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EXPERIMENTAL STUDY ON RECOVERY OF SPENT HYDROCRACKING CATALYST

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Abstract

The spent catalysts are one of the environmental concerns in the refineries. This problem can be solved by returning them to the process via regenerating and rejuvenating. In this paper, an experimental study is presented which the recovery of spent catalyst of hydrocracking unit in order to use in kerosene hydrotreatment process is investigated. The result shows that the regenerated catalyst is suitable for kerosene HDS at 300°C, 35 bar and H2/HC=100.

Key words: Hydrocracking; Spent Catalyst; Kerosene; Hydrotreatment.

1. Introduction

Sulfur compounds have a poison role for catalysts in the catalytic processes and also cause corrosion in equipments of refineries. Therefore they should be decreased to their allowable standard ranges.

Hydrotreatment is common method for sulfur treating from petroleum cuts, wherein hydrogen is used in presence of catalyst[1-2].

The catalysts deactivate with time and when the activity of the catalyst declines below the acceptable level. It is usually regenerated and reused. But, regeneration is not always possible and after a few cycles of regeneration and reuse, the catalyst activity may decrease to very low levels and further regeneration may not be economically feasible. The spent catalysts are discarded as solid wastes. In most refineries, a major portion of the spent catalyst waste comes from the residue hydrotreating and hydroprocessing units. This is because the catalysts used in these processes deactivate rapidly by coke and metal (V and Ni) deposits, and have a short life. Furthermore; regeneration and reactivation of the catalysts deactivated by metal fouling is not possible for the refiners.

Attempts have been made to find new outlets for spent non-regenerable catalysts. In this regard, attention must be paid to the environmental issues because spent hydroprocessing catalysts have been designated as hazardous toxic wastes[3-4].

Several methods such as disposal in landfills, reclamation of metals, reuse by regeneration & rejuvenation and utilization as raw materials to produce other useful products are available for the refiners which deal with the spent catalyst problem.

As the disposal of spent catalysts as landfill is environmentally restricted, increasing emphasis has been placed on the development of processes for recycling the waste catalyst materials as much as possible emitted. Recovery of metals and other components from the spent catalysts is possible particularly for the catalysts containing valuable metals[5].

A wide range of new applications for spent hydroprocessing catalysts have been identified. Among several options, reutilization of the metal-fouled non-regenerable catalysts in a reprocessed (regenerated and rejuvenated) form in hydroprocessing operations has been explored that is the subject of present paper.

2. Material and method

Two types of spent catalysts were used in the experiments. They contained some residual oil from the process.Table-1 shows the catalyst specification which is used in this experimental research.

Table 1: Catalyst Specification

Name	F1
Type	Hydrocracking catalyst
Shape	Extrude
Catalyst base	Silica-alumina
Active metal	Tungsten
Promoter	Nickel

1. The analysis of sulfur in liquid feed and products was performed using XRF analysis.
2. A mercury porosimeter was used for pore volume and pore size distribution determination in catalyst samples.
3. Surface area of the catalysts was determined by BET method using an autosorb-adsorption unit.
4. The concentrations of metals were determined using Atomic Absorption Spectrometer.

The spent catalyst is first washed with naphtha to remove hydrocarbons from the surface of catalyst and then will be dried. After that, its physical properties such as surface area, mechanical strength, actual density and pore volume are determined.

The spent catalyst is investigated to report the chemical specification and component content. The catalyst rejuvenation is performed in order to separation of deposited metals with acetic acid and oxalic acid in a soxhlet apparatus.

Then it is followed catalyst decoking in a horizontal rotary furnace by air under programmed and controlled temperature conditions in the range 400–700^{o}C to obtain the best condition. Finally, the activity of regenerated catalyst is evaluated by applying it in an experimental set-up.

Hydrotreating activities of the prepared catalysts were tested in a micro-reactor unit using sour kerosene as feed. The feedstock contained 0.247 wt% sulfur and 110.7 ppm RSH.

About 4gr catalyst was used for each run. The catalyst was presulfided before introducing the feed by a standard procedure. After presulfiding the test conditions were adjusted to desired operating temperature, pressure, hydrogen to oil ratio and liquid hourly space velocity (LHSV).

A commercial HDS catalyst was also tested under the same operational conditions. For each run product samples were collected every 12 hours for analysis of total sulfur, mercaptan, specific gravity, etc. The experiment is performed based on following steps:

- Catalyst loading (60 cc.) in reactor
- Pressure testing to operating pressure (by hydrogen)
- Catalyst sulphidation in contact with a feed containing sulphur (isomax diesel mixing : 1 wt% dimethyl-disulphide) along with passing hydrogen for activating the catalyst
- Substitution of the feed with the main feed (sour kerosene) and adjusting the conditions (temperature, pressure, hydrogen flow rate and feed flow rate)

Product gathering and analyzing it after washing with cadmium chloride for removing hydrogen sulfide in order to assess of the catalyst’s performance.

3. Result and discussion

Table-2 shows the physical properties of the fresh and spent catalyst samples. As it can see, the strength of catalyst grain has no considerable change, but due to deposition of materials on the surface of spent catalyst, its density has been increased and its surface area has been decreased.

Table 2: Physical properties of fresh and spent catalyst

Sample	Surface area (m^2/g)	Mechanical resistance (MPa)	Density (g/cm^3)	Pore volume (cm^3/g)	Mean pore radius (^{o}A)
F1	232.5	1.01	2.3	0.306	38.6
S1	155	0.86	2.5	0.304	66.3
S2	150.8	0.84	2.65	0.235	-
S3	176.9	1.01	2.38	0.218	-
S4	162	1.05	3.92	0.222	-

The pore volume of spent catalyst is decreased more than 20 percent. The low surface area and pore volume values indicate that the catalyst is deactivated by pore blockage and fouling of the active catalyst sites by coke and metal deposits. Although the coke deposits are removed during the calcinations of the catalyst in air, the metal deposits will remain in the pores. Therefore a gradual decrease in the surface area and pore volume of catalyst is not unexpected. Table-3 shows the metal content of fresh and spent catalyst.

Table 3: Chemical Analysis of Fresh and Spent Catalyst

Sample	Component (wt%)						
	Fe	Na	V	Si	Al	Ni	W
F1	0.054	0.30	trace	13.68	19.75	2.61	19.9
S1	0.079	0.03	trace	11.55	17.93	2.68	19.37
S2	0.075	0.12	trace	14.11	16.5	2.63	19.7
S3	0.08	0.04	trace	-	16.7	4.2	20.35
S4	0.1	0.03	trace	-	16.8	3.54	22.1

The spent catalyst contains low levels of iron and sodium. Acid leaching is performed by Acetic and Oxalic acid, which is considered various acid concentrations. Table-4 shows the metal content of spent catalyst after the metal-leaching treatment.

Table 4: Chemical Specification of Acid Leaching Solution

Acid	Normality	Component (ppm)						
		Fe	Na	V	Si	Al	Ni	W
Acetic Acid	0.1	4.48	6.77	trace	27.4	168.8	463.7	2857.1
	0.05	4.11	6.43	trace	36.1	157.6	478.6	2857.1
	0.01	4.7	6.33	trace	32.88	138.6	478.6	3035.7
Oxalic Acid	0.1	3.65	7.8	trace	33.8	126.6	74.8	2678.5
	0.01	4.36	9.2	trace	16.9	127.1	448.7	2857.1
	0.001	4.15	7.3	trace	25.1	124.5	448.7	3035.7

Table 5 shows the catalyst surface area after decoking and leaching by acetic acid and oxalic acid.

Substantial improvement in the surface area and pore volume of the catalyst is occurred as a result of extraction of the metals.

Leaching of the foulant metal deposits blocking the catalyst's pores could open the pores and consequently increase the pore volume and surface area of the catalyst.

Higher surface area values are observed for the leached spent catalyst. This is not surprising since leaching of the deposited metals from the spent catalyst opens the pores and increases the pore volume and surface area.

The optimal condition of catalyst regeneration is 500°C during 5 hours, which can satisfy carbon content and surface area. Table-6 shows the experimental result of hydrotreatment of sour feed by fresh and spent catalyst.

Table 5: Regeneration Results

Sample	Surface Area (m^2/g)	Component (wt %)	
		Sulfur	Carbon
F1	232.5	0.056	0.21
S1	155	1.30	0.612
S2	150.8	-	-
S1-400	134.28	1.14	0.169
S1-500	160.1	0.680	0.124
S1-600	154.57	0.218	0.121
S1-700	86.02	0.089	0.120
S1-1	149.22	0.872	0.144
S1-3	154.38	0.701	0.137
S1-5	160.1	0.680	0.124
S1-7	148.91	0.586	0.116
S1-A	238.1	-	-
S1-O	268.54	-	-

Table 6: Feed & Product Specification in present of Fresh and Spent Catalyst

Sample	kerosene	S4	S3	S2	S1	F2	Sour Feed
Total Sulfur (wt%)	Max. 0.15	0.083	0.0672	0.0883	0.0577	0.0728	0.247
Mercaptan (ppm)	Max. 10	<5	<5	4.77	3.94	<5	110.7
Color (Saybolt)	Min. 25	25	25	30	30	30	26
Flash Point (^oC)	Min. 43	38	39	42	40	44	47
Sp.gr. @15.56 (^oC)	Max. 0.82	0.7907	0.7917	0.7926	0.7921	0.7922	0.794
Distillation (^oC)							
IBP		144.3	141.9	145.7	146.2	143.5	149
5%		153.3	156.8	153.9	158.5	156.1	157
10%		162.5	160.3	157.3	163.4	159.7	160
20%		169.5	169.6	166.1	170.9	167.8	165
30%		175.7	175.3	173.9	176.2	174.9	175
40%		181.7	181.9	180.6	182.5	182	181.5
50%	185	188.2	189.1	188	189.5	189	188
60%		196.5	196.2	196.5	197.7	197.4	196
70%		205.5	206.2	205.6	206.7	206.3	205
80%	200	218	216.6	215.9	216.7	216.4	216
90%	210	229	228.5	228.2	228.7	228.6	228
95%	235	-	236.6	235.9	236.7	236.6	233
FBP	275	259.3	244.1	243.1	243	244.5	238
HDS (wt%)	-	66.4	72.8	64.25	76.64	70.5	-

Based on the experimental data, it's obtained following result for fresh catalyst:

- Excepting the flash point (which is modifiable) in other properties there is an approximately good conformity with standard ones of kerosene.
- The flash point of the consumed feed (sour kerosene) in HDS was found to be 47°C, which after desulphurization it was decreased and maximum reached to 42°C. This shows that due to the cracking property of the spent catalyst, the kerosene has been a little cracked.
- The maximum desulphurization is obtained in 35 bar pressure, 300°C temperature, and H2/HC=100. In the reactor tests for the spent and F2 catalysts, these conditions were used.

The spent catalyst is also tested in experimental set-up and obtained following results:

- The levels of sulphur and mercaptan existing in feed have been decreased to the acceptable limits (the desulfurization levels for different samples have been ranged between 45-77 weight percent). The lowest level of desulphurization is related to sample S1-O.
- The results of color, smoke point, specific weight, flash point, and D86 distillation are also satisfactory.

4. Conclusion

It is obvious that because of variety in the impurities available in each kind of the kerosene cut (in each refinery) and difference among the catalysts types as well as the last situation of spent catalysts; to make a final decision in relation to possibility of this project, the reactor tests must be applied on the different samples of spent catalysts. However, according to the results of the carried out tests it can be expressed that: usage of the rejuvenated spent catalyst for hydrogen treating of kerosene in the conditions of 300°C, 35bar, and H2/HC=100, is suitable.

Nomenclature

F1 : Fresh catalyst (catalyst of ISOMAX units)
F2 : Fresh catalyst (catalyst of Hydrotreater units)
S1, S2 : Spent catalyst of first Refinery
S3, S4 : Spent catalyst of second Refinery
S1-400: Spent catalyst regenerated in 400^{o}C for 5 hours
S1-500: Spent catalyst regenerated in 500^{o}C for 5 hours
S1-600: Spent catalyst regenerated in 600^{o}C for 5 hours
S1-700: Spent catalyst regenerated in 700^{o}C for 5 hours
S1-1 : Spent catalyst regenerated in 500^{o}C for 1 hour
S1-3 : Spent catalyst regenerated in 500^{o}C for 3 hours
S1-5 : Spent catalyst regenerated in 500^{o}C for 5 hours
S1-7 : Spent catalyst regenerated in 500^{o}C for 7 hours
S1-A : Spent catalyst washed with acetic acid (0.01 Normal) for 3 hours
S1-O : Spent catalyst washed with oxalic acid (0.01 Normal) for 3 hours

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