

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF NEW CATALYSTS

(71) We, SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ, B.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 present invention relates to a process for the preparation of novel catalysts comprising one or more metals having hydrogenation activity on a carrier. The invention further relates to the application of these catalysts in the treatment of hydrocarbon oils with hydrogen, in particular to their application in the treatment of high-boiling hydrocarbon oils with hydrogen with the object of, among other things, reducing the metal content, the asphaltenes content and the viscosity.

High-boiling hydrocarbon oils, such as residual oils obtained in the distillation of crude oils at atmospheric or reduced pressure, as well as certain heavy crude oils, in particular those originating from South America, contain considerable amounts of high-molecular-weight, non-distillable compounds such as asphaltenes and metal compounds, in particular vanadium and nickel compounds. Besides, such high-boiling hydrocarbon oils often have a high viscosity. If these high-boiling hydrocarbon oils are applied as feed for catalytic processes such as cracking, hydrocracking and hydrodesulphurization, metals such as vanadium and nickel are deposited 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 Applicant into the hydrodemetallization of high-boiling 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 can be prepared according to the well-known granulation (also called nodulizing) technique, according to which technique catalyst or catalyst-carrier particles, for example, having a diameter of at most 0.1 mm are agglomerated with the aid of a granulation liquid to form larger particles, for example, having a diameter of at least 1.0 mm, provided that the catalysts and the particles to which the nodulizing technique is applied meet certain requirements. An optimum catalyst for the hydrodemetallization of high-boiling hydrocarbon oils should be taken to mean in this patent application a catalyst whose activity and stability are of a sufficiently high level for this purpose.

It has been found that for the catalytic hydrodemetallization of high-boiling hydrocarbon oils the requirements of the catalyst with respect to particle diameter and porosity, which should be met by optimum catalysts prepared according to the nodulizing techniques, are as follows. In the first place the catalysts should have such a specific average pore diameter (p in nm) and specific average particle diameter (d in mm) that the quotient p/d is larger than 15. Furthermore, the percentage (v) of the total pore volume of the

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catalysts that consists of pores with a diameter larger than 100 nm should be at least 50. Further, the pore volume (y) of the catalysts that consists of pores with a diameter larger than 50 nm should at least be 0.2 ml/g. Finally, the catalysts should have a specific surface area larger than 150 m²/g. The material used as starting material in the nodulizing technique should have a specific surface area of more than 200 m²/g.

Based on the method of determination, the above-mentioned values of p and d are defined as follows.

After a complete sieve analysis of the material to be investigated has been carried out, d is read from a graph in which for each successive sieve fraction the percentage by weight, based on the total weight of the 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.

After determination of the complete pore diameter distribution of a sample of the material to be investigated, p is read from a graph in which for the pore diameter range of 0-100 nm, for each 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 have 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 material 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 material 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 material 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 total pore volume mentioned in this patent application is defined as follows. 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 mentioned in this patent application have been determined according to the B.E.T. method.

Besides their suitability for the application as optimum catalysts in the hydrodemetalization of high-boiling hydrocarbon oils, which oils are subsequently used for instance, as feed for a catalytic process such as cracking, hydrocracking or hydrodesulphurization, the present catalysts have also been found eminently suitable as optimum catalysts in processes for the reduction of the asphaltenes content and the viscosity of heavy hydrocarbon oils. In such processes, which are often referred to as processes for upgrading heavy oils, oils with a C₅-asphaltene content above 5 %w and a V_k²¹⁰ above 30 cSt are con-

tacted 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, in order to reduce the C₅-asphaltene content by at least 30% and the V_k²¹⁰ by at least 50% (C₅-asphaltene

content and V_k²¹⁰ of the feed compared with

that of the liquid reaction product obtained). An optimum catalyst for upgrading heavy hydrocarbon oils should be taken to mean in this patent application a catalyst whose activity and stability are of a sufficiently high level for this purpose.

The present catalysts are novel compositions.

According to the present invention there is provided a process for the preparation of a catalyst in which a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst meets the following requirements:

- (1) the quotient p/d is larger than 15,
- (2) v is at least 50%,
- (3) y is at least 0.2 ml/g, and
- (4) the specific surface area is larger than 150 m²/g,

is prepared according to the nodulizing technique from particles with a specific surface area above 200 m²/g.

In the process according to the invention preference is given to the preparation of catalysts of which y is at least 0.40 ml/g and which have a specific surface area above 200 m²/g. As regards the particles which form the starting material for the nodulizing step preference is given to a material having a specific surface area above 250 m²/g. In

carrying out the nodulizing technique catalyst particles or catalyst-carrier particles, for example, having a diameter of at most 0.1 mm are agglomerated with the aid of a granulation liquid to larger particles, for example, having a diameter of at least 1.0 mm. In actual practice the nodulizing technique is usually effected as follows. Catalyst-carrier material having a diameter of at most 0.1 mm is placed on a rotating disc provided with a raised edge and a scraping device. The disc is disposed at a specific angle to the horizontal plane. A granulation liquid is sprayed onto the carrier material that is in continuous motion on the disc. In practice, when alumina is used as a carrier, a dilute aqueous solution of acetic acid or citric acid is usually employed as the granulation liquid. During the residence of the small particles on the disc larger particles are formed from the small ones by agglomeration. The nodulizing technique can be carried out both batchwise and continuously. When the continuous process is used finely dispersed material is continuously supplied to the rotating disc and agglomerated material continuously leaves the disc via the top of the raised edge when this is in its lowest position. After the agglomerated particles have left the disc a sieve fraction with the desired diameter is separated from it. Particles with a diameter smaller than that of the desired sieve fraction may be recycled to the disc. If the agglomerated material contains particles with a diameter larger than that of the desired sieve fraction, these particles, after reduction of the particle size, for instance by grinding, may also be recycled to the disc. The conversion of the agglomerated material with the desired particle size into a suitable carrier material takes place by drying and calcination. The emplacement of one or more metals with hydrogenation activity on the carrier material thus prepared, is usually affected by impregnation with an aqueous solution of compounds of the respective metals, followed by drying and calcination of the impregnated material.

Catalysts according to the invention preferably comprise 0.1—15 pbw of one or more metals having hydrogenation activity per 100 pbw carrier material. As metals having hydrogenation activity preference is given to one or more of nickel, cobalt, molybdenum and vanadium. It is further preferred that the catalysts should comprise at least one of nickel and cobalt and at least one of molybdenum and vanadium and further that the atomic ratio between nickel and/or cobalt on the one hand and molybdenum and/or vanadium on the other hand is between 0.05 and 3.0. Suitable metal combinations are nickel-vanadium, cobalt-molybdenum and nickel-molybdenum. The quantity of metals having hydrogenation activity present in the catalysts preferably amounts to 0.5—10 pbw

and in particular 2.0—7.5 pbw per 100 pbw carrier material. Very attractive catalysts according to the invention are catalysts comprising about 0.5 pbw nickel and about 2 pbw vanadium per 100 pbw carrier material, as well as catalysts comprising about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier material. 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 carrier in the form of their sulphides. Sulphidation of the present catalysts may be carried out by any technique for the sulphidation of catalysts known in the art.

Suitable carriers for the present 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, silica-alumina and silica-magnesia. If for the preparation of the present catalysts use is made of any of the above-mentioned oxidic carriers, preference is given to the application of alumina or silica for this purpose. Another type of material that is very suitable to serve as a carrier for the present catalyst is soot, in particular a soot obtained as by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam. Apart from the fact that soot is a suitable carrier for the present catalysts its use for this purpose has an additional advantage when the catalysts are employed for treating hydrocarbon oils having a high metal content with hydrogen, which advantage is not achieved when any of the oxidic carriers mentioned hereinbefore is employed. This can be explained as follows. Although the catalysts according to the invention show a long life in the treatment of hydrocarbon oils having a high metal content with hydrogen, even these catalysts are in the long run deactivated as a result of the deposition of large amounts of metals, in particular vanadium and nickel, and therefore, after a certain time of operation, they have to be replaced. If it is intended to recover the deposited metals from the deactivated catalyst, the use of a catalyst on soot as the carrier offers the considerable advantage over catalysts on other carrier materials that the carrier can simply be removed from the deactivated catalyst by combustion, after which a mixture of the metals concerned is left behind in the form of their oxides for further working up.

During the investigation concerning the preparation of catalysts according to the nodulizing technique five modifications of the usual procedure were found by the Applicant, which modifications will each produce a favourable effect. These modifications will be described in more detail hereinafter.

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1. In the preparation of catalysts on the basis of alumina as a carrier an aqueous solution of acetic acid or citric acid is usually applied as the granulation liquid. It has been found that when dilute nitric acid is applied as the granulation liquid, alumina-based catalysts can be obtained with a crushing strength and density that are considerably higher than when an aqueous solution of citric acid or acetic acid is applied.
2. When in the preparation of the catalysts the starting material is mixed with a certain amount of glass powder and, in addition, the particles formed by the nodulizing technique are subjected to a calcination at a temperature above the softening temperature of glass, catalysts can be obtained with a considerably increased crushing strength. The amount of glass powder applied is preferably 0.5—15 %w based on the amount of starting material with which it is mixed.
3. When phosphorus is incorporated in the catalysts they become more suitable for the demetallization of metal-containing hydrocarbon oils as well as for the upgrading of hydrocarbon oils with a high viscosity and a high asphaltene content. The demetallization of metal-containing hydrocarbon oils by incorporation of phosphorus into the catalysts can take place during any stage in the catalyst preparation. The incorporation of phosphorus can, for instance, very suitably take place by addition of a phosphorus compound to the granulation liquid and/or to the impregnation liquid that is applied for the emplacement of the metals with hydrogenation activity on the particles formed. The amount of phosphorus compound is preferably chosen in such a way that a catalyst is obtained comprising a 0.5—5 pbw phosphorus per 100 pbw carrier material.
4. In the catalyst preparation according to the nodulizing technique larger particles, which are more or less spherical, are formed from the starting material. The size of the particles formed is determined, among other factors, by the residence time of the material on the rotating disc. After the particles have attained approximately the desired size they are removed from the disc and are dried and calcined. It has been found that catalysts with a considerably higher density can be prepared, when the particles formed, after they have left the rotating disc but before drying and calcination, are rotated for some time, for instance in a rotating drum. Such rotation of the particles formed preferably takes place during a period of time at least equal to the residence time of the material on the rotating disc.

5. In the catalyst preparation according to the nodulizing technique the usual procedure is for the carrier particles, after they have been formed on the disc, to be dried and calcined, followed by emplacement of the desired metals with hydrogenation activity on the calcined material, for instance by impregnation with an aqueous solution containing salts of the relevant metals. Finally, the impregnated material is dried and calcined. It has been found that this catalyst preparation can be considerably simplified by incorporating the metal salts into the granulation liquid. When the emplacement of the metals in the catalyst is carried out in this way the separate impregnation step as well as the second drying and calcination steps can be omitted, which in the large-scale preparation of the present catalysts obviously affords a considerable saving.
- Examples of suitable water-soluble metal compounds which may be applied in the preparation of the present catalysts are nitrates, chlorides, formates and acetates of nickel and cobalt, ammonium molybdate, vanadyl oxalate, vanadyl sulphate, vanadyl acetylacetonate and ammonium vanadate.
- As has already been stated hereinbefore, the catalysts according to the invention are suitable for treating hydrocarbon oils with hydrogen and in particular for demetallizing metal-containing hydrocarbon oils and for upgrading hydrocarbon oils with a high viscosity and a high asphaltene content. The two latter processes are preferably carried out by passing the hydrocarbon oils at elevated temperature and pressure and in the presence of hydrogen in an upward, downward or radial direction, through one or more vertically disposed reactors containing a fixed or moving bed of the catalyst particles concerned. The two processes 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 velocities used being such that expansion of the catalyst bed occurs (processing in ebullated bed operation). A very attractive embodiment of the two processes is one in which the hydrocarbon oil is passed through a vertically disposed catalyst bed, while during operation fresh catalyst is periodically introduced at the top of the catalyst bed and spent catalyst is withdrawn at the bottom thereof (processing in bunker flow operation). Another, very attractive embodiment of the two processes is one in which several reactors containing a fixed catalyst bed are used, which reactors are alternately used for the relative process, while the process is carried out in one or more of these reactors, the catalyst in the other reactors is replenished (processing in fixed-bed swing operation). If desired, the two processes may also be carried out by

suspending the catalyst in the hydrocarbon oil to be treated (processing in slurry phase operation).

If the catalysts according to the invention are employed for the demetallization of metal-containing hydrocarbon oils or for upgrading hydrocarbon oils with a high viscosity and a high asphaltenes content, preference is given to catalyst particles having a d of 1.04–4.0 mm and in particular of 1.5–3.5 mm.

Hydrodemetallization of metal-containing hydrocarbon oils using a catalyst according to the invention is 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. Hydrodemetallization of metal-containing hydrocarbon oils is of importance especially if the oil is subsequently subjected to catalytic cracking, hydrocracking or hydrodesulphurization. As a result of the hydrodemetallization, deactivation of the catalyst applied in these processes is suppressed to a considerable extent. Hydrocracking and hydrodesulphurization of 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.

Upgrading of hydrocarbon oils having a high viscosity and a high asphaltenes content using a catalyst according to the invention takes place at a temperature of 400–500°C, a hydrogen partial pressure of 100–300 bar and a space velocity of 0.2–2.0 l.l⁻¹.h⁻¹.

Examples of hydrocarbon oils eligible for treatment with hydrogen using catalysts according to the invention in order to reduce their metal content or their viscosity and asphaltenes contents are crude oils and residues obtained from the distillation of crude oils at atmospheric or reduced pressure, such as topped crude oils and long and short residues.

The invention will now be illustrated with the aid of the following three examples. Example I refers to the preparation of the novel catalysts according to the invention. Example II relates to the application of the catalysts to the demetallization of metal-containing hydrocarbon oils. Example III describes the use of the catalysts for upgrading heavy hydrocarbon oils.

Example I.

Catalyst preparation.

Catalyst A

As starting material use was made of an alumina obtained by spray-drying with a d

smaller than 0.05 mm and a specific surface area of 380 m²/g. Of this alumina 100g was put on a rotating disc and 100 ml of an aqueous solution containing 2.5 g citric acid was gradually sprayed onto it. The rotating disc, which was provided with a raised edge of 10 cm high, had a diameter of 40 cm. The disc made 40 revolutions per minute and was disposed at an angle of 45° to the horizontal plane. After 15 minutes' residence time the nodules formed were removed from the disc. After drying at 120°C a sieve fraction with a d of 2.8 mm was isolated from the dried material. After 1 hour's calcination at 600°C the particles were impregnated with an aqueous solution comprising nickel nitrate and ammonium molybdate. Finally, the impregnated material was dried at 120°C and calcined for 1 hour at 500°C. The catalyst thus prepared comprised 1 pbw nickel and 4 pbw molybdenum per 100 pbw alumina.

Catalyst B

This catalyst was prepared in substantially the same way as catalyst A, the difference being, however, that in the present case 100 ml of an aqueous solution comprising 2.5 g nitric acid was used as the granulation liquid.

Catalyst C

This catalyst was prepared in substantially the same way as catalyst A, the difference being, however, that in the present case 2 g glass powder with a d smaller than 0.05 mm was added to the alumina starting material and that after calcination at 600°C another calcination was carried out for 1 hour at 800°C.

Catalyst D

This catalyst was prepared in substantially the same way as catalyst A, the difference being, however, that in the present case so much NH₄H₂PO₄ was added to the impregnation liquid comprising nickel and molybdenum that a catalyst was obtained comprising in addition to 1 pbw nickel and 4 pbw molybdenum, 1 pbw phosphorus per 100 pbw alumina and that in the present case the nodules formed, after having left the disc, were rotated for another hour in a rotating drum.

Catalyst E

This catalyst was prepared in substantially the same way as catalyst D, the difference being, however, that in the present case the starting material was an alumina obtained by spray-drying with a d smaller than 0.01 mm and a specific surface area of 269 m²/g.

Catalyst F

The starting material was a soot with a d smaller than 0.01 mm and a specific surface area of 410 m²/g. The soot had been obtained

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5 as a by-product of the partial oxidation of hydrocarbon with air. The soot, being available in the form of a slurry in water, was isolated from it by filtering, drying of the filter cake and grinding of the dried material to the particle size mentioned. The nodules were prepared from the soot in substantially the same way as the nodules from alumina as described for catalyst A, the difference being, however, that in the present case an aqueous solution of lignosulphonate was used as the granulation liquid. After 15 minutes' residence time the nodules were removed from the disc. After drying at 120°C a sieve fraction with a d of 2.3 mm was isolated from the dried material. After 1 hour's calcination in a nitrogen stream at 700°C these

particles were impregnated with an aqueous solution comprising nickel nitrate and vanadyl oxalate. Finally, the impregnated material was dried at 120°C and calcined for 1 hour at 500°C in a nitrogen stream. The catalyst thus prepared comprised 0.5 pbw nickel and 2 pbw vanadium per 100 pbw soot.

Catalyst G

This catalyst was prepared in substantially the same way as catalyst A, the difference being, however, that in the present case the starting material was an alumina obtained by spray-drying with a d smaller than 0.5 mm and a specific surface area of 98 m²/g.

The properties of the catalysts prepared are shown in Table A.

TABLE A

Catalyst No.	A	B	C	D	E	F	G
Specific surface area, m ² /g	333	295	340	280	241	348	81
Total pore volume, ml/g	1.32	1.23	1.45	1.18	1.49	1.40	1.38
y, ml/g	0.76	0.82	0.85	0.73	0.89	0.82	0.79
v, %	54	52	56	53	57	56	54
d, mm	2.8	2.6	2.5	3.2	3.3	2.3	3.2
p, nm	145	107	210	105	300	150	109
p/d	52	41	84	33	91	65	34
Crushing strength, kg/cm ²	7.6	9.2	9.1	7.8	8.0	6.2	7.5
Density g/cm ³	0.29	0.34	0.30	0.33	0.32	0.30	0.29

35 Of the catalysts mentioned in Table A, catalysts A—F are catalysts according to the invention. These catalysts with p/d > 15, v > 50%, y > 0.2 ml/g and a specific surface area > 150 m²/g were prepared according to the nodulizing technique, starting from a material with a specific surface area > 200 m²/g. Catalyst G falls outside the scope of the present invention and has been included for comparison. Admittedly, this catalyst with a specific surface area < 150 m²/g was prepared according to the nodulizing technique, but starting from a material with a specific surface area < 200 m²/g.

50 Comparison of the crushing strengths and the densities of catalysts A and B shows the favourable effect of the use of dilute nitric acid as the granulation liquid instead of an aqueous citric acid solution.

The favourable effect of the incorporation

of glass powder in the starting material in combination with calcination at a temperature above the softening temperature of glass is found when comparing the crushing strengths of catalysts A and C.

Comparison of the densities of catalysts A and D shows the favourable effect of post-rotation of the nodules after these have attained the desired size on the rotating disc.

Example II.

Demetallization.

A residual hydrocarbon oil having a total vanadium and nickel content of 62 ppmw, which oil had been obtained as a residue in the atmospheric distillation of a Middle East crude oil was catalytically hydrodemetallized at different space velocities using four of the catalysts given in Table A. 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 and an exit gas

rate of 250 NI H₂/kg of feed. The catalysts were applied in the form of their sulphides. The results of the demetallization experiments are shown in Table B.

TABLE B

Experiment No.	1	2	3	4
Catalyst No.	D	E	F	G
Space velocity, l.l ⁻¹ .h ⁻¹	4.6	4.6	3.5	2.0
V+Ni removal (%w), after processing 5 tons feed/kg catalyst	49	50	48	39

10 A catalyst is optimum under the conditions applied during these demetallization experiments when the criterion is met that the catalyst is still capable of removing more than 40% of the total amount of vanadium and nickel present in this oil, after 5 tons of this oil has been processed over 1 kg of the catalyst at a space velocity of at least 2.9 l.l⁻¹.h⁻¹.

15 Experiments 1—3 given in Table B (in which the catalysts met the above-mentioned requirement concerning %w Ni+V removal) are demetallization experiments within the scope of the present invention. Experiment 4 has been included for comparison.

20 The influence of the specific surface area of the catalysts as well as of the specific surface area of the material from which they have been prepared by the nodulizing technique, on the demetallization activity of the catalysts becomes apparent when comparing the results of experiments 1 and 2 with those of experiment 4. It appears that catalysts D and E (with a specific surface area >150 m²/g and prepared from a material with a specific surface area >200 m²/g) are still capable of removing 49 and 50 %w V+Ni,

respectively, after processing 5 tons feed/kg catalyst at a space velocity of 4.6 l.l⁻¹.h⁻¹, whereas catalyst G (with a specific surface area <150 m²/g and prepared from a material with a specific surface area <200 m²/g), is only capable of removing 39 %w V+Ni after processing the same amount of feed/kg catalyst, while, in addition, the space velocity is only 2.0 l.l⁻¹.h⁻¹.

Example III.

Upgrading.

Four of the catalysts mentioned in Table A were tested for the upgrading of three residual hydrocarbon oils obtained as residues in the atmospheric distillation of three different crude oils originating from South America. To this end the residual oils, together with hydrogen, were passed downwards through a cylindrical, vertically disposed fixed catalyst bed at a temperature of 410°C and an exit gas rate of 250 NI H₂/kg of feed. The catalysts were applied in the form of their sulphides. The results of the upgrading experiments, the space velocities and hydrogen partial pressures applied and the properties of the residual oils have been collected in Table C.

TABLE C

Oil No.	A			B			C	
C_5 -asphaltenes content, %w	11.0			11.4			12.1	
$V_{k_{210}}$, cSt	183			128			140	
Experiment No.	5	6	7	8	9	10	11	
Catalyst No.	D	E	F	G	D	D	D	
Hydrogen partial pressure, bar	125	125	125	125	150	150	150	
Space velocity, $l.l^{-1}.h^{-1}$	0.4	0.4	0.4	0.4	0.9	0.4	0.6	
Reduction in C_5 -asphaltenes Content, %								
After processing 2 tons feed/kg catalyst	39	40	32	14			50	
After processing 4 tons feed/kg catalyst					33	40		
Reduction in $V_{k_{210}}$, %								
After processing 2 tons feed/kg catalyst	85	86	77	52			85	
After processing 4 tons feed/kg catalyst					73	80		

A catalyst is optimum under the conditions applied during these upgrading experiments when the criterion is met that the catalyst is still capable of reducing the C_5 -asphaltenes content and the $V_{k_{210}}$ of oil A by at least 30% and at least 50%, respectively, after 2 tons of the oil have been processed over the catalyst at a temperature of 410°C, a hydrogen partial pressure of 125 bar and a space velocity of 0.4 $l.l^{-1}.h^{-1}$.

Experiments 5—7 and 9—11 given in Table C (in which catalysts were applied which met the above-mentioned requirements concerning reduction of asphaltenes content and viscosity) are upgrading experiments within the scope of the present invention. Experiment B was included for comparison.

The influence of the specific surface area of the catalysts as well as of the specific surface area of the material from which they have been prepared by the nodulizing technique on the upgrading activity of the catalysts becomes apparent when comparing the results of experiments 5 and 6 with those of experiment 8. It appears that catalysts D and E (with a specific surface area $>150 \text{ m}^2/\text{g}$ and prepared from a material with a specific surface area $>200 \text{ m}^2/\text{g}$), are still capable

of reducing the C_5 -asphaltenes content and the $V_{k_{210}}$ of oil A by 39 and 85%, respectively, (for catalyst D) and by 40 and 86%, respectively, (for catalyst E) after processing of 2 tons of this oil per kg catalyst at a temperature of 410°C, a hydrogen partial pressure of 125 bar and a space velocity of 0.4 $l.l^{-1}.h^{-1}$, whereas catalyst G (with a specific surface area $<150 \text{ m}^2/\text{g}$ and prepared from a material with a specific surface area $<200 \text{ m}^2/\text{g}$), is only capable of reducing the C_5 -asphaltenes content and the $V_{k_{210}}$ by 14 and 52%, respectively, after processing of the same quantity of oil under the same conditions.

WHAT WE CLAIM IS:—

1. A process for the preparation of a catalyst, in which a catalyst comprising one or more metals having hydrogenation activity on a carrier and which catalyst meets the following requirements:

- (1) the quotient of the specific average pore diameter (p in nm) and the specific average particle diameter (d in nm) is larger than 15,

(17)



TABLE C

Oil No.	A				B		C	
C ₃ -asphaltenes content, %w	11.0				11.4		12.1	
V _{k₂₁₀} , cSt	183				128		140	
Experiment No.	5	6	7	8	9	10	11	
Catalyst No.	D	E	F	G	D	D	D	
Hydrogen partial pressure, bar	125	125	125	125	150	150	150	
Space velocity, l.l ⁻¹ .h ⁻¹	0.4	0.4	0.4	0.4	0.9	0.4	0.6	
Reduction in C ₃ -asphaltenes Content, %								
After processing 2 tons feed/kg catalyst	39	40	32	14				50
After processing 4 tons feed/kg catalyst					33	40		
Reduction in V _{k₂₁₀} , %								
After processing 2 tons feed/kg catalyst	85	86	77	52				85
After processing 4 tons feed/kg catalyst					73	80		

A catalyst is optimum under the conditions applied during these upgrading experiments when the criterion is met that the catalyst is still capable of reducing the C₃-asphaltenes content and the V_k of oil A by at least 30% and at least ²¹⁰50%, respectively, after 2 tons of the oil have been processed over the catalyst at a temperature of 410°C, a hydrogen partial pressure of 125 bar and a space velocity of 0.4 l.l⁻¹.h⁻¹.

Experiments 5—7 and 9—11 given in Table C (in which catalysts were applied which met the above-mentioned requirements concerning reduction of asphaltenes content and viscosity) are upgrading experiments within the scope of the present invention. Experiment B was included for comparison.

The influence of the specific surface area of the catalysts as well as of the specific surface area of the material from which they have been prepared by the nodulizing technique on the upgrading activity of the catalysts becomes apparent when comparing the results of experiments 5 and 6 with those of experiment 8. It appears that catalysts D and E (with a specific surface area >150 m²/g and prepared from a material with a specific surface area >200 m²/g), are still capable

of reducing the C₃-asphaltenes content and the V_k of oil A by 39 and 85%, respectively, (for catalyst D) and by 40 and 86%, respectively, (for catalyst E) after processing of 2 tons of this oil per kg catalyst at a temperature of 410°C, a hydrogen partial pressure of 125 bar and a space velocity of 0.4 l.l⁻¹.h⁻¹, whereas catalyst G (with a specific surface area <150 m²/g and prepared from a material with a specific surface area <200 m²/g), is only capable of reducing the C₃-asphaltenes content and the V_k by 14 and 52%, respectively, after processing of the same quantity of oil under the same conditions.

WHAT WE CLAIM IS:—

1. A process for the preparation of a catalyst, in which a catalyst comprising one or more metals having hydrogenation activity on a carrier and which catalyst meets the following requirements:

(1) the quotient of the specific average pore diameter (p in nm) and the specific average particle diameter (d in mm) is larger than 15,



- (2) the percentage (v) of the total pore volume that consists of pores with a diameter larger than 100 nm is at least 50,
- 5 (3) the pore volume (y) that consist of pores with a diameter larger than 50 nm is at least 0.2 ml/g, and
- (4) the specific surface area is larger than 150 m²/g,
- 10 is prepared according to the nodulizing technique from a starting material with a specific surface area above 200 m²/g.
2. A process according to claim 1, in which process a catalyst is prepared whose y is at least 0.40 ml/g.
- 15 3. A process according to claim 1 or 2, in which process a catalyst is prepared having a specific surface area above 200 m²/g.
4. A process according to any one of claims 20 1—3, in which process the specific surface area of the starting material is larger than 250 m²/g.
5. A process according to any one of claims 1—4, in which process the catalyst comprises 25 0.1—15 pbw of one or more metals having hydrogenation activity per 100 pbw carrier material.
6. A process according to claim 5, in which process the catalyst comprises 0.5—10 pbw of one or more metals having hydrogenation activity per 100 pbw carrier material.
- 30 7. A process according to any one of claims 1—6, in which process the catalyst comprises as metals with hydrogenation activity one or more of nickel, cobalt, molybdenum and vanadium.
- 35 8. A process according to claim 7, in which process the catalyst comprises at least one of nickel and cobalt and at least one of molybdenum and vanadium.
- 40 9. A process according to claim 8, in which process in the catalyst the atomic ratio between nickel and/or cobalt on the one hand and molybdenum and/or vanadium on the other hand is between 0.5 and 3.0.
- 45 10. A process according to claim 9, in which process the catalyst comprises either about 0.5 pbw nickel and about 2 pbw vanadium, or about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier material.
- 50 11. A process according to any one of claims 1—10, in which process the catalyst comprises silica, alumina or soot as the carrier.
- 55 12. A process according to claim 11, in which process the catalyst comprises soot as the carrier, which soot has been obtained as a by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam.
- 60 13. A process according to any one of claims 1—12, in which process the catalyst comprises the metals with hydrogenation activity in the form of their sulphides.
- 65 14. A process according to any one of claims 1—13, in which process the catalyst comprises alumina as a carrier and that the catalyst has been prepared using dilute nitric acid as the granulation liquid.
- 70 15. A process according to any one of claims 1—14, in which process the starting material from which larger particles are formed by the nodulizing technique is mixed with a certain amount of glass-powder and the particles formed by the nodulizing technique are subjected to a calcination at a temperature above the softening temperature of glass.
- 75 16. A process according to claim 15, in which process the amount of glass powder applied is 0.5—15 %w based on the amount of starting material with which it is mixed.
- 80 17. A process according to any one of claims 1—16, in which process the catalyst comprises phosphorus, preferably in amounts of 0.5—5.5 pbw per 100 pbw carrier material.
- 85 18. A process according to any one of claims 1—17, in which process the particles formed are rotated for some time after they have left the rotating disc but before drying and calcination and preferably for a period of time at least equal to the residence time of the material on the rotating disc.
- 90 19. A process according to any one of claims 1—18, in which process a granulation liquid is applied into which one or more compounds of the metals with hydrogenation activity have been incorporated.
- 95 20. A process for the preparation of a catalyst substantially as described hereinbefore and with particular reference to Example I as far as it relates to the preparation of catalysts A—F.
- 100 21. A catalyst prepared according to a process as claimed in any one of claims 1—20.
- 105 22. A process for the treatment of hydrocarbon oils with hydrogen, in which process the treatment is carried out in the presence of a catalyst as claimed in claim 21.
- 110 23. A process for upgrading a heavy hydrocarbon oil, in which process of a hydrocarbon oil having a C₅-asphaltenes content above 5 %w and a V_k²¹⁰ above 30 cSt, the C₅-asphaltenes content is reduced by at least 30% and the V_k²¹⁰ by at least 50%, by contacting the oil at a temperature of 400—500°C, a hydrogen partial pressure of 100—300 bar and a space velocity of 0.2—2.0 l.l⁻¹.h⁻¹ with a catalyst as claimed in claim 21.
- 115 24. A process for the demetallization of a metal-containing hydrocarbon oil, in which process the oil together with hydrogen is contacted 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 with a catalyst as claimed in claim 21.
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25. A process according to claim 23 or 24, which process is carried out in bunker flow operation or fixed-bed swing operation.

5 26. A process for the catalytic conversion of a metal-containing hydrocarbon oil, in particular by cracking, hydrocracking or hydrodesulphurization, in which the oil is first demetallized and subsequently catalytically converted, in which process the demetallization is carried out as described in claim 24 or 25.

10 27. A process according to any one of claims 23—26, in which process catalysts are applied with a d of 1.0—4.0 mm.

28. A process for the treatment of hydro-

carbon oils with hydrogen substantially as described hereinbefore and with particular reference to Examples II and III as far as they relate to the application of catalysts A—F. 15

29. Hydrocarbon oils obtained by a process as claimed in any one of claims 22—28. 20

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