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(54) "HYDROCARBON CONVERSION PROCESS"

(71) We, Shell Internationale Research Maatschappij B.V. (formerly N.V.), a company organised under the laws of The Netherlands, 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 particularly described in and by the following statement:—

The invention relates to a process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted.

Most residual hydrocarbon oils, such as residues obtained in the distillation of crude oils under atmospheric or reduced pressure, contain high-molecular weight non-distillable metal compounds, in particular vanadium and nickel compounds. If these residual hydrocarbon oils are applied as feed for catalytic processes such as cracking, hydrocracking and hydrodesulphurization, metals such as vanadium and nickel deposit on the catalyst particles. As a result of the increasing concentration of vanadium and nickel on the active sites of the catalyst, a very rapid deactivation of the catalyst occurs.

To prolong catalyst life, it has already been suggested that the metals should be removed from the feed before the latter is contacted with the metal-sensitive catalyst. This may be performed by contacting the feed at elevated temperature and pressure and in the presence of hydrogen with a suitable demetallization catalyst. For this purpose several catalysts comprising one or more metals having hydrogenation activity on a carrier have already been suggested.

An investigation by the applicants into the hydrodemetallization of residual hydrocarbon oils with the aid of catalysts comprising one or more metals having hydrogenation activity on a carrier, has revealed that optimum catalysts for this purpose should meet a number of requirements with regard to their particle diameter and porosity. An optimum catalyst for the hydrodemetallization of residual hydrocarbon oils is a catalyst which shows a low degree of deactivation for a sufficiently long period and has a satisfactory activity, so that at acceptable space velocity a product with a sufficiently low metal content is obtained.

It has been found that for the catalytic hydrodemetallization of residual hydrocarbon oils the requirements with respect to particle diameter and porosity which an optimum catalyst should meet are as follows.

For catalysts which have such a specific average pore diameter (p in nm) and specific average particle diameter (d in mm) that the quotient p/d meets the requirement: $p/d > 10.0 - 0.15 v$, the catalysts should have a surface area larger than $100 \text{ m}^2/\text{g}$ and a total pore volume above 0.40 ml/g , which the percentage of the total pore volume that consists of pores with a diameter above 100 nm (v) should be smaller than 50.

For catalysts that have such a p and d that the quotient p/d is larger than $3.5 - 0.02 v$ but at most $10.0 - 0.15 v$, the catalysts should meet the following requirements:

- (1) the nitrogen pore volume should be larger than 0.60 ml/g ,
- (2) the surface area should be larger than $150 \text{ m}^2/\text{g}$, and
- (3) p should be larger than 5 nm ,
- (4) v is smaller than 50.

The above-mentioned values of d and p are determined by the following method, which is referred to hereinafter as "the herein defined".

The way in which d is determined depends on the shape of the catalyst particles. If the shape is such that the particle diameter distribution of the catalyst can be determined with the aid of a sieve analysis, d is determined as follows. After a complete sieve analysis of a representative catalyst sample has been carried out, d is read off from a graph in which for every successive sieve

fraction the percentage by weight, based on the total weight of the catalyst sample, has been cumulatively plotted as a function of the linear average particle diameter of the relevant sieve fraction; d is the particle diameter corresponding to 50% of the total weight. This method can be used to determine d of spherical and granular materials and materials with a similar shape, such as extrudates and pellets having a length/diameter ratio between 0.9 and 1.1. The determination of d of extrudates and pellets having a length/diameter ratio smaller than 0.9 or larger than 1.1 and similar cylindrically shaped materials, of which the particle diameter distribution cannot be determined with the aid of a sieve analysis, is carried out as follows. After a complete length distribution analysis (in case the length/diameter ratio is smaller than 0.9) or after a complete diameter distribution analysis (in case the length/diameter ratio is larger than 1.1) of a representative catalyst sample has been carried out, d is read off from a graph in which for every successive length and diameter fraction, respectively, the percentage by weight, based on the total weight of the catalyst sample, has been cumulatively plotted as a function of the linear average size of the relevant fraction; d is the value corresponding to 50% of the total weight.

After the complete pore diameter distribution of a catalyst sample has been determined, p is read off from a graph in which for the pore diameter range of 0–100 nm, for every successive pore volume increment smaller than or equal to 10% of the pore volume, the quotient of the pore volume increment and the corresponding pore diameter, interval has been cumulatively plotted as a function of the linear average pore diameter over the relevant pore diameter interval; p is the pore diameter corresponding to 50% of the total quotient at 100 nm.

A determination of the complete pore diameter distribution of the catalyst may very suitably be carried out with the aid of the nitrogen adsorption/desorption method (as described by E.V. Ballou and O.K. Doolen in *Analytical Chemistry* 32, 532 (1960)) combined with the mercury penetration method (as described by H.L. Ritter and L.C. Drake in *Industrial and Engineering Chemistry, Analytical Edition* 17, 787 (1945)), applying mercury pressures of 1–2000 bar. In this case, the pore diameter distribution of the catalyst in the pore diameter range below and including 7.5 nm is calculated from the nitrogen desorption isotherm (assuming cylindrical pores) according to the method described by J.C.P. Broekhoff and J.H. de Boer in *Journal of Catalysis* 10, 377 (1968) and the pore diameter distribution of the catalyst in the pore diameter range above 7.5 nm is calculated with the aid of the formula:

$$\text{pore diameter (in nm)} = \frac{15000}{\text{absolute mercury pressure (in bar)}}$$

The nitrogen pore volume and the total pore volume referred to herein are defined herein as follows. The nitrogen pore volume of a catalyst is the pore volume determined with the aid of the above-mentioned nitrogen adsorption/desorption method. The total pore volume of a catalyst is the sum of the nitrogen pore volume present in pores with a diameter below and including 7.5 nm (determined with the aid of the above-mentioned nitrogen adsorption/desorption method) and the mercury pore volume present in pores with a diameter above 7.5 nm (determined with the aid of the above-mentioned mercury penetration method). The surface areas referred to herein are those determined by the B.E.T. method.

According to the present invention there is provided a process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more having hydrogenation activity on a carrier, which catalyst comprises particles which meet the following requirements, in which d and p are determined by the method of a determination herein defined, surface area is determined by the B.E.T. method, and the nitrogen pore volume and the total pore volume are as herein defined.

- (1) $p/d > 3.5-0.02 v$, in which p is the specific average pore diameter in nm, d is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm,
 - (2) the total pore volume is larger than 0.40 ml/g,
 - (3) v is smaller than 50, and
 - (4) the surface area is larger than 100 m²/g, with the proviso that when the catalyst particles have such a p and d that the quotient p/d is larger than 3.5–0.02 v but at most 10–0.15 v , the following requirements apply:
 - (a) the nitrogen pore volume is larger than 0.60 ml/g,
 - (b) the surface area is larger than 150 m²/g, and
 - (c) p is larger than 5 nm,
- or agglomerates of said particles.

The demetallization catalysts used in carrying out the invention are characterized, among other things, by a given relation between their average pore diameter and average particle diameter. It is essential that the average pore diameter and average particle diameter used for the characterization of the catalysts should be determined according to the method specified above for the specific

average pore diameter and specific average particle diameter because, if for the characterization of the catalysts use is made of an average pore diameter or an average particle diameter determined by methods other than those specified above for the specific average pore diameter and specific average particles diameter (for example an average pore diameter calculated as four times the quotient of the pore volume and the surface area or an average particle diameter calculated as the linear average), entirely different results may be obtained.

The relation between p and d makes it possible at a certain d of the catalyst particles to determine the minimum value above which p of the catalyst particles should be selected to obtain an optimum catalyst. Consequently, it is also possible to derive from the relation found the maximum value below which d of catalyst particles having a certain p should be selected to obtain an optimum catalyst. The most suitable values for p and d , respectively, within the ranges found are determined by, among other factors, the composition of the hydrocarbon oil to be demetallized. According as the hydrocarbon oil to be demetallized has a higher C_5 -asphaltenes content, a catalyst with a higher p/d is preferably applied.

The hydrodemetallization of residual hydrocarbon oils in the processes according to the invention is preferably carried out in the presence of a catalyst comprising 0.1–15 pbw metals having hydrogenation activity per 100 pbw carrier. The metals having hydrogenation activity are preferably selected from nickel, cobalt, molybdenum, vanadium and tungsten. It is further preferred that the catalyst should comprise at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum, vanadium and tungsten and further that the atomic ratio between nickel and/or cobalt on the one hand and molybdenum, vanadium and/or tungsten on the other hand is between 0.05 and 3.0. Suitable metal combinations are nickel-vanadium, cobalt-molybdenum, nickel-molybdenum and nickel-tungsten.

Residue demetallization in the processes according to the invention is preferably carried out over a catalyst comprising a combination of nickel and vanadium. This preference is based on the results of a comparative investigation into the activity for residue demetallization of catalysts according to the invention, which catalysts comprised nickel, vanadium, cobalt-molybdenum and nickel-vanadium, and which catalysts comprised the same carrier. In contrast with the other catalysts, the nickel-vanadium catalyst was the only one to show a stable activity right from the start of the demetallization process. The nickel catalyst and the vanadium catalyst showed a lower initial activity, whereas the cobalt-molybdenum catalyst and the nickel-molybdenum catalyst, showed a higher initial activity compared with the nickel-vanadium catalyst. The activities of these catalysts levelled out to that of the nickel-vanadium catalyst after a certain amount of metal-containing feed had been processed over these catalysts. Although the nickel-molybdenum catalyst and the cobalt-molybdenum catalyst show a higher initial activity for demetallization, these catalysts also show desulphurization activity, which may lead to an undesired temperature increase in the catalyst bed. The metal load of the demetallization catalysts applied according to the present invention preferably amounts to 0.5–10 pbw and in particular 2.0–7.5 pbw per 100 pbw carrier. An especially preferred demetallization catalyst according to the invention is a catalyst comprising about 0.5 pbw nickel and about 2.0 pbw vanadium per 100 pbw carrier. The metals may be present on the carrier in the metallic form or in the form of their oxides or sulphides. Preference is given to catalysts in which the metals are present on the carriers in the form of their sulphides. Sulphidation of the catalysts may be carried out by any technique for the sulphidation of catalysts known in the art. Sulphidation may, for instance, be carried out by contacting the catalysts with a sulphur-containing gas such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide, or a mixture of hydrogen and carbon disulphide, or a mixture of hydrogen and a mercaptan such as butyl mercaptan. Sulphidation may also be carried out by contacting the catalysts with hydrogen and with a sulphur-containing hydrocarbon oil, such as a sulphur-containing kerosine or gas oil. In addition to the above-mentioned catalytically active metals, the catalysts may contain other catalytically active metals and promoters such as phosphorus, boron and halogens, such as fluorine and chlorine. Very suitable carriers for the catalysts are oxides of the elements of Group II, III or IV of the Periodic Table of Elements or mixtures of the said oxides, such as silica, alumina, magnesia, zirconia, thoria, boria, hafnia, silica-alumina, silica-magnesia and alumina-magnesia.

The preparation of these catalysts may be carried out by depositing the metals concerned on a carrier having such a pore diameter distribution and specific average pore diameter that after deposition of the metals thereon a catalyst is obtained which meets the requirements of the invention, either as such or after the specific average catalyst particle diameter has been decreased.

The porosity of the finished catalyst depends to a certain extent on the metal load applied. In general, it may be said that when starting from a carrier with a given porosity, the porosity of the finished catalyst will be lower according as the metal load is higher. This phenomenon plays only a minor role if relatively low metal loads are applied. This means that at the relatively low metals loads which are preferred for the catalysts according to the invention, the porosity of the finished catalyst is mainly determined by the porosity of the applied carrier so that for the preparation of these catalysts carriers should be selected having a porosity which differs only little from the

desired porosity of the finished catalyst. The porosity of a carrier may also be influenced by means of a high-temperature treatment, either in the presence or in the absence of steam.

The porosity of a carrier is mainly determined by the way in which the carrier has been prepared. Catalyst carriers of the metal-oxide type are usually prepared by adding to one or more aqueous solutions of the salts of the metals concerned one or more gelating agents, as a result of which the metals precipitate in the form of metal hydroxide gels, which are subsequently shaped and calcined. Usually, before being shaped the metal hydroxide gels are allowed to age for some time. During the preparation of the carrier there is ample opportunity of influence the porosity of the carrier. The porosity of the final carrier depends, among other factors, on the rate of addition of the gelating agents, and on the temperature and pH applied during the formation of the gel. The porosity of the final carrier may also be influenced by addition of certain chemicals to the gel, such as phosphorus and/or halogen compounds. If ageing is applied, the porosity of the final carrier also depends on the ageing time and the temperature and pH applied during ageing. In the preparation of mixed metal oxide carriers a further aspect that is important with respect to the porosity of the final carrier, is the way in which the metal hydroxide gels are precipitated: simultaneously or separately, e.g. one on top of the other. The porosity of the final carrier further depends on the way in which the carrier particles are shaped, on the conditions applied during shaping, and on the temperature applied during calcination.

During shaping the porosity of the carrier particles is influenced, for example, by the type and amount of peptizing agents and binders which are usually added during this stage of carrier manufacture, by the addition of certain chemicals, and by the addition of small amounts of inert materials. If the carrier particles are shaped by extrusion or tableting, the porosity of the final carrier is influenced by the extrusion or tableting pressure applied. If use is made of the spray-drying technique, the porosity of the carrier is influenced by the spray temperature and spray pressure applied.

The catalysts may be prepared by any technique for the preparation of supported catalysts known in the art. It is not necessary that the catalytically active metals are deposited on a finished carrier; they may also be incorporated into the carrier material during the preparation thereof, for example, prior to shaping. Incorporating the catalytically active metals into the carrier at an early stage of catalyst preparation may also have a strong influence on the porosity of the finished catalyst.

As has already been mentioned hereinbefore, catalyst carriers of the metal-oxide type are usually prepared by precipitating the metals in the form of metal hydroxide gels, followed by shaping and calcining. Usually, before being shaped the metals hydroxide gels are aged. Very active demetallization catalysts according to the invention can be prepared by incorporating the catalytically active metals, into the metal hydroxide gels before the latter are being shaped. The incorporation of the catalytically active metals into the metal hydroxide gels is preferably carried out after the latter have been aged. Incorporating the catalytically active metals into the metal hydroxide gels before the latter are being shaped offers the advantage that the catalyst preparation requires only on calcination, which may mean a considerable saving in catalyst preparation costs. A very active demetallization catalyst according to the invention has e.g. been prepared by incorporating a nickel and a vanadium compound, in an amount corresponding to about 0.5 pbw nickel and about 2.0 pbw vanadium per 100 pbw final carrier, into a silica hydrogel, after the latter had been precipitated and aged but before shaping and calcining.

Another attractive way of preparing the demetallization catalysts used in carrying out the invention is by single or multistep coimpregnation of a carrier with an aqueous solution comprising one or more nickel and/or cobalt compounds and one or more molybdenum, vanadium and/or cobalt compounds and one or more molybdenum, vanadium and/or tungsten compounds, followed by drying and calcining. If the impregnation is carried out in several steps, the material may be dried and calcined, if desired, between the successive steps of impregnation. Drying and calcining are preferably carried out at temperatures between 50 and 150°C and between 150 and 550°C, respectively. Examples of suitable water-soluble compounds of nickel, cobalt, vanadium, molybdenum and tungsten which may be applied in the preparation of the present catalysts are nitrates, chlorides, carbonates, formates and acetates of nickel and cobalt, vanadyl oxalate, vanadyl sulphate, ammonium vanadate, and vanadyl acetyl acetate, ammonium molybdate and ammonium tungstate. In order to increase the solubility of these compounds and to stabilize the solutions, certain compounds such as ammonium hydroxide, monoethanolamine and sorbitol may be added to the solutions.

As carriers for the catalysts used in carrying out the invention aluminas, silicas and silica-aluminas are preferred. Very suitable carriers are alumina or silica particles prepared by spray-drying of an alumina or silica gel, followed by shaping of the spray-dried microparticles into larger particles, e.g., by extrusion, and spherical alumina or silica particles obtained by the well-known oil drop method. The latter method comprises formation of an alumina or silica hydrosol, combining the hydrosol with a suitable gelating agent and dispersing the mixture as droplets into an oil which may be kept at an elevated temperature; the droplets are allowed to remain in the oil

until they have solidified to spherical hydrogel particles, which are subsequently isolated, washed, dried and calcined. Very suitable silica-alumina carriers for the present catalysts are cogels of aluminium hydroxide gel on silica hydrogel. These cogels are preferably prepared by the first precipitating a silica hydrogel from an aqueous, silicate-ions containing solution by the addition of a mineral acid, subsequently adding a water-soluble aluminium salt to the solution, and then precipitating an aluminium hydroxide gel by adding an alkaline-reacting compound. It is preferred that the silica hydrogel produced be allowed to age for some time at an elevated temperature before the cgel preparation is continued. The ageing conditions, particularly the ageing time and the ageing temperature, have a strong influence on the porosity of the final cgel. The preparation of catalysts according to the invention based on the above cogels may e.g. be carried out as follows. First the cgel is shaped, e.g. by extrusion, followed by drying and calcining of the hydrogel particles. Subsequently, the xerogel particles thus obtained are neutralized with a nitrogen base and dried. Finally, the catalytically active metals are deposited on the carrier by impregnating the latter with one or more aqueous solutions comprising salts of the metals concerned, followed by drying and calcining of the composition. The preparation of catalysts according to the invention based on the above cogels may also be carried out by the following simplified procedure. The catalytically active metals are incorporated into the cgel by mixing the latter with one or more aqueous solutions comprising salts of the metals concerned, after which the composition is shaped, e.g. by extrusion, dried and calcined.

In addition to extrusion and tableting which have already been mentioned hereinbefore as attractive shaping techniques for the present catalysts and catalyst carriers, another attractive shaping technique is granulation. According to this technique small particles of the catalyst or carrier material are intimately mixed with a liquid in such proportion that agglomeration of the small particles to larger particles (granules) occurs. If desired, the liquid may comprise salts of the catalytically active metals. Optionally a binder may be added to the solid and/or liquid phase.

The relationship found between p and d enables the preparation of catalysts for the hydrodemetallization of residual hydrocarbon oils, which possess optimum properties. If a catalyst or catalyst carrier is available of which d is too large in relation to p , it is possible to prepare therefrom an optimum catalyst or catalyst carrier by adapting d to p . This can be effected in a simple way by reducing the particle size of the catalyst or catalyst carrier, for example by grinding the particles.

If, in the preparation of demetallization catalysts to be used in carrying out invention starting from a certain catalyst or catalyst carrier material, the required d corresponding to the p of the material from which the catalyst must be prepared is so small that practical plant difficulties would arise when such small catalyst particles are used for catalyst hydrodemetallization (as is particularly likely to arise when dealing with materials having a small p and v), it is preferred that agglomerates (granules) be formed from the small particles. The porous catalyst agglomerates may very suitably be prepared from the small catalyst particles by binding them with or without the use of a binding agent in the presence of a material which is incorporated in the agglomerates and subsequently removed therefrom by evaporation, combustion, solution, leaching or otherwise, leaving sufficient pores with a diameter above 100 nm in the agglomerates. Suitable compounds for this purpose are cellulose-containing materials, polymers and compounds soluble in organic or inorganic solvents. Such agglomeration can also be effected with particles of the catalyst carrier prior to impregnation to form similar agglomerated catalysts.

The catalytic demetallization of residual hydrocarbon oils is preferably carried out by passing the hydrocarbon oils at elevated temperature and pressure and in the presence of hydrogen in upward, downward or radial direction through one or more vertically disposed reactors comprising a fixed or moving bed of the catalyst particles concerned. The demetallization may, for instance, be carried out by passing the hydrocarbon oils together with hydrogen through a vertically disposed catalyst bed in the upward direction, the liquid and gas velocity used being such that expansion of the catalyst bed occurs (demetallization in ebullated bed operation). If several reactors are used in series for the demetallization, the catalysts present in these reactors may differ from each other for instance with respect to their p , d and/or chemical composition. A very attractive embodiment of the present demetallization process is one in which the hydrocarbon oil is passed through a vertically disposed catalyst bed in which during operation fresh catalyst is periodically introduced at the top of the catalyst bed and spent catalyst is withdrawn at the bottom thereof (demetallization in bunker flow operation). Another very attractive embodiment of the present demetallization process is one in which several reactors comprising a fixed catalyst bed are used, which reactors are alternately used for demetallization; while the demetallization is carried out in one or more of these reactors, the catalyst in the other reactors is replenished (demetallization in fixed bed swing operation). If desired, the present demetallization may also be carried out by suspending the catalyst in the hydrocarbon oil to be demetallized (demetallization in slurry phase operation).

For the catalytic hydrodemetallization of residual hydrocarbon oils use is generally made of catalyst particles having a d of 0.4–5.0 mm. Catalyst particles having a d of 0.5–4.0 mm and in particular of 0.6–3.0 mm are preferred for this purpose.

The catalyst particles preferably have a total pore volume of at least 0.50 ml/g and a surface are above 150 m²/g.

The reaction conditions applied in the hydrodemetallization process according to the invention may vary widely. The hydrodemetallization is preferably carried out at a temperature of 300–450°C, a total pressure of 75–250 bar, a space velocity of 0.1–25 pbv of fresh feed pbv of catalyst per hour, and a hydrogen/feed ratio of 100–2000 N1 H₂/kg feed. Particularly preferred are a temperature of 350–425°C, a total pressure of 100–200 bar, a space velocity of 1–10 pbv of fresh feed per pbv of catalyst per hour and a hydrogen/feed ratio of 200–1000 N1 H₂/kg feed.

The process according to the invention is especially of importance for the conversion of residual hydrocarbon oils by hydrocracking, hydrodesulphurization and catalytic cracking. As a result of the hydrodemetallization, deactivation of the catalyst applied in these processes is considerably suppressed. Hydrocracking and hydrodesulphurization of residual hydrocarbon oils may be carried out by contacting the oils at elevated temperature and pressure and in the presence of hydrogen with a suitable catalyst which may be present in the form of a fixed bed, a moving bed or a suspension of catalyst particles. An attractive combination of demetallization and hydrocracking or hydrodesulphurization according to the invention, is one in which the demetallization is carried out in fixed bed swing operation or in bunker flow operation and the hydrocracking or hydrodesulphurization in conventional fixed bed operation. If the demetallization is carried out in combination with hydrocracking or hydrodesulphurization, it is customary that these processes are carried out at the same total pressure. For the combination of demetallization and hydrodesulphurization it may be of advantage to carry out the demetallization at a higher hydrogen partial pressure than the hydrodesulphurization. This may be accomplished by carrying out the demetallization step with the fresh hydrogen which is supplied to the process and the hydrodesulphurization step with the hydrogen which is recycled in the process.

Examples of residual hydrocarbon oils which can be demetallized and subsequently catalytically converted by the processes of the present invention are residues obtained from the distillation of crude oils at atmospheric or reduce pressure.

The demetallization step of the process of the present invention will now be further described with the aid of the following experimental data:

30 CATALYST PREPARATION 30

Catalyst 1

A catalyst comprising 2.0 pbw vanadium per 100 pbw alumina was prepared as follows:

An aqueous solution of vanadyl oxalate was prepared by boiling an aqueous mixture comprising 6.25 g vanadium pentoxide and 14 g oxalic acid. After cooling down, the solution was diluted with water to a volume of 100 ml and used to impregnate 175 g of an alumina carrier. After 30 minutes, the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 2

A catalyst comprising 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw alumina was prepared as follows:

An aqueous solution of vanadyl oxalate (prepared from 6.3 g vanadium pentoxide and 12 g oxalic acid) was mixed with an aqueous solution of 4.4 g nickel nitrate 6 aq. After diluting the solution with water to a volume of 110 ml, it was used to impregnate 175 g of an alumina carrier. After 30 minutes, the impregnated material was dried at 120°C and calcined for one hour at 500°C.

Catalyst 3

This catalyst, which comprised 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw alumina, was prepared in substantially the same way as catalyst 2.

Catalysts 4-11

These catalysts, which comprised 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica, were prepared in substantially the same way as catalyst 2. In the present case, however, silicas instead of alumina were used in carriers.

Catalyst 12

94.7 g of a silica, which had been calcined for 3 hours at 500°C, was stored for 4 hours in a desiccator over water and subsequently mixed with a solution of 100 ml 25% ammonia in 300 ml water. After 5 minutes' stirring, the silica was filtered off and washed with water. This silica was used as carrier for a catalyst comprising 0.1 pbw nickel and 1.1 pbw vanadium per 100 pbw silica. The catalyst was prepared as follows:

An aqueous solution of vanadyl oxalate (prepared from 4.4 g vanadium pentoxide and 9.25 g oxalic acid) was mixed with an aqueous solution of 3.06 g nickel nitrate 6 aq. After diluting the solution with water to a volume of 500 ml, it was mixed with the above-mentioned silica and the mixture was stirred for 3 hours. After 12 hours the solid material was filtered off, washed with water, dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 13

The pH of a quantity of 6750 ml of an aqueous solution of 1500 g sodium silicate (SiO₂ content: 27 %w) was decreased from 11.5 to 6 by addition of 600 ml of 6 N nitric acid with stirring. The silica gel obtained was aged for 24 hours at 100°C, filtered off and washed with

water until it was sodium-free. This silica gel (13.6 %w dry material) was used as carrier for a catalyst comprising 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica. The catalyst was prepared as follows:

An aqueous solution of vanadyl oxalate (prepared from 14.6 g vanadium pentoxide and 29 g oxalic acid) was mixed with an aqueous solution of 10.1 g nickel nitrate 6 aq. After diluting the solution with water to a volume of 250 ml, it was mixed with the above-mentioned silica gel which had been taken up in 250 ml water. After the mixture had been stirred for 2 hours, it was dried on a steam bath, subsequently dried at 120°C and finally calcined for 3 hours at 500°C.

10 Catalyst 14

A catalyst comprising 4.0 pbw cobalt and 11.0 pbw molybdenum per 100 pbw alumina was prepared as follows:

15 An aqueous solution comprising 608 g ammonium molybdate and 780 ml 30% hydrogen peroxide was mixed with an aqueous solution of 594 g cobalt nitrate 6 aq. After the mixture had been diluted with water to a volume of 2350 ml, it was used to impregnate 3000 g of an alumina carrier. After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalysts 15-20

20 These catalysts, which comprised 4.0 pbw cobalt and 11.0 pbw molybdenum per 100 pbw alumina, were prepared in substantially the same way as catalyst 14.

Catalysts 21 and 22

These catalysts, which comprised 2.5 pbw cobalt and 6.0 pbw molybdenum per 100 pbw alumina, were prepared in substantially the same way as catalyst 14.

Catalysts 23-25

25 These catalysts, which comprised 3.7 pbw cobalt and 9.5 pbw molybdenum per 100 pbw alumina, were prepared in substantially the same way as catalyst 14.

Catalyst 26

This catalyst, which comprised 3.0 pbw cobalt and 8.7 pbw molybdenum per 100 pbw alumina, was prepared in substantially the same way as catalyst 14.

30 Catalyst 27

A catalyst comprising 1.0 pbw nickel and 8.0 pbw molybdenum per 100 pbw alumina was prepared as follows.

35 An aqueous solution comprising 781 g ammonium molybdate and 941 ml 30% hydrogen peroxide was mixed with an aqueous solution of 247 g nickel nitrate 6 aq. After the mixture had been diluted with water to a volume of 6670 ml, it was used to impregnate 5000 g of an alumina carrier. After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Silica-alumina cogel A

40 A quantity of 116.25 kg of an aqueous solution containing 26.25 kg sodium silicate (SiO₂ content: 26.5 %w) was warmed up to 40°C. The pH of the solution was decreased to 6 by addition of 6 N nitric acid in 30 minutes with stirring. The silica gel obtained was aged for 140 hours at 40°C stirring. A quantity of 30 l of an aqueous solution containing 7.66 kg aluminium nitrate 9 aq and having a temperature of 40°C was added to the mixture in 5 minutes with stirring. After another 45 10 minutes' stirring the pH of the mixture was increased to 4.8 by addition of 25% ammonia. After 10 minutes the pH of the mixture was further increased to 5.5. The silica-alumina cogel was isolated by centrifuging and washed with water until sodium-free.

Silica-alumina cogels B-H

These cogels were prepared in substantially the same way as cogel A.

Silica-alumina cogel J

50 This cogel was prepared in substantially the same way as cogel A. In the present case, however, the silica gel was aged for 24 hours at 100°C (instead of for 140 hours at 40°C) and washing of the isolated silica-alumina cogel was omitted.

Catalyst 28

A catalyst comprising 2.0 pbw nickel per 100 pbw silica-alumina was prepared as follows:

55 A sample of cogel A was dried at 120°C and calcined for one hour at 500°C. A quantity of 85 g of this calcined silica-alumina was impregnated with 100 ml of an aqueous solution of 8.42 g nickel nitrate 6 aq. After 30 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 29

60 This catalyst was prepared from cogel B by drying at 120°C and calcining for 3 hours at 500°C.

Catalyst 30

A catalyst comprising 2.0 pbw vanadium per 100 pbw silica-alumina was prepared as follows:

65 A quantity of 150 ml of an aqueous solution of vanadyl oxalate (prepared from 21.42 g vanadium oxide and 45 g oxalic acid) was added to 4580 g of cogel C. The mixture was kneaded for one hour and subsequently dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 31

A catalyst comprising 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica-alumina was prepared as follows.

Cogel D was dried at 120°C and calcined for 3 hours at 500°C. An aqueous solution of vanadyl oxalate (prepared from 1.37 g vanadium pentoxide and 3 g oxalic acid) was mixed with an aqueous solution of 0.95 g nickel nitrate 6 aq. The solution thus obtained was diluted with water to a volume of 47.8 ml and used to impregnate 38.25 g of the above-mentioned calcined silica-alumina. After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 32

A catalyst comprising 0.5 pbw nickel and 4.0 pbw molybdenum per 100 pbw silica-alumina was prepared as follows:

A quantity of 4580 g of cogel E was kneaded for 10 minutes. After addition of 9.4 g nickel formate 2 aq the material was again kneaded for 20 minutes. Subsequently a solution of 44.2 g ammonium molybdate in 150 ml water was added and the mixture was kneaded for one hour. Finally the material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 33

A catalyst comprising 2.0 pbw vanadium per 100 pbw silica-alumina was prepared as follows.

Cogel F was heated for one hour at 100°C with 0.1 N ammonium nitrate solution. The silica-alumina was filtered off, dried at 120°C and calcined for 3 hours at 500°C. A quantity of 150 g of this calcined silica-alumina was impregnated with 150 ml of an aqueous solution of vanadyl oxalate (prepared from 5.3 g vanadium pentoxide and 11 g oxalic acid). After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 34

A catalyst comprising 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica-alumina was prepared as follows.

Cogel G was dried at 120°C and calcined for 3 hours at 500°C. A quantity of 113 g of this silica-alumina was impregnated with 140 ml of an aqueous solution of vanadyl oxalate (prepared from 4.0 g vanadium pentoxide and 8 g oxalic acid). After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C. The V/SiO₂-Al₂O₃ composition obtained was subsequently impregnated with 105 ml of an aqueous solution of 2.79 g nickel nitrate 6 aq. After 15 minutes the impregnated material was dried at 120°C and calcined for one hour at 500°C.

Catalyst 35

A catalyst comprising 2.0 pbw nickel and 16.0 pbw molybdenum per 100 pbw silica-alumina was prepared as follows.

A quantity of 1131 g of cogel H was mixed with 11310 ml 0.1 N ammonium nitrate. The pH of this mixture was increased from 4.6 to 7 by the addition of 23.4 ml concentrated ammonia. After 2 hours the silica-alumina was filtered off washed with water and dried at 100°C.

An aqueous solution of 23 g nickel formate 2 aq was mixed with an aqueous solution of 108 g ammonium molybdate. After addition of 70 ml monoethanolamine the mixture was diluted with water to a volume of 500 ml. This mixture was used to impregnate 386 g of the above-mentioned dried silica-alumina. After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 36

This catalyst, which comprised 1.0 pbw nickel and 8.0 pbw molybdenum per 100 pbw silica-alumina, was prepared from cogel H in substantially the same way as catalyst 35.

Catalyst 37

A catalyst comprising 2.0 pbw vanadium per 100 pbw silica-alumina was prepared as follows.

Cogel I was mixed with 0.1 N ammonium nitrate and the mixture was stirred for 12 hours. After filtering off the cogel was dried at 120°C and calcined for 3 hours at 500°C. A quantity of 59 g of this calcined silica-alumina was impregnated with 104 ml of an aqueous solution of vanadyl oxalate (prepared from 2.11 g vanadium pentoxide and 4.22 g oxalic acid). After 15 minutes the impregnated material was dried at 120°C and calcined for 3 hours at 500°C.

Catalyst 38

This catalyst, which comprised 2.0 pbw vanadium per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 1. In the present case, however, silica-alumina instead of alumina was used as carrier.

Catalyst 39

This catalyst, which comprised 1.0 pbw nickel and 8.0 pbw molybdenum per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 27. In the present case, however, silica-alumina instead of alumina was used as carrier.

Hydrodemetalization experiments

Two residual hydrocarbon oils (A and B) were catalytically hydrodemetalized at different space velocities and with the use of catalysts 1-39. To this end the oils together with hydrogen were passed downwards through a cylindrical vertically disposed fixed catalyst bed at a temperature of 420°C, a total pressure of 150 bar and an exit gas rate of 250 NI H₂/kg of fresh feed. The

18

catalysts were applied in the form of their sulphides. The oils applied as feeds had the following properties:

5 OIL A: Residual hydrocarbon oils having a total vanadium and nickel content of 245 ppmw, a C₅-asphaltenes content of 7.2 %w and a sulphur content of a 2.1 %w, which oil had been obtained as a residue in the atmospheric distillation of a Caribbean crude oil. 5

OIL B: Residual hydrocarbon oil having a total vanadium and nickel content of 62 ppmw, a C₅-asphaltenes content of 6.4 %w and a sulphur content of 3.9 %w, which oil had been obtained as a residue in the atmospheric distillation of a Middle East crude oil.

10 The results of the demetallization experiments together with the applied space velocities and the properties of the applied catalysts have been collected in Table I. For determining p and v as well as the total and nitrogen pore volumes of the catalysts, use was made of the nitrogen adsorption method and the mercury penetration method, as mentioned hereinbefore. 10

TABLE I

Exp. No.	Cat. No.	Residual hydro-carbon oil applied as feed	Space velocity, $l \cdot l^{-1} \cdot h^{-1}$	Surface area, m^2/g	Total pore vol., ml/g	Nitrogen v. % pore vol., ml/g	d, mm	p, mm	V-Ni removal (%w given in column I) after processing a fixed number of tons feed/kg cat. (number of tons given in column II)	I	II	II
1	1	A	4.0	225	0.57	0.56	0.7	10.2		44	2	
2	1	B	4.6	225	0.57	0.56	0.7	10.2		51	5	4
3	2	B	4.6	270	0.49	0.40	0.75	7.4		62	5	
4	3	B	4.6	236	0.86	0.72	2.0	14.6		41	5	7
5	4	B	4.6	331	0.95	0.95	0.8	14.2		66	5	
6	5	B	4.6	449	0.80	0.80	0.8	12.0		54	5	
7	8	B	4.6	137	0.76	0.72	1.8	17.6		47	5	
8	13	B	5.0	222	1.30	1.04	0.8	17.0		52	5	
9	14	B	4.6	353	0.74	0.59	1.0	9.4		52	5	
10	17	A	2.9	154	0.57	0.56	1.5	16.8		36	2	
11	19	A	2.9	177	0.58	0.58	1.5	18.3		37	2	
12	24	A	2.9	254	0.51	0.46	0.2	4.6		70	2	1.3
13	24	B	2.9	254	0.51	0.46	0.2	4.6		75	5	3
14	26	A	2.9	185	0.62	0.50	0.8	6.9		41	2	1
15	28	A	4.6	402	1.06	0.99	0.8	8.8		39	2	
16	30	A	4.0	393	0.70	0.66	0.8	8.9		48	2	
17	31	A	4.0	353	0.65	0.65	0.8	8.7		42	2	
18	32	A	4.0	355	0.60	0.57	0.8	12.0		55	2	
19	33	A	4.6	341	0.87	0.78	0.8	7.8		41	2	4
20	34	A	4.6	332	0.96	0.82	0.8	8.7		45	2	3
21	35	A	2.9	278	0.81	0.76	0.76	10.4		48	2	4
22	26	A	2.9	271	0.81	0.78	0.76	10.2		47	2	
23	27	A	4.0	208	1.18	1.17	0.8	20.2		41	2	4
24	6	B	4.6	206	0.82	0.80	1.8	12.0		46	5	
25	7	B	4.6	272	0.94	0.89	1.8	9.4		51	5	
26	9	B	4.6	408	1.00	0.93	1.8	10.8		53	5	
27	10	B	4.6	346	0.96	0.87	1.8	8.6		49	5	
28	11	B	4.6	243	0.81	0.74	2.2	9.0		50	2	5
29	12	B	4.6	300	0.93	0.88	1.8	10.0		48	5	3
30	15	A	3.0	201	0.63	0.61	1.7	11.5		36	2	

TABLE I (continued)

Exp. No.	Cat. No.	Residual hydrocarbon oil applied as feed	Space velocity $l \cdot l^{-1} \cdot h^{-1}$	Surface area, m^2/g	Total pore vol., ml/g	Nitrogen v. pore vol., ml/g	d, mm	p, mm	V-Ni removal (%w given in column I) after processing a fixed number of tons feed/kg cat. (number of tons given in column II)	I	II
31	18	A	2.9	221	0.61	0.61	1.5	12.6	37		
32	20	A	3.1	202	0.62	0.63	1.5	14.1	37		
33	16	A	3.4	185	0.53	0.51	1.6	10.0	0		
34	21	B	2.9	303	0.45	0.45	1.5	4.8	20	30	2.5
35	21	A	2.9	303	0.45	0.45	1.5	4.8	0	25	1
36	22	A	2.9	253	0.50	0.50	1.5	12.0	28	40	1
37	23	A	2.9	254	0.51	0.46	1.5	4.6	<10	12	1.4
38	25	A	2.9	254	0.51	0.46	0.8	4.6	33	50	1.2
39	27	A	2.9	210	0.78	0.55	1.5	7.6	8	10	1.5
40	29	A	2.9	470	0.70	0.66	0.8	8.8	0	5	0.2
41	38	A	2.9	110	0.35	0.34	0.8	10.0	21	19	2.5
42	39	B	2.9	239	0.66	0.58	1.5	9.4	35	55	2.5

The criteria for a catalyst to be optimum under the conditions applied in these demetallization experiments are that the catalyst is still capable of removing more than 35 %w of the total amount of vanadium and nickel present in oil A after 2 tons of this oil have been processed over the catalyst at a LHSV of at least $2.9 \text{ l.l}^{-1} \cdot \text{h}^{-1}$, and that the catalyst is still capable of removing more than 40 %w of the total amount of vanadium and nickel present in oil B after 5 tons of this oil have been processed over the catalyst at a LHSV of at least $2.9 \text{ l.l}^{-1} \cdot \text{h}^{-1}$.

Experiments 1-32 (in which the catalysts met the above requirements concerning %w Ni + V removal after processing a fixed number of tons feed/kg catalyst (illustrate the demetallization step of the present invention.

In experiments 1-23, in which catalysts were applied with $p/d > 10.0-0.15 \text{ v}$, these catalysts also satisfied the further requirements of the invention concerning $v (< 50\%)$, total pore volume ($> 0.40 \text{ ml/g}$) and surface area ($> 100 \text{ m}^2/\text{g}$).

In experiments 24-32, in which catalysts were applied with $10.0-0.15 \text{ v} > p/d > 3.5-0.02 \text{ v}$, these catalysts also satisfied the further requirements of the invention concerning $v (< 50\%)$, $p (> 5 \text{ nm})$, nitrogen pore volume ($> 0.60 \text{ ml/g}$) and surface area ($> 150 \text{ m}^2/\text{g}$).

The experiments 33-42 (in which the catalysts did not meet the above requirements concerning %w Ni + V removal after processing a fixed number of tons feed/kg catalyst) illustrate demetallization which is outside the scope of the demetallization step of the present invention.

In experiments 33, 36, 39 and 42 catalysts were applied with $10.0-0.15 \text{ v} > p/d > 3.5-0.02 \text{ v}$, but a nitrogen pore volume smaller than 0.60 ml/g .

In experiments 34, 35 and 37 catalysts were applied with $p/d < 3.5-0.02 \text{ v}$.

In experiment 38 a catalyst was applied with $10.0-0.15 \text{ v} > p/d > 3.5-0.02 \text{ v}$, but $p < 5 \text{ nm}$ and a nitrogen pore volume smaller than 0.60 ml/g .

In experiment 40 a catalyst was applied which did not contain a metal component with hydrogenation activity.

In experiment 41 a catalyst was applied with $p/d > 10.0-0.15 \text{ v}$, but a total pore volume smaller than 0.40 ml/g .

Further catalyst preparation

A silica-alumina cogel K was prepared in substantially the same way as cogel A. Five catalysts according to the invention (catalysts 40-44 with $p/d > 10.0-0.15 \text{ v}$; v smaller than 50; total pore volume larger than 0.40 ml/g ; and surface area larger than $100 \text{ m}^2/\text{g}$) were prepared from this cogel K as follows.

Catalyst 40

This catalyst, which comprised 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 31.

Catalyst 41

This catalyst, which comprised 2.0 pbw nickel per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 31. In the present case, however, an aqueous nickel nitrate solution was used as impregnation liquid.

Catalyst 42

This catalyst, which comprised 2.0 pbw vanadium per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 31. In the present case, however, an aqueous solution of vanadyl oxalate was used as impregnation liquid.

Catalyst 43

This catalyst, which comprised 0.5 pbw nickel and 4.0 pbw molybdenum per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 31. In the present case, however, an aqueous solution, comprising nickel nitrate, ammonium molybdate and hydrogen peroxide was used as impregnation liquid.

Catalyst 44

This catalyst, which comprised 0.5 pbw cobalt and 4.0 pbw molybdenum per 100 pbw silica-alumina, was prepared in substantially the same way as catalyst 31. In the present case, however, an aqueous solution comprising cobalt nitrate, ammonium molybdate and hydrogen peroxide was used as impregnation liquid.

Catalyst 45

This catalyst was prepared from cogel K by drying at 120°C and calcining for 3 hours at 500°C.

Hydrometalization experiments

Residual hydrocarbon oil A was catalytically demetallized with the use of catalysts 40-45. To this end the oil together with hydrogen was passed downwards through a cylindrical vertically disposed fixed catalyst bed at a temperature of 420°C, a total pressure of 150 bar, a space velocity of 4.0 l.l⁻¹.h⁻¹ and an exit gas rate of 250 Nl H₂/kg fresh feed. The catalysts were applied in the form of their sulphides. The results of the demetallization experiments have been collected in Table II.

TABLE II

Cat. No. (composition)	%w V + Ni removal after processing 0.5, 4 and 6 tons of feed/kg cat., respectively		
	after 0.5 ton	after 4 tons	after 6 tons
40 (Ni/V/SiO ₂ -Al ₂ O ₃)	49	49	49
41 (Ni/SiO ₂ -Al ₂ O ₃)	38		
42 (V/SiO ₂ -Al ₂ O ₃)	43	49	49
43 (Ni/Mo/SiO ₂ -Al ₂ O ₃)	48	51	49
44 (Co/Mo/SiO ₂ -Al ₂ O ₃)	56	49	49
45 (SiO ₂ -Al ₂ O ₃)	7	4	0

The figures given in Table II demonstrate that in contrast with the other catalysts, the nickel-vanadium catalyst is the only one to show a stable activity right from the start of the demetallization process.

The following additional information is provided in order to facilitate understanding of the present invention:

By means of the nitrogen adsorption/desorption method combined with the mercury penetration method a complete pore radius distribution of two Ni/Mo/Al₂O₃ catalysts (catalysts I and II) was determined. Tables III and IV show the percentage of the pore volume being present in pores with a given pore radius.

TABLE III

Catalyst I

pore radius, nm		% of the pore volume
0 - 1		9.9
1 - 2		9.3
2 - 3		7.0
3 - 4		6.4
4 - 5		5.7
5 - 6		5.7
6 - 7		5.1
7 - 8		5.1
8 - 10		7.0
10 - 15		9.0
15 - 20		3.8
20 - 50		3.8
> 50		22.2
pore volume: 0.78 ml/g		
surface: 238 m ² /g		

TABLE IV

Catalyst II

pore radius, nm

% of the pore volume

0 - 1	6.4
1 - 2	6.4
2 - 3	7.2
3 - 4	5.6
4 - 5	3.1
5 - 6	3.1
6 - 7	7.9
7.0 - 7.5	6.3
7.5 - 8.0	6.4
8.0 - 8.5	6.4
8.5 - 9.0	6.3
9.0 - 9.5	5.6
9.5 - 10.0	5.5
10 - 15	7.9
15 - 20	1.6
20 - 50	3.2
> 50	11.1

pore volume : 0.63 ml/g
surface: 133 m²/g

Of the catalysts I and II the average pore diameter was determined by three different methods, each used as such in practice.

Method 1: Calculated by means of the formula

$$\text{pore diameter} = \frac{4 \times \text{pore volume}}{\text{surface}} \times 10^3$$

Method 2: Read off from a graph composed by means of a

complete pore radius distribution and in which for the pore diameter range of from 0 to 100 nm, for each pore volume increment smaller than or equal to 10% of the pore volume, the quotient of the pore volume increment and the corresponding pore diameter interval has been plotted as a function of the linear average pore diameter over the relevant pore diameter interval; the pore diameter is read off at the point where the curve reaches a maximum.

Method 3: Read off from a graph composed by means of a complete

pore radius distribution and in which for the pore diameter range of from 0 to 100 nm, for each pore volume increment smaller than or equal to 10% of the pore volume, the quotient of the pore volume increment and the corresponding pore diameter interval has been cumulatively plotted as a function of the linear average pore diameter over the relevant pore diameter interval; the pore diameter is read off at the point corresponding to 50% of the total quotient at 100 nm. For catalyst I the following average pore diameter values were found by the different methods.

By method 1: 13.1 nm.

By method 2: Undeterminable, since there is no distinct maximum in the curve.

By method 3: 7.6 nm.

For catalyst II the following average pore diameter values were found by the different methods.

By method 1: 18.9 nm.

By method 2: 16.0 nm.

By method 3: 13.6 nm.

It is seen that the different methods for determining the average pore diameter of the catalyst lead to widely varying results. For determining the specific average pore diameter (p) in connection with the invention method 3 is used.

A complete sieve analysis was carried out of a crushed Ni/Mo/Al₂O₃ catalyst having a particle diameter between 0.115 and 0.10. The results of this sieve analysis are shown in Table V.

TABLE V

	Sieve No. (US mesh)	Particle diameter range, mm	% by weight	Average particle diam. mm	Cumulative % by weight	
5	16 - 18	1.00 - 1.19	1.0	1.10	100.0	5
	18 - 20	0.84 - 1.00	2.3	0.92	99.0	
	20 - 25	0.71 - 0.84	3.5	0.77	96.7	
10	25 - 30	0.59 - 0.71	5.2	0.65	93.2	10
	30 - 35	0.50 - 0.59	5.5	0.55	88.0	
	35 - 40	0.42 - 0.50	6.6	0.46	82.5	
	40 - 45	0.35 - 0.42	8.1	0.38	75.9	
	45 - 50	0.297 - 0.35	7.1	0.32	67.8	
15	50 - 60	0.250 - 0.297	9.3	0.27	60.7	15
	60 - 70	0.210 - 0.250	8.9	0.23	51.4	
	70 - 80	0.177 - 0.210	8.5	0.19	42.5	
	80 - 100	0.149 - 0.177	9.9	0.165	34.0	
	100 - 120	0.125 - 0.149	10.8	0.13	24.1	
20	120 - 140	0.105 - 0.125	13.3	0.115	13.3	20

Of this catalyst the average particle diameter was determined by two different methods which are both used in practice.

Method 1: Calculated as linear average by means of the formula.

25 particle diameter = $\frac{d_1 + d_2}{2}$, in which d_1 and d_2 represent the particle diameter of the largest and the smallest particle respectively.

Method 2: Read off from a graph composed by means of a complete

30 sieve analysis and in which for every successive sieve fraction the percentage by weight, based on the total weight of the catalyst sample, has been plotted cumulatively as a function of the linear average diameter of the relevant sieve fraction; the particle diameter is read off at the point corresponding to 50% of the total weight.

For this catalyst the following average particle diameter values were found by the different methods.

35 By method 1: 0.61 mm
By method 2: 0.225 mm

It is seen that the different methods for determining the average particle diameter of the catalyst lead to widely varying results. For determining the specific average particle diameter (d) in connection with the invention method 2 is used.

40 WHAT WE CLAIM IS:-

1. A process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst comprises particles which meet the following requirements, in which d and p are determined by the method of determination herein defined, surface area is determined by the B.E.T. method, and the nitrogen pore volume and the total pore volume are as herein defined:

- 45 (1) $10.0 - 0.15 v > p/d > 3.5 - 0.02 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm, 50
(2) v is smaller than 50,
(3) the nitrogen pore volume is larger than 0.60 ml/g,
(4) the surface area is larger than 150 m²/g, and
(5) p is larger than 5 nm.
55 or agglomerates of said particles.

2. A process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst comprises particles which meet the following requirements, in which d and p are determined by the method of determination herein defined, surface area is determined by the B.E.T. method, and the nitrogen pore volume and the total pore volume are as herein defined:

- 60 (1) $p/d > 10.0 - 0.15 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm, 65



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TABLE V

	Sieve No. (US mesh)	Particle diameter range, mm	% by weight	Average particle diam. mm	Cumulative % by weight	
5	16 - 18	1.00 - 1.19	1.0	1.10	100.0	5
	18 - 20	0.84 - 1.00	2.3	0.92	99.0	
	20 - 25	0.71 - 0.84	3.5	0.77	96.7	
10	25 - 30	0.59 - 0.71	5.2	0.65	93.2	10
	30 - 35	0.50 - 0.59	5.5	0.55	88.0	
	35 - 40	0.42 - 0.50	6.6	0.46	82.5	
	40 - 45	0.35 - 0.42	8.1	0.38	75.9	
	45 - 50	0.297 - 0.35	7.1	0.32	67.8	
15	50 - 60	0.250 - 0.297	9.3	0.27	60.7	15
	60 - 70	0.210 - 0.250	8.9	0.23	51.4	
	70 - 80	0.177 - 0.210	8.5	0.19	42.5	
	80 - 100	0.149 - 0.177	9.9	0.165	34.0	
	100 - 120	0.125 - 0.149	10.8	0.13	24.1	
20	120 - 140	0.105 - 0.125	13.3	0.115	13.3	20

Of this catalyst the average particle diameter was determined by two different methods which are both used in practice.

Method 1: Calculated as linear average by means of the formula.

particle diameter = $\frac{d_1 + d_2}{2}$, in which d_1 and d_2 represent the particle diameter of the largest and the smallest particle respectively.

Method 2: Read off from a graph composed by means of a complete

sieve analysis and in which for every successive sieve fraction the percentage by weight, based on the total weight of the catalyst sample, has been plotted cumulatively as a function of the linear average diameter of the relevant sieve fraction; the particle diameter is read off at the point corresponding to 50% of the total weight.

For this catalyst the following average particle diameter values were found by the different methods.

By method 1: 0.61 mm

By method 2: 0.225 mm

It is seen that the different methods for determining the average particle diameter of the catalyst lead to widely varying results. For determining the specific average particle diameter (d) in connection with the invention method 2 is used.

WHAT WE CLAIM IS:-

1. A process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst comprises particles which meet the following requirements, in which d and p are determined by the method of determination herein defined, surface area is determined by the B.E.T. method, and the nitrogen pore volume and the total pore volume are as herein defined:

(1) $10.0 - 0.15 v > p/d > 3.5 - 0.02 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm,

(2) v is smaller than 50,

(3) the nitrogen pore volume is larger than 0.60 ml/g,

(4) the surface area is larger than 150 m²/g, and

(5) p is larger than 5 nm.

or agglomerates of said particles.

2. A process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst comprises particles which meet the following requirements, in which d and p are determined by the method of determination herein defined, surface area is determined by the B.E.T. method, and the nitrogen pore volume and the total pore volume are as herein defined:

(1) $p/d > 10.0 - 0.15 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm,



- (2) v is smaller than 50,
(3) the total pore volume is larger than 0.40 ml/g, and
(4) the surface area is larger than 100 m²/g,
or agglomerates of said particles.

5 3. A process as claimed in claim 1 or 2, in which process the demetallization is carried out in the presence of a catalyst comprising 0.1–1.15 pbw metals having hydrogenation activity per 100 pbw carrier. 5

10 4. A process as claimed in claim 3, in which process the demetallization is carried out in the presence of a catalyst comprising 0.5–10 pbw and preferably 2.0–7.5 pbw metals having hydrogenation activity per 100 pbw carrier. 10

5. A process as claimed in any one of claims 1-4, in which process the demetallization is carried out in the presence of a catalyst in which the metals having hydrogenation activity are selected from nickel, cobalt, molybdenum, vanadium and tungsten.

15 6. A process as claimed in claim 5, in which the demetallization is carried out in the presence of a catalyst comprising at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum, vanadium and tungsten. 15

7. A process as claimed in claim 6, in which process the demetallization is carried out in the presence of a catalyst in which the atomic ratio between nickel and/or cobalt on the one hand and molybdenum, vanadium and tungsten on the other hand is between 0.05 and 3.0.

20 8. A process as claimed in claim 6 or 7, in which process the demetallization is carried out in the presence of a catalyst comprising as metals having hydrogenation activity a combination of nickel and vanadium. 20

25 9. A process as claimed in claim 8, in which process the demetallization is carried out in the presence of a catalyst comprising about 0.5 pbw nickel and about 2.0 pbw vanadium per 100 pbw carrier. 25

10. A process as claimed in any one of claims 1-9, in which process the demetallization is carried out in the presence of a catalyst which comprises the metals having hydrogenation activity in the form of their sulphides.

30 11. A process as claimed in anyone of claims 1-10, in which process the demetallization is carried out in the presence of a catalyst comprising a metal oxide carrier, which catalyst has been prepared by incorporating the catalytically active metals into a metal hydroxide gel of the carrier material before the latter is being shaped and preferably after it has been aged. 30

35 12. A process as claimed in claim 11, in which process the demetallization is carried out in the presence of a catalyst which has been prepared by incorporating a nickel and a vanadium compound, in an amount corresponding to about 0.5 pbw nickel and about 2.0 pbw vanadium per 100 pbw final carrier, into a silica hydrogel, after the latter has been precipitated and aged but before shaping and calcining. 35

40 13. A process as claimed in anyone of claims 1-10, in which process the demetallization is carried out in the presence of a catalyst which has been prepared by single or multistep co-impregnation of a carrier with an aqueous solution comprising one or more nickel and/or cobalt compounds and one or more molybdenum, vanadium and/or tungsten compounds, followed by drying and calcining. 40

45 14. A process as claimed in anyone of claims 1-13, in which process the demetallization is carried out in the presence of a catalyst comprising silica, alumina or silica-alumina as a carrier. 45

15. A process as claimed in claim 14, in which process the demetallization is carried out in the presence of a catalyst comprising as carrier alumina or silica particles which have been prepared by spray-drying of an alumina or silica gel, followed by shaping the spray-dried microparticles into larger particles.

50 16. A process as claimed in claim 14, in which process the demetallization is carried out in the presence of a catalyst comprising as carrier spherical alumina or silica particles which have been prepared by the "oil drop" method. 50

17. A process as claimed in claim 14, in which process the demetallization is carried out in the presence of a catalyst comprising as carrier a cogel of aluminium hydroxide gel on silica hydrogel.

55 18. A process as claimed in claim 17, in which process the demetallization is carried out in the presence of a catalyst comprising as carrier a silica-alumina cogel, which cogel has been prepared by first precipitating a silica hydrogel from an aqueous silicate-ions containing solution by the addition of a mineral acid, subsequently adding a water-soluble aluminium salt to the solution and then precipitating an aluminium hydroxide gel by adding an alkaline-reacting compound. 55

60 19. A process as claimed in claim 18, in which process the demetallization is carried out in the presence of a catalyst comprising as carrier a silica-alumina cogel, in the preparation of which the silica hydrogel produced is allowed to age for some time at an elevated temperature before the cogel preparation is continued. 60

65 20. A process as claimed in anyone of claims 17-19, in which process the demetallization is carried out in the presence of a catalyst which has been prepared by a method in which a silica-alumina cogel is shaped e.g. by extrusion, followed by drying and calcining of the hydrogel 65



26

particles, in which subsequently the xerogel particles thus obtained are neutralized with a nitrogen base and dried and in which finally the catalytically active metals are deposited on the cogel carrier by impregnating the latter with one or more aqueous solutions comprising salts of the metals concerned, followed by drying and calcining of the composition.

5 21. A process as claimed in claim 14, in which process the demetallization is carried out in the presence of a catalyst, which catalyst or the carrier on which it has been based, has been prepared according to the granulation technique.

10 22. A process as claimed in anyone of claims 1-21, in which process the demetallization step is carried out by passing the hydrocarbon oil at elevated temperature and pressure and in the presence of hydrogen in upward, downward or radial direction through one or more vertically disposed reactors comprising a fixed or moving bed of the catalyst particles concerned.

15 23. A process as claimed in claim 22, in which process the demetallization is carried out by passing the hydrocarbon oil through a vertically disposed catalyst bed in which during operation fresh catalyst is periodically introduced at the top of the catalyst bed and spent catalyst is withdrawn at the bottom thereof (demetallization in bunker flow operation).

24. A process as claimed in claim 22, in which process the demetallization is carried out in several reactors comprising a fixed catalyst bed, which reactors are alternately used for the demetallization; while the demetallization is carried out in one or more of these reactors, the catalyst in the other reactor is replenished (demetallization in fixed bed swing operation).

20 25. A process as claimed in anyone of claims 1-24, in which process the demetallization is carried out in the presence of a catalyst having a d of 0.4-5.0 mm.

26. A process as claimed in claim 25, in which process the demetallization is carried out in the presence of a catalyst having a d of 0.5-4.0 mm and preferably of 0.6-3.0 mm.

25 27. A process as claimed in anyone of claims 2-26, in which process the demetallization is carried out in the presence of a catalyst having a total pore volume of at least 0.50 ml/g.

28. A process as claimed in anyone of claims 2-27, in which process the demetallization is carried out in the presence of a catalyst having a surface area above 150 m²/g.

30 29. A process as claimed in anyone of claims 1-28, in which process the demetallization is carried out at a temperature of 300-450°C and preferably of 350-425°C, a total pressure of 75-250 bar and preferably of 100-200 bar, a space velocity of 0.1-26 pbv and preferably of 1-10 pbv of fresh feed per pbv of catalyst per hour and a hydrogen feed ratio 100-2000 NI and preferably of 200-1000 NI H₂/kg feed.

30. A process as claimed in anyone of claims 1-29, in which process the hydrocarbon oil is first demetallized and subsequently hydrocracked, hydrodesulphurized or catalytically cracked.

35 31. A process as claimed in claim 30, in which process the hydrocarbon oil is first demetallized and subsequently hydrocracked or hydrodesulphurized and in which the demetallization is carried out in fixed swing operation or in bunker flow operation and the hydrocracking or hydrodesulphurization is carried out in conventional fixed bed operation.

40 32. A process as claimed in claim 30 or 31, in which process the hydrocarbon oil is first demetallized and subsequently hydrodesulphurized and in which the demetallization is carried out at a higher hydrogen partial pressure than the hydrodesulphurization.

45 33. A process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out substantially as described hereinbefore and with particular reference to any of the experiments 1-32.

34. Hydrocarbon oils obtained by a process as claimed in anyone of claims 1 to 33.

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