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PHYSICOCHEMICAL STUDY OF SPENT HYDRODESULPHURIZATION (HDS) CATALYST

A spent hydrodesulphurization (HDS) catalyst $Ni,Mo/Al_2O_3$ has been studied by means of X-ray diffraction, scanning electron microscope, electron microprobe and chemical analysis. Chemical analysis of catalyst confirmed its partial chemical composition as follows: Ni (5.26%), Mo (5.08%), Al (24.57%), V (5.36%), S (9.64%), C (17.63%), H (1.14%). Powder XRD analysis showed that the main phase of studied catalyst is γ-Al_2O_3 while V_5S_8 and Ni_3S_4 were also detected. SEM results confirmed that V and Ni sulphides are deposited on the surface. The surface area of the catalyst determined by nitrogen adsorption (BET method) was found equal to 80.1 m^2/g. Leaching tests of the spent catalyst in solutions of sulphuric acid as well as oxalic acid with oxidizing agents such as NH_4NO_3, $(NH_4)_2S_2O_8$ and H_2O_2 have been carried out.

Key words: spent catalyst, critical metals, leaching

INTRODUCTION

Catalysts containing valuable metals such as nickel, cobalt and molybdenum are commonly used in the oil industry and especially for the hydrodesulphurization of petroleum fractions. This process results in generation of spent catalysts that contain S, C, V, Fe, Ni, Si and traces of As, P (Trim et al.,1989; Diez and Gattes, 1990; Furimsky and Massoth, 1990). Spent catalysts can be classified as hazardous materials (Loehr et al., 1993). Due to their toxic nature, the disposal of spent catalysts can pollute the environment since heavy metals are leached out. To avoid pollution in land disposal as well as to minimize landfill space, the spent catalysts are subjected to metal extraction by various solubilization processes and reused in variety of applications (Furimsky, 1996; Marafi and Stanislaus, 2003; Angelidis et al., 1995).

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Leached residue of a spent hydrodesulphurization catalyst has been combined for instance with ladle furnace slag for making of a high value added anorthite glass-ceramic materials (Sun et al., 2001).

In this investigation the spent hydrodesulphurization catalyst was characterized physically and chemically. Additional chemical leaching tests were also performed using solutions of sulphuric acid as well as oxalic acid with oxidizing agents: NH_4NO_3, $(NH_4)_2S_2O_8$ and H_2O_2.

EXPERIMENTAL

MATERIALS AND METHODS

The spent catalyst, as cylindrical extrudates of approximate diameter 0.3-0.4 mm and length 4-6 mm was studied. It contained residual oil which was washed out with hot toluene by Soxhlet process and then dried at 110^oC before experiments. The surface area of the deoiled catalyst was determined by nitrogen adsorption (BET method). X-ray diffraction (XRD) analysis was performed on STOE model powder diffractometer. SEM-EDX analysis was made with scanning electron microscope (JEOL JSM 580 LV) coupled with the link ISIS 300 X- ray microanalysis system (Oxford Instrument). Prior to scanning electron microscopy (SEM) analysis samples were dried at room temperature, dispersed on a specimen holder, and coated with carbon film for SEM examination. Transmission electron microscopy (TEM) measurements were performed with CM 20 Philips instrument.

The concentrations of metals (V, Ni, Mo and Al) in the catalyst samples and leach liquids were measured by the atomic emission spectrometry with inductively coupled argon plasma as the excitation source. A Jobin-Yvon 38S spectrometer was equipped with a cross-flow nebuliser and Scott-type spray chamber. The high-pressure microwave sample decomposition was performed using Milestone digestion system (MLS-1200 MEGA). For CHNS analysis of the spent catalyst CHNS analyzer (VarioEl) was used.

LEACHING EXPERIMENTS

Leaching tests were carried out in a flask containing 200 ml of the leaching solution. The flask was submerged in a task, temperature of which was kept constant to within 0.1^oC. When the required temperature was reached, a 0.5g charge of spent catalyst was added and stirring started. Leaching lasted three hours, during which six 1 ml samples of the solution were taken to determine the metal concentration by ICP-OES.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION (XRD)

X-ray diffractograms of the deoiled and oiled spent catalysts are given in Fig. 1. Both show that studied catalyst is amorphous. Its main phase is $\gamma-Al_2O_3$, however V_5S_8 and Ni_3S_4 compounds were also visible. No additional peaks are observed. This indicates that molybdenum and nickel atoms are well dispersed over the alumina support.
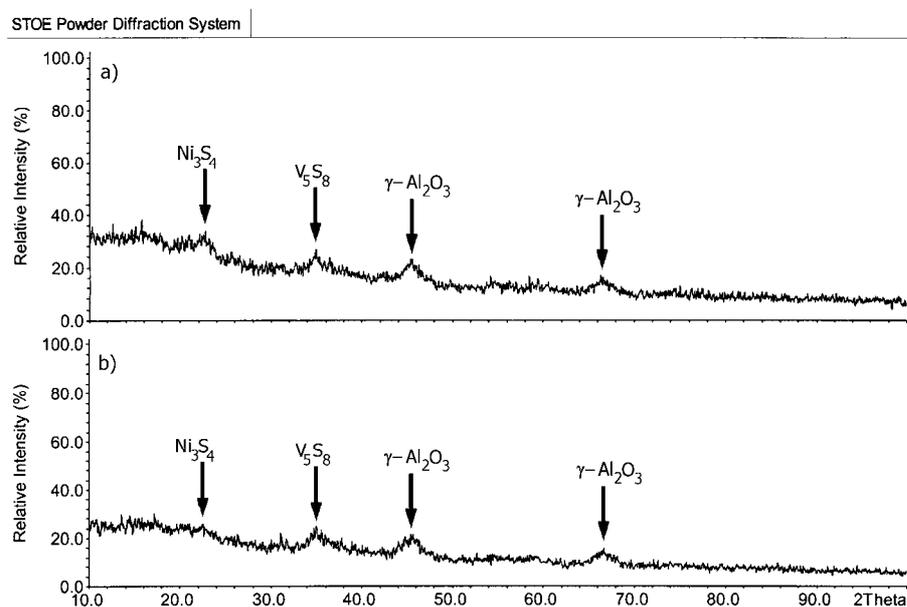

Fig. 1. X-ray diffractograms of the spent catalyst; a) deoiled, b) oiled

MISROSCOPIC ANALYSIS

Scanning electron micrograph of the spent catalyst extrudate is shown in Fig. 2. Fig. 2a presents the shape of the sample. Morphology of its surface (Fig. 2b) evidenced that it consists of aggregated small particles of diameter ranging from 0.4 to 1.7 μm.

The microprobe analysis of the surface of two different extrudates of the spent catalyst depicted in Fig. 3 (indicated by circle and square) resulted in comparable peaks of the elements.
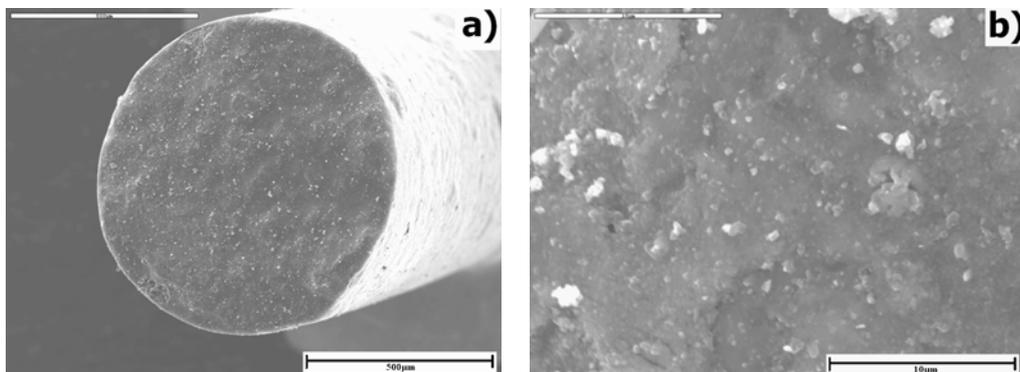
Fig. 2. Scanning electron micrograph of the spent catalyst;
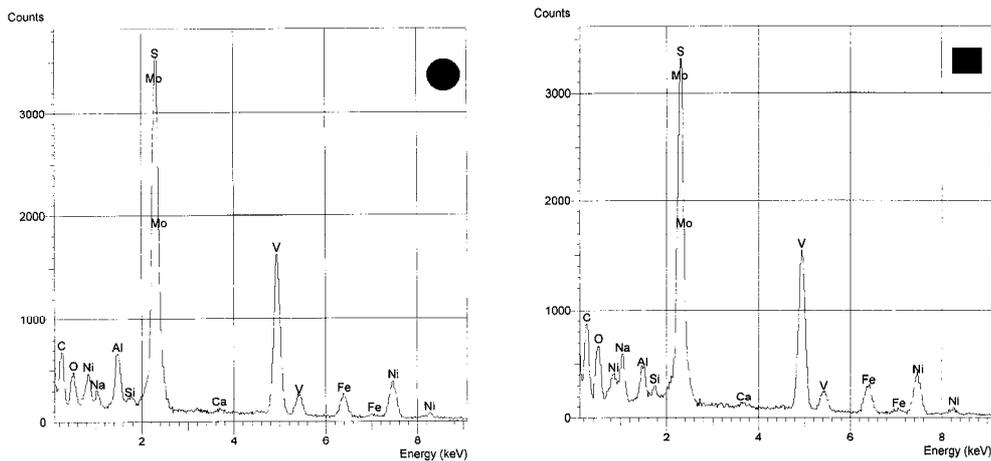a) shape of an extrudate,   b) morphology of its surface

Fig. 3. Microprobe analysis of the surface of two different extrudates of the spent catalyst

The most interesting microscope evidence found in this study is provided by the cross-section of the spent catalyst extrudate shown in Fig. 4.

Microprobe analysis of the surface of edge extrudate cross-section (marked by circle in Fig. 4) proved high contents of V (19.35%), Ni (9.48%), Fe (4.20%), and sulphur (18.38%) but small amounts of Al (3.42%) and Mo (1.44%) (Fig. 5).

The middle part of the extrudate cross-section (indicated by square in Fig. 4) showed dominating contents of Al (32.39%), Mo (3.89%), S (7.01%) and Ni (2.25%), whereas practically no amounts of V and Fe were found. 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 within pores. TEM analysis confirmed the existence of γ-Al_2O_3, Ni_3S_4, and V_5S_8 and revealed molybdenum sulphide (MoS_2). All metal sulphide deposits on a HDS catalyst are crystallites of 10 – 30 nm.
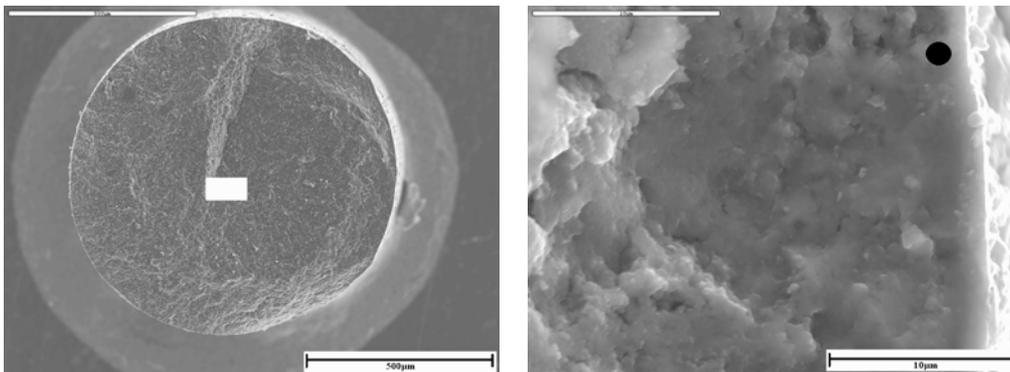

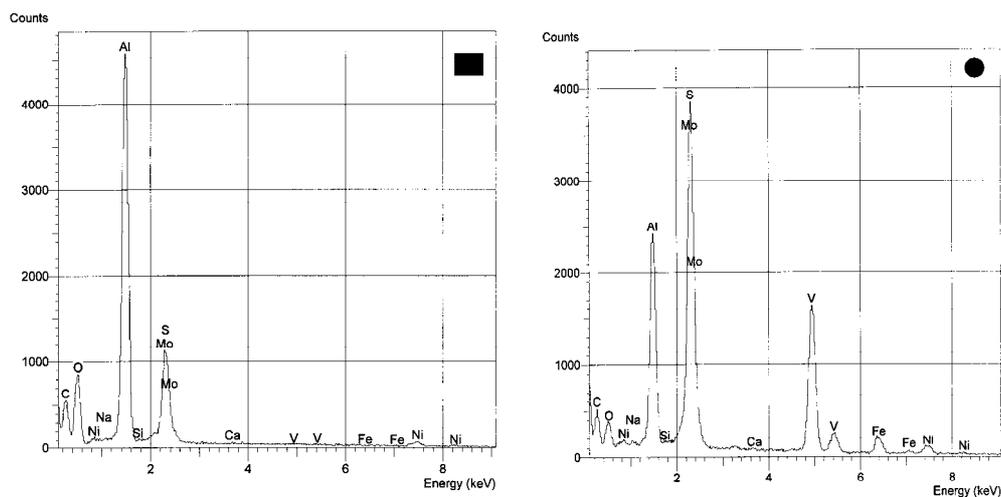Fig. 4. SCM micrograph of the spent catalyst extrudate cross-section

Fig. 5. Microprobe analysis of the surface cross-section showed in Fig. 4;
■ middle of the catalyst extrudate, ● edge of the catalyst extrudate

BET SURFACE AREA

The BET measurements were made in a conventional glass apparatus giving a base pressure of 10^{-6} Torr. The BET surface area of the deoiled, spent catalyst was measured by nitrogen adsorption at liquid nitrogen temperature, assuming 0.162 nm^2 as the area per one N_2 molecule. Prior to measurements the catalysts were degassed for 3h at 200°C. The surface area found is equal to 80.1 m^2/g.

CHEMICAL ANALYSIS

About 0.3 g of powdered spent catalyst was accurately weighted into a Teflon digestion vessel. Then 3 ml of concentrated hydrochloric acid, 7 ml of concentrated nitric acid and 3 ml of hydrogen peroxide (30 %) were added. Decomposition of the sample was carried out the next day with microwave digestion system. Samples microwave heated at maximum power of 500 W for 35 minutes. After cooling, the sample solution was quantitatively transferred into 100 ml volumetric flask and made up to the volume with distilled water. Before analysis all the solutions were filtered through the hard filter paper. The resulting solutions were diluted to the concentration range required for analysis. Results are as follows: 5.08 Mo, 5.36 V, 5.26 Ni and 24.57 Al (wt.%).

CHNS ANALYSIS

One to two milligrams of the spent catalyst was used to C, H, N and S analysis, following the procedure outlined in Aung and Ting (2004). The CHNS analysis showed that the spent catalyst contained (wt.%) carbon, 17.63; hydrogen, 1.14; nitrogen, 0.38 and sulphur, 9.64.

LEACHING TESTS

In order to choose a suitable leachant: sulphuric acid as well as oxalic acid without and with additional oxidants: NH_4NO_3, $(NH_4)_2S_2O_8$ and H_2O_2 were tested.

The leaching was performed at 70^oC for three hours. Reproducibility of leaching experiments was determined to be of order of ± 2% by repeating selected experiments under identical conditions. Summarised results of extraction of metals with different reagents after 3 hours leaching at 70^oC are given in Table 1.

Table 1. Metal extraction in various leaching solutions

Leaching solution	Metal extraction, %			
	Mo	Ni	V	Al
2 M H_2SO_4	2.1	40.4	5.1	12.4
2 M H_2SO_4 + 0.66 M H_2O_2	32.8	84.7	53.5	41.3
2 M H_2SO_4 + 0.5 M NH_4NO_3	38.1	83.5	58.3	67.1
2 M H_2SO_4 + 0.5 M $NaNO_3$	48.7	74.8	57.2	66.9
2 M H_2SO_4 + 0.1 M $Na_2S_2O_8$	31.1	70.8	39.1	59.0
2 M H_2SO_4 + 0.1 M $(NH_4)_2S_2O_8$	33.5	82.8	53.9	65.0
0,5 M $H_2C_2O_4$	11.9	33.1	12.8	18.7
0.4 M $H_2C_2O_4$ + 0.66 M H_2O_2	62.1	70.3	80.0	57.5
0.5 M $H_2C_2O_4$ + 0.5 M NH_4NO_3	7.4	36.1	11.7	12.9
0.5 M $H_2C_2O_4$ + 0.1 M $(NH_4)_2S_2O_8$	28.0	57.2	34.0	26.5

From Table 2 it comes that sulphuric and oxalic acids alone exhibit very poor efficiency for the leaching of metals from studied catalyst. The oxalic acid with H_2O_2 addition evidenced the highest leaching efficiency for vanadium (80.0%), molybdenum (62.1%) and nickel (70.3%). The 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 after leaching with H_2SO_4 in the presence of H_2O_2. Leaching of the spent catalyst in oxalic acid as well as in sulphuric acid containing H_2O_2 resulted in 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 H_2O_2 is comparable for nickel (82.8%), vanadium (53.9%) and molybdenum (33.5%) but extraction of aluminium is of about 24% lower in the presence of H_2O_2 than $(NH_4)_2S_2O_8$.

CONCLUSIONS

1. Powder XRD analysis of the spent HDS catalyst showed that its main phase is γ-Al_2O_3 but V_5S_8 and Ni_3S_4 were also detected. No sharp peaks corresponding to nickel or molybdenum sulphides or other phases were observed.
2. SEM-EDX analysis of the spent catalyst extrudate cross-section illustrated that the metal foulants (vanadium, nickel and iron) are concentrated near the outer surface of the catalyst pellets.
3. Chemical analysis of the spent catalyst is as follows: Ni (5.26%), Mo (5.08%), V (5.36%) and Al (24.57%).
4. CHNS analysis revealed that the spent catalyst contained (wt.%): C (17.64), H (1.14%), N (0.38) and S (9.64).
5. Oxalic acid with H_2O_2 addition exhibited the highest leaching efficiency towards metals contained in the studied catalyst. After 3 hours of leaching at 70°C with solution of 0.4 M $H_2C_2O_4$ + 0.66 M H_2O_2, extraction of metals from the spent catalyst were: 80.0% of V, 70.3% of Ni, 62.1% of Mo and 42.4% of Al.

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Szymczycha-Madeja A., Mulak W., Leśniewicz A., *Badania fizykochemiczne zużytego katalizatora hydroodsiarczania (HDS),* Physicochemical Problems of Mineral Processing, 41 (2007) 125-132 (w jęz. ang.).

Charakterystykę fizykochemiczną zużytego katalizatora HDS wykonano stosując: analizę rentgenograficzną (XRD), skaningową mikroskopię elektronową z mikrosondą rentgenowską (SEM-EDX), transmisyjną mikroskopię elektronową (TEM) oraz analizę chemiczną i elementarną. Analiza XRD wykazała dużą amorficzność katalizatora i jako główną fazę określono γ-Al$_2$O$_3$. Stwierdzono również słabe piki siarczku wanadu (V$_5$S$_8$) i niklu (Ni$_3$S$_4$). Analiza TEM potwierdziła fazę γ-Al$_2$O$_3$ oraz obecność V$_5$S$_8$ i Ni$_3$S$_4$ oraz wykazała zawartość MoS$_2$ w postaci cienkich płytek. Stwierdzono również , że siarczki metali występują w formie małych kryształków o wymiarach od 10 do 30 nm. Na podstawie wyników analizy SEM-EDX wykazano, że zanieczyszczenia katalizatora (V, Ni, Fe, S) osadzają się głównie na jego powierzchni w postaci siarczków. Analiza chemiczna i elementarna określiły następujące zawartości pierwiastków: 5.08% Mo; 5.36% V; 5.26% Ni; 24.87% Al oraz 17.63% C; 1.14% H; 0.38% N oraz 9.64% S. Przeprowadzono również ługowania testujące w roztworach kwasu siarkowego (VI) i szczawiowego w obecności utleniaczy (NH$_4$NO$_3$; (NH$_4$)$_2$S$_2$O$_8$ i H$_2$O$_2$. Najwyższy stopień wyługowania metali uzyskano w roztworach kwasu szczawiowego z dodatkiem H$_2$O$_2$, po 3 godzinach ługowania do roztworu przechodziło: 62% Mo, 70% Ni, 80% V oraz 57% Al.