of sulfur by Na<sub>2</sub>CO<sub>3</sub> solution was higher than that of NaOH solution. The reason may be ascribed to the fact that some metal sulfides like MoS<sub>2</sub> can react with Na<sub>2</sub>CO<sub>3</sub> solution at high temperature (see Eq. (5)). Although the removal percentage of sulfur by alkaline solutions was not high, proper temperature control can effectively remove sulfur from spent catalyst.



The highest sulfur removal was obtained in the presence of an oxidizing agent like H<sub>2</sub>O<sub>2</sub>. Half of the sulfur has been removed from spent catalyst at ambient temperature. Moreover, the removal percentage of sulfur has increased to 58% with the aid of ultrasound. The role of H<sub>2</sub>O<sub>2</sub> is to convert sulfur to soluble sulfate. During the pretreatment of spent catalyst, H<sub>2</sub>O<sub>2</sub> could be decomposed to yield oxygen and water. In order to obtain the combined effect of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> as an oxidizing agent, oxygen gas was also supplied to the solution. Meanwhile, the function of ultrasound is to promote the dispersion of sulfur on the spent catalyst surface into the solution. Under the impact of ultrasonic cavitation over time, the particle size and shape of material can be deformed, which can affect the metal components inside spent catalyst. The conversion reaction of sulfur and metal sulfides by H<sub>2</sub>O<sub>2</sub> can be described by Eqs. (6-10):



Among various solutions employed in this work, aqueous solutions showed better removal efficiency of sulfur than non-aqueous solutions. Therefore, NaOH solution and oxidative treatment with H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> were selected for the further experiments to investigate the effect of some factors on the removal of sulfur from the spent catalyst.

### 3.3. Removal of sulfur from spent catalyst by NaOH solution

In the removal of sulfur from spent catalyst by NaOH solution, the effect of some variables such as temperature, NaOH concentration, pulp density, and reaction time was investigated. The experimental conditions are provided in Table 3. In order to investigate the effect of temperature on the removal of sulfur from the spent catalyst by using NaOH solution, the temperature was varied from 50 to 90°C. In these experiments, NaOH concentration, pulp density, and reaction time were fixed at 0.5 M, 20 g/dm<sup>3</sup>, and 1.5 h, respectively. The obtained results are shown in Fig. 3. The removal of sulfur was constant at 16% as the temperature increased from 50 to 60°C and then decreased with the further increase in temperature. Since Al and Si oxides dissolved well in alkaline solutions, their leaching percentage increased in the range of temperature. The temperature had a negligible influence on the leaching percentage of the other elements such as Fe, Ni, and Co by NaOH solution. High temperature was not effective in removing sulfur, and thus a temperature of 60°C was selected for the removal of sulfur from spent catalyst.

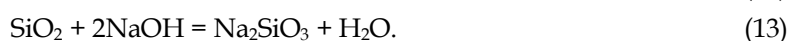
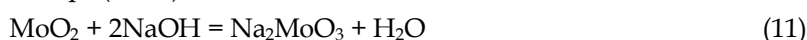
Table 3. Summary of experimental conditions

Conditions	Values
Temperature, °C	50, 60*, 70, 80, 90
NaOH concentration, M	0.1, 0.5*, 1, 3, 5
Pulp density, g/dm <sup>3</sup>	10, 20*, 30, 40, 50
Reaction time, h	1, 1.5*, 2, 2.5, 3
Stirring speed, rpm	800*

\* denotes the values kept constant

Among the variables investigated in this work (NaOH concentration, pulp density, and reaction time and temperature), only temperature affected the removal of sulfur but the removal percentage of sulfur was below 20%. The optimum NaOH concentration was found to be 0.5 M at which sulfur removal percentage was 16.4%. In the case of pulp density, the highest removal percentage of sulfur was 18.5% at 10 g/dm<sup>3</sup> pulp density. A small amount of Al and Si was dissolved into the solution at low pulp density (10 g/dm<sup>3</sup>). When the pulp density was high, the interaction between the spent catalyst and NaOH solution would decrease the mass-transfer rate at the liquid-solid interface. Therefore, the pulp density of 20 g/dm<sup>3</sup> was selected for further experiments. To obtain the optimum reaction time for the removal of sulfur, reaction time was varied from 1 to 3 h. The results are shown in Fig. 4. The removal of sulfur increased from 9.5 to 16.4% as reaction time increased from 1 to 1.5 h and slightly increased with the further increase of the reaction time. As can be seen from Fig. 4, the longer the reaction time, the more soluble metals would dissolve into the solution. Therefore, the experiments were conducted at a reaction time of 1.5 h.

During the removal of sulfur from spent catalyst, some metal components were dissolved. However, the leaching percentage of these metals was lower than 15% by varying the above variables except Al and Si at high temperatures (80-90°C). In general, metal sulfides are more difficult to dissolve than metal oxides in alkaline solutions (Zeng and Cheng, 2009). Therefore, most of the dissolution of metal results from the dissolution of metal oxides. The dissolution reaction of metal oxides from spent catalyst in NaOH solution can be represented as Eqs. (11-13):



In order to achieve highest removal of sulfur as well as the suppression of the dissolution of metals, the experiments were carried out at 60°C for 1.5 h reaction time at a pulp density of 20 g/dm<sup>3</sup> in 0.5 M

NaOH solution with a stirring speed of 800 rpm. From these results, it can be said that the removal of sulfur from spent catalyst by NaOH solution was still low. Moreover, there was some difference in the content of sulfur between the surface and the inside of spent catalyst. Experimental results are consistent with the XRD pattern data which shows that most of sulfur exists in the form of metal sulfides and a small amount of sulfur exists in the elemental state on the surface of the spent catalyst.

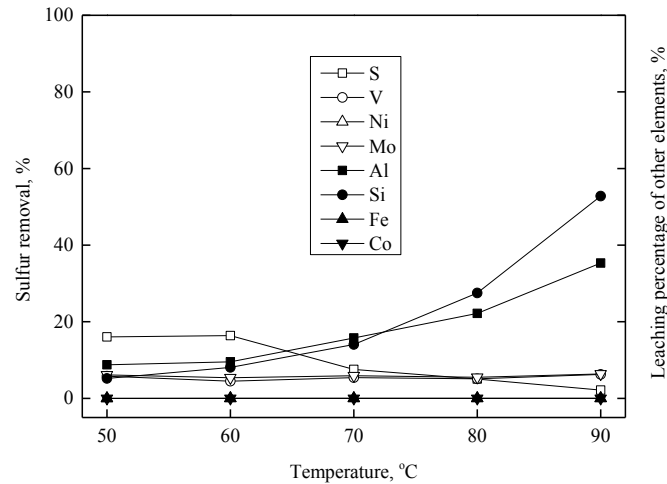


Fig. 3. Effect of temperature on the removal of sulfur from the spent catalyst. Conditions: NaOH concentration: 0.5 M, pulp density: 20 g/dm<sup>3</sup>, reaction time: 1.5 h, stirring speed: 800 rpm

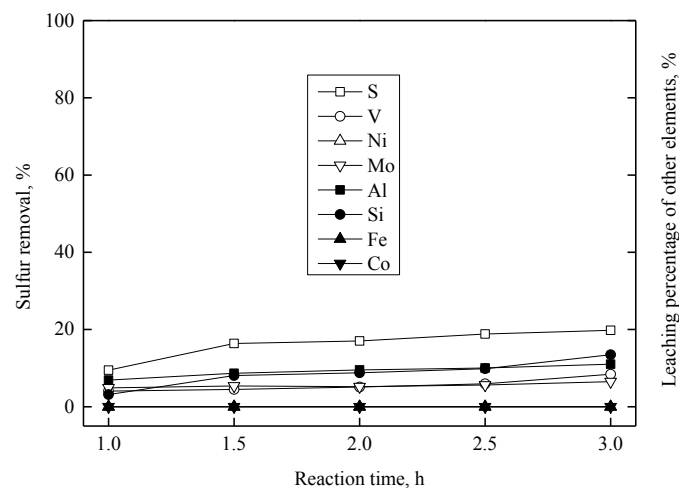


Fig. 4. Effect of reaction time on the removal of sulfur from the spent catalyst. Conditions: Temperature: 60°C, NaOH concentration: 0.5 M, pulp density: 20 g/dm<sup>3</sup>, stirring speed: 800 rpm

### 3.4. Removal of sulfur from spent catalyst by oxidizing agent

Fig. 5 shows the effect of temperature on the removal of sulfur from spent catalyst by oxidative treatment with H<sub>2</sub>O<sub>2</sub> solution. In these experiments, the temperature was varied from 25 to 60°C at a pulp density of 20 g/dm<sup>3</sup> in 5 vol.% H<sub>2</sub>O<sub>2</sub> solution for 2 h reaction time. Oxygen gas was provided to the system with a flow rate of 50 cc/min. The results showed that the removal percentage of sulfur decreased from 52 to 38% with the increase of temperature. Sulfur removal percentage in the spent catalyst by H<sub>2</sub>O<sub>2</sub> was higher than that by NaOH solution. It means that the other sulfides can be dissolved into H<sub>2</sub>O<sub>2</sub> solution. Since H<sub>2</sub>O<sub>2</sub> is an active oxidizing agent, sulfur present as metal sulfides can be oxidized by H<sub>2</sub>O<sub>2</sub> according to Eqs. (7-10). Besides the removal of sulfur, some valuable metal oxides such as V, Al, Mo, Co, and Ni also were dissolved into the solution. The dissolution reactions of metal oxides can be represented as Eqs. (14-18):



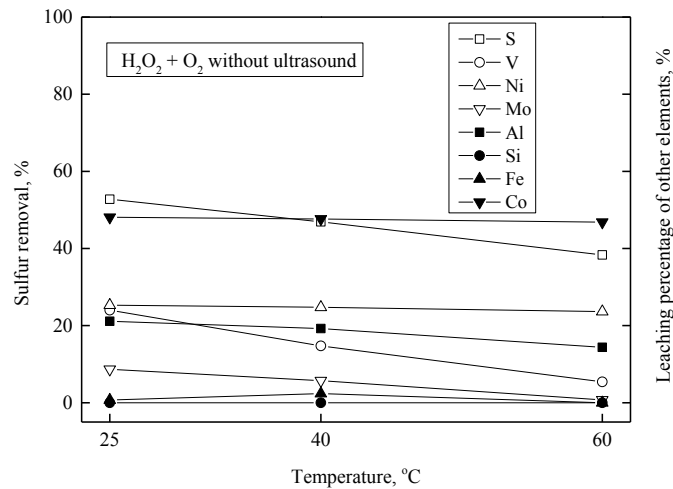
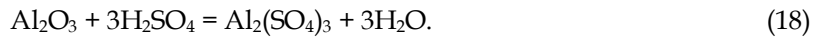


Fig. 5. Effect of temperature on the removal of sulfur from the spent catalyst. Conditions:  $\text{H}_2\text{O}_2$  concentration: 5 vol.%, pulp density: 20 g/dm<sup>3</sup>, reaction time: 2 h, stirring speed: 500 rpm, flow oxygen rate: 50 cc/min

As can be seen in Fig. 5, the leaching percentage of V, Al, Mo slightly decreased with the increase in temperature. The leaching percentage of Co and Ni was constant in the temperature range, while most of Fe and Si remained in the residue. The highest leaching percentage of cobalt, nickel, vanadium, and aluminium was obtained as 48, 25, 24, and 21%, respectively at 25°C. Eqs. (7-10) indicate that the stoichiometric coefficients of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  for the dissolution reaction of NiS and CoS is less than those of  $\text{MoS}_2$  and  $\text{V}_2\text{S}_3$ . Therefore, the dissolution of NiS and CoS can occur readily when the amount of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  is not enough to dissolve all the metal sulfides. The treatment of sulfur by  $\text{H}_2\text{O}_2$  results in the generation of sulfuric acid which can dissolve metal oxides. According to Eqs. (17) and (18), one mole of  $\text{H}_2\text{SO}_4$  is sufficient to dissolve  $\text{V}_2\text{O}_5$ , while three moles of  $\text{H}_2\text{SO}_4$  are needed to dissolve  $\text{Al}_2\text{O}_3$ . In the case of molybdenum, molybdenum(VI) oxide sulfates ( $\text{MoO}_2\text{SO}_4$ ) resulted from Eq. (16) was bulky and unstable in solution (Christiansen et al., 2001). Therefore, the leaching percentage of Mo was lower than the above metals. Since the solubility of oxygen decreases with temperature, the removal percentage of sulfur as well as the leaching percentage of metals decreases with temperature.

The effect of temperature on the removal of sulfur from spent catalyst by ultrasound-assisted oxidative treatment with  $\text{H}_2\text{O}_2$  solution was investigated. The experiments by ultrasound-assisted oxidative treatment were performed at the same conditions as without ultrasound. The obtained results are presented in Fig. 6. The highest sulfur removal percentage was 58.1% at 25°C. When the reaction temperature increased, the removal percentage of sulfur decreased. This behavior of sulfur was almost similar to the case of without ultrasound. When metal sulfides which had been converted to metal oxides by  $\text{H}_2\text{O}_2$  undergo Eqs. (7-10), the metal oxides should be dissolved in the solution. Fig. 6 also indicated that the leaching percentage of V and Mo decreased, while that of Al, Ni, and Co kept almost constant with the increase of temperature. Compared to the treatment without ultrasound, there was not much change in the leaching percentage of metals. The removal of sulfur was significantly enhanced with the help of ultrasound. Elemental sulfur and sulfur in metal sulfide came into the aqueous solution, which led to the highest removal of sulfur at 25°C. Hence, further experiments were done at room temperature.

Fig. 7 depicts the obtained results on the effect of  $\text{H}_2\text{O}_2$  concentration on sulfur removal of the spent catalyst by ultrasound-assisted oxidative treatment with  $\text{H}_2\text{O}_2$ . The concentration of  $\text{H}_2\text{O}_2$  was varied from 5 to 30% by volume, while other factors were fixed at the following conditions: temperature of 25°C, pulp density of 20 g/dm<sup>3</sup>, reaction time of 2 h with a flow oxygen rate of 50 cc/min. As shown in Fig. 7, the removal percentage of sulfur increased from 58 to 71% with the increase in  $\text{H}_2\text{O}_2$  concentration

from 5 to 30% by volume. The improvement of sulfur removal revealed strong oxidation of spent catalyst by ultrasound-assisted oxidative treatment with  $H_2O_2$  in the solution. On the other hand, the leaching percentage of metals such as Co, V, Al, and Mo slightly increased in the  $H_2O_2$  concentration range of 5-10 vol.% and remained constant with the increase of oxidizing concentration. 10 vol.% of  $H_2O_2$  was the optimal condition for the dissolution of metals.

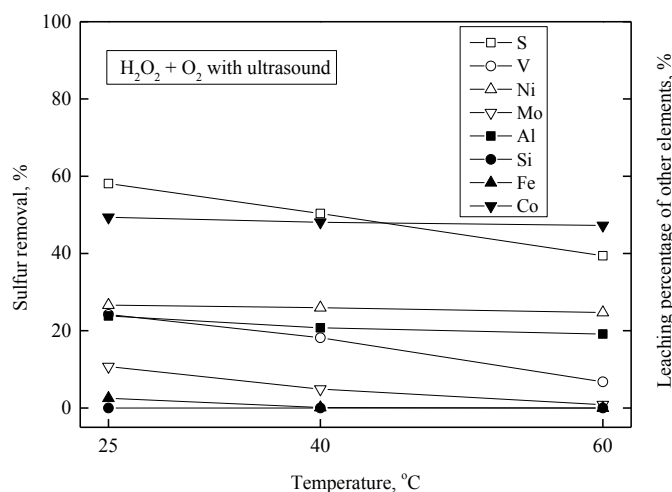


Fig. 6. Effect of temperature on the removal of sulfur from the spent catalyst with ultrasound. Conditions:  $H_2O_2$  concentration: 5 vol.%, pulp density: 20 g/dm<sup>3</sup>, reaction time: 2 h, stirring speed: 500 rpm, flow oxygen rate: 50 cc/min

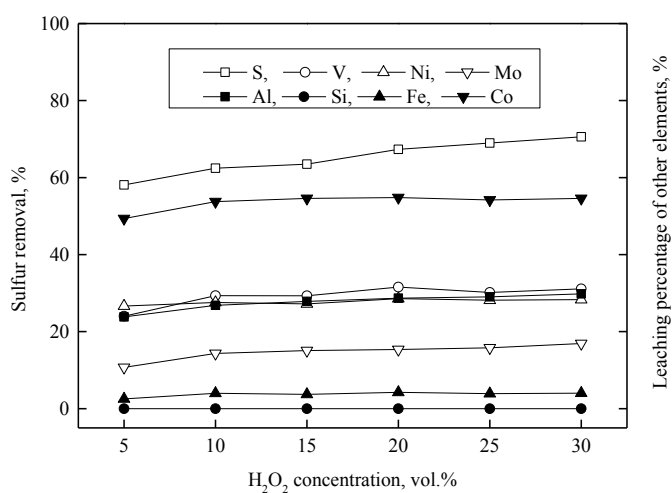


Fig. 7. Effect of  $H_2O_2$  concentration on the removal of sulfur from the spent catalyst with ultrasound. Conditions: pulp density: 20 g/dm<sup>3</sup>, reaction time: 2 h, stirring speed: 500 rpm, flow oxygen rate: 50 cc/min

Although a large amount of sulfur was removed from the spent catalyst by employing the ultrasound-assisted oxidative method, some metals were together dissolved into solution. The purpose of this work was to remove only sulfur from the spent catalyst while suppressing the dissolution of metal components. The pretreatment of spent catalyst with NaOH solution was considered to be the most optimal condition among the solutions employed in this work. It should be mentioned that the treatment of spent catalyst should be selected in the light of the process objective, namely either sulfur removal or metal recovery. In terms of metal recovery from the spent catalysts, the existence of metals as metal oxides is preferred because metal oxide can be easily dissolved into acidic solutions. Once the metal components are dissolved into acidic solution, some separation processes such as precipitation, solvent extraction, and ion exchange can be employed to separate and purify the dissolved components.

To the best of our knowledge, few works have been reported on the removal of elemental sulfur from the spent catalysts although there are some studies related to this topic. For instance, a process has



been reported on the utilization of sulfur-oxidizing bacteria to treat the sulfur in the spent catalysts (Kim et al., 2009). The necessity of keeping favorable conditions for bacterial growth and the slow kinetics are the disadvantages of this method. It has been reported that the use of ultrasound technology combined with hydrogen peroxide could remove more than 75% of sulfur from the hydrotreated petroleum products (Duarte et al., 2011). Compared with our work, the removal of sulfur by ultrasound-assisted oxidative treatment with  $H_2O_2$  solution was higher than it is reported in Table 2. The reason may be ascribed to the difference in the chemical composition of the catalyst material. Since sulfur can be removed from the spent catalyst, the dissolution behavior of valuable metals and then their recovery should be investigated in detail in further work.

#### 4. Conclusions

In order to develop a process to remove sulfur on the surface of spent catalysts resulted from petroleum refining, several solutions were investigated including aqueous and non-aqueous solutions such as NaOH,  $Na_2CO_3$ ,  $H_2O_2$ ,  $CS_2$ , and decanol. Either decanol or  $CS_2$  had a negligible effect on the removal of sulfur. The highest removal of the sulfur was obtained by ultrasound-assisted oxidative treatment with  $H_2O_2$  at room temperature. However, both sulfur and some valuable metals dissolved together to the solution. The dissolution of components from spent catalyst in  $H_2O_2$  solution occurred by oxidation/reduction reactions. In choosing a suitable reagent for the removal of sulfur, NaOH solution showed the best sulfur removal effect among the solutions employed in this work. By employing NaOH solution, the elemental sulfur that covered the surface of the spent catalyst could be removed without affecting the dissolution of other metal components in spent catalyst. The disproportionation reaction was responsible for the removal of sulfur from spent catalyst. The optimum conditions for removal efficiency of sulfur were achieved after 1.5 h reaction time in 0.5 M NaOH solution containing 20 g/dm<sup>3</sup> pulp density at 60°C. This work also indicated that most of the sulfur existed as metal sulfides in spent catalysts. After removing sulfur from the spent catalyst by NaOH solution, further works need to be done to investigate the leaching behavior of metals in spent catalyst.

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