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(54) IMPROVED PROCESS FOR EXTRACTING  
 VANADIUM FROM DEACTIVATED CATALYSTS

(71) We, SHELL INTERNATIONALE RE-  
 SEARCH MAATSCHAPPIJ B.V., a company  
 organised under the laws of The Netherlands,  
 of 30 Carel van Bylandtlaan. The Hague,  
 5 The Netherlands, do hereby declare the  
 invention, for which we pray that a patent  
 may be granted to us, and the method by  
 which it is to be performed, to be particu-  
 larly described in and by the following  
 10 statement:—

Patent 1,526,927 to which the present ap-  
 plication is an addition, relates to a pro-  
 cess for extracting vanadium from a catalyst  
 which has been deactivated by use in the  
 15 treatment of a hydrocarbon oil containing  
 vanadium with hydrogen at elevated tem-  
 perature and pressure, during which treat-  
 ment the vanadium content of the catalyst  
 has increased by at least 10 pbw. According  
 20 to the said patent 1,526,927 the extraction  
 of the vanadium, whereby the vanadium  
 content of the catalyst is decreased by at  
 least 40% of the amount by which it has  
 risen during the deactivation, is carried out  
 25 by extracting the deactivated catalyst with  
 an aqueous solution of a mineral acid,  
 after which vanadium is separated from the  
 vanadium-containing solution thus obtained.  
 If the process is applied to a catalyst that has  
 30 been deactivated in the hydrotreatment of a  
 hydrocarbon oil containing nickel in addi-  
 tion to vanadium, during which treatment  
 the nickel content of the catalyst has in-  
 creased as well, nickel is also removed from  
 35 the catalyst in the process. Besides the ex-  
 traction of vanadium and optionally nickel  
 from deactivated catalysts, the process is  
 also applicable to the regeneration of de-  
 activated catalysts so that they can be used  
 40 again for catalytic purposes.

According to the said patent 1,526,927  
 the acid extraction is preferably carried out  
 in the presence of a reducing agent. Also,  
 according to the said patent 1,526,927 it is  
 45 preferred to treat the deactivated catalyst

first with steam to remove sulphur and then  
 with an oxygen-containing gas to remove  
 carbon, prior to subjecting it to acid extrac-  
 tion. It should be remarked that, when the  
 aim is not only to extract vanadium and  
 optionally nickel from the catalyst, but also  
 to regenerate the catalyst, the treatment of  
 the deactivated catalyst with an oxygen-  
 containing gas in the way indicated in the  
 examples of the said patent 1,526,927 where-  
 50 by a small portion of the deactivated catalyst  
 is treated with air for three hours at 550°C,  
 is not suitable for larger quantities of de-  
 activated catalyst because of the large  
 amount of heat that would be liberated. 60

When larger quantities of deactivated  
 catalyst had to be treated with a view to  
 extracting vanadium and optionally nickel  
 from the catalyst as well as regenerating the  
 catalyst, the following three-stage procedure  
 65 was until recently considered to be the most  
 attractive embodiment of the process accord-  
 ing to the said patent 1,526,927. The de-  
 activated catalyst is first treated for 1-5  
 hours at 250-450°C and atmospheric pres-  
 70 sure with a mixture of steam and nitrogen,  
 then for 1-5 days at 350-600°C and atmos-  
 pheric pressure with a mixture of air and  
 nitrogen and finally it is subjected to acid  
 extraction in the presence of a reducing agent  
 75 for 0.5-3 hours at 50-150°C. The treat-  
 ment times required in the various stages  
 are dependent upon, inter alia, the quantities  
 of sulphur, carbon and metals which are  
 present on the deactivated catalyst and the  
 80 conditions chosen, viz. treatment tempera-  
 tures, gas flow rates and compositions of  
 treating gases and extraction liquid. Up  
 to now the long treatment time required in  
 the second stage of the three-stage pro-  
 85 cedure has been considered a serious draw-  
 back for using the process according to the  
 said patent 1,526,927 on a commercial scale.

Continued investigation of the process as  
 described in the said patent 1,526,927 has 90

now led to the finding that a comparable result can be obtained as regards vanadium and nickel removal and activity of the regenerated catalyst to that achieved by conducting the process according to the three-stage procedure described hereinbefore, but in a much shorter time, if the acid agent in the presence of a reducing agent is preceded by treatment of the deactivated catalyst at a temperature above 250°C with a mixture of steam and air of which the steam/air ratio is more than 1.0 at a steam partial pressure above 1 bar. In addition to the fact that with the process now found a much shorter treatment time will suffice for achieving a comparable result as regards vanadium and nickel removal and activity of the regenerated catalyst, this process has two additional advantages over the above-mentioned three-stage procedure in that both the number of treatment stages and the number of gases necessary for treating the deactivated catalyst prior to the acid extraction have decreased by one.

The present patent application therefore relates to an improved process for extracting vanadium from a deactivated catalyst according to the patent 1,526,927 in which process vanadium is extracted from a catalyst which has been deactivated by use in the treatment of a vanadium-containing hydrocarbon oil with hydrogen at elevated temperature and pressure, during which treatment the vanadium content of the catalyst has increased by at least 10 pbw, and in which process the said vanadium extraction, whereby the vanadium content of the catalyst is reduced by at least 40% of the amount by which it has risen during the deactivation (vanadium content of the catalyst expressed in pbw vanadium/100 pbw catalyst carrier), is carried out by extracting the deactivated catalyst with an aqueous solution of a mineral acid (called hereinafter "acid extraction"), after which the vanadium is separated from the vanadium-containing solution thus obtained.

The improvement consists in that the acid extraction which is carried out in the presence of a reducing agent, is preceded by a treatment of the deactivated catalyst at a temperature above 250°C with a mixture of steam and air in which the steam/air ratio is more than 1.0 at a steam partial pressure above 1 bar.

In the process according to the present invention the treatment with the mixture of steam and air is conducted at a temperature above 250°C, but preferably below 600°C and in particular at a temperature between 325 and 425°C. In the treatment of the deactivated catalyst with the mixture of steam and air the steam partial pressure is more than 1 bar, but preferably below 5 bar and in particular between 2 and 4 bar. The

steam/air ratio of the steam/air mixture used is more than 1.0, but preferably lower than 10 and in particular between 4 and 8.

The acid extraction in the presence of a reducing agent to which the deactivated catalyst should be subjected in the process according to the invention, is preferably carried out at elevated temperature, in particular at a temperature above 50°C. The said extraction is preferably conducted with an aqueous solution of sulphuric acid which has been saturated with sulphur dioxide.

When the process according to the invention is applied to deactivated catalysts which contain nickel in addition to vanadium, it may be advisable to extract the deactivated catalyst with water after the treatment with the steam/air mixture. By this extraction with water, which is preferably carried out at elevated temperature and in particular at a temperature above 50°C, an aqueous nickel-containing solution is obtained from which the nickel can be extracted.

The process according to the present invention is particularly important in those cases in which the aim is not only to extract vanadium and optionally nickel from the deactivated catalyst, but also to regenerate the catalyst (which may, in the fresh condition, contain one or more metals with hydrogenation activity) so that it can be used again for catalytic purposes. The present patent application relates therefore not only to a process for extracting vanadium and optionally nickel from a deactivated catalyst, but also to a process in which this extraction is conducted in such a way that a regenerated catalyst is obtained which can be used again for catalytic purposes, either as such, or after a complementary quantity of metals with hydrogenation activity has been added to it. The process according to the invention is especially important for extracting vanadium and optionally nickel from a catalyst substantially consisting of silica, in combination with regeneration of the catalyst, which catalyst has been used in a process for the hydrodemetallization of a hydrocarbon oil.

Applicants copending application 11404/78 (Serial No. 1 567 139) also relates to an improved process for extracting vanadium from deactivated catalysts.

The invention will now be explained with reference to the following examples.

#### EXAMPLE I

A catalyst comprising 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica carrier was prepared by impregnating a silica carrier with an aqueous solution of nickel nitrate and vanadium oxalate, after which the composition was dried and calcined. (catalyst A) was used in the sulphidic form for the hydrodemetallization of

a hydrocarbon oil (oil A) with a total vanadium and nickel content of 62 ppmw, a C<sub>5</sub>-asphaltenes content of 6.4 %w and a sulphur content of 3.9 %w, which oil had been obtained as the residue in the atmospheric distillation of a crude oil from the Middle East. The hydrodemetallization was carried out by passing the oil together with hydrogen in a downward direction through a cylindrical, vertically disposed fixed catalyst bed at a temperature of 420°C, a total pressure of 150 bar, a space velocity of 5 kg.l<sup>-1</sup>.h<sup>-1</sup> and a gas flow rate (measured at the reactor outlet) of 250 NI H<sub>2</sub>.kg<sup>-1</sup>. The activity of the catalyst, expressed as "% vanadium removed" (= average vanadium removal over the period of catalyst age from 1 tonne oil/kg catalyst to 4 tonnes oil/kg catalyst), was 51. After the catalyst had been deactivated in this process, it was extracted with toluene to remove remnants of residual oil and after evaporation of the toluene from the catalyst the latter was analysed. The deactivated catalyst (catalyst B) contained 9.7 pbw carbon, 20.6 pbw sulphur, 4.1 pbw nickel and 24.3 pbw vanadium per 100 pbw silica.

#### EXAMPLE II

5 kg of Catalyst B was treated with a 4:1 steam/nitrogen mixture for three hours at 350°C, atmospheric pressure and a gas flow rate of 2 NI gas mixture. (g catalyst)<sup>-1</sup>.h<sup>-1</sup>. The catalyst was then treated with a 1:9 air/nitrogen mixture for 50 hours at 400°C, atmospheric pressure and a gas flow rate of 1 NI gas mixture (g catalyst)<sup>-1</sup>.h<sup>-1</sup>. Finally, the catalyst was extracted for two hours at 90°C with stirring with 40 l 2 N sulphuric acid which had been saturated with sulphur dioxide. After the extracted catalyst had been washed with water, it was dried at 120°C and calcined for three hours at 550°C. On analysis of the catalyst thus obtained (catalyst C), 96% of the vanadium and 95% of the nickel were found to have been removed from the catalyst by this treatment.

#### EXAMPLE III

5 kg of Catalyst B was treated with a 7:1 steam/air mixture for 25 hours at 400°C, a steam partial pressure of 3.5 bar and a gas rate of 0.6 NI gas mixture. (g catalyst)<sup>-1</sup>.h<sup>-1</sup>. The catalyst was then extracted for two hours at 90°C with stirring with 40 l 2 N sulphuric acid which had been saturated with sulphur dioxide. After the extracted catalyst had been washed with water, it was dried at 120°C and calcined for three hours at 550°C. On analysis of the catalyst thus obtained (catalyst D), 96% of the vanadium and 95% of the nickel were found to have been removed from the catalyst by this treatment.

#### EXAMPLE IV

5 kg of Catalyst B was treated with a 5:1 steam/air mixture for 20 hours at 350°C, a steam partial pressure of 3.0 bar and a gas flow rate of 0.6 NI gas mixture. (g catalyst)<sup>-1</sup>.h<sup>-1</sup>. The catalyst was then subjected to acid extraction in the same way as described in Example III. On analysis of the catalyst thus obtained (catalyst E), 94% of the vanadium and 92% of the nickel were found to have been removed from the catalyst by this treatment.

#### EXAMPLE V

5 kg of Catalyst B was treated with a 1:2 steam/air mixture for 20 hours at 400°C, a steam partial pressure of 0.6 bar and a gas flow rate of 0.4 NI gas mixture. (g catalyst)<sup>-1</sup>.h<sup>-1</sup>. The catalyst was then subjected to acid extraction in the same way as described in Example III. On analysis of the catalyst thus obtained (catalyst F), 95% of the vanadium and 95% of the nickel were found to have been removed from the catalyst by this treatment.

#### EXAMPLE VI

5 kg of Catalyst B was treated with a 2:1 steam/air mixture for 25 hours at 150°C, a steam partial pressure of 1.5 bar and a gas flow rate of 2 NI gas mixture. (g catalyst)<sup>-1</sup>.h<sup>-1</sup>. The catalyst was then subjected to acid extraction in the same way as described in Example III. On analysis of the catalyst thus obtained (catalyst G), 40% of the vanadium and 45% of the nickel were found to have been removed from the catalyst by this treatment.

#### EXAMPLE VII

Catalysts containing 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica carrier were prepared by impregnating catalysts C and F with an aqueous solution of nickel nitrate and vanadyl oxalate, after which the compositions were dried and calcined. Catalysts C' and F' thus obtained were used in the sulphidic form for the hydrodemetallization of oil A under the same conditions as the hydrodemetallization of this oil by catalyst A described in Example I. The activities of catalysts C' and F', expressed as "percentage vanadium removed", were 48 and 10, respectively.

#### EXAMPLE VIII

In the same way as described in Example VII, catalysts D' and E' were prepared from catalysts D and E and used for the hydrodemetallization of oil A. The activities of catalysts D' and E', expressed as "percentage vanadium removed", were 50 and 49, respectively.

Of the examples I-VIII, Nos. III, IV and VIII are examples according to the present

invention. The other examples have been included for comparison.

Example I relates to a hydrodemetallization in which a fresh catalyst A deactivates 5 to the deactivated catalyst B.

Example II relates to the three-stage procedure described hereinbefore in which a regenerated catalyst C is prepared from the deactivated catalyst B and in which it takes 10 53 hours in all to carry out the first two stages.

Examples III and IV relate to the improved process according to the invention in which regenerated catalysts D and E are 15 prepared from the deactivated catalyst B. Comparison of examples II, III and IV shows that the process according to the invention leads to the same excellent metal removal as the three-stage procedure. However, the treatment with the steam/air mixture, which has replaced the first and the second stage of the three-stage procedure, takes only 20-25 hours.

Examples V and VI relate to the treatment 25 of the deactivated catalyst with a mixture of steam and air followed by acid extraction, in which "regenerated" catalysts F and G are prepared from deactivated catalyst B. During the treatment with the steam/air 30 mixture, the steam partial pressure and the steam/air ratio employed were too low in Example V and the temperature was too low in Example VI. This resulted in an insufficient metal removal for catalyst G (and consequently in a low activity!) and, as is 35 seen from Example VII, in a low activity for catalyst F.

From Examples VII and VIII it is seen that catalysts which have been regenerated 40 according to the present invention (catalysts D' and E') show the same high activity as a catalyst which has been regenerated according to the three-stage procedure (catalyst C').

45 WHAT WE CLAIM IS:—

1. An improved process for extracting vanadium from a deactivating catalyst according to patent 1,526,927 in which process 50 vanadium is extracted from a catalyst which has been deactivated by use in the treatment of a vanadium-containing hydrocarbon oil with hydrogen at elevated temperature and pressure, during which treatment 55 the vanadium content of the catalyst has increased by at least 10 pbw, and in which process the said vanadium extraction, whereby the vanadium content of the catalyst is reduced by at least 40% of the amount 60 by which it has risen during the deactivation (vanadium content of the catalyst expressed in pbw vanadium/100 pbw catalyst), is carried out by extracting the deactivated 65 catalyst with an aqueous solution of a min-

eral acid (called hereinafter "acid extraction"), after which the vanadium is separated from the vanadium-containing solution thus obtained wherein the improvement consists in that the acid extraction which is carried 70 out in the presence of a reducing agent, is preceded by a treatment of the deactivated catalyst at a temperature above 250°C with a mixture of steam and air in which the steam/air ratio is more than 1.0 at a steam 75 partial pressure above 1 bar.

2. A process according to claim 1, characterized in that the treatment of the deactivated catalyst with a mixture of steam and air is conducted at a temperature below 80 600°C.

3. A process according to claim 2, characterized in that the said temperature is between 325 and 425°C.

4. A process according to any one of 85 claims 1-3, characterized in that the treatment of the deactivated catalyst with a mixture of steam and air is conducted at a steam partial pressure below 5 bar.

5. A process according to claim 4, 90 characterized in that the said pressure is between 2 and 4 bar.

6. A process according to any one of claims 1-5, characterized in that the treatment of the deactivated catalyst with a mixture 95 of steam and air is conducted with a gas mixture in which the steam/air ratio is lower than 10.

7. A process according to claim 6, characterized in that the said ratio is between 4 and 8. 100

8. A process according to any one of claims 1-7, characterized in that the acid extraction in the presence of a reducing agent is carried out at a temperature above 105 50°C.

9. A process according to any one of claims 1-8, characterized in that the acid extraction in the presence of a reducing agent is carried out with an aqueous solution of sulphuric acid which has been saturated 110 with sulphur dioxide.

10. A process according to any one of claims 1-9, characterized in that nickel is removed from the deactivated catalyst by extraction with water at a temperature above 115 50°C, after the deactivated catalyst has been treated with the steam/air mixture.

11. A process according to any one of claims 1-10, characterized in that it is applied to a catalyst substantially consisting 120 of silica, which catalyst has been used in a process for the hydrodemetallization of a hydrocarbon oil.

12. A process for extracting vanadium 125 and optionally nickel from a deactivated catalyst, whether or not with regeneration of the catalyst, substantially as described hereinbefore and in particular with reference to Examples III, IV and VIII. 130

13. Vanadium and optionally nickel extracted from a deactivated catalyst according to a process as described in claim 12.

14. Catalysts that have been regenerated according to a process as described in claim 12.

15. Catalytic processes in which a catalyst according to claim 14 is used.

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