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PRELIMINARY RESULTS OF METALS LEACHING FROM A SPENT HYDRODESULPHURIZATION (HDS) CATALYST

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A spent industrial HDS catalyst Ni,Mo/γ–Al_2O_3 used for reducing sulphur in petroleum products was physically and chemically characterized by X-ray diffraction, scanning electron microscope, electron microprobe and chemical analysis. The leaching efficiency of Mo, Ni, V and Al from the spent catalyst in oxalic acid solution with hydrogen peroxide addition was investigated. The effects of oxalic acid and hydrogen peroxide concentrations and the stirring speed on the rate of metal leaching were studied. The results revealed that addition of hydrogen peroxide to oxalic acid up to 3.0M H_2O_2 concentration enhanced leaching of metals remarkably, and thereafter remained relatively constant. The highest extraction of metals from the spent catalyst (at 50°C in solution of 0.5M $H_2C_2O_4$ with 3.0M H_2O_2) was found to be 90% Mo, 94% V, 65% Ni and 33% Al in 4 hour leaching.

Key words: spent hydrodesulphurization catalyst, metal foulants, acidic leaching

INTRODUCTION

The petroleum refining industry makes extensive use of catalysts for desulphurization of various fractions. The most common hydrodesulphurization (HDS) catalysts are Ni,Mo and Co,Mo on the γ-alumina support. During hydrodesulphurization the catalysts are deactivated by compounds of S, C, V, Fe, Ni, Si and traces of As and P (Furimsky and Massoth, 1999). As a result, the spent catalysts are classified as hazardous materials. However, such waste materials containing high metal concentrations may be considered as "artificial ores", since they can serve as secondary raw materials with a consequent reduction in the demand for primary mineral resources. Recycling of spent catalysts became an unavoidable task

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not only for lowering catalysts costs but also for reducing their waste to prevent the environmental pollution. A variety of processing approaches for recovering metals from the spent catalysts has been proposed and most of the literature in this field is patented (Furimsky, 1996; Yoo, 1998). The spent catalysts are subjected to hydrometallurgical or hydropyrometallurgical treatment for metals recovery. In both cases the metals are recovered as mixed solutions and then separated by conventional separation techniques (solvent extraction, selective precipitation, ion-exchange). Hydrometallurgical processes involve leaching with alkaline or acidic solutions. Many reagents, such as NaOH, H_2SO_4, NH_3, $(NH_4)_2SO_4$ and oxalic acid with H_2O_2 and $Fe(NO_3)_2$, have been tested (Queneau et al., 1989; Rabah et al., 1997; Siemens et al., 1986; Stanislaus et al., 1993; Marafi et al., 1994; Marafi and Stanislaus, 2003). Hydropyrometallurgical processes involve roasting with Na_2CO_3, NaCl or Cl_2 gas (Kar et al., 2004; Biswas, 1985; Gaballah et al., 2002). The main aim of the present research work was to investigate the possibility and efficiency of leaching of the spent hydrodesulphurization catalyst in oxalic and sulphuric acids with oxidizing agents addition.

EXPERIMENTAL

CHARACTERIZATION OF SPENT CATALYST

The spent HDS catalyst was in the form of cylindrical extrudates of approximate diameter 0.3-0.4 mm and length 4-6 mm. It contained residual oil and was washed with hot toluene by Soxhlet process and dried at 110°C before experiments. The surface of the deoiled catalyst has been determined by nitrogen adsorption (BET method) and is equal to 80.0 m^2/g. Powder XRD analysis of the spent catalyst showed that its main phase is $\gamma{-}Al_2O_3$, but V_5S_8 compound was also detected. Chemical analysis of the spent catalyst confirmed its partial composition as follows: 5.08% Mo, 5.26% Ni, 5.36% V and 24.57% Al. In turn, CHNS analysis showed that the spent catalyst contained (wt. %) carbon 17.6, hydrogen 1.14, nitrogen 0.38 and sulphur 9.64. The most interesting microscope evidence found in this study is provided by the cross-section of the spent catalyst extrudate. Electron microprobe analysis of the edge extrudate cross-section proved a high content of vanadium (23.37%), iron (4.12%) and sulphur (22.56%), but low content of nickel (2.71%) and molybdenum (3.42%). The middle extrudate cross-section did not evidence vanadium and iron. The results of microprobe analysis at the edge and middle part of the cross-section of the spent catalyst extrudate are given in Table 1 and in Fig. 1.

Table 1. Microprobe analysis of the cross-section of the spent catalyst extrudate

Part of the cross-section	Element content, %										
	C	O	Na	Al	Si	S	Ca	V	Fe	Ni	Mo
(1) edge	5.31	21.35	0.84	15.94	0.28	22.58	0.11	23.37	4.12	2.31	3.42
(2) middle	17.62	36.25	0.18	32.39	0.16	7.01	0.13	0.11	0.00	2.25	3.89

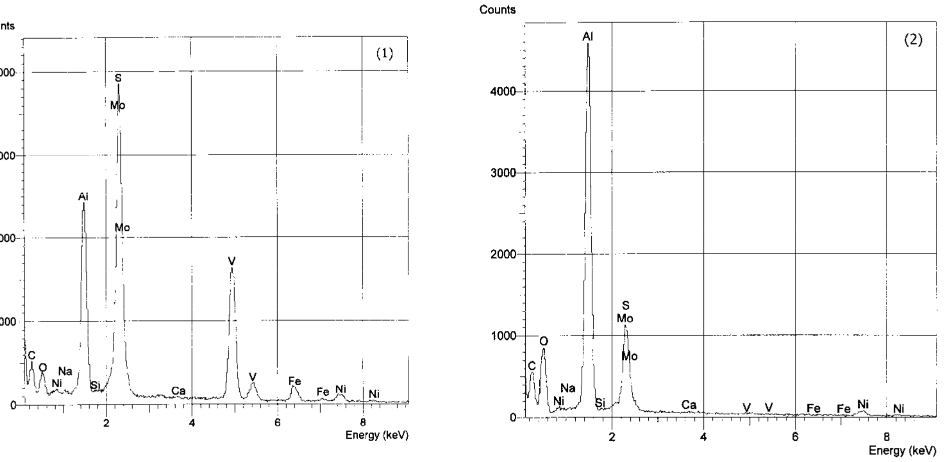

Fig. 1. Microprobe analysis of the cross-section of the spent HDS catalyst extrudate: (1) edge, (2) middle

It is clearly shown that metal foulants such as vanadium, nickel and iron are concentrated near the outer surface of the catalyst extrudate, blocking the pore mouths and retarding the access of the reactants to the active sites of the catalyst with the pores.

LEACHING EXPERIMENTS

In each experiment a flask containing 200 ml of leaching solution of the desired concentration was submerged in a tank the temperature of which was kept constant to within 0.1°C. When the required temperature had been reached a charge of 0.5 g of the spent catalyst was added and the stirring was started. A mechanical glass agitator of L shape with 25 mm impeller was applied. Its tip speed converted from 600 m^{-1} was equal to 0.785 m/s. The leaching was carried out for 3 and 4 hours during which nine 1 ml samples of the solution were taken for determination of the molybdenum, nickel, vanadium and aluminium concentration by the atomic emission spectrometry with inductively coupled plasma as the excitation source. The reproducibility of the leaching experiments was determined to be of order of ± 2% by repeating selected experiments under identical conditions.

RESULTS AND DISCUSSION

SELECTION OF THE PROPER LEACHING SOLUTION

In order to choose a suitable leachant the solutions of sulphuric and oxalic acids were tested with H_2O_2, $NaNO_3$, NH_4NO_3 and $(NH_4)_2S_2O_8$ addition. The leaching was performed at 70°C with the constant stirring speed of 600 min^{-1}. The results of the leaching efficiencies at various solutions after three hour leaching are shown in Fig. 2 and Fig. 3.

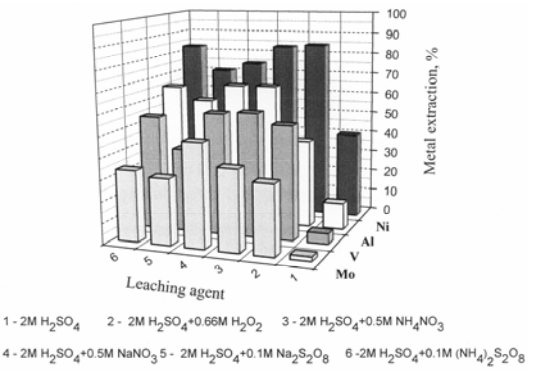

Fig. 2. Effect of adding various oxidizing agents to sulphuric acid solution on metal extraction

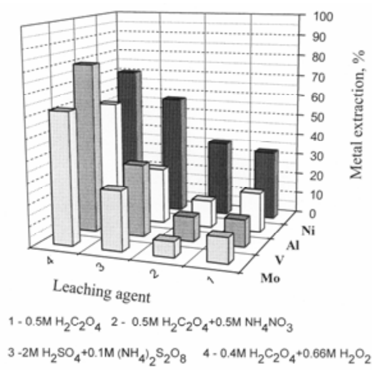

Fig. 3. Effect of adding various oxidizing agents to oxalic acid solution on metal extraction

From these figures it can be seen that oxalic acid as a chelating agent forms soluble metal complexes with molybdenum and vanadium (Marafi and Stanislaus, 1989), causing that the extraction of Mo and V is higher than that in the leaching with H_2SO_4 in the presence of H_2O_2. Leaching of the spent HDS catalyst in oxalic acid as well as in sulphuric acid with H_2O_2 addition is followed by the loss of the alumina catalyst support (about 40%). Leaching efficiency of nickel and vanadium in sulphuric acid solution with $(NH_4)_2S_2O_8$ and then with H_2O_2 is comparable for nickel (82.8%), vanadium (53.9%) and molybdenum (33.5%), but the extraction of aluminium was about 24.0% lower in the presence of H_2O_2 than $(NH_4)_2S_2O_8$.

EFFECT OF STIRRING SPEED

The effect of stirring speed on the metal leaching efficiency from the spent catalyst was investigated in solution containing 0.5M $H_2C_2O_4$ and 3M H_2O_2 at 50°C in the range of speed from 300 to 1200 min^{-1}.

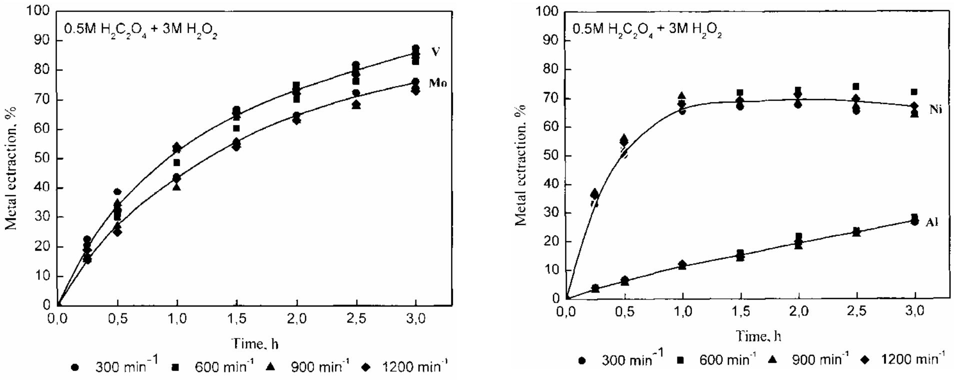

Fig. 4. Effect of stirring speed on metal extraction as a function of time at 50°C in solution containing $H_2C_2O_2$ and H_2O_2 after 3 hour leaching

The results presented in Figs 4a and 4b show that the leaching of molybdenum, nickel, vanadium and aluminium is independent of the stirring speed. This indicates that the diffusion of the reactants from the solution towards the surface of a catalyst particle, and the products away from the surface of the particle was fast, and hence did not control the leaching rate within the range of the stirring speeds tested. All subsequent experiments were carried out at a stirring speed of 600 min^{-1} to assure the invariance of this parameter.

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION

The influence of H_2O_2 concentration on the leaching of molybdenum, nickel, vanadium and aluminium from the spent HDS catalyst was determined by varying the initial concentration of H_2O_2 from 0.5 to 3.0M at 50°C in 0.5M $H_2C_2O_4$ solution. Fig. 5 shows summarized metals extraction after 4 hour leaching. Generally, the extraction of Mo, Ni, and V gradually increased up to 3.0M and then remained constant. The extraction of Al was practically not affected by the concentration of H_2O_2 within the whole range. The highest extraction of molybdenum (90%), vanadium (94%) and nickel (65%) was observed in 0.5M $H_2C_2O_4$ solution with 3.0M H_2O_2 at 50°C during 4 hour leaching.

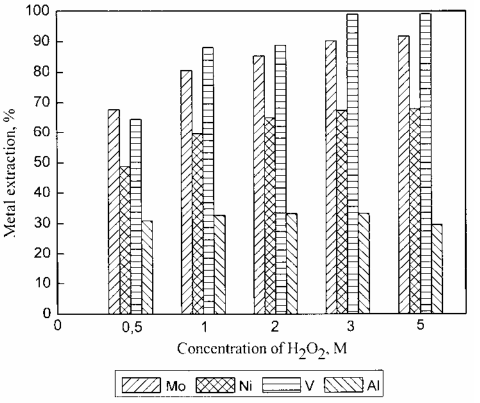

Fig. 5. Effect of H_2O_2 concentration on metal leaching efficiency at 50°C in 0.5M $H_2C_2O_4$ solution after 4 hour leaching

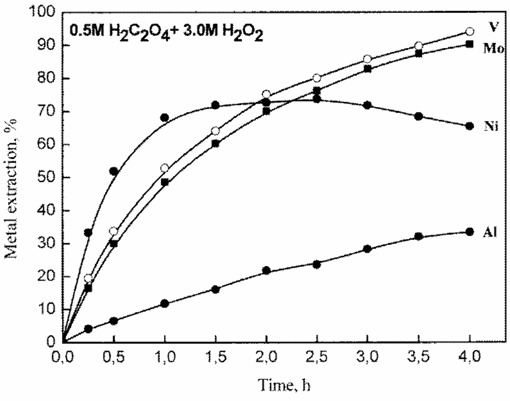

Fig. 6. Influence of leaching time on metal extraction from the spent HDS catalyst at 50°C in solution containing oxalic acid and hydrogen peroxide

Figure 6 depicts the kinetics of leaching of Mo, Ni, V and Al at 50°C in 0.5M $H_2C_2O_4$ solution with 3.0M H_2O_2 addition. As is seen the extraction of vanadium is quite similar to that of molybdenum and gradually increases with time. It was also found, that the extraction of nickel increased with time up to about two hours (74%) and then gradually decreased to about 65% after 4 hour leaching. This unexpected decrease is due to the precipitation of nickel as nickel oxalate (Santhiya and Ting, 2005).

EFFECT OF OXALIC ACID CONCENTRATION

The experiments were carried out at a leaching temperature of 50°C. The concentrations of $H_2C_2O_4$ used were 0.25, 0.375, 0.50 and 0.70M. The effect of $H_2C_2O_4$ concentration on the extraction of molybdenum, vanadium, nickel and aluminium at 50°C in 3.0M H_2O_2 solution after 4 hour leaching is presented in Fig. 7. These experimental results showed that the change in concentration of $H_2C_2O_4$ solution within the range 0.25-0.70M causes a gradual increase of the extraction of Mo (90%), V (94%), Ni (65%) and Al (33%) up to 0.5M $H_2C_2O_4$ and then it slowly falls down to 76% Mo, 84% V, 49% Ni and 28% Al in 0.7M $H_2C_2O_4$ solution. The kinetics of leaching of Mo, Ni, V and Al from the spent HDS catalyst at 50°C solution containing 0.7M $H_2C_2O_4$ and 3.0M H_2O_2 is illustrated in Fig. 8.

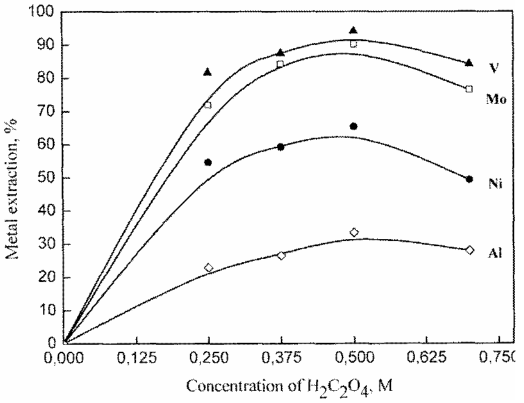

Fig. 7. Effect of $H_2C_2O_4$ concentration on metal leaching efficiency at 50°C in 3.0 M H_2O_2 solution after 4 hour leaching

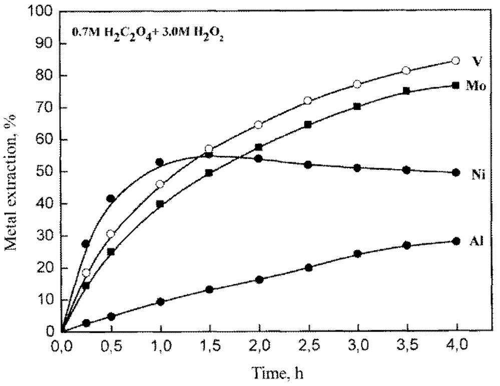

Fig. 8. Influence of leaching time on metal extraction from the spent HDS catalyst at 50°C in solution containing oxalic acid and hydrogen peroxide

The leaching plots in Figs 6 and 8 are generally similar although those for more concentrated solution of $H_2C_2O_4$ are lowered. Especially the decrease of nickel extraction is the deepest (only 75% of the optimal value) and the downfall begins already after 1.5 hours of the process.

CONCLUSION

1. X-ray diffraction analysis of the spent hydrodesulphurization (HDS) catalyst shows that its main phase is γ–Al_2O_3, however V_5S_8 compound was also detected.
2. Scanning electron microscopy and microprobe analysis of the spent catalyst extrudate cross-section revealed that vanadium, nickel, iron and sulphur are deposited near the outer surface of the catalyst extrudate.

3. Leaching rate of molybdenum, nickel, vanadium and aluminium from the spent HDS catalyst in oxalic acid with H_2O_2 addition is independent of the stirring speed. That indicates that the reaction is not controlled by the diffusion in the liquid phase.
4. Rise in H_2O_2 concentration up to 3.0M gradually increases the extraction of Mo, V and Ni, but thereafter it remains constant. The extraction of Al is practically not affected by H_2O_2 concentration within the range from 0.5 to 5.0M.
5. The change in the concentration of $H_2C_2O_4$ solution from 0.25 to 0.5M increases metals extraction, and thereafter gradually decreases it.
6. The highest leaching efficiency of the metals was obtained after 4 hour leaching in the solution containing 0.5M $H_2C_2O_4$ and 3.0M H_2O_2. The extraction of metals at the above conditions are: 90% Mo, 94% V, 65% Ni and 33% Al in 4 hours of leaching.

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Katalizatory hydroodsiarczania HDS o składzie Ni,Mo/Al_2O_3 oraz Co,Mo/Al_2O_3 należą do najszerzej stosowanych w procesach rafineryjnych. Ich dezaktywacja następuje głównie na skutek osadzania się na powierzchni związków węgla i siarczków metali. Tego typu zużyte katalizatory zaliczane są do niebezpiecznych odpadów: są one łatwopalne, wybuchowe, toksyczne, korozyjne, a w kontakcie ze środowiskiem naturalnym wydzielają trujące gazy. Recykling tych katalizatorów jest konieczny ze względów ekologicznych i ekonomicznych. Do badań stosowano zużyty katalizator Ni,Mo/Al_2O_3 uprzednio odolejony toluenem. Jego charakterystykę fizykochemiczną wykonano na podstawie wyników analizy chemicznej, elementarnej, rentgenowskiej oraz skaningowym mikroskopem elektronowym z mikrosondą rentgenowską. Analiza chemiczna katalizatora wykonana metodą ICP-OES po uprzednim przeprowadzeniu próbki do roztworu wykazała następujące zawartości metali: 5,08% Mo, 5,26% Ni, 5,36% V oraz 24,57% Al. Wyniki analizy skaningowym mikroskopem elektronowym wykazały obecność wanadu, niklu, żelaza oraz siarki głównie na powierzchni katalizatora. W celu ustalenia optymalnego czynnika ługującego metale z katalizatora wykonano ługowania testujące w czasie trzech godzin w temperaturze 70^oC w roztworach kwasu siarkowego (VI) oraz kwasu szczawiowego z dodatkiem takich utleniaczy jak: H_2O_2, $NaNO_3$, NH_4NO_3 oraz $(NH_4)_2S_2O_8$. Wykazano, że najlepszym czynnikiem ługującym molibden i wanad jest roztwór kwasu szczawiowego z dodatkiem ditlenku diwodoru, natomiast najlepszym czynnikiem ługującym nikiel jest roztwór zawierający kwas siarkowy (VI) z dodatkiem H_2O_2 lub $(NH_4)_2S_2O_8$. Określono wpływ stężenia $H_2C_2O_4$ oraz H_2O_2 na wydajność ługowania Mo, Ni, V oraz Al. Najwyższe wydajności wyługowania metali wynoszące 90% Mo, 94% V, 65% Ni oraz 33% Al uzyskano w roztworze zawierającym 0,5M $H_2C_2O_4$ z dodatkiem 3,0M H_2O_2 w temperaturze 50^oC po 4 godzinach ługowania.