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(54) PROCESS FOR RECOVERING VANADIUM FROM DEACTIVATED CATALYSTS

(71) We, SHELL INTERNATIONALE
 RESEARCH MAATSCHAPPIJ B.V., a com-
 pany organised under the laws of The Nether-
 lands, of 30 Carel van Bylandtlaan, The
 Hague, 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 state-
 ment:—

The invention relates to a process for the
 recovery of vanadium from a catalyst which
 has become deactivated in a process wherein
 a vanadium-containing hydrocarbon oil has
 been treated with hydrogen at elevated tem-
 perature and pressure.

In catalytic processes wherein vanadium-
 containing hydrocarbon oils are treated at ele-
 vated temperature and pressure with hydrogen,
 vanadium from the feed deposits on the cata-
 lists, as a result of which the activity of the
 catalyst decreases. As more vanadium is de-
 posited, the activity of the catalyst further
 decreases and in the long run the catalyst be-
 comes deactivated and has to be replaced by a
 fresh batch. In catalytic processes wherein
 hydrocarbon oils are treated with hydrogen
 at elevated temperature and pressure, the cata-
 lyst cost is only a minor cost factor in the
 overall process. If, however, vanadium-con-
 taining hydrocarbon oils are applied as feed
 in these processes, the required catalyst re-
 placements during the process may easily in-
 crease the catalyst cost to a level where the
 process becomes economically unattractive.
 This is particularly important in those cases
 where a rapid deactivation of the catalyst
 occurs and consequently a rapid cata-
 lyst replacement is required. Since
 vanadium is a valuable metal, the
 higher catalyst cost incurred when vana-
 dium-containing hydrocarbon oils are used as
 the feed, can be greatly compensated for by
 recovering vanadium from the deactivated
 catalyst, provided that a considerable quantity

of vanadium has been deposited on the cata-
 lyst during the process and that a recovery
 procedure is available which is capable of
 removing a considerable part of the vana-
 dium present on the catalyst. In general it
 may be said that recovery of vanadium from
 the present deactivated catalysts is only re-
 garded as being attractive if during the pro-
 cess in which the catalyst has become deacti-
 vated the vanadium content of the catalyst
 has increased by at least 10 pbw, whereas dur-
 ing the recovery of vanadium from the deacti-
 vated catalyst, the vanadium content of the
 catalyst has decreased by at least 40% of the
 increase of the vanadium content of the cata-
 lyst which occurred during the deactivation
 (vanadium content of the catalyst expressed in
 pbw vanadium/100 pbw catalyst carrier).

An investigation by the Applicant into the
 recovery of vanadium from the present deacti-
 vated catalysts, which meet the above-men-
 tioned requirement with respect to increase
 of the vanadium content during deactivation,
 has revealed that a vanadium recovery com-
 plying with the above-mentioned requirement
 with respect to decrease of the vanadium con-
 tent during recovery may be performed in a
 simple way by extracting the deactivated cata-
 lyst with an aqueous solution of a mineral acid
 followed by isolation of vanadium from the
 vanadium-containing solution thus obtained.

The invention therefore relates to a process
 for the recovery of vanadium from a catalyst
 which has become deactivated in a process
 wherein a vanadium-containing hydrocarbon
 oil has been treated with hydrogen at elevated
 temperature and pressure, during which pro-
 cess the vanadium content of the catalyst has
 increased by at least 10 pbw, said recovery
 of vanadium, in which the vanadium content
 of the catalyst is decreased by at least 40%
 of the increase of the vanadium content of the
 catalyst which occurred during the deactiva-
 tion (vanadium content of the catalyst ex-
 pressed in pbw vanadium/100 pbw catalyst

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carrier), being carried out by extracting the deactivated catalyst with an aqueous solution of a mineral acid followed by isolation of vanadium from the vanadium-containing solution thus obtained.

For the sake of brevity extraction of the deactivated catalyst with an aqueous solution of a mineral acid will be referred to herein as "acid extraction".

The acid extraction is preferably carried out at elevated temperature, in particular at a temperature above 50°C. As a mineral acid sulphuric acid is very suitable. It is further preferred that the acid extraction is preceded by a treatment with a reducing agent or that the acid extraction is carried out under reducing conditions. Acid extraction under reducing conditions may very suitably be performed by application of a mineral acid having reducing properties or by carrying out the acid extraction in the presence of a reducing agent. As examples of attractive embodiments of the process according to the invention in which the acid extraction is preceded by a treatment with a reducing agent or in which the acid extraction is carried out under reducing conditions, the following may be mentioned.

- a) treatment of the deactivated catalyst with sulphur dioxide followed by an acid extraction using an aqueous solution of sulphuric acid.
- b) an acid extraction in which an aqueous solution of sulphurous acid containing no dissolved sulphur dioxide is used.
- c) an acid extraction in which water containing dissolved sulphur dioxide is used, in particular water which has been saturated with sulphur dioxide.
- d) an acid extraction as in (c) in which said water also contains sulphuric acid, in particular an aqueous solution of sulphuric acid which has been saturated with sulphur dioxide.

If in the process according to the invention sulphur dioxide is applied as reducing agent, it may be of advantage that the process is carried out at elevated pressure.

Vanadium-containing hydrocarbon oils contain as a rule a considerable amount of sulphur. If these oils are treated with hydrogen at elevated temperature and pressure in the presence of a catalyst, part of the sulphur deposits on the catalysts mainly in the form of sulphides of vanadium and if nickel is present in the hydrocarbon oil, also in the form of sulphides of nickel. In addition to metals and sulphur, coke also deposits on the catalyst during the process in which the catalyst is applied. This coke originates from decomposition of components of the hydrocarbon feed. It has been found that the results of the process according to the invention can be improved if at least part of the sulphur and/or the coke present on the deactivated catalyst is removed before the acid extraction,

or, when the acid extraction is preceded by a treatment with a reducing agent, before the treatment with a reducing agent is carried out. Removal of at least part of the sulphur and/or coke present on the deactivated catalyst may suitably be performed by treating the catalyst at elevated temperature with an oxygen-containing gas, e.g. air or a mixture of air and nitrogen. This treatment is preferably carried out at a temperature above 250°C, in particular above 350°C. A drawback of the treatment of the deactivated catalyst at elevated temperature with an oxygen-containing gas is that a large amount of heat is evolved as a result of the exothermic reactions which take place. To avoid the occurrence of extremely high temperatures during this treatment, which may unfavourably influence the results of the recovery procedure and/or damage the equipment in which the treatment is performed, it will be appreciated by those in the art that it is necessary that the treatment is carried out very carefully under strict temperature control. This may cause the treatment to be a very time-consuming operation. It has, however, been found that the above-mentioned drawback of the sulphur and coke removal step may be avoided if first of all at least part of the sulphur present on the deactivated catalyst is removed therefrom by treating the catalyst at elevated temperature with steam. This treatment is preferably carried out at a temperature above 200°C and in particular above 250°C. As a result of the treatment of the deactivated catalyst with steam, the subsequent treatment of the catalyst with an oxygen-containing gas at elevated temperature is much easier to control and requires much less time. If it is the intention to remove only part of the sulphur from the deactivated catalyst and no coke, the above-mentioned steam treatment of the catalyst may be carried out without a subsequent treatment of the catalyst with an oxygen-containing gas. A treatment of the deactivated catalyst with steam is also very suitable to remove remnants of residual oil from the catalyst. This may also be achieved by extracting the deactivated catalyst with an organic solvent.

Vanadium-containing hydrocarbon oils also often contain nickel, although the nickel content in such case is usually considerably lower than the vanadium content. If these vanadium and nickel-containing oils are treated in a catalytic process with hydrogen at elevated temperature and pressure, as a result of which vanadium deposits on the catalyst, the vanadium deposition is accompanied by nickel deposition. This nickel deposition also contributes to the deactivation of the catalyst. If the process according to the invention is applied to this type of deactivated catalyst, a vanadium-containing solution is obtained which also contains nickel. As the nickel con-

tent of the solution increases, the isolation of pure vanadium from this solution may become more difficult. It has been found that the nickel content of the solution from which vanadium should be isolated, can be considerably decreased by extracting the deactivated catalyst with water, after it has been treated at elevated temperature with an oxygen-containing gas. In this way a major part of the nickel present on the deactivated catalyst is removed therefrom and an aqueous nickel-containing solution is obtained which contains only a slight amount of vanadium. The extraction of the deactivated catalyst with water for the removal of nickel is preferably carried out at elevated temperature, in particular at a temperature above 50°C. If in the process according to the invention aqueous nickel-containing solutions are obtained with a sufficiently high nickel concentration, it may become attractive to use the process not only for recovering vanadium from deactivated catalysts but also for recovering nickel, which may easily be performed by isolating nickel from these solutions.

Catalysts which are used for the treating of hydrocarbon oils with hydrogen at elevated temperature and pressure comprise as a rule one or more metals with hydrogenating activity on a carrier. Preferred catalysts for this purpose are catalysts which contain one or more metals selected from the group consisting of nickel, cobalt, molybdenum, tungsten and vanadium on alumina, silica or silica-alumina as carrier, in particular catalysts which contain at least one of nickel and cobalt and at least one of molybdenum, tungsten and vanadium, such as catalysts containing the metal combinations nickel-vanadium, nickel-molybdenum, nickel-tungsten and cobalt-molybdenum. The catalysts are preferably used in their sulphidic form. For this purpose the metals present on the carrier are converted into the corresponding metal sulphides before the catalyst is contacted with the hydrocarbon oil to be treated in the catalytic process. During the initial stage of the process in which the catalysts are used, a rather rapid deposition of coke on the catalyst takes place, until the coke content of the catalyst has reached a certain level. When this coke level has been reached, it hardly increases any further during the remaining part of the process. As has been mentioned already hereinbefore, catalysts which are applied for the treating of hydrocarbon oils with hydrogen at elevated temperature and pressure usually contain one or more metals with hydrogenating activity. Under certain conditions it is, however, also possible to use for this purpose catalysts which do not contain such metals and consist entirely of e.g. alumina or silica.

So far, the description of the process according to the invention has been restricted to the recovery of vanadium and possibly nickel from

deactivated catalysts. It has, however, been found that the process also offers the possibility of regenerating the deactivated catalysts so that they can be used again for catalytic purposes. This regeneration is of course only possible if the fresh catalyst or at least the carrier thereof is a material that can stand the treatment according to the invention without serious damage being inflicted upon the catalytic properties of the catalyst.

If the process according to the invention is not only performed to recover vanadium and possibly nickel from the deactivated catalyst, but also to regenerate the catalyst, the way in which the process should be carried out depends, among other things, on whether or not metals with hydrogenating activity have been present on the fresh catalyst, the type and quantity of these metals and whether or not the regenerated catalyst is intended to be applied in the same type of process wherein the fresh catalyst has become deactivated.

If the regenerated catalyst is to be employed in a process wherein the presence of vanadium or nickel is undesired, the recovery process according to the invention should be carried out in such a way that vanadium and nickel are removed from the deactivated catalyst as completely as possible.

If the fresh catalyst contained one or more metals with hydrogenating activity other than vanadium and nickel, such as cobalt, molybdenum or tungsten, there is a fair chance that in the recovery process according to the invention at least part of these metals is removed from the deactivated catalyst together with vanadium and nickel. Thus, if the regenerated catalyst is to be used in a process wherein the original load of these metals is required, and additional amount of these metals should be supplied to the regenerated catalyst to restore the metal content of the catalyst to its original level. This may easily be achieved by impregnating the regenerated catalyst with an aqueous solution of salts of the metals concerned followed by drying and calcining of the composition.

An interesting situation arises when the regenerated catalyst is to be applied in a process wherein a vanadium and/or nickel-containing catalyst is required. Since the process according to the invention is highly flexible with respect to the amounts of vanadium and/or nickel which remain on the catalyst, the process can be carried out in such a way that a regenerated catalyst is obtained which contains the required amount of vanadium and/or nickel either as such or after an additional impregnation with a vanadium and/or nickel-containing solution.

In view of the above, the present invention not only relates to a process for the recovery of vanadium and possibly of nickel from a deactivated catalyst, but also to a pro-

cess wherein this recovery is carried out in such a way that a regenerated catalyst is obtained which can be used again for catalytic purposes, either as such or after an additional amount of metals with hydrogenating activity has been supplied to the catalyst. The present invention further relates to the resulting regenerated catalysts as well as to their application.

With respect to sulphur and coke which may be present on the deactivated catalyst the following is remarked. As has already been mentioned hereinbefore, catalysts comprising one or more metals with hydrogenating activity which are used in processes wherein hydrocarbon oils are treated with hydrogen at elevated temperature and pressure, are usually used in their sulphidic form. During the initial part of the process coke deposits on the catalyst until a certain coke level is reached, whereafter the coke content of the catalyst remains practically constant during the further process. In view of this it is in principle not necessary for sulphur and coke to be removed from the deactivated catalyst during the process of the invention, if the catalyst is to be used again.

The recovery process according to the invention is applied to catalysts which have become deactivated in a process wherein a vanadium-containing hydrocarbon oil is treated with hydrogen at elevated temperature and pressure. Examples of such treating processes are hydrosulphurization and hydrocracking. The recovery process according to the invention is of special importance for the recovery of vanadium and possibly nickel from a catalyst, either or not in combination with regeneration of the catalyst, which catalyst has been applied in a process for the hydrodemetallization of a hydrocarbon oil or in a process for improving the quality of a heavy hydrocarbon oil.

Processes for the hydrodemetallization of hydrocarbon oils are usually applied to oils having a high vanadium content, which oils are to be used as feed for catalytic processes such as cracking, hydrocracking and hydrosulphurization. Hydrodemetallization processes are usually carried out at a temperature of 350—450°C, a total pressure of 75—175 bar and a space velocity of 2.5—10 l.l⁻¹.h⁻¹. The purpose of the hydrodemetallization processes is to extend the life of the catalyst applied in the subsequent catalytic process.

Processes for improving the quality of heavy hydrocarbon oils are applied to oils having a C₈-asphaltene content of more than 5%w and a V_k²¹⁰ above 30 cSt. These processes

are carried out by contacting the oil in the presence of hydrogen with a catalyst at a temperature of at least 400°C, a hydrogen partial pressure of at least 100 bar and a space velocity of at most 2.0 l.l⁻¹.h⁻¹. The purpose of

these processes is to obtain a reduction of the C₈-asphaltene content and the V_k²¹⁰ of at least 30 and 50%, respectively (C₈-asphaltene content and V_k²¹⁰ of the feed compared with those

of the liquid reaction product obtained). Heavy hydrocarbon oils which are eligible for quality improvement, as a rule contain a large amount of vanadium.

In view of the rapid catalyst deactivation which as a rule occurs in processes for the hydrodemetallization or quality improvement of vanadium-containing hydrocarbon oils, these processes are preferably carried out either by passing the hydrocarbon oil through a vertically disposed catalyst bed and introducing at certain intervals during the operation fresh catalyst at the top of the catalyst bed and withdrawing at certain intervals spent catalyst at the bottom thereof (operation according to the "bunker flow" principle), or by using several reactors each comprising a fixed catalyst bed, which reactors are alternately used for the process concerned; while the process is carried out in one or more of these reactors, the catalyst in the other reactors is replenished (operation according to the "fixed bed swing" principle).

The invention is illustrated by the following examples, in which the percentages quoted for vanadium and nickel removal are based on the increase in the vanadium content or vanadium and nickel contents of the catalyst which occurred during the deactivation. In those examples in which vanadium removal, or vanadium and nickel removal, yielded solutions, the vanadium or vanadium and nickel was recovered from these solutions in conventional manner.

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 vanadyl oxalate followed by drying and calcining the composition. The catalyst (catalyst A) was applied in the sulphidic form for the hydrodemetallization of a hydrocarbon oil (oil A) having a total vanadium and nickel content of 62 ppmw, a C₈-asphaltene content of 6.4 %w and a sulphur content of 3.9 %w, which oil has been obtained as a residue in the atmospheric distillation of a Middle East crude oil. The hydrodemetallization was carried out by passing the oil together with hydrogen downwardly through a cylindrical vertically arranged fixed catalyst bed at a temperature of 420°C, a total pressure of 150 bar a space velocity of 5 l.l⁻¹.h⁻¹ and a gas velocity (measured at the reactor outlet) of 250 NH₃.kg⁻¹. The activity of the catalyst, expressed as "% vanadium removed" was 51. After the catalyst had become deactivated

in this process, it was extracted with toluene to remove remnants of residual oil and after evaporation of the toluene from the catalyst it was analysed. The deactivated catalyst (catalyst B) comprised 9.7 pbw carbon, 20.6 pbw sulphur, 4.1 pbw nickel and 24.3 pbw vanadium per 100 pbw silica.

EXAMPLE II

50 g of the deactivated catalyst B was extracted for 2 hours at 90°C, while stirring with 1.8 l 2N sulphuric acid. After washing the extracted catalyst with 2 l water it was dried at 120°C and calcined for 3 hours at 550°C. Analysis showed that by this treatment 45% of the vanadium and 46% of the nickel had been removed from the catalyst.

EXAMPLE III

Catalyst B was treated in substantially the same way as described in Example II, however, with the difference that in the present case instead of 1.8 l 2N sulphuric acid, 1.8 l water was used which had been saturated with sulphur dioxide. Analysis showed that by this treatment 48% of the vanadium and 55% of the nickel had been removed from the catalyst.

EXAMPLE IV

Catalyst B was treated in substantially the same way as described in Example II, however, with the difference that in the present case the sulphuric acid had been saturated with sulphur dioxide. Analysis showed that by this treatment 78% of the vanadium and 81% of the nickel had been removed from the catalyst.

EXAMPLE V

Catalyst B was treated in substantially the same way as described in Example II, however, with the difference that in the present case instead of 1.8 l 2N sulphuric acid, 0.2 l 2N sulphuric acid was used which had been saturated with sulphur dioxide. Analysis showed that by this treatment 58% of the vanadium and 60% of the nickel had been removed from the catalyst.

EXAMPLE VI

Catalyst B was treated in substantially the same way as described in Example IV, however, with the difference that in the present case the catalyst was treated for 3 hours at 350°C with steam (0.8 bar steam, 0.2 bar nitrogen) before the extraction with sulphuric acid. Analysis showed that by this treatment 84% of the vanadium and 79% of the nickel had been removed from the catalyst.

EXAMPLE VII

Catalyst B was treated in substantially the same way as described in Example VI, however, with the difference that in the present

case the catalyst was heated in air for 3 hours at 550°C, in between the treatment with steam and the extraction with sulphuric acid. Analysis showed that by this treatment 93% of the vanadium and 98% of the nickel had been removed from the catalyst.

EXAMPLE VIII

Catalyst B was treated in substantially the same way as described in Example II, however with the difference that the catalyst was heated in air for 3 hours at 550°C before the extraction with sulphuric acid. Analysis showed that by this treatment 81% of the vanadium and 97% of the nickel had been removed from the catalyst.

EXAMPLE IX

Catalyst B was treated in substantially the same way as described in Example II, however, with the difference that in the present case the catalyst was heated in air for 3 hours at 550°C, before the extraction with water saturated with sulphur dioxide. Analysis showed that by this treatment 89% of the vanadium and 94% of the nickel had been removed from the catalyst.

EXAMPLE X

Catalyst B was treated in substantially the same way as described in Example IV, however, with the difference that in the present case the catalyst was heated in air for 3 hours at 550°C, before the extraction with sulphuric acid saturated with sulphur dioxide. Analysis of the catalyst thus obtained (catalyst C) showed that by this treatment 96% of the vanadium and 95% of the nickel had been removed from the catalyst B.

EXAMPLE XI

A catalyst comprising 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica carrier was prepared by impregnating catalyst C (see Example X) with an aqueous solution of nickel nitrate and vanadyl oxalate followed by drying and calcining the composition. This catalyst (catalyst D) was applied in sulphidic form for the hydrodemetallization of oil A under the same conditions as applied in the hydrodemetallization of this oil with catalyst A, as described in Example I. The activity of the catalyst, expressed as "% vanadium removed", was 43.

EXAMPLE XII

Catalyst B was treated in substantially the same way as described in Example V, however, with the difference that in the present case the catalyst was heated in air for 3 hours at 550°C before the extraction with sulphuric acid saturated with sulphur dioxide. Analysis showed that by this treatment 89% of the vanadium and 89% of the nickel had been removed from the catalyst.

EXAMPLE XIII

Catalyst B was treated in substantially the same way as described in Example XII, however with the difference that in the present case the water wash after the extraction with sulphuric acid saturated with sulphur dioxide was omitted. The catalyst thus obtained (catalyst E), which comprised 0.8 pbw nickel and 4.9 pbw vanadium per 100 pbw silica carrier, was applied in sulphidic form for the hydrodemetallization of oil A under the same conditions as applied in the hydrodemetallization of this oil with catalyst A, as described in Example I. The activity of the catalyst, expressed as "% vanadium removed", was 41.

EXAMPLE XIV

Catalyst B was treated in substantially the same way as described in Example X, however, with the difference that in the present case the catalyst was extracted for 2 hours at 90°C, while stirring with 1.8 l water in between the heating in air and the extraction with sulphuric acid saturated with sulphur dioxide. Analysis showed that by the extraction with water 74% of the nickel and 2% of the vanadium had been removed from the catalyst, whereas by the extraction with sulphuric acid saturated with sulphur dioxide an additional amount of 92% of the vanadium and 23% of the nickel had been removed from the catalyst.

EXAMPLE XV

Catalyst B was treated in substantially the same way as described in Example IX, however, with the difference that in the present case the saturation of the water with sulphur dioxide and the extraction of the catalyst were carried out at a sulphur dioxide pressure of 3 bar. Analysis showed that by this treatment 90% of the vanadium and 91% of the nickel had been removed from the catalyst.

EXAMPLE XVI

Catalyst B was treated in substantially the same way as described in Example XII, however, with the difference that in the present case the saturation of the sulphuric acid with sulphur dioxide and the extraction of the catalyst were carried out at a sulphur dioxide pressure of 2 bar. Analysis showed that by this treatment 91% of the vanadium and 89% of the nickel had been removed from the catalyst.

EXAMPLE XVII

This example was carried out in substantially the same way as Example I, however, with the difference that in the present case instead of extracting the deactivated catalyst with toluene, the catalyst was steamed for 1 hour at 150°C at a steam pressure of 1.5 bar to remove remnants of residual oil. The deactivated catalyst (catalyst F) was treated in

the same way as catalyst B in Example XII. Analysis showed that by this treatment 85% of the vanadium and 87% of the nickel had been removed from the catalyst.

EXAMPLE XVIII

Catalyst B was treated in substantially the same way as described in Example II, however, with the difference that in the present case instead of 1.8 l 2N sulphuric acid, 1.8 l 10 %w aqueous nitric acid was used. Analysis showed that by this treatment 97% of the vanadium and 96% of the nickel had been removed from the catalyst.

EXAMPLE XIX

A catalyst comprising 1 pbw nickel and 4 pbw molybdenum per 100 pbw alumina was prepared by impregnating an alumina carrier with an aqueous solution of nickel nitrate and ammonium molybdate followed by drying and calcining the composition. The catalyst (catalyst G) was applied in the sulphidic form for the hydrodemetallization of oil A under the same conditions as applied in the hydrodemetallization of this oil with catalyst A, as described in Example I. The activity of the catalyst, expressed as "% vanadium removed", was 52. After the catalyst had become deactivated in this process, it was extracted with toluene to remove remnants of residual oil and after evaporation of toluene from the catalyst it was analysed. The deactivated catalyst (catalyst H) comprised 35.5 pbw carbon, 45.0 pbw sulphur, 9.6 pbw nickel, 81.0 pbw vanadium, and 4.0 pbw molybdenum per 100 pbw alumina.

EXAMPLE XX

Catalyst H was treated in the same way as catalyst B in Example IX. Analysis showed that by this treatment 64% of the vanadium, 21% of the nickel and 23% of the molybdenum had been removed from the catalyst.

The examples II—X, XII—XVIII and XX demonstrate the suitability of the process according to the invention for the recovery of vanadium and nickel from a vanadium and nickel-containing catalyst which has become deactivated in a hydrodemetallization process of a vanadium and nickel-containing hydrocarbon oil. The examples XI and XIII demonstrate the suitability of the process according to the invention for the regeneration of a catalyst which has become deactivated in a hydrodemetallization process of a vanadium and nickel-containing hydrocarbon oil.

WHAT WE CLAIM IS:—

1. A process for the recovery of vanadium from a catalyst which has become deactivated in a process wherein a vanadium-containing hydrocarbon oil has been treated with

**EXAMPLE XIII**

Catalyst B was treated in substantially the same way as described in Example XII, however with the difference that in the present case the water wash after the extraction with sulphuric acid saturated with sulphur dioxide was omitted. The catalyst thus obtained (catalyst E), which comprised 0.8 pbw nickel and 4.9 pbw vanadium per 100 pbw silica carrier, was applied in sulphidic form for the hydrodemetallization of oil A under the same conditions as applied in the hydrodemetallization of this oil with catalyst A, as described in Example I. The activity of the catalyst, expressed as "% vanadium removed", was 41.

EXAMPLE XIV

Catalyst B was treated in substantially the same way as described in Example X, however, with the difference that in the present case the catalyst was extracted for 2 hours at 90°C, while stirring with 1.8 l water in between the heating in air and the extraction with sulphuric acid saturated with sulphur dioxide. Analysis showed that by the extraction with water 74% of the nickel and 2% of the vanadium had been removed from the catalyst, whereas by the extraction with sulphuric acid saturated with sulphur dioxide an additional amount of 92% of the vanadium and 23% of the nickel had been removed from the catalyst.

EXAMPLE XV

Catalyst B was treated in substantially the same way as described in Example IX, however, with the difference that in the present case the saturation of the water with sulphur dioxide and the extraction of the catalyst were carried out at a sulphur dioxide pressure of 3 bar. Analysis showed that by this treatment 90% of the vanadium and 91% of the nickel had been removed from the catalyst.

EXAMPLE XVI

Catalyst B was treated in substantially the same way as described in Example XII, however, with the difference that in the present case the saturation of the sulphuric acid with sulphur dioxide and the extraction of the catalyst were carried out at a sulphur dioxide pressure of 2 bar. Analysis showed that by this treatment 91% of the vanadium and 89% of the nickel had been removed from the catalyst.

EXAMPLE XVII

This example was carried out in substantially the same way as Example I, however, with the difference that in the present case instead of extracting the deactivated catalyst with toluene, the catalyst was steamed for 1 hour at 150°C at a steam pressure of 1.5 bar to remove remnants of residual oil. The deactivated catalyst (catalyst F) was treated in

the same way as catalyst B in Example XII. Analysis showed that by this treatment 85% of the vanadium and 87% of the nickel had been removed from the catalyst.

EXAMPLE XVIII

Catalyst B was treated in substantially the same way as described in Example II, however, with the difference that in the present case instead of 1.8 l 2N sulphuric acid, 1.8 l 10 %w aqueous nitric acid was used. Analysis showed that by this treatment 97% of the vanadium and 96% of the nickel had been removed from the catalyst.

EXAMPLE XIX

A catalyst comprising 1 pbw nickel and 4 pbw molybdenum per 100 pbw alumina was prepared by impregnating an alumina carrier with an aqueous solution of nickel nitrate and ammonium molybdate followed by drying and calcining the composition. The catalyst (catalyst G) was applied in the sulphidic form for the hydrodemetallization of oil A under the same conditions as applied in the hydrodemetallization of this oil with catalyst A, as described in Example I. The activity of the catalyst, expressed as "% vanadium removed", was 52. After the catalyst had become deactivated in this process, it was extracted with toluene to remove remnants of residual oil and after evaporation of toluene from the catalyst it was analysed. The deactivated catalyst (catalyst H) comprised 35.5 pbw carbon, 45.0 pbw sulphur, 9.6 pbw nickel, 81.0 pbw vanadium, and 4.0 pbw molybdenum per 100 pbw alumina.

EXAMPLE XX

Catalyst H was treated in the same way as catalyst B in Example IX. Analysis showed that by this treatment 64% of the vanadium, 21% of the nickel and 23% of the molybdenum had been removed from the catalyst.

The examples II—X, XII—XVIII and XX demonstrate the suitability of the process according to the invention for the recovery of vanadium and nickel from a vanadium and nickel-containing catalyst which has become deactivated in a hydrodemetallization process of a vanadium and nickel-containing hydrocarbon oil. The examples XI and XIII demonstrate the suitability of the process according to the invention for the regeneration of a catalyst which has become deactivated in a hydrodemetallization process of a vanadium and nickel-containing hydrocarbon oil.

WHAT WE CLAIM IS:—

1. A process for the recovery of vanadium from a catalyst which has become deactivated in a process wherein a vanadium-containing hydrocarbon oil has been treated with



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- hydrogen at elevated temperature and pressure, during which process the vanadium content of the catalyst has increased by at least 10 pbw, said recovery of vanadium, in which the vanadium content of the catalyst is decreased by at least 40% of the increase of the vanadium content of the catalyst which occurred during the deactivation (vanadium content of the catalyst expressed in pbw vanadium/100 pbw catalyst carrier), being carried out by extracting the deactivated catalyst with an aqueous solution of a mineral acid (further called "acid extraction") followed by isolation of vanadium from the vanadium-containing solution thus obtained.
2. A process as claimed in claim 1, in which the acid extraction is carried out at elevated temperature.
3. A process as claimed in claim 1 or 2, in which an aqueous solution of sulphuric acid is applied in the acid extraction.
4. A process as claimed in claim 1 or 2, in which the acid extraction is preceded by a treatment with a reducing agent or in which the acid extraction is carried out under reducing conditions.
5. A process as claimed in claim 4, in which process the deactivated catalyst is treated with sulphur dioxide followed by an acid extraction in which an aqueous solution of sulphuric acid is used.
6. A process as claimed in claim 4, in which the acid extraction under reducing conditions is performed with the aid of a mineral acid having reducing properties or by carrying out the acid extraction in the presence of a reducing agent.
7. A process as claimed in claim 6, in which water containing dissolved sulphur dioxide is used in the acid extraction.
8. A process as claimed in claim 7, in which said water also contains sulphuric acid.
9. A process as claimed in claim 6, in which an aqueous solution of sulphurous acid containing no dissolved sulphur dioxide is used in the acid extraction.
10. A process as claimed in any one of claims 4—8, in which sulphur dioxide is applied at elevated pressure.
11. A process as claimed in any one of claims 1—10, in which at least part of the sulphur and/or the coke present on the deactivated catalyst is removed before the acid extraction, or, when the acid extraction is preceded by a treatment with a reducing agent, before the treatment with the reducing agent is carried out.
12. A process as claimed in claim 11, in which at least part of the sulphur present on the deactivated catalyst is removed therefrom by treating the catalyst at elevated temperature with steam.
13. A process as claimed in claim 11, in which at least part of the sulphur and/or coke present on the deactivated catalyst is removed therefrom by treating the catalyst at elevated temperature with an oxygen containing gas.
14. A process as claimed in claim 13, in which nickel is recovered from the deactivated catalyst by extraction with water after the deactivated catalyst has been treated at elevated temperature with an oxygen-containing gas.
15. A process as claimed in claim 13, in which at least part of the sulphur present on the deactivated catalyst is removed therefrom by treating the catalyst at elevated temperature with steam prior to the treatment with an oxygen-containing gas.
16. A process as claimed in any one of claims 1—15, in which a regenerated catalyst is obtained which can be used again for catalytic purposes, either as such or after an additional amount of metals with hydrogenating activity has been supplied to the catalyst.
17. A process as claimed in any one of claims 1—16, which is applied to a deactivated catalyst which contains nickel as well as vanadium, both nickel and vanadium being recovered.
18. A process for the recovery of vanadium or vanadium and nickel from a deactivated catalyst, either or not in combination with regeneration of the catalyst, which is carried out substantially as hereinbefore described with reference to any one of Examples II—X, XII—XVIII and XX.
19. Vanadium which has been recovered from a deactivated catalyst by the process claimed in any one of claims 1—18, and nickel which has been recovered by the process claimed in claim 17 or 18.
20. A regenerated catalyst obtained by the process claimed in claim 16.
21. A catalyst prepared by supplying an additional amount of metals with hydrogenating activity to a regenerated catalyst according to claim 20.
22. A catalytic process in which a catalyst according to claim 20 or 21 is used.
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