

# REUSE OF HYDROTREATING SPENT CATALYST

A.M. Habib<sup>\*</sup>, M.F. Menoufy<sup>\*\*</sup>, and H.S. Amhed<sup>\*\*</sup>.

\* Faculty of Science, Tanta University

\*\* Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

## ABSTRACT

All hydro treating catalysts used in petroleum refining processes gradually lose activity through coking, poisoning by metal, sulfur or halides or lose surface area from sintering at high process temperatures.

Waste hydrotreating catalyst, which have been used in re-refining of waste lube oil at Alexandria Petroleum Company (after 5 years lifetime) compared with the same fresh catalyst were used in the present work.

Studies are conducted on partial extraction of the active metals of spent catalyst (Mo and Ni) using three leaching solvents, 4% oxidized oxalic acid, 10% aqueous sodium hydroxide and 10% citric acid. The leaching experiments are conducting on the decoked extrudate [uncrushed] spent catalyst samples. These steps are carried out in order to rejuvenate the spent catalyst to be reused in other reactions.

The results indicated that 4% oxidized oxalic acid leaching solution gave total metal removal 45.6 for decoked catalyst samples while Naoh gave 35% and citric acid gave 31.9 %

The oxidized leaching agent was the most efficient leaching solvent to facilitate the metal removal, and the rejuvenated catalyst was characterized by the unchanged crystalline phase

The rejuvenated catalyst was applied for hydrodesulfurization (HDS) of vacuum gas oil as a feedstock, under different hydrogen pressure 20-80 bar in

order to compare its HDS activity, diesel index and other quality product characteristics with both the fresh and spent samples.

The results indicated that the rejuvenation techniques introduce a catalyst have an HDS-activity nearly approached to that of the fresh of the same type, depending on the reaction temperature, i.e. at 50 bar, the treated catalyst restored nearly 81% its HDS activity at 340 °C and 96% at 380 °C.

## **INTRODUCTION**

Large quantities of catalysts are used in the refining industry for purification and upgrading of various petroleum streams and residues <sup>(1)</sup>. The catalysts deactivate with time and the spent catalysts are usually discarded as solid wastes. The quantity of spent catalysts discharged from different processing units depends largely on the amount of fresh catalysts used, their life and the deposits formed on them during use in the reactors. In most refineries, a major portion of the spent catalysts wastes come from the hydroprocessing units.

The volume of spent hydroprocessing catalysts discarded as solid wastes has increased significantly with a rapid growth in the distillates hydroprocessing capacity to meet the increasing demand for low sulfur fuels <sup>(2)</sup>.

Environmental laws concerning spent catalyst disposal have become increasingly more severe in recent years. Spent hydroprocessing catalysts have been classified as hazardous waste by the Environmental protection Agency (EPA)<sup>(3)</sup>. Several alternative methods such as disposal in land fills, reclamation of metals, regeneration/ rejuvenation and reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with spent catalyst problem <sup>(4,5,6,7)</sup>. In the present study, leaching runs were conducted in order to recover contaminants metals from spent catalyst using different chemical leaching agents, namely; 4% oxidized oxalic acid,

10% citric acid, and 10% NaOH. The treatments were focused on treating and reusing the catalyst in refining reactions.

## **EXPERIMENTAL**

Spent catalyst originally provided from Sud-Chime designated as (20-7-05 TRX) was obtained from the re-refining waste-lube oil hydrotreating unit of Alexandria petroleum company. The catalyst was in the form of extrudates and contained residual lube oils sulfur, carbon, metal deposits in addition to the catalyst metals.

### **Spent Catalyst Pretreatment**

The catalyst contaminates, such as residual lube oil, sulfur and coke were removed as follows;

- 0 Washing the spent catalyst first with naphtha and then with toluene in a soxhlet extractor in order to remove residual oil.
- 1 The clean catalyst containing coke, sulfur, and metals was then dried in an oven at 120°C for 24h. The dried catalyst was subjected to carbon disulfide (100 ml/10g) with agitation at room temperature in a closed flask for 12h. The filtered catalyst was then dried in air at room temperature, followed by heating in an electric oven to 450°C at 25°C/h maintained constant for 20h in order to remove both carbon (decoked) and the remained sulfur.

### **Leaching Treatments**

#### **A- 4% oxidized oxalic acid solution.**

4% oxalic acid solution with addition of 5% H<sub>2</sub>O<sub>2</sub><sup>(8)</sup> as oxidizing agents was used for leaching experiments. 500ml of this solution was added to 10g of the pretreated decoked spent catalyst (extrudate) in a 1L pyrex conical flask equipped with a reflux condenser at higher temperature (100°C), and agitated for one hour in a thermostated water bath.

### **B- 10% NaOH leaching solution**

10g of the decoked pretreated spent catalyst (Extrudate) was added to 100ml of alkali leaching solution in a 500ml flask heated in water bath at 100°C for 24h with stirring and adjusted the pH to 8 .

### **C- 10% citric acid leaching solution**

The pretreated spent catalyst sample (10g) was added to 500ml of the organic acid solution in 1L flask, then heated for 75 min at 95-100°C with stirring.

At the end of the different leaching times of leaching treatments, the content was cooled to room temperature, filtered, dried in air, heated, at 110°C and calcined at 450°C for 4h, which represents the treated catalyst sample. The concentration of various metals (Mo, Ni, Al and P) present in the catalyst samples were determined by an atomic absorption spectra photometer (Perkin Elmer 800) and silica by the gravimetric method. The physical characteristics of the Fresh, spent and treated catalyst samples, such as surface area and average pore diameter were determined by nitrogen adsorption (BET method) using a quanta sorb adsorption unit (Nova Automated Gas Sorption-2002).

The structure profile of the metals within the catalyst was measured using x-ray fluorescence Philips DX-90, EDAX, at 10.25 Kv tube and 10, 120m

### **2- Activity test.**

The hydrodesulfurization (HDS) activity tests of the treated catalyst samples were calculated in a fixed bed cat-test unit using 100ml catalyst charge. Vacuum gas oil containing 0.99% sulfur was used as feedstock. The operating conditions were; hydrogen pressure, 20-80 bar, reactor temperature, 340°C, H<sub>2</sub>/feed ratio, 450l/l and LHSV, 2h<sup>-1</sup>. The catalyst samples were presulfided in situ before use <sup>(9)</sup>. The sulfur content in the feed and products were determined according to the IP-366 standard method.

### **III- RESULT AND DISCUSSION**

#### **III.1. Effect of chemical leaching on total metal removal**

The study was conducted on decoked samples. It was known that during decoking, carbon is burned in an oxygen-containing atmosphere, the sulfide form (coked) was oxidized to the, high valence metal oxides and sulfates these metals in the higher oxidation states were more soluble by the leaching agents in case of the coked samples<sup>(8)</sup>. Crushing is an energy consuming procedure and increases significantly the metal recovery cost. Since the catalyst extrudes were of small size, the uncrushed samples were used for the treatment study. The data in figure (1) indicated that the oxidized oxalic acid is the most leaching agents for spent catalyst total metal recovery than the other leaching agents 10% citric acid and 10%NaOH.

The data indicated that oxalic H<sub>2</sub>O<sub>2</sub> system was more effective for leaching total metals than NaOH and citric acid. It means that the oxidizing agents increases the leaching efficiency towards amount of metals in the catalyst pores.

#### **III.2 Effect of chemical leaching solutions on selective metal recovery.**

The data in tables (1&2) indicated that the effects of oxidized oxalic acid, alkali and citric acid on selective metals (Mo, Ni and Al) recovered were in the order;

- For Mo-recovery  
10% NaOH > 10% citric acid > 4% oxidized oxalic acid.
- For Ni-recovery  
10% citric acid > 10% NaOH > 4% oxidized oxalic acid
- For Al-recovery  
10% Citric-acid > 4% oxidized oxalic acid > 10% NaOH .

It means that NaOH, citric acid leached the active metals (Mo, Ni) more than the oxidized oxalic acid, and hence their metallic ratios to the total active metals were less than in case of 4% oxidized oxalic acid. Figs. (2-6) represents

the XRF-charts of fresh, spent, and treated catalysts, and indicates the extent of the metals remaining after leaching effect.

Therefore, the catalysts was redistributed, according to the remaining active metals on the catalyst surface during the leaching process, beside the unleashed silicon. In addition, a part of the inactive metal atoms present in the tetrahedral sites of the alumina support may be leached by the agents and redistributed over the molybdate layer. In the sometime, some of the molybdenum may be interacted between these metals, especially nickel, which lead to the formation of an active Ni-Mo-S phase structures in the final catalyst.

During the leaching runs, it was found a certain correlation between the treatment procedure and the catalyst characteristics, such as surface area and average pore diameter which is the major objective of the present work, i.e reuse (rejuvenate) the spent catalyst.

### **III.3. Effect of metal leaching on physical characteristics of spent catalyst.**

Fig. (7) compares the effect of chemical treatments for rejuvenating the spent catalyst. The characteristics were greatly improved depending on the extent of metal recovered. The improvement in surface area was resulted due to opening the catalyst pores through interaction with leaching agent. In case of the aqueous leaching, the selective metals complexed with sodium ions and may be redistributed inside the pore, resulting in reducing its pore diameter. Therefore, oxidized oxalic acid leaching agents was the suitable agent for inhuding and reusable catalyst can be used in many reactions.

### **III.4 Effect of metal recovered on catalyst activity**

The hydrodesulfurization (HDS) activity of the rejuvenated catalyst as a result of contacting with 4% acid concentration was studied at different operating hydrogen pressure range (20-80bar) compared with fresh or spent catalyst.

The data of Table (3) represents the hydrodesulfurization activity test of fresh catalyst using VGO. The data show the quality of the treated VGO under the tested operating conditions which revealed that the quality was improved by increasing the hydrogen pressure especially the HDS-activity, within the refineries conditions.

In comparing the rejuvenated catalyst with both the fresh and spent catalyst it was found that the treated catalyst restored nearly the fresh catalyst activity at higher temperature (380°C) under constant hydrogen pressure, 50 bar (Fig. 8).

On the other hand, depending on reactor temperature, the treated catalyst restored nearly 81% the fresh HDS activity at 340°C and 96% of the fresh HDS-activity, at 380°C.

## **CONCLUSION**

The rejuvenation process promotes formation of a valuable catalyst from spent derived from waste-lube re-refining unit. The improvements in the physical characteristics were obtained due to the interaction of 4% oxidized oxalic acid leaching agents with the spent catalyst compared with 10% citric acid sodium hydroxide for recovered the active metals in the spent catalyst.

The selected leaching agents succeeded in improving the surface area and average pore diameter of the spent catalyst. These improvements caused recovery in the HDS-activated of the treated catalyst depending on the reactor temperature.

Therefore, it is clearly possible to reuse the rejuvenated catalyst, especially in the refining processes, as a second layer on top-layer of the fresh catalyst as guard-bed.

**Table (1) Metal contents of fresh spent and leached catalysts Extraction by different leaching agents**

Catalyst type	Fresh	Spent	Treated catalyst		
			4% oxidized oxalic acid	10% NaOH	10% critic acid
Catalyst composition wt%					
MO	15.03	9.79	2.95	2.62	2.73
Ni	3.57	2.68	2.02	2.01	1.21
AL	34.74	32.81	25.90	27.25	25.44
P	---	3.12	1.71	2.30	1.73
SI	---	11.55	12.71	11.71	13.31
(2n, Fe, Mg, Ca, Na,K)	0.550	0.713	0.67	0.42	0.43

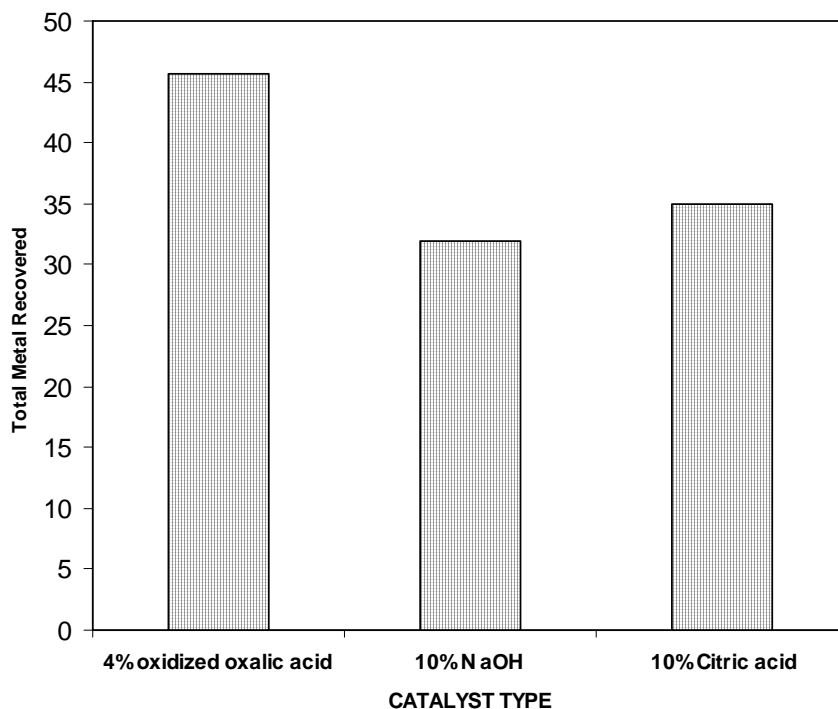
**Table (2) Effect of leaching agents on spent catalyst metal recovery**

Catalyst type	4% oxidized oxalic acid	10% NaOH	10% critic acid
Metal removal (wt%)			
MO	69.87	73.24	72.11
Ni	24.63	25.00	54.85
AL	21.06	16.95	22.46
P	45.19	26.28	44.55
(2n, Fe, Mg, Ca, Na,K)	6.03	41.70	40.45

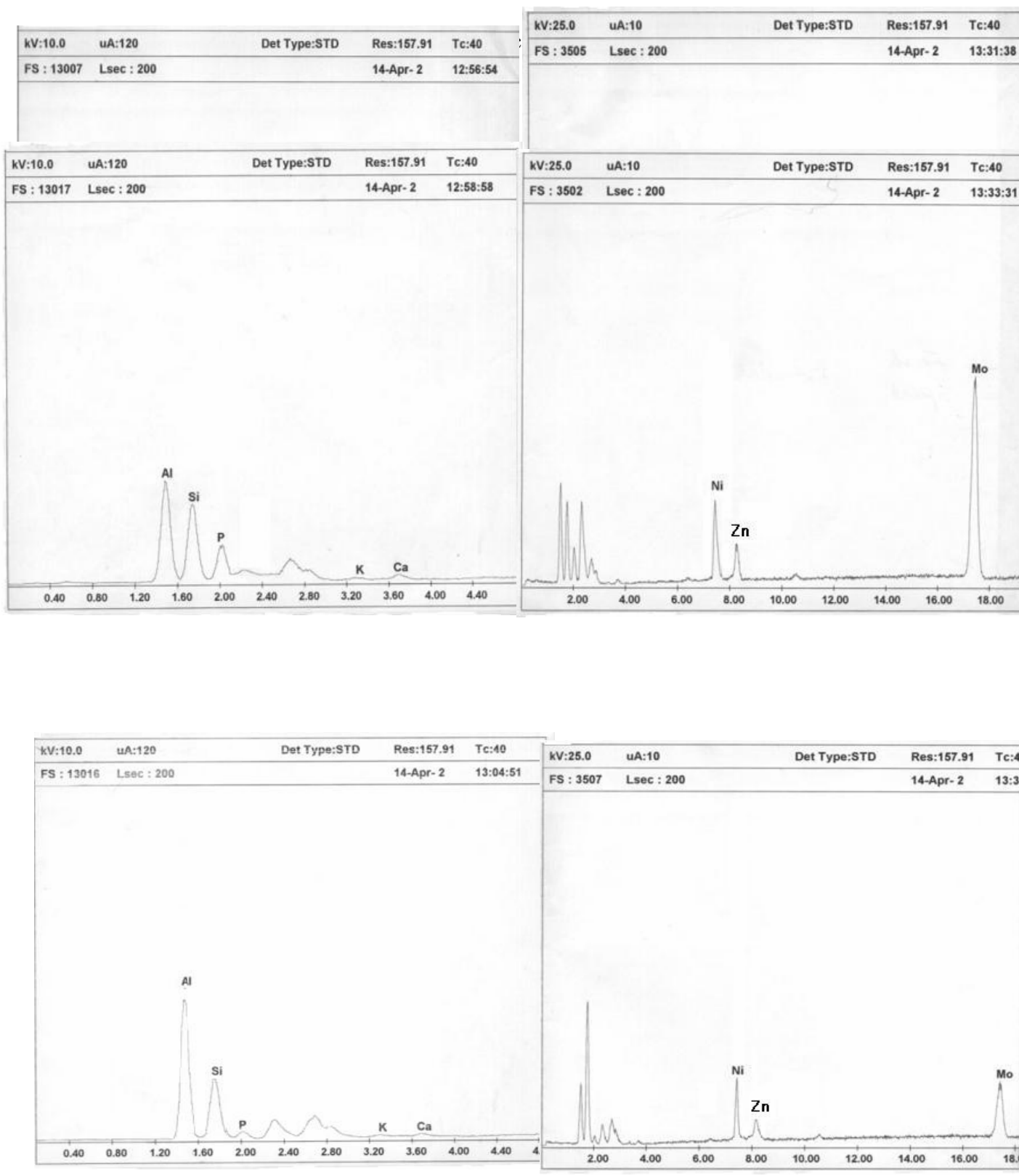


**Table (3) Hydrotreating Activity of Fresh Catalyst Using VGO (at the temperature, 340°C, LHSV, 2h<sup>-1</sup>, and H<sub>2</sub>/feed ratio 450 L/L)**

Catalyst Type Characteristics	Fresh Catalyst					
	Total Hydrogen Pressure, bar					
	Feed	20	35	50	65	80
Density@15 <sup>0</sup> C	0.8374	0.8295	0.8290	0.8281	0.8281	0.8276
Yield, wt%	--	97.00	95.8	93.00	87.00	80.00
Sulfur content, wt%	0.9933	0.1547	0.0762	0.0484	0.0374	0.0256
ASTM-Colour	1.5	1.0	1.0	0.5	0.5	0.5
Pour point, °C	-6	-9	-9	-9	-9	-9
Aniline point, °C	79	82	86	90	91	93
Diesel Index	31.70	35.17	38.08	41.10	41.81	43.35
HDS-activity, %	--	84.43	92.33	95.17	96.23	97.42



**Fig. (1) Effect of Chemical Leaching on spent catalyst total metal removal**



**Fig (4) XRF of Spent Catalyst Extrudate (uncrushed) Treated by 4% Oxalic Acid .**



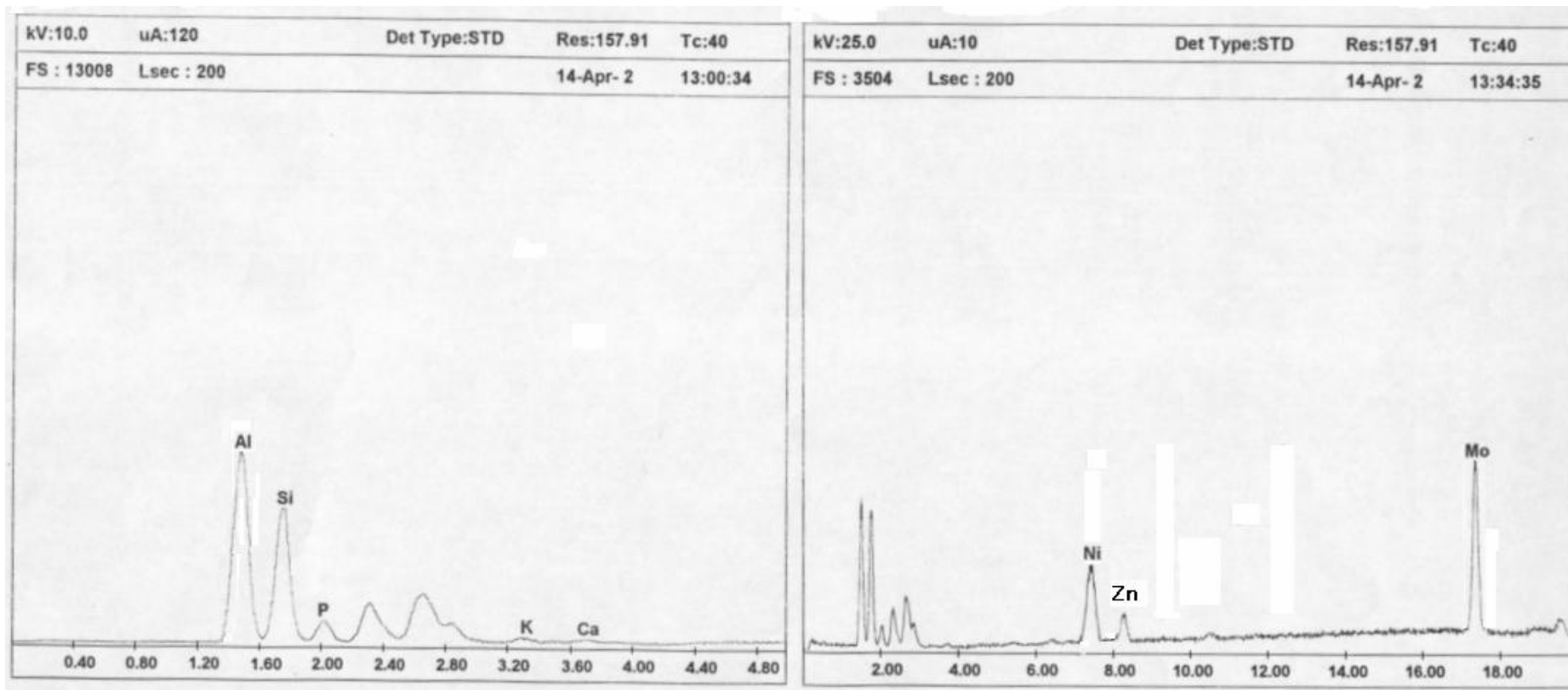


Figure (5) XRF of Spent Catalyst as Extrudate (uncrushed) Treated by 10% Citric Acid Solution

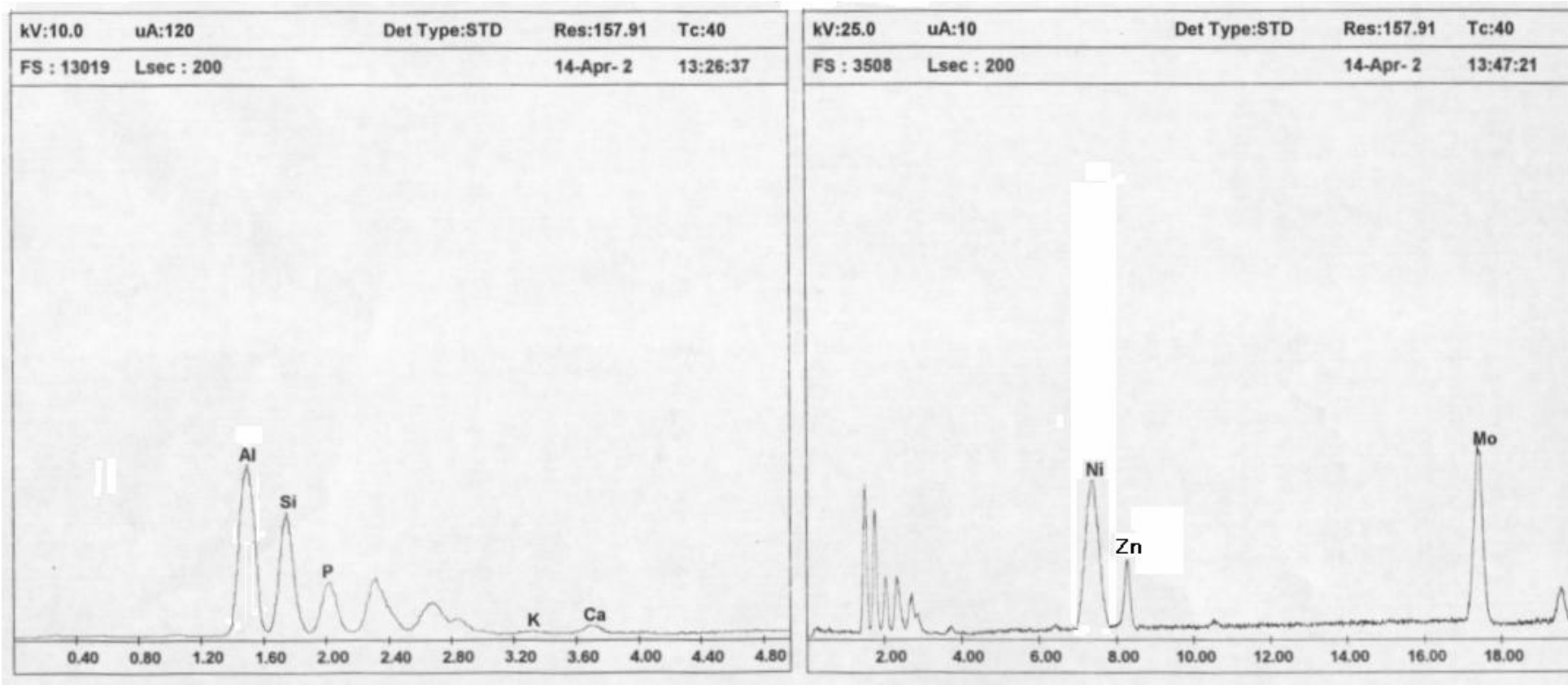


Figure (6) XRF of Spent Catalyst as Extrudate (uncrushed) Treated by 10% Stiochmetric NaOH Solution

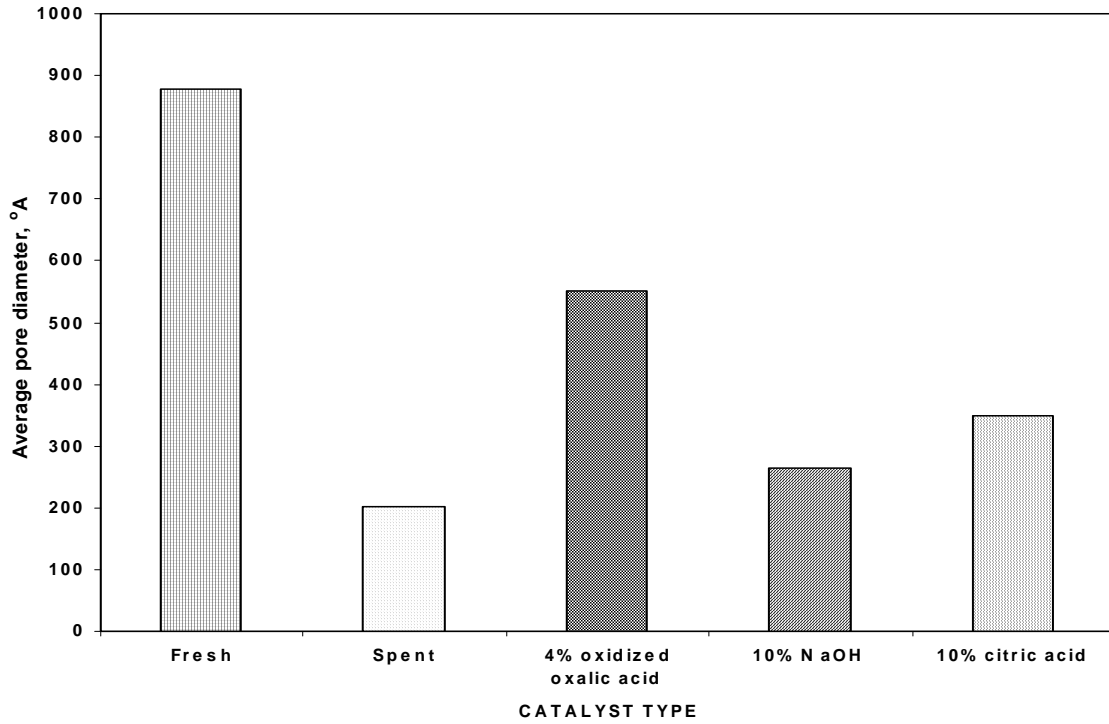


Fig.( 7 ) Effect of leachant agents on physical-characteristics of spent catalyst

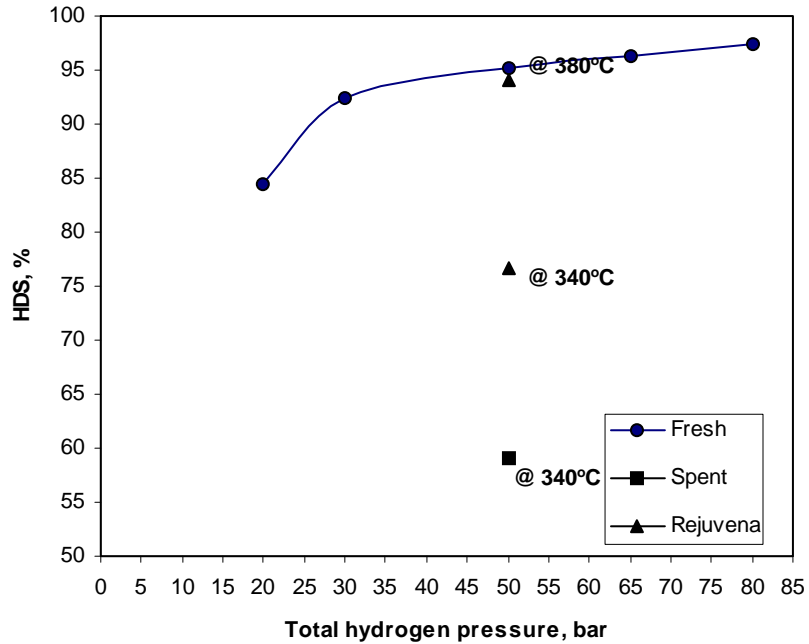


Fig. (8) Comparison of HDS Activity of Spent, Fresh and Rejuvenated (Leached by 4% oxalic acid) Catalysts

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