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Extraction of molybdenum from a spent HDS catalyst using alkali leaching reagent

Chatisa KANSOMKET[1], Piamsak LAOKHEN[1], Tanongsak YINGNAKORN[1], Tapany PATCHARAWIT[1], and Sakhob KHUMKOA[1,*]

[1] *School of Metallurgical Engineering, Institute of Engineering, Suranaree University of Technology, Suranaree, Muang, Nakhon Ratchasima 30000, Thailand*

***Corresponding author e-mail:** sakhob@sut.ac.th

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Abstract

This research investigated extraction of molybdenum from spent hydrodesulfurization (HDS) catalyst used in petroleum refinery. The spent HDS catalyst still however contains significant amounts of valuable metals such as molybdenum and nickel for example, thereby recovery of such metals are of great interest. Pyro-hydrometallurgical process was utilized in this research to selectively extract molybdenum from the spent HDS catalyst using alkali leaching reagent. The process start from calcination of spent HDS catalyst, alkali leaching using sodium carbonate, purification by carbon adsorption-desorption, precipitation of ammonium molybdate and finally calcination to give molybdenum trioxide (MoO_3) as the final recycling product. Effects of calcination temperature (450°C to 650°C) together with alkali concentration (1 M to 3 M Na_2CO_3), solid to liquid ratio (100 $g\cdot L^{-1}$ to 300 $g\cdot L^{-1}$) and leaching time (30 min to180 min) have been investigated. Calcination at 450°C has shown to give the highest leaching efficiency. The optimum leaching condition, giving 97% leaching efficiency was determined to be 40 $g\cdot L^{-1}$ sodium carbonate concentration, 2 h-leaching time, 100 $g\cdot L^{-1}$ solid to liquid ratio and 90°C leaching temperature, by controlling the temperature at 90°C and the pH at 2, ammonium molybdate then precipitated. Calcination at 450°C finally converted the obtained precipitate to molybdenum trioxide as the final recycling product of 99.5% purity.

1. Introduction

In the petroleum refinery process, to meet fuel specification with clean and low-sulfur level for environmental requirements, undesirable sulfur must be removed from the oil via hydrodesulfurization (HDS) process in a temperature range of 260°C to 280°C over 5 bar to 160 bar [1]. To capture sulfur which appears as organosulfur compounds or sulfides, HDS catalyst is used and where the HDS involves the breakage of C-S bonds and give the resultant hydrogen sulfide (H_2S) gas and sulfur free from hydrocarbon, causing much reduced toxic SOx emission. Clean and high quality oil with low sulfur level then results to meet high specification of fuel production. HDS catalysts used are mostly based on MoS_2 with Ni and Co in small amounts, which are incorporated on inert supports such as cost effective γ-Al_2O_3 or more stable SiO_2. Nominal composition for the Ni/Mo HDS catalyst is typically 4% to 13% Mo, 1% to 5% Ni, 8% to 10% S, and 15% to 30% Al for example [2]. It was shown from ex-situ microscopic data [3] that MoS_2 nanoislands comprise one or more layers of S-Mo-S sandwich in the truncated triangle shape where their active edges serve as active sites during catalytic reactions [4].

When activation reaction efficiency has gone under an acceptable level after several years of operation, several approaches dealing with the spent HDS catalyst are necessary. The first approach involves regeneration of the spent HDS catalyst to reuse them in the system, which is the first priority prior to disposal if possible. Secondly, deactivated HDS catalyst waste may be disposed to landfill. However, such an approach is restricted to waste management and environmental regulations since the spent HDS catalyst is categorized as hazardous [5]. Disposal to landfill is harmful and not preferred since it requires large area. Moreover, heavy metals such as molybdenum, nickel, iron and cobalt along with hazardous elements, i.e. arsenic might be leached out to land and water resources in communities unfortunately. The third approach is been the recovery of valuable metals such as molybdenum, cobalt and nickel to be recycled back as the raw materials for re-manufacturing of spent HDS catalyst, applicable to the zero waste scheme. The amount of the spent HDS catalyst is estimated to be approximately 150,000 ton/year to 170,000 tons/year in the worldwide [6]. Therefore, recovery of valuable metals from the large amount of the spent HDS catalysts is interested from an environmental and economical point of view.

Many research works have focused on recycling of valuable metals from the spent HDS catalyst, following the conventional pyrometallurgical and hydrometallurgical process routes along with the bioleaching route [6-14]. The hydrometallurgical route includes leaching by using different agents for example; i) acidic agents, i. e., sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), oxalic acid $(COOH)_2$, and citric acid ($C_6H_8O_7$) to selectively recover molybdenum or vanadium, ii) alkali leaching, i.e., sodium hydroxide

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(NaOH) and potassium hydroxide (KOH), iii) ammonium salts leaching using ammonium hydroxide (NH_4OH), ammonium carbonate $(NH_4)_2CO_3$, and ammonium sulfate $(NH_4)_2SO_4$, and iv) bio-reagents involving microorganisms in which their metabolisms require aerobic oxidation of reduced sulfur compounds such as bacteria and fungi. The bioleaching has been claimed to be more environmental friendly due to less chemicals used. The pyrometallurgical process involves salt roasting the discarded spent HDS catalyst with NaOH, sodium nitrate (Na_2NO_3) or sodium chloride (NaCl) followed by leaching in water or in sodium carbonate (Na_2CO_3). Other routes such as roasting in air carried out over 500°C to 700°C followed by acid leaching and smelting directly or after calcination have also been studied [7]. Nevertheless, effectiveness of individual recycling routes selected has been also based on original waste compositions. Therefore, more investigation should be further explored in order to extent to the commercial scale of recycling to serve both environmental and economic issues.

The pyro-hydrometallurgical route or (roasting-extraction method) has been of great interest and reported to be effective. However, limited research works have explored the use of Na_2CO_3 as the leaching agent. Recent technology has been reported to obtain 92% Mo efficiency via roasting followed by pressure leaching using 45 wt% Na_2CO_3 over temperatures of 180°C to 190°C [2]. The process nevertheless consumed quite large amount of Na_2CO_3. In addition, work by K. H. Park, *et al.* [13] employed alkali leaching using Na_2CO_3 at 40 $g \cdot L^{-1}$ concentration with 6 vol% H_2O_2 as an oxidant without preceding spent HDS catalyst calcination. Work notable molybdenum leaching efficiency approaching 85%. Though spent HDS catalyst calcination has been incorporated and studied in some research works and patents [7,15,16], the investigated temperature ranges were in the regime of higher than 600°C. Further, the effect of calcination temperature in the lower temperature range of 200°C to 600°C on leaching efficiency has been reported [17], which defined the optimum calcination temperature at 500°C for the recovery of spent Co/Mo-γ Al_2O_3 HDS catalyst.

Accordingly, pyro-hydrometallurgical process has therefore been applied to recover molybdenum from spent Ni/Mo HDS catalyst in this present study. Waste treatment or calcination prior to alkali (Na_2CO_3) leaching has been incorporated to investigate effects of calcination temperature in the range of 450°C to 650°C on leaching efficiency. The proposed recycling route started from pyrometallurgical process via calcination of spent HDS catalyst to remove excessive organic pollutant (carbon) and also to convert metal sulfides into metal oxides. Following the subsequent hydrometallurgical process, alkali (Na_2CO_3) leaching has been selected due to its selective leaching especially to molybdenum. Variables such as alkali concentration, leaching time, and solid to liquid ratio were investigated to assess extraction efficiency and determine the optimum condition required for the succeeding steps of purification, precipitation and finally calcination to obtain the recycling product.

2. Experimental

The extraction and recovery of molybdenum from spent HDS catalyst obtained domestically from a petroleum plant can be envisaged in experimental flow chart in Figure 1. Through sequential steps, spent HDS catalyst will be subjected to waste preparation, calcination, leaching, adsorption-desorption, precipitation and calcination. Analysis of the starting waste and products obtain from individual recycling steps has been performed using various techniques such as ICP-OES, XRD, WD-XRF, and SEM coupled with EDS to identify phase evolution of the products obtained from certain recycling steps and also to quantify the final product's composition, % purity and % recovery.

2.1 Waste preparation and calcination

The as-received spent HDS catalyst appeared in a cylindrical shape having 2 mm diameter and 4 mm high was subjected to crushing into the form of fine powder. The particle size of the powder prior to calcination and leaching steps was less than 210 micron (70 mesh). Chemical composition of the crushed spent HDS catalyst was analyzed using WD-XRF model: Rigaku ZSX Primus IV.

In order to remove residual oils and carbonaceous species, the ground spent HDS catalyst was calcined at 450, 550 and 650°C for 5 h, and with the intention of converting metal sulfides into metal oxides prior to proceed to the next step of leaching. Phases obtained after calcination at different temperatures were identified using XRD model: BRUKER model D2 phaser. Comparison was made to that of the as-received condition to identify phase evolution taking place in order to determine the optimum calcination temperature.

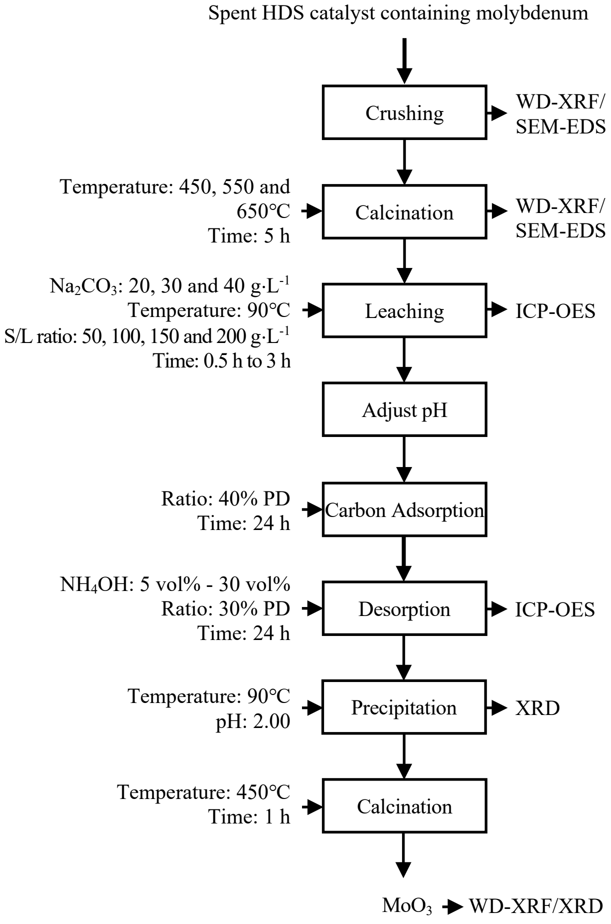


Figure 1. Experimental flow chart of molybdenum recovery from spent HDS catalyst.

2.2 Leaching

The as received and calcined samples were subsequently leached using Na_2CO_3 as the alkali reagent. In order to determine the optimum condition, variables such as Na_2CO_3 concentration at 20, 30 and 40 $g{\cdot}L^{-1}$ were investigated. The catalyst to leachant (or solid to liquid; S/L) ratios were varied at 50, 100, 150, and 200 $g{\cdot}L^{-1}$ with leaching time ranging from 30 min to 180 min. Leaching was controlled at a temperature of 90°C and a stirring speed of 250 rpm. Chemical compositions of the leached solution were analyzed by ICP-OES model: Perkin Elmer/Optima 8000).

2.3 Carbon adsorption-desorption

Activated carbon of analytical reagent (AR) grade was utilized as an adsorbent for the purification of the leached solution in order to selectively adsorb molybdenum on the activated carbon surface. The adsorption was controlled by using ratio of the activated carbon to the leached solution of 40 w/v% together with pre-adjustment of the solution pH within a range of 0.5-2.0 using hydrochloric acid. Desorption of molybdenum loaded on activated carbon was then followed by using NH_4OH varying at 5 vol% to 30 vol% and at the adsorbed activated carbon to solution ratio of 30% pulp density (PD). Both adsorption and desorption were controlled at ambient temperature for 24 h. ICP-OES analysis was performed to characterize the composition of the obtained desorption products.

2.4 Precipitation and calcination

Precipitation was carried out at 90°C using HCl till pH of the solution reached 2.0. Finally, the precipitate was calcined at 450°C for 1 h to obtain molybdenum trioxide (MoO_3) as the final recycling product. Phases obtained after precipitation and calcination were identified using XRD analysis while composition of the final product was determined using XRF analysis.

3. Results and discussion

3.1 Waste characterization and calcination

Chemical composition of the as-received spent HDS catalyst analyzed by XRF technique is listed in Table 1. It can be seen that the key element is molybdenum having 11.40 wt%, with other elements such as nickel (2.55 wt%), carbon (6.81 wt%), and while aluminum (28.2 wt%) and oxygen (40.55 wt%) are present as the support materials.

3.1.1 Effects of calcination temperatures on phase evolution of the calcined spent HDS catalyst

Since leaching of the originally obtained spent HDS catalyst might be somehow inefficient, calcination was then first performed to convert metal sulfides to metal oxides to facilitate the succeeding step of leaching. Therefore, effects of calcination temperature over 450°C to 650°C on phase transformation of the spent HDS catalyst have been investigated. It can be seen in Figure 2 that the ground spent HDS catalyst in the as-received condition appearing as black powder has changed its color to yellow, pale yellow and yellowish white as the calcination temperature increased. This color change has been linked to phase evolution of the calcined products detected by XRD analyses as illustrated in Figure 3. The results showed comparison of XRD spectra of the as-received and the calcined spent HDS catalyst over the range of 450°C to 650°C. The XRD spectra of the as-received spent HDS catalyst exhibited peaks of various compounds in which the main peaks being Al_2O_3 and the minor peaks being MoS_2. After calcination, transformation of molybdenum sulfide (MoS_2) to molybdenum oxides (MoO_2 and MoO_3) has been detected, as addressed in equation (1). It appeared that the higher the calcination temperature, the more evident the molybdenum oxide peaks observed.

$$2MoS_{2\,(s)} + 7O_{2\,(g)} \rightarrow 2MoO_{3\,(s)} + 4SO_{2\,(g)} \qquad (1)$$

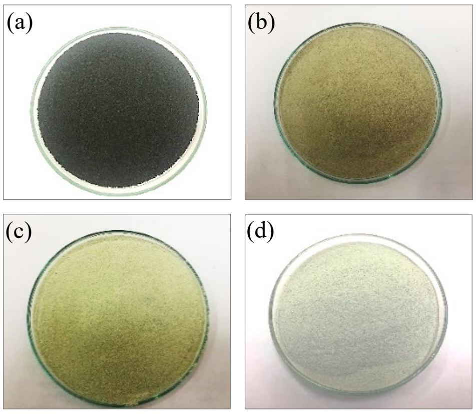


Figure 2. Ground spent HDS catalyst (a) as received, calcined at (b) 450°C, (c) 550°C and (d) 650°C for 5 h.

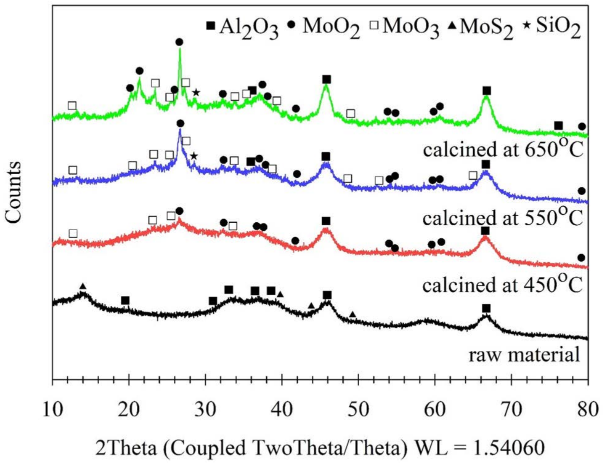


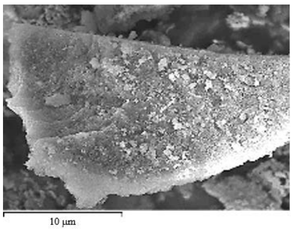
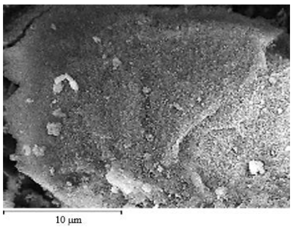
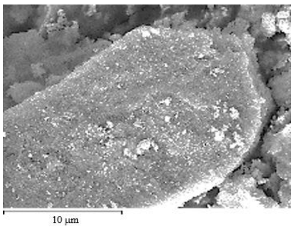
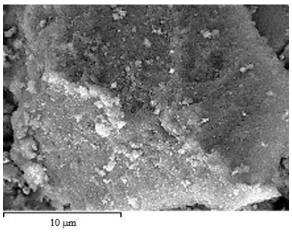
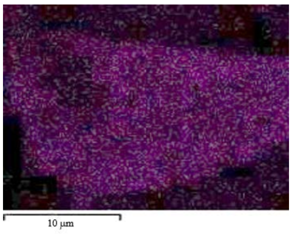
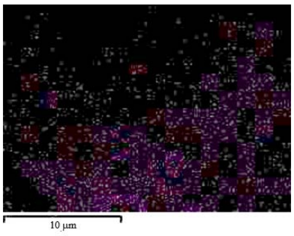
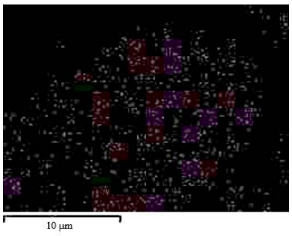
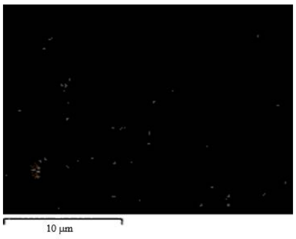
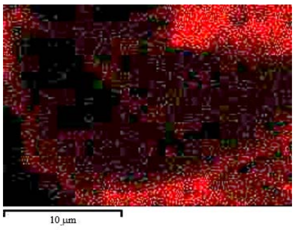
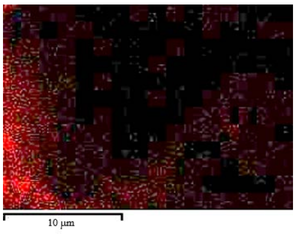
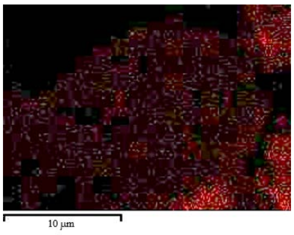
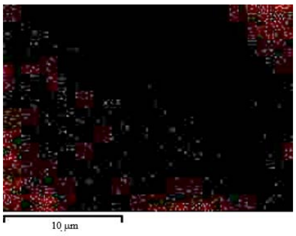
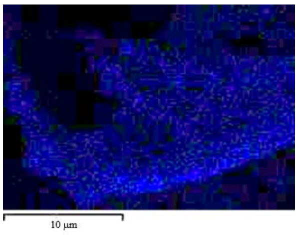
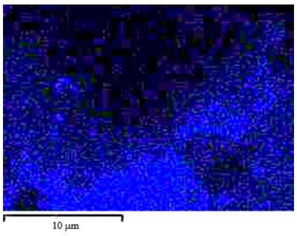
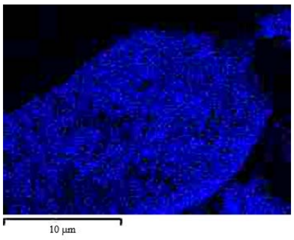
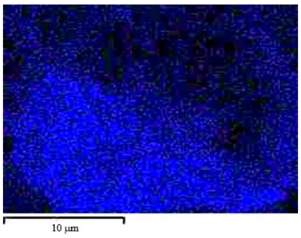
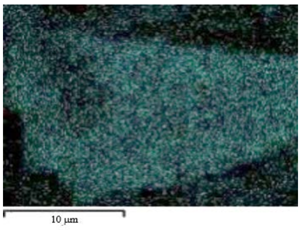
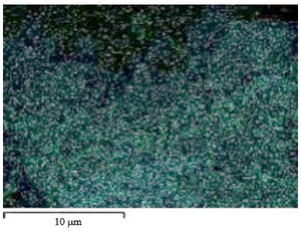
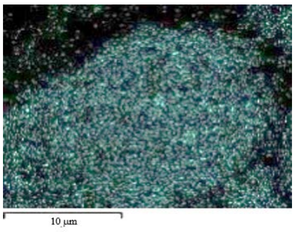
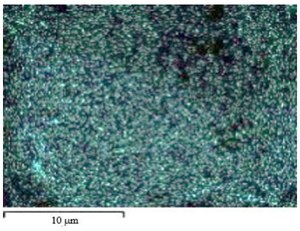
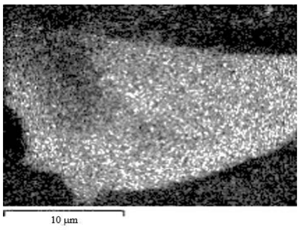
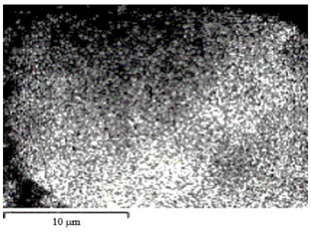
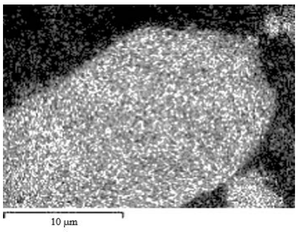
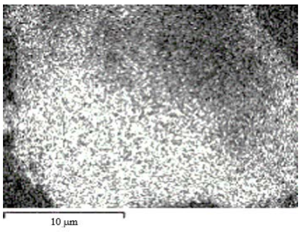
Figure 3. XRD spectra of as-received and calcined spent HDS catalyst samples.

Table 1. Chemical composition of spent HDS catalyst.

Element	**Mo**	**Ni**	**Al**	**P**	**C**	**O**	**S**	**Fe**	**Ca**	**Na**	**Other**
Mass %	11.40	2.55	28.20	2.21	6.81	40.55	7.18	0.12	0.06	0.29	balanced

In addition, it is worthy to mention that after calcination at the lower temperature of 450°C, phase evolution has been towards the formation of mainly MoO_3 with the relative minor being MoO_2. Then by raising the calcination temperature up to 550°C and 650°C, the appearance of MoO_2 was much more evident than that of MoO_3. This might be due to the tendency for MoO_3 sublimation toward a temperature of higher than 600°C reported by [17,18]. No evidence of insoluble complex compound formation was detected since the calcination temperature was less than 700°C [7]. Furthermore, SEM and EDS investigation on as-received and calcined samples revealed the depletion of sulfur and carbon (organic pollutant) after calcination, as depicted in Table 2, corresponding to work by D. Mohapatra, and K.H. Park [17].

Table 2. SEM images and EDS maps of as-received and calcined spent HDS catalyst samples at different temperatures (scale bar at 10 µm).

	As received sample	**Calcined at 450°C**	**Calcined at 550°C**	**Calcined at 650°C**
SEM				
S				
C				
O				
Mo				
Al				

3.2 Alkali (sodium carbonate) leaching

3.2.1 Effects of calcination temperature on molybdenum leaching efficiency of spent HDS catalyst

Effects of calcination over 450°C to 650°C on molybdenum leaching efficiency of the spent HDS catalyst using Na_2CO_3 will be first discussed. As illustrated in Figure 4 showing effects of calcination temperature on leaching efficiency, it was found that non-calcined spent HDS catalyst obviously gives inferior leaching efficiency in comparison to those of calcined spent HDS catalyst. Calcination at lower temperature at 450°C seemed to give better leaching efficiency in this case. By considering at 20 g·L^{-1} Na_2CO_3 concentration, leaching of calcined spent HDS catalyst sample at 450°C gave the highest efficiency of 93% whereas that of spent HDS catalyst sample calcined at 650°C gave the lower efficiency at 89%. It could be explained that this slight reduction in molybdenum extraction efficiency as the calcination temperature increased from 450°C to 650°C might be due to the preferential alkali leaching among molybdenum oxide species, i.e. MoO_2 and MoO_3 compounds. Since the XRD result previously revealed more evident MoO_2 spectra towards the higher calcination temperature and subsequently become the dominant phase at 650°C. The greater content of MoO_2 attained at higher calcination temperature might be responsible for a less tendency for Na_2CO_3 alkali leaching accordingly.

3.2.2 Effects of sodium carbonate concentration on molybdenum leaching efficiency of spent HDS catalyst

By considering effects of Na_2CO_3 concentration over 20 g·L^{-1} to 40 g·L^{-1} on leaching efficiency, it was found that molybdenum extraction efficiency tended to increase slightly with increasing Na_2CO_3 concentration. For leaching of spent HDS catalyst sample calcined at 450°C, it was found that molybdenum extraction efficiency increased from 93% to 97% when the Na_2CO_3 concentration increased from 20 g·L^{-1} to 40 g·L^{-1}. The proposed equation is as follows where sodium molybdate (Na_2MoO_4) and carbon dioxide (CO_2) are the reaction products;

$$MoO_{3\,(s)} + Na_2CO_{3\,(aq)} \rightarrow Na_2MoO_{4\,(aq)} + CO_{2\,(g)} \qquad (2)$$

3.2.3 Effect of solid to liquid (S/L) ratio on molybdenum leaching efficiency

The effect of the solid to liquid ratio varied from 50 g·L^{-1} to 200 g·L^{-1} on the molybdenum leaching was examined at the following condition: 450°C calcination temperature, 40 g·L^{-1} Na_2CO_3 concentration, 2 h-leaching time, 90°C leaching temperature and 250 rpm stirring spend as presented in Figure 5. It was observed that the optimum S/L ratio was at 100 g·L^{-1}. Beyond such an S/L ratio, molybdenum dissolution declined due to insufficient amount of leachate ions to leach molybdenum into the solution.

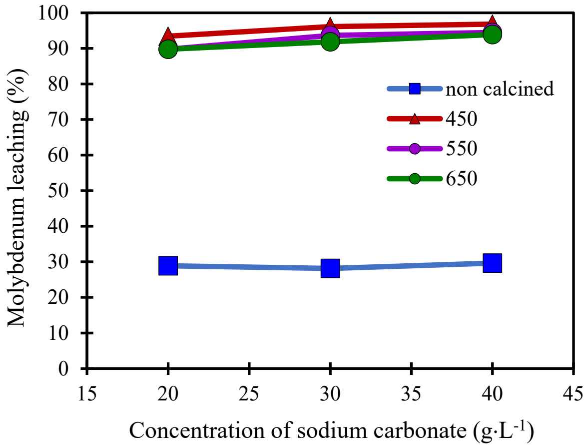


Figure 4. Effects of sodium carbonate concentration and calcination temperature on molybdenum leaching (condition: 1 h-leaching time, 100 g·L^{-1} S/L ratio, 90°C leaching temperature, 250 rpm stirring speed).

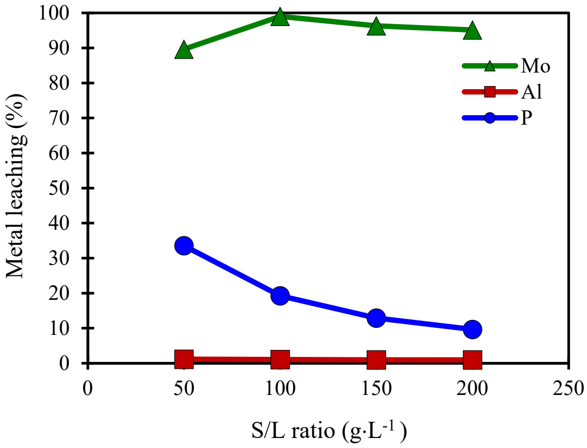


Figure 5. Effect of S/L ratio on metal leaching (condition: 450°C calcination temperature, 40 g·L^{-1} sodium carbonate concentration, 90°C leaching temperature, 2 h-leaching time, 250 rpm stirring speed).

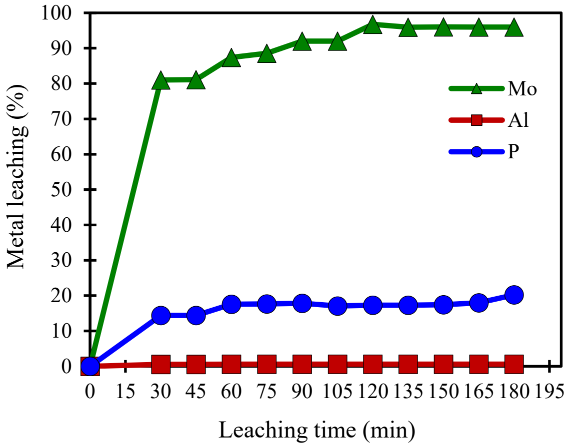


Figure 6. Effect of leaching time on metal leaching (condition: 450°C calcination temperature, 40 g·L^{-1} sodium carbonate concentration, 90°C leaching temperature, 100 g·L^{-1} S/L ratio, 250 rpm stirring speed).

3.2.4 Effects of leaching time on molybdenum leaching efficiency of spent HDS catalyst

Over the investigated leaching time of 30 min to 180 min (0.5 h to 3 h) using spent HDS catalyst sample calcined at 450°C as shown in Figure 6, it was observed that the extraction rate of molybdenum increased significantly during the early period of leaching till about 1 h and then becoming stabilized when the leaching time approached 2 h (120 min). The maximum molybdenum extraction efficiency was found at 96%. Leaching of aluminium however did not show a significant increase over the leaching time investigated while leaching of phosphorus appeared to increase slightly with time to less than 20% efficiency.

3.3 Carbon adsorption-desorption

Carbon adsorption of the leached solution, by using activated carbon at S/L ratio at 40 w/v% at room temperature for 24 h, offered high molybdenum adsorption efficiency >99%. There was no significant effect in molybdenum adsorption efficiency when leaching the solution having pH varying from 0.5 to 2.0. Subsequently, desorption of molybdenum from load activated carbon was carried out at 30%w/v of load activated carbon to NH_4OH for 24 h.

3.3.1 Effect of ammonium hydroxide concentration on molybdenum desorption efficiency

On the desorption of molybdenum from the load activated carbon, effect of NH_4OH concentration of 5 vol% to 30 vol% on molybdenum desorption efficiency is demonstrated in Figure 7. It can be seen that molybdenum desorption increased from 84% to 98% with increasing NH_4OH concentration from 5 vol% to 15 vol%. The desorption of molybdenum became level off when NH_4OH concentration was greater than 15 vol%.

3.4 Precipitation of ammonium molybdate and calcination

After molybdenum desorption, the pH of the solution increased up to 9.3 due to NH_4OH addition. When proceeding to the next step of precipitation, the solution was subjected to hydrochloric acid addition to adjust its pH to 2.0, and the temperature was controlled at 90°C. Precipitation of ammonium molybdates ($(NH_4)_2MoO_4$) then resulted, according to the following equations [19].

$$Na_2MoO_{4\,(aq)} + 8HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + MoCl_{6\,(aq)} + 4H_2O_{(aq)} \quad (3)$$

$$MoCl_{6\,(aq)} + 3NH_4OH_{(aq)} \rightarrow (NH_4)_2MoO_{4\,(\text{ammonium molybdates})} + NH_4Cl_{(aq)} \quad (4)$$

After desorption of molybdenum from activated carbon using ammonium hydroxide, the solution reached the pH of around 9.30. Subsequently, HCl was added to the solution till the pH reduced to 2.0 with the controlled temperature at 90°C. This proceeded to precipitation of ammonium molybdate appearing as greenish grey powder. After filtered, rinsed with deionized water and dried, the precipitate was subjected to calcination at 450°C for 1 h such that ammonium molybdate precipitate has transformed into MoO_3 as the desired recycling product. XRD spectra as illustrated in Figure 8 also confirmed the presence of molybdenum trioxide in comparison to that of pre-calcined ammonium molybdate. Result acquired by XRF analysis revealed the composition of the obtained molybdenum trioxide to be of 99.5% purity. Based on this experiment, the recovery efficiency of molybdenum from spent HDS catalyst as molybdenum trioxide was approximately 82%.

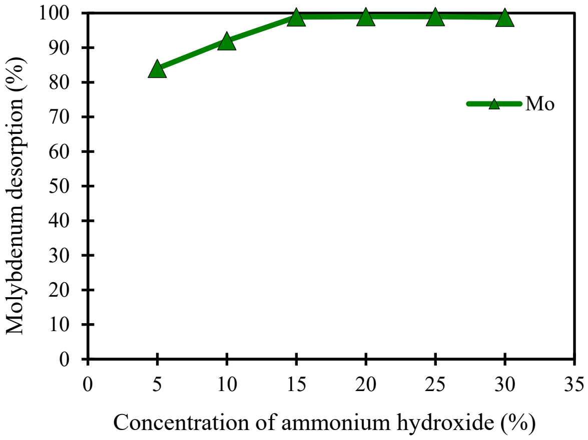


Figure 7. Effect of ammonium hydroxide concentration on molybdenum desorption.

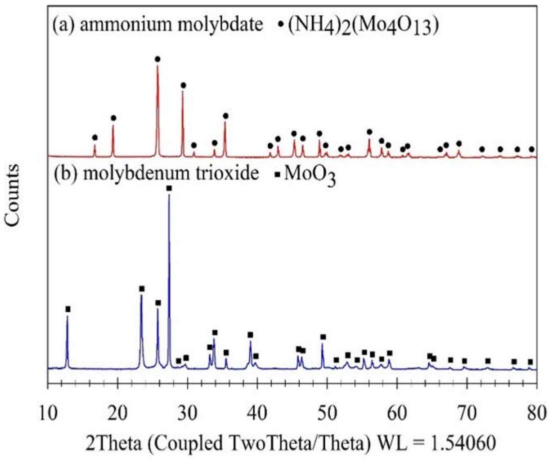


Figure 8. XRD spectra of ammonium molybdate and molybdenum trioxide.

4. Conclusions

In present study, the combination of pyro-hydrometallurgy process has been utilized to recovery molybdenum from spent HDS catalyst; detailing in the 5 key steps of i) calcination of the spent HDS catalyst, ii) alkali leaching, iii) carbon adsorption-desorption, iv) precipitation and v) calcination to obtain molybdenum trioxide as the recycling product.

Effects of calcination temperature, on molybdenum leaching efficiency have been evidenced, giving the optimum condition at 450°C for 5 h. Increasing calcination temperature above 450°C led to the formation of molybdenum dioxide (MoO_2) compound in a greater extent, which might not be readily leached by alkali in comparison to molybdenum trioxide compound. Apart from leaching efficiency dependence on calcination temperature, effects of sodium carbonate concentration, leaching time and solid to liquid ratio have also been observed, giving the optimum condition at 40 g·L^{-1} sodium carbonate concentration, 2 h-leaching time, 100 g·L^{-1} solid to liquid ratio and 90°C leaching temperature.

To produce molybdenum trioxide of high purity, purification has proceeded. Carbon adsorption followed by desorption with ammonium hydroxide assured the promising molybdenum desorption efficiency of 98% at 15 vol% of ammonium hydroxide addition. After precipitation by using hydrochloric acid to control the solution pH at 2.0 and the temperature of 90°C, ammonium molybdate was subsequently obtained. Finally, the precipitate was subjected to calcination at 450°C for 1 h to achieve the desired molybdenum trioxide of 99.5% purity. The recovery efficiency of molybdenum from spent HDS catalyst as molybdenum trioxide was approximately 82%.

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