Preparation and characterization of molybdenum trioxide from spent hydrodesulfurization catalyst

Barsha Dash†, Indra Narayan Bhattacharya, Bhaskara Venkata Ramanamurthy, and Raja Kishore Paramguru

Institute of Minerals and Materials Technology, Bhubaneswar-751013, Orissa, India

Abstract−An approach to produce molybdenum trioxide from spent hydrodesulfurization (HDS) catalyst, obtained from a petroleum refinery, is presented here. The spent catalyst was devolatilized at 600 ℃ so as to make it free from oils, organics and other volatile species. It was then roasted with sodium carbonate at a temperature of 850 ℃ for 30 min. The leaching efficiency for 20% soda roasted sample at 10% pulp density was 99.8%. From the solution molybdenum was precipitated out as ammonium molybdate at pH 1.0 with HCl and ammonium chloride. This ammonium molybdate was calcined at 750 ℃ to get MoO_3. The product was characterized by XRD. Its purity was determined titrimetrically and by ICP-AES.

Key words: Spent Catalyst, Soda Roasting, Leaching, Molybdenum, Molybdenum Trioxide

INTRODUCTION

Molybdenum is a metal of group six. It readily forms hard, stable carbides, and for this reason it is often used in high-strength steel alloys. Silvery in appearance, molybdenum helps in keeping our environment green by desulfurizing carbon-based fossil fuels. Industrially, molybdenum compounds are used in high-pressure and temperature resistant greases as pigments and catalysts. As the demands for catalysts are increasing in modern industry, the utilization of spent catalysts calls for research and developmental efforts. Many types of catalysts are used; however, the catalysts used in petroleum refineries have received much attention in recent years. Recovery of transition metals from spent petroleum refining catalysts is an important problem. These industries mostly use molybdenum containing catalyst for desulfurization and mild hydrogenation process. During the hydrorefining the catalyst gets poisoned due to contamination with different elements such as S, Fe, Si and Zn etc.

The only way to avoid disposing these spent catalysts directly in the environment is to process them, meeting the acceptable environmental demands, to get a value added product. Various options such as soda roasting [1] and salt roasting [2] are there for molybdenum recovery where a water soluble molybdate product is obtained. Carbothermic reduction can also be done for hydrorefining spent catalyst to extract molybdenum metal [3]. Molybdenum can also be recovered through hydrometallurgical processing via leaching with sodium carbonate mixed with hydrogen peroxide [4]. Direct ammonical or alkali leaching is another option for spent catalyst processing [5,6]. Processing via fusion is also an option for utilization of spent catalyst [7]. Recovery of molybdenum compound from the leached liquor is another course like carbon adsorption-desorption studies [3,8] and solvent extraction [9-12]. In this paper the preparation and characterization of molybdenum trioxide from the HDS spent catalyst through roasting, leaching and precipitation has been carried out.

†To whom correspondence should be addressed.
E-mail: barsha.dash@gmail.com

Table 1. Chemical composition of roasted catalyst

Element	Mo	V	Fe	Cu	Ni	Co	Zn
Percentage	14.4	0.635	0.28	0.1	4	Nil	0.03

EXPERIMENTAL

1. Materials

The original hydrodesulfurization catalyst was crushed, sieved and roasted at 600 ℃ to remove oils and organics. The weight loss was found to be 44%. The chemical composition of the devolatilsed catalyst is given in Table 1.

2. Characterization

2-1. XRD

Phase determination by X-ray diffractometry study was done by using Phillips powder diffractometer PW 1830 X'pert system in the 2θ range of 10 to 70º with voltage of 30 kV and CuKα was used to characterize the samples.

2-2. ICP-AES

The constitutional elemental analysis was done by ICP-AES of model No. Perkin- Elmer Plasma 4000 ICP-AES.

2-3. AAS

Other trace metals were estimated by Perkin Elmer 300A atomic absorption spectrophotometer.

2-4. Analyses

Volumetric estimation of molybdenum was done by following the complexometric determination of Mo [13]. EDTA reacts with Mo^V ion to form a stable complex compound. Mo^{VI} is reduced to Mo^V by hydrazine in sulphuric acid medium in the presence of excess EDTA which is titrated with a standard solution of zinc salt with erichrome black T. The method is applicable to analysis of alloys containing Bi, Cd, Co, Zn, Ni, Cu, Hg, V, Cr and Pb. All accompanying elements are first titrated in one portion of the solution without reducing Mo^{VI}. The total amount of Mo and the accompanying elements is titrated in the other portion after reduction. Substracting the former titration value from the later gives the value of molyb-

denum titration.

Volumetric estimation of vanadium was carried out by titrimetric determination method [14] of vanadium in ores with Mohr's salt. The method is based on the titration of the pentavalent vanadium ion in a medium of 5N solution of sulphuric acid using standard solution of Mohr's salt in the presence of excess phosphoric acid, which binds the Fe^{3+} ion in a colorless complex.

3. Roasting

The catalyst was roasted in a 6"x6" electrically heated 4 kW muffle furnace (horizontal type). A charge consisting of devolatized HDS catalyst mixed with 20% (w/w) anhydrous sodium carbonate (Merck, India) was introduced in the furnace and heated to the desired temperature. The rate of heating was set as 5 °C per minute. The effect of temperature of roasting was studied from 550 °C to 950 °C while that of duration was carried out at 850 °C.

4. Leaching

Leaching of the soda roasted materials was carried out by taking 20 g soda roasted material with 100 ml water in a 250 ml conical flask fitted in a condenser. Heating and stirring were done through a hot plate with magnetic stirrer at around 250 rpm. After the leaching was completed, the slurry was filtered. The liquor contains dissolved molybdenum and vanadium.

5. Precipitaion

For the precipitation of the leach liquor, ammonium chloride (Merck, India) and HCl (Merck, India) were added in two sequences, i.e., route 1 and route 2. In route 1 HCl was first added to acidify 40 ml leach liquor to pH 1.0 taken in a 100 ml glass beaker. After that 8 g ammonium chloride was added with stirring by a magnetic stirrer. In another two similar sets of experiments, 1 g and 3 g ammonium chloride were aded to study the variation in the amount of ammonium chloride. In route-2 again 1, 3 and 8 g of ammonium chloride were added followed by addition of HCl upto pH 1.0 in each case. Precipitates obtained from all cases through both the routes were filtered and dried in a hot air oven at 80 °C for 24 h.

RESULTS AND DISCUSSION

The detailed chemical analyses, spectrophotometric analyses, leaching procedure and precipitation are given below in different sections. Fig. 1 shows the XRD pattern of the devolatilized catalyst. It indicates major presence of alumina, MoO_3 and NiO to a lesser extent.

1. Roasting

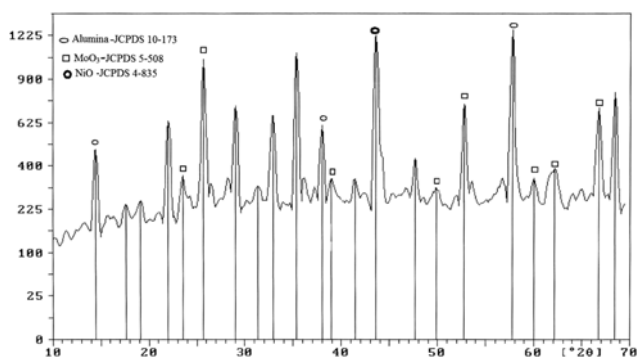The catalyst was initially devolatilized at 600 °C to remove oils
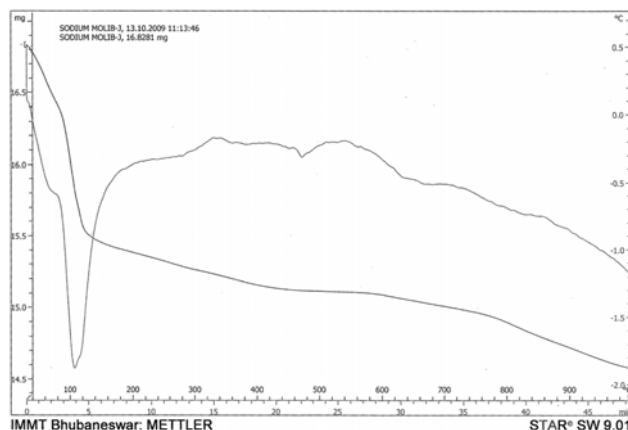

Fig. 1. XRD of devolatilized catalyst.

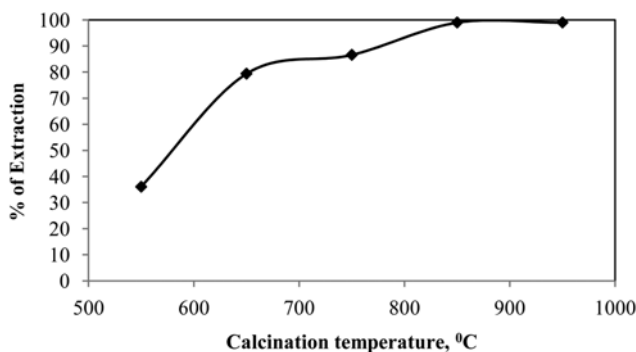**Fig. 2. TG and DTA analysis of mixture of catalyst and sodium carbonate.**

Fig. 3. Variation of roasting temperature, Condn: 20% soda, time-1 h.

and other volatile matters and organics. TG and DTA analysis of soda (20% w/w) mixed catalyst was done, which is shown in Fig. 2. The first weight loss of 7.84% was observed at 100 °C, showing the loss of moisture. Then the second weight loss for the rest of the region up to 1,000 °C was 5.34% in the thermogram. This loss can be attributed to loss of carbon dioxide.

In the process of soda roasting, molybdenum trioxide reacts with sodium carbonate giving sodium molybdate and carbon dioxide. The reaction is as follows:

$$MoO_3 + Na_2CO_3 \rightarrow Na_2MoO_4 + CO_2 \qquad (1)$$

The roasting temperature was varied from 550 to 950 °C and the percentage of extraction of Mo in the leach liquor was plotted as shown in Fig. 3. The extraction of molybdenum was in increasing order up to 850 °C.

The highest extraction was found at 850 °C and above due to the complete diffusion of sodium carbonate. This is because the melting point of anhydrous sodium carbonate is 850 °C. At 750 °C and above molybdenum has a tendency to form polymeric species. But when it is alkalized the polymolybdate ion converts into MoO_4^{2-} [15]. Thus, molybdenum forms soluble sodium molybdate ($Na_2MoO_4^{2-}$).

The kinetics of roasting is given in Fig. 4. The time period of 45 minutes was optimized.

2. Leaching

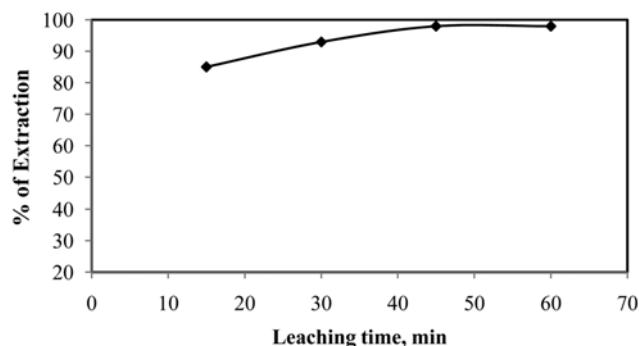Leaching experiments were carried out by taking the soda roasted

Fig. 4. Kinetic of leaching with soda roasting of spent catalyst, Condn; temp.- 850 °C, 20% sodium carbonate.
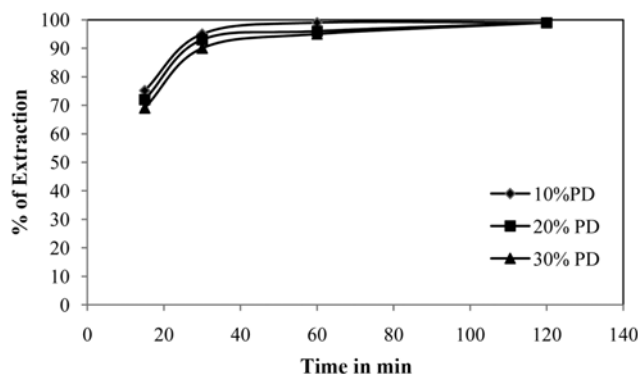

Fig. 5. Kinetics of leaching with variation of pulp densities, Condn: Temp.-80 °C.

catalyst and demineralized water so as to dissolve the soluble sodium molybdate salt formed during the roasting.

2-1. Kinetics of Leaching

The kinetics of leaching was studied and given here in Fig. 5 with variation in pulp densities.

The optimized leaching time was 30 min. After 30 min the kinetic became slower and the plot was found to be almost horizontal, indicating exhaustion of sodium molybdate. The nature of the plot shows that molybdenum extraction has reached the limit. No further extraction could occur in that condition.

2-2. Effect of Leaching Temperature

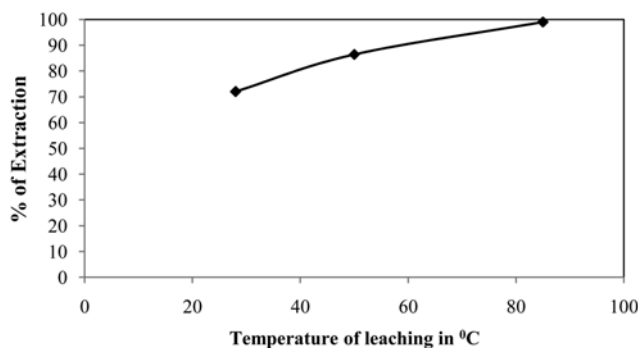The temperature of leaching was varied from room temperature

Fig. 6. Effect of leaching temperature, Condn: time- 30 min, pulp density- 10%.

Table 2. Recovery of Mo from route 1

Amount of NH₄Cl	Recovery of Mo
8 g	94.24%
3 g	94.19%
1 g	90.03%

Table 3. Recovery of Mo from route 2

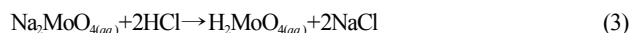| Amount of NH₄Cl	Recovery of MoO₃
8 g	89%
3 g	87.5%
1 g	78.44%

(28 °C) to 80 °C as shown in Fig. 6. At 28 °C the leaching efficiency was found to be 77%, and it increased to 99% at 80 °C.

3. Precipitation

To precipitate ammonium molybdate, from the alkaline leach liquor, HCl and ammonium chloride were added. The sequence of addition of HCl and ammonium chloride was carried out by following two routes.

3-1. Addition of HCl Followed by Ammonium Chloride

To the leach liquor conc. HCl was added dropwise to bring the pH to 1.00. Sodium molybdate present in the solution when acidified in aqueous media gives molybdic acid given in Eq. (3). Ammonium chloride was then added to get a precipitate of ammonium molybdate as shown in Eq. (4).

$$Na_2MoO_{4(aq.)}+2HCl \rightarrow H_2MoO_{4(aq.)}+2NaCl \tag{3}$$

$$7 H_2MoO_{4(aq.)}+6NH_4Cl \rightarrow (NH_4)_6Mo_7O_{24.} 4 H_2O+6HCl \tag{4}$$

The weight percentage of the precipitate through route 1 is given in Table 2.

3-2. Addition of Ammonium Chloride Followed by HCl

To the leach liquor, ammonium chloride was added. First, some cloud-like turbidity developed, which dissolved by subsequent acid addition. A precipitate was obtained at a pH around 2.00. The acid addition was continued up to pH 1.00. The weight percentage of the precipitate through route 2 is given in Table 3.

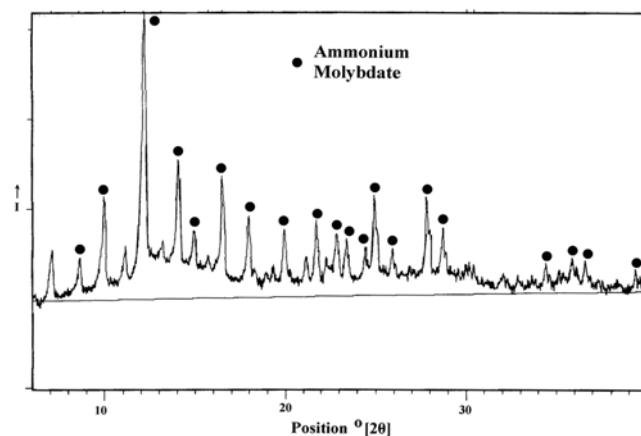Out of the above two routes, the first one is preferable as it gives

Fig. 7. XRD of Ammonium molybdate.

90.03% recovery in 1 g ammonium chloride. The XRD pattern of the obtained ammonium molybdate is given in Fig. 7, which matches perfectly with standard ammonium molybdate (JCPDS-9-412). Ammonium molybdate precipitated as given by Eq. (4). It was dried in a hot air oven at 80 °C for 24 h. This sample was calcined at 750 °C for 1 h to get MoO_3.

3-3. XRD

The XRD patterns of molybdenum trioxide obtained through precipitation followed by calcinations matches with that of standard MoO_3 pattern as shown in Fig. 8.

The 100% peak with d-value of 3.26 A° corresponds to MoO_3. Subsequent peaks also match with molybdenum trioxide standard peaks.

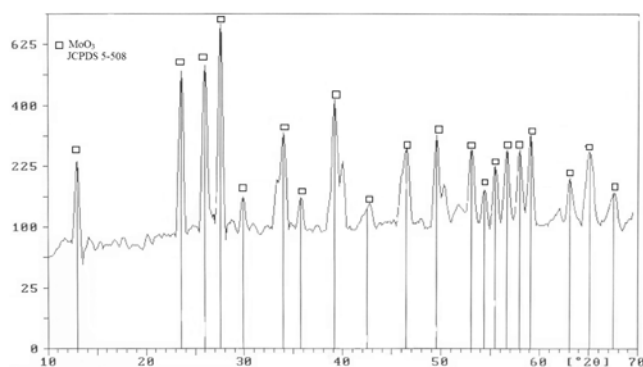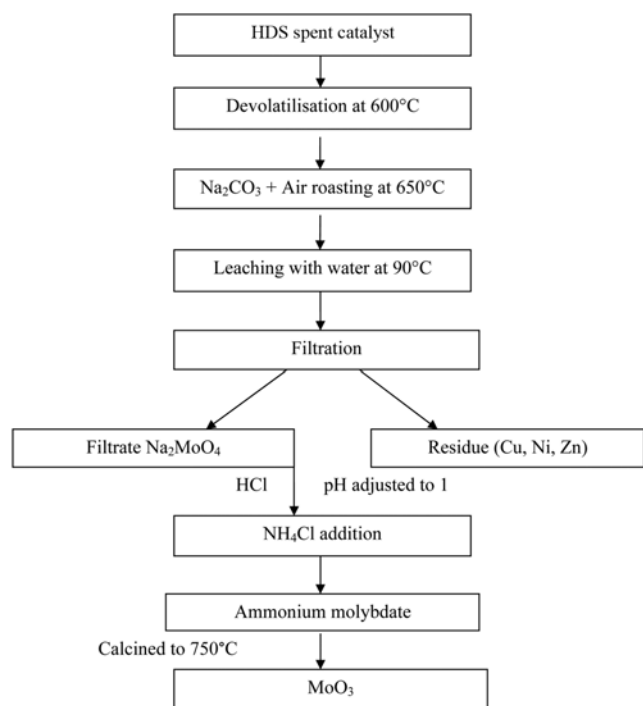To test the purity of the material it was digested and Mo was analyzed titrimetrically, while all other impurities were analyzed through ICP-AES. Table 4 below shows the total composition of the finally obtained material.

A complete flow sheet from spent catalyst to value added MoO_3 is given below.

CONCLUSIONS

HDS spent catalyst obtained from petroleum refinery was heated as such to 600 °C so as to make it free from oils, organics and other volatile species. It was then roasted with sodium carbonate at 850 °C for 1 h. The leaching efficiency for 20% soda roasted sample at 10% pulp density was 99%. From the above solution molybdenum was precipitated out as ammonium molybdate with addition of HCl upto pH 1.0 followed by ammonium chloride. This ammonium molybdate was calcined at 750 °C to get MoO_3. The required characterizations like XRD of the product obtained after calcination were carried out. The purity was determined titrimetrically and through ICP-AES.

ACKNOWLEDGEMENT

Fig. 8. XRD of obtained product.

Table 4. Total composition of obtained MoO_3

Element	MoO_3	V_2O_5	Al_2O_3	SiO_2	WO_3
%	95%	2.85%	1.13%	0.98%	0.025%

Flow sheet for MoO_3 preparation.

REFERENCES

1. B. B. Kar, P. Datta and V. N. Misra, *Hydrometallurgy*, **72**, 87 (2004).
2. B. B. Kar, B. V. R. Murthy and V. N. Mishra, *Int. J. Miner Process.*, **76**, 143 (2005).
3. B. B. Kar, *Int. J. Miner Process.*, **75**, 249 (2005).
4. K. H. Park, D. Mohapatra and B. R. Reddy, *J. Hazard. Mater.*, **138**, 311 (2006).
5. Y. Chen, Q. Feng, Y. Shao, G. Zhang, L. Ou and Y. Lu, *Int. J. Miner. Process.*, **79**, 42 (2006).
6. M. S. Villarreal, B. I. Kharisov, L. M. Torres-Martnez and V. N. Elizondo, *Ind. Eng. Chem. Res.*, **38**, 4624 (1999).
7. R. G. Busnardo, N. G. Busnardo, G. N. Salvato and J. C. Afonso, *J. Hazard. Mater. B*, **139**, 391 (2007).
8. V. S. Bhave, P. R. Menon, P. P. Shukla and T. K. Mukherjee, *Hydromet-90*, Research and Practice in Hydrometallurgy, 6.11.1-6.11. 4 (1990).
9. J. W. An, Y. H. Lee, S. J. Kim, T. Tran, S. O. Lee and M. J. Kim, *Miner. Eng.*, **22**, 1020 (2009).
10. K. H. Park, B. R. Reddy, D. Mohapatra and C.-W. Nam, *Int. J. Miner Process.*, **80**, 261 (2006).
11. K. H. Park, D. Mohapatra and C.-W. Nam, *J. Hazard. Mater.*, **148**, 287 (2007).
12. A. Saily, U. Khurana, S. K. Yadav and S. N. Tondon, *Hydrometallurgy*, **41**, 99 (1996).
13. A. I. Busev, V. G. Tiptsova and V. M. Ivanov, *Analytical chemistry of rare elements*, Mir Publishers Moscow, 228 (1981).
14. A. I. Busev, V. G. Tiptsova and V. M. Ivanov, *Analytical chemistry of rare elements*, Mir Publishers Moscow, 176 (1981).
15. A. I. Busev, V. G. Tiptsova and V. M. Ivanov, *Analytical chemistry of rare elements*, Mir Publishers Moscow, 221 (1981).