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STUDYING OF THE EFFECTIVE PARAMETERS ON HYDROTREATING CATALYSTS REGENERATION

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Abstract:
Nowadays hydrotreating processes especially hydrodesulphurization of platinum reforming feeds stocks for upgrading the quality and in preventing the environmental pollution are very important.
This article is relates to a method of rejuvenation of spent hydrodesulphurization (HDS, a type of hydrotreating catalyst) and discussed on regenerating porous hydrodesulphurization catalysts having an alumina substrate or base which have been deactivated incidental to use in a hydrodesulphurization process by build-up of exogenous nickel and vanadium compounds on the surface of and in the pores of the HDS catalyst. To achieve this aim, contaminated metals are eliminated by acid wash. The effects of time and concentration of acid were also studied; the results showed that washing by acetic acid (0.1 N) in 3-hour periods is suitable. After this step, specification and ability of catalyst samples were tested.

Keywords: hydrotreatment, catalyst, hydrodesulphurization and rejuvenation

Introduction

In the refinery, sulfur in the form of organic compounds is removed from the distillate streams by a process called hydrodesulphurization (HDS), where compounds containing sulfur undergo reaction with hydrogen and form the corresponding hydrocarbon and hydrogen sulfide (H_2S), is then removed as a gas.

The reaction of aliphatic compounds is schematically shown in Equation (1), where R stands for alkyl.

$$R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S \qquad (1)$$

A similar reaction applies to aromatic and polyaromatic sulfur compounds, where a desulphurized hydrocarbon and H_2S again are the final products. However, the mechanism of the reaction of sulfur compounds containing aromatic ring(s) is not as simple as presented in Equation (1), but can proceed through several reaction pathways, as is schematically shown for thiophene in Figure 1.

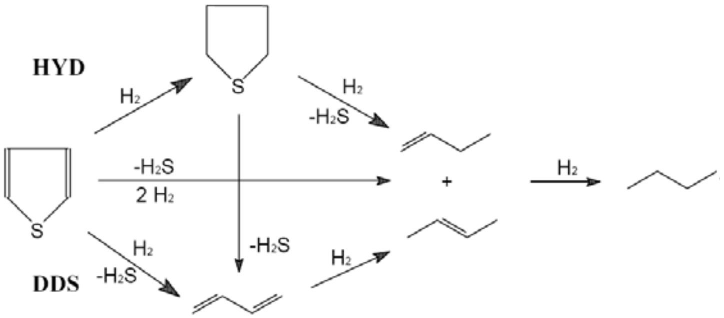

Fig (1): Reaction scheme for thiophene hydrodesulphurization

There it will be shown that a similar reaction network exists for all polyaromatic sulfur compounds. Hydrodesulphurization is a heterogeneously catalyzed reaction. Supported metal sulfides have been found to be the best catalysts for the HDS reaction. Both molybdenum and tungsten sulfides are active catalysts in the hydrodesulphurization reaction. Nowadays however, mainly molybdenum-based catalysts are used worldwide in the processes connected with sulfur removal. Different promoters have been tested and nickel and cobalt were found to give the highest enhancement of the activity towards desired products. Alumina support has a very important role in the activity and stability of the hydrodesulphurization catalyst as well and the γ-phase is the most suitable for the operation. Catalyst Hydrotreating are important components of petroleum refining processes. These catalysts are used to improve the yield of high-quality light oil fractions from heavier crude oil and petroleum feedstock containing high levels of impurities. Residuum hydrotreating catalysts are susceptible to irreversible deactivation caused by adsorption of sulfur and by metals impurities, such as vanadium and nickel. The gradual buildup of these impurities in a hydrotreating catalyst eventually plugs the pores and deactivates it. Nickel and vanadium adversely affect the behavior of cracking catalysts, reducing product yield and quality.

In a method for regenerating a spent HDS catalyst having an alumina support by removing contaminating nickel and vanadium compounds there from while increasing the BET surface area and the pore diameter thereof to attain a porosity effective to allow the regenerated HDS catalyst to be reused as HDS catalyst. Replacing deactivated catalysts represents a significant cost in petroleum refining [3-9]. Equally important are the costs and potential liabilities associated with treating and disposing spent catalysts.

Experimental tests and discussion

The spent catalyst is washed with naphtha to remove hydrocarbon and placed in the oven (120° C, 24hr) for drying. After this step, acid washing is done for contaminant metal removing. Acid acetic is used with different molarities (0.05, 0.1, 0.2 and 0.3 M) for this purpose.

Figure 2 is shown experimental setup. Acid acetic in the round bottomed flask is heated to boiling and the vapors rise through the outer chamber and into the condenser. The vapors condense into liquid and fall back into the bottom of the Soxhlet chamber. The Acid extracts the contaminant As the Acid level rises, the solution is forced through the small inner tube, and the chamber is flushed due to a siphoning effect. The flushed Acid returns to the flask taking the extracted compounds with it.

Fig (2): Experimental Setup

The HDS catalyst was dried at 110° C in an atmospheric oven. Samples were subjected to sulfiding pretreatment to convert metal impurities into sulfides and provide protection of the alumina, and leaching to remove metal impurities. Conditions for sulfiding pretreatment involve packing the spent HDS catalyst in a quartz tube, heating the tube at 400° C. while a mixture of 5% hydrogen sulfide in helium gas was passed through the bed at a flow rate of 10 cm^3 /min/g HDS catalyst for 2 hours. This calculates to a total amount of hydrogen sulfide per gram of catalyst equal to 60 cm^3 /gm of catalyst and represents about the minimum of sulfiding, based on hydrogen sulfide, to which the spent HDS catalyst should be pretreated. After acid washing, calcination is done. Conditions for calcination include packing the HDS catalyst in a stainless steel tube, heating and maintaining the tube at about 500° C and passing with using a continuous air stream through the bed for 5 hours. After calcinations, it was allowed to cool down to ambient temperature as inert gas was passed through the bed. Table I is shown acid wash and calcination condition of samples.

Table (I): Acid wash and calcination condition of samples

Sample Codes	**Type**	**Acid wash**		**Calcination**		**Remark**
		Acid Normality	**Time (hr)**	**Temperature (° C)**	**Time (hr)**	
F	Fresh catalyst	-	-	-	-	Hydrotreating catalyst
S	Spent catalyst	-	-	-	-	
S-1	Treated catalyst	0.05	3	500	5	
S-2	Treated catalyst	0.1	3	500	5	
S-3	Treated catalyst	0.2	3	500	5	
S-4	Treated catalyst	0.3	3	500	5	
S-5	Treated catalyst	0.1	3	500	5	Mixed S-2 and F (1:1)
S-6	Treated catalyst	-	-	500	5	Only calcination
S-7	Treated catalyst	0.1	1	500	5	
S-8	Treated catalyst	0.1	2	500	5	
S-9	Treated catalyst	0.1	3	500	5	First calcination then acid wash
S-10	Treated catalyst	0.1	4	500	5	

Metal contain of samples is determined with an atomic absorber (table 2). Then, catalyst samples are tested in reactor system. In this test, presulfurization is done and then sulfiding step in 340°C.

In any event, the above Tables show that the best removals of vanadium and nickel are obtained by calcination followed by sulfiding or by sulfiding alone.

Accordingly, it is of principal concern in this method to so control and/or combine the regeneration steps as will achieve the requisite regenerating removal of the contaminating vanadium and nickel compounds while also enhancing the BET surface area of the spent HDS catalyst sufficiently to allow the regenerated HDS catalyst to be reused for its intended purpose.

Table (II): Metal content of experimental samples

Metal / **Sample**	**Mo (% wt)**	**Ni (% wt)**	**Co (% wt)**	**Fe (% wt)**	**Na (% wt)**	**Pb (% wt)**	**As (ppm)**
F	7.71	3.2	0.04	0.03	0.025	0.007	Trace
S	6.9	2.95	0.04	0.35	0.46	0.01	35
S-1	6.81	2.85	0.04	0.3	0.15	Trace	30
S-2	6.7	2.83	0.04	0.07	0	Trace	>20
S-3	6.6	2.81	0.04	0.07	0	Trace	23

S-4	6.5	2.80	0.04	0.07	0	Trace	23
S-5	7.2	3	0.04	0.05	0.001	0.003	23
S-6	6.6	2.83	Trace	0.07	0	Trace	Trace
S-7	6.89	2.9	Trace	0.3	0.3	Trace	Trace
S-8	6.8	2.89	Trace	0.18	0.1	Trace	Trace
S-9	6.7	2.83	Trace	0.07	0	Trace	Trace
S-10	4.8	2.8	Trace	0.04	0	Trace	Trace

Three samples are prepared in 3,6 and 12hr period. Removing sulfur content, nitrogen content and cetane number of samples are determined for samples. These results are evaluated and rejuvenation condition of spent catalyst is determined.

Table (III): Results of Reactor Tests

Test **Sample**	**Sulfur ppm**	**Nitrogen ppm**	**Aromatic wt%**	**Non-Aromatic wt%**	**Cetane Number**
Light diesel	9530	260	19.49	80.51	52.14
F	3038	160	8.5	91.75	53.45
S	4850	220	18.11	81.89	52.15
S-1	4000	200	14.6	85.5	52.31
S-2	3400	170	10.99	89.01	52.76
S-3	3820	180	12.78	87.24	52.36
S-4	3950	190	15.74	84.26	52.34
S-6	4100	205	16.88	83.12	52.22
S-7	3932	200	14.76	8.24	52.33
S-8	3825	185	14.6	8.5	52.59
S-9	3400	170	10.99	89.01	52.76
S-10	4445	190	12.82	87.18	52.37

Surface of samples are determined with BET method, table IV is shown results. We have found that the average pore diameter of the regenerated catalyst invariably is increased in accord with this invention as compared to the original catalyst material so that it is not possible to restore this parameter to the original value. However, we have found that if the BET surface area of the regenerated catalyst is significantly enhanced over the value from that displayed by the spend catalyst, the porous nature of the regenerated catalyst will be sufficient to operate successfully in the HDS process.

Table (IV): Samples surface

Sample	**F**	**S**	**S-1**	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	**S-10**
Surface (m^2/g. catalyst)	187	131	152	165	164	165	169	150	152	160	165	164

The spent HDS catalyst typically will display a BET surface area much lower than that which the HDS catalyst originally possessed and we have found that the combination of enhanced BET surface area and the increased pore diameter resulting from the regeneration results in a regenerated catalyst which is reusable in the HDS process. As used hereinafter, the term "porosity" as relating to regenerated HDS catalyst means that the increased pore diameter in combination with the enhanced BET surface area is effective to allow the regenerated HDS catalyst to operate effectively in the HDS process.

Results

The results of the experiments to rejuvenation HDS catalyst showed that spent catalyst could reuse in hydrotreating process.

The research accomplishes its objective of removing nickel and vanadium compounds from the surface and pores of the HDS catalyst and correspondingly enhancing the BET surface area without significant removal of the alumina base by selecting and controlling the processing steps. It has been found that for best contaminant metals removal, the pretreatment steps of calcination following by sulfiding or of sulfiding alone, prior to the leaching, is most effective. With respect to protection of the alumina substrate and restoration of the porosity characteristics of the HDS catalyst material, the sulfiding step and in particular the temperature at which it is carried out is vital. Moreover, it has been found that protection of the alumina substrate is also effected if the oil from the catalysis process is not removed, i.e., if the spend HDS catalyst is not washed with a solvent such as naphtha or the like as a pretreatment step. However, it may be necessary in a particular case to wash the spent HDS catalyst with solvent prior to the sulfiding step and subsequent leaching step in order to achieve the desired degree of regeneration. Therefore, the proper balancing of the pretreatment steps, including the conditions carried out during them is essential to successful regeneration of the spent HDS catalyst.

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