

- 1 -

THIS SHEET HAS BEEN REPLACED

CATALYST, USE THEREOF AND PREPARATION PROCESS

The present invention relates to a novel catalyst and to its use in hydroconversion processes, wherein a hydrocarbon oil comprising aromatic compounds is contacted with hydrogen in the presence of such a catalyst. Furthermore, the present invention relates to a process for the preparation of the novel catalyst.

Hydrotreating catalysts are well known in the art. Conventional hydrotreating catalysts comprise at least one Group VIII metal component and/or at least one Group VIB metal component supported on a refractory oxide support. The Group VIII metal component may be either based on a non-noble metal, such as nickel (Ni) and/or cobalt (Co), or may be based on a noble metal, such as platinum (Pt) and/or palladium (Pd). Useful Group VIB metal components include those based on molybdenum (Mo) and tungsten (W). The most commonly applied refractory oxide support materials are inorganic oxides such as silica, alumina and silica-alumina and aluminosilicates, such as modified zeolite Y. Specific examples of conventional hydrotreating catalysts are NiMo/alumina, CoMo/alumina, NiW/silica-alumina, Pt/silica-alumina, PtPd/silica-alumina, Pt/modified zeolite Y and PtPd/modified zeolite Y.

Hydrotreating catalysts are normally used in processes wherein a hydrocarbon oil feed is contacted with hydrogen to reduce its content of aromatic compounds, sulphur compounds and/or nitrogen compounds. Typically, hydrotreating processes wherein reduction of the aromatics content is the main purpose are referred to as hydrogenation processes, whilst processes predominantly focusing on reducing sulphur and/or

This Sheet Has Been Replaced



- 2 -

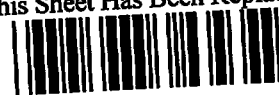
nitrogen content are referred to as hydrodesulphurisation and hydrodenitrogenation, respectively. Current environmental standards require that both aromatic content and sulphur and nitrogen content of oil products are very low and it is generally expected that specifications for aromatics, sulphur and nitrogen will become more and more severe in the future. Accordingly, in the refining of hydrocarbon oil fractions the ability to deeply hydrogenate, deeply hydrodesulphurise and deeply hydrodenitrogenate will become increasingly important.

In US-4,469,590 a process for hydrogenating aromatic hydrocarbons is disclosed, wherein said aromatic hydrocarbons are contacted at hydrogenation conditions with a certain catalyst in the presence of hydrogen and in the absence of an inorganic sulphur compound, particularly hydrogen sulphide. The catalyst employed comprises (i) a metal of Group VIII, preferably palladium, and (ii) a steamed support comprising a transition metal oxide selected from tungsten oxide, niobium oxide and mixtures thereof, composited with a non-zeolitic inorganic oxide, preferably alumina. The steamed support may additionally comprise a metal oxide selected from tantalum oxide, hafnium oxide, chromium oxide, titanium oxide, zirconium oxide and mixtures thereof.

In EP-A-0,653,242 a catalyst is disclosed comprising platinum and/or palladium and molybdenum and/or tungsten on a refractory oxide support. This catalyst is described to be very effective in hydrogenating aromatic compounds present in a hydrocarbon oil, even in the presence of relatively large amounts of sulphur and/or nitrogen, whilst its performance in hydrodesulphurisation and hydrodenitrogenation is also good. The catalyst is described to be particularly useful for

hydrotreating gas oils, whereby also mono-aromatic compounds are effectively hydrogenated which is more difficult with the traditional hydrotreating catalysts. In EP-A-0,653,242 it is furthermore described that the catalysts, due to their excellent hydrogenation activity and good desulphurisation and denitrogenation activity, could be very useful in the development of a single stage process for reducing the amount of aromatics and sulphur- and nitrogen-containing compounds. The conventional way for reducing the amounts of aromatics and sulphur- and nitrogen-containing compounds, namely, is via a two-stage process with in the first stage mainly hydrodesulphurisation and/or hydrodenitrogenation occurring and in the second stage mainly hydrogenation of the aromatic compounds still left. Such two-stage process is necessary, as conventional aromatics hydrogenation catalysts have a relatively low sulphur and/or nitrogen tolerance, so that they exhibit poor hydrogenation activity in the presence of substantial amounts of sulphur- and/or nitrogen-containing compounds. This applies in particular for the saturation of monoaromatics.

Like the invention which is the subject of EP-A-0,653,242, the present invention aims to provide a hydrotreating catalyst having an excellent aromatics hydrogenation activity, even in the presence of substantial quantities of sulphur- and nitrogen-containing compounds. The present invention also aims to provide a hydrotreating catalyst enabling an effective reduction of the contents of aromatics, sulphur-containing compounds and nitrogen-containing compounds in a single stage. The present invention moreover aims to provide catalysts exhibiting an excellent hydrogenation activity towards aromatics, which is at least equal to the hydrogenation activity of the



THIS SHEET HAS BEEN REPLACED

5 catalysts disclosed in EP-A-0,653,242, and having an improved hydrodesulphurisation and/or hydro-denitrogenation activity. It will be understood that such a process offers an increased potential for meeting
10 future low-content specifications for (mono)aromatics, sulphur and nitrogen.

Accordingly, the present invention in a first aspect relates to a catalyst comprising from 0.1 to 15% by weight of platinum and/or palladium and from 2 to 40% by
15 weight of at least one metal of the actinium series as the catalytically active metals, said weight percentages indicating the amount of metal based on the total weight of carrier, supported on an acidic carrier.

The actinium series refers to those elements of the
15 Periodic Table of Elements having an atomic number ranging from 89 (Actinium, Ac) to 103 (Lawrentium, Lr). These elements are also sometimes referred to as actinides. For the purpose of the present invention the enriched forms of the actinides, i.e. the radio-active isotopes, are not likely to be used in practice. The
20 catalytically active metals, i.e. platinum and/or palladium and the actinium series metal component, may be present in elemental form, as an oxide, as a sulphide or as a mixture of two or more of these forms. As will
25 be discussed in detail hereinafter, a suitable preparation method used to prepare the present catalyst includes a final step of calcination in air, which will cause the catalytically active metals to be at least partially converted into their oxides. Usually such
30 final calcination step will cause substantially all catalytically active metals to be converted into their oxides. If the catalyst is subsequently contacted with a sulphur-containing feed, then at least a part of these oxides will be sulphided and hence converted into the
35 corresponding sulphides ("in situ" sulphidation). Very



THIS SHEET HAS BEEN REPLACED

good catalyst performance has been observed in this situation and therefore it is considered a preferred embodiment of the present invention to have the catalytically active metals at least partly present in the catalyst as sulphides. Accordingly, the catalyst may also be subjected to a separate presulphiding treatment prior to being contacted with the feed. The degree of sulphidation of the metal oxides can be controlled by relevant parameters such as temperature and partial pressures of hydrogen, hydrogen sulphide, water and/or oxygen. The metal oxides may be completely converted into the corresponding sulphides, but suitably an equilibrium state between the oxides and sulphides of the catalytically active metals will be formed, so that the catalytically active metals are present both as oxides and as sulphides.

As will be discussed in more detail below, the catalyst according to the present invention can suitably be used in a variety of hydroconversion processes. The catalyst has been found to be particularly useful in the hydrotreatment of gas oils, thermally and/or catalytically cracked distillates (such as light cycle oils and cracked cycle oils) and mixtures of two or more of these. These oils usually contain a relatively large amount of aromatic compounds, sulphur-containing compounds and nitrogen-containing compounds. The amounts of such compounds must usually be reduced in view of environmental regulations. Aromatic compounds reduction may also be desirable for reaching certain technical quality specifications, such as cetane number in the case of automotive gas oils, smoke point in the case of jet fuels and colour and stability in the case of lubeoil fractions. When using the catalyst according to the present invention in the hydrotreatment of gas oils, thermally and/or catalytically cracked distillates and

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

mixtures of two or more of these, the required reduction for e.g. meeting automotive gas oil specifications can be attained in a single stage. It has been found that the catalysts of the present invention are especially active in reducing the amount of mono-aromatics in the final product, even in the presence of substantial amounts of sulphur containing compounds, such as hydrogen sulphide, and nitrogen containing compounds.

The catalyst according to the present invention comprises as catalytically active metals from 0.1 to 15% by weight of platinum and/or palladium and from 2 to 40% by weight of at least one metal of the actinium series. It has been found that if lower amounts of catalytically active metals are applied, the activity of the catalyst becomes too low to be commercially attractive. If, on the other hand, the amount of catalytically active metals is higher than the upper limits indicated, the further increase in catalytic activity does not warrant the costs of the extra amount of metal. This applies in particular for platinum and palladium. Good results can be obtained with catalysts comprising from 3 to 10% by weight of platinum and/or palladium and from 5 to 30% by weight of at least one metal of the actinium series.

As has already been indicated above the actinium series covers those elements of the Periodic Table of Elements which have an atomic number from 89 (actinium) to 103 (lawrentium). Suitably, the catalyst according to the present invention comprises one metal of the actinium series and preferred candidates are thorium and uranium. Of these, uranium is most preferred. With respect to the noble metal component, it is preferred to use palladium only. A very much preferred catalyst, accordingly, is a catalyst comprising palladium and uranium as the catalytically active metals.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

The carrier used to support the catalytically active metals is an acidic carrier. Acidic carriers are known in the art. Examples of suitable carriers for the purpose of the present invention, then, include acidic carriers comprising an aluminosilicate or silico-aluminophosphate zeolite, amorphous silica-alumina, alumina, fluorided alumina or a mixture of two or more of these. It will be appreciated that the type of acidic carrier to be used largely depends on the intended application of the catalyst. For most applications it is, however, preferred that the carrier comprises a zeolite. Examples of suitable zeolites are silico-aluminophosphates, such as SAPO-11, SAPO-31 and SAPO-41 and aluminosilicate zeolites like ferrierite, ZSM-5, ZSM-23, SSZ-32, mordenite, beta zeolite and zeolites of the faujasite type, such as faujasite and the synthetic zeolite Y. The use of silicoaluminophosphates may, for instance, be considered when using the present catalyst in a process for producing lubricating base oils which involves a hydroconversion step. In general, however, the use of aluminosilicate zeolites is preferred. A particularly preferred aluminosilicate zeolite is zeolite Y, which is usually used in a modified, i.e. dealuminated, form. Particularly when using the catalyst according to the present invention as a hydrotreating catalyst for reducing the content of aromatics and sulphur- and nitrogen-containing compounds, the use of an acidic carrier comprising a modified zeolite Y is very much preferred. A particularly useful modified zeolite Y is one having a unit cell size below 24.60 Å, preferably from 24.20 to 24.45 Å and even more preferably from 24.20 to 24.35 Å, and a SiO₂/Al₂O₃ molar ratio in the range of from 10 to 150, preferably from 15 to 110 and more preferably from 30 to 90. Such carriers are known in the art and examples are, for instance,



THIS SHEET HAS BEEN REPLACED

described in EP-A-0,247,678; EP-A-0,303,332 and EP-A-0,512,652. Modified zeolite Y having an increased alkali(ne) metal -usually sodium- content, such as described in EP-A-0,519,573, can also be suitably applied.

In addition to any of the aforementioned carrier materials the carrier may also comprise a binder material. The use of binders in catalyst carriers is well known in the art and suitable binders, then, include inorganic oxides, such as silica, alumina, silica-alumina, boria, zirconia and titania, and clays. Of these, the use of silica and alumina is preferred for the purpose of the present invention, whereby the use of alumina is most preferred. If present, the binder content of the carrier may vary from 5 to 95% by weight based on total weight of carrier. In a preferred embodiment, the carrier comprises 10 to 60% by weight of binder. A binder content of from 10 to 40% by weight has been found particularly advantageous.

The catalyst according to the present invention can be used in a variety of hydroconversion processes, wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen. Specific examples of such processes are hydrocracking, luboil manufacture (hydrocracking/hydroisomerization) and hydrotreating.

Accordingly, the present invention also relates to the use of the catalyst described above in a process wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen. Since the present catalysts are active not only in hydrogenating aromatic compounds, but also in removing sulphur and/or nitrogen compounds, hydrocarbon



THIS SHEET HAS BEEN REPLACED

feedstocks comprising sulphur and/or nitrogen containing compounds in addition to the aromatic compounds are particularly suitable.

5 If the catalyst is to be applied in a hydrocracking process, the carrier will usually comprise either an amorphous silica-alumina or an aluminosilicate zeolite with silica and/or alumina as a binder. A carrier which is preferably used comprises zeolite Y and alumina. A hydrocracking process typically comprises contacting a
10 hydrocarbon feedstock boiling between 100 and 500 °C in the presence of hydrogen with a suitable catalyst at a temperature of between 300 and 500 °C and a hydrogen partial pressure of up to 300 bar. The catalyst according to the present invention is, due to its
15 excellent hydrotreating performance, particularly useful as the first stage catalyst in a two stage hydrocracking process.

In lubricating base oil manufacture processes at least one hydroconversion step may be included for
20 removal of sulphur and/or nitrogen containing contaminants from the feedstock and/or hydrogenation of aromatic compounds and/or hydroisomerisation of straight chain and slightly branched hydrocarbons into further branched hydrocarbons and/or hydrocracking of waxy
25 molecules (usually long chain paraffinic molecules or molecules containing tails of this type) into smaller molecules. For application in such lubricating base oil manufacture process, the catalyst according to the present invention will preferably comprise a carrier
30 comprising amorphous silica-alumina, fluorided alumina or a zeolite with silica and/or alumina as binder. If the hydrotreating reactions are intended to occur predominantly, the use of carriers comprising modified zeolite Y is preferred. If cracking and/or hydro-
35 isomerisation of the waxy molecules is the main

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

objective, preferred carriers comprise fluorided alumina, amorphous silica-alumina or zeolites, such as ferrierite, ZSM-5, ZSM-23, SSZ-32 and SAPO-11. A hydroconversion step in a lubricating base oil manufacture process typically comprises contacting a luboil feedstock at a temperature of between 200 and 450 °C and a pressure up to 200 bar with a suitable catalyst in the presence of hydrogen. Examples of lubricating base oil manufacturing processes, wherein the catalyst according to the present invention may be used, are disclosed in GB-A-1,546,504 and EP-A-0,178,710.

The catalyst according the present invention has been found to be particularly suitable for use in a hydrotreating process. Suitable hydrotreating operating conditions are a temperature in the range of from 200 to 450 °C, preferably between 210 and 350 °C, and a total pressure in the range of from 10 to 200 bar, preferably between 25 and 100 bar. Examples of suitable hydro-treatment processes have been described in European patent applications 0,553,920 and 0,611,816. Suitable feedstocks for such a hydrotreating process are gas oils, light gas oils, gas oils, thermally and/or catalytically cracked distillates (such as light cycle oils and cracked cycle oils) and mixtures of two or more of these. All these feedstocks normally comprise at least 70% by weight of hydrocarbons boiling between 150 and 450 °C. When used in such a hydrotreating catalyst, it is preferred that the carrier comprises a binder in an amount as indicated above. The preferred acidic material in the carrier in case of hydrotreating is an aluminosilicate zeolite, most preferably modified zeolite Y. It has been found that the present catalyst exhibits an excellent hydrotreating activity and is particularly effective in hydrogenating mono-aromatics,

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

even in the presence of substantial amounts of sulphur-
and nitrogen-containing compounds. In addition, the
present catalyst is also very effective in the
hydrogenation of di-aromatics and higher aromatics (tri+
aromatics).

5

The present invention also relates to a process for
preparing the catalysts described above, which process
comprises incorporating the catalytically active metals
into the refractory oxide carrier, suitably by means of
impregnation or ion-exchange techniques, followed by
drying and calcining and optionally presulphiding. In
order to obtain catalysts having a particularly good
catalytic activity, this process can be carried out by
the subsequent steps of:

10

15

(a) impregnating the carrier with a solution containing
at least one compound of a metal of the actinium series
and a solution containing a platinum and/or palladium
compound; and

20

(b) drying and calcining the thus impregnated carrier at
a temperature in the range of from 250 to 650 °C.

25

A preferred method of impregnating the carrier is
the so-called pore volume impregnation, which involves
the treatment of a carrier with a volume of impregnating
solution, whereby said volume of impregnating solution
is substantially equal to the pore volume of the
carrier. In this way, full use is made of the
impregnating solution. For the purpose of the present
invention this impregnation method has been found to be
particularly suitable as the resulting catalysts show a
particularly good performance. The impregnation step (a)
can be carried out using one impregnation solution
containing all metal components or can be carried out in
two separate impregnation steps, one step for
impregnation with platinum and/or palladium and one step

30

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

for impregnation with the actinide, possibly with an intermediate drying and/or calcining step.

5 Metal compounds which can be used in the impregnating solutions for preparing the catalysts according to the present invention, are known in the art. Typical actinide compounds are salts thereof which are soluble in water, such as chlorides, sulphates, nitrates and acetates. In case of uranium, uranyle nitrate, uranium sulphate, ammonium diuranate, uranyle chloride and uranium acetate may conveniently be applied
10 in a water-based impregnating solution. Additionally, uranium salts soluble in alcohol and/or hydrocarbon solvents may be used in impregnating solutions based on such solvents. An example of a suitable uranium salt in this connection is uranyle acetylacetonate. Typical
15 palladium compounds for use in impregnating solutions are tetrachloropalladium acid (H_2PdCl_4), palladium nitrate, palladium(II) chloride and its amine complex. The use of H_2PdCl_4 is preferred. Typical platinum
20 compounds for use in an impregnating solution are hexachloroplatinic acid, optionally in the presence of hydrochloric acid, platinum amine hydroxide and the appropriate platinum amine complexes.

25 It is common practice in catalyst preparation, to subject the catalysts in the final step to calcination in air, whereby the metals are brought in the form of their oxides. To convert the metals at least partially into their sulphides, the catalyst can be presulphided after the final calcination step and prior to contact
30 with the feedstock. Suitable presulphiding methods are known in the art, such as for instance from EP-A-0,181,254. Accordingly, in a further embodiment of the present invention, the process for preparing the catalyst comprises the further step of:

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

(c) subjecting the dried and calcined catalyst to a presulphiding treatment.

5 In stead of the aforementioned presulphiding methods, presulphiding can take place via in situ presulphidation, i.e. by contacting the calcined catalyst with a sulphur-containing hydrocarbon feedstock. In most cases, namely, the hydrocarbon feed to the hydroconversion process contains substantial amounts of sulphur-containing compounds and if not, it
10 can be spiked with sulphur-containing compounds like di-tertiary nonyl polysulphide for presulphiding purposes, so that the metal oxides present on the calcined catalyst are at least partially converted into the corresponding sulphides when contacted with the said
15 hydrocarbon feedstock. Suitably, such contact is conducted at conditions which are less severe than the actual hydroconversion operating conditions. For instance, in situ presulphidation can be carried out at a temperature which is gradually increased from ambient
20 temperature to a temperature of between 150 and 250 °C. The catalyst is to be maintained at this temperature for between 10 and 20 hours. Subsequently, the temperature is to be raised gradually to the operating temperature for the actual hydroconversion process. In general, in
25 situ presulphidation can take place, if the hydrocarbon feedstock has a sulphur content of at least 0.5% by weight, said weight percentage indicating the amount of elemental sulphur relative to the total amount of feedstock. It will be understood that in situ
30 presulphidation of the catalyst may be advantageous for both process-efficiency and economic reasons.

The catalyst according to the present invention will usually slowly deactivate during use in a hydrocarbon conversion process. If the activity of the catalyst
35 becomes too low, the catalyst can be regenerated.

This Sheet Has Been Replaced



Suitable methods for regeneration of catalysts are known in the art. In some cases, however, the catalyst will not be regenerated. In those cases, the catalytically active metals will usually be recovered before disposal of the catalyst. Recovery of these metals can be achieved via known methods. A typical method for recovery of the catalytically active metals from spent catalyst comprises removing the deactivated catalyst from the reactor, washing the catalyst to remove the hydrocarbons, burning off the coke and subsequently recovering the platinum and/or palladium and the actinide.

The invention is illustrated by the following examples without restricting the invention to these particular embodiments.

Example 1

An acidic carrier consisting of 80% by weight dealuminated zeolite Y (unit cell size of 24.25 Å and silica/alumina molar ratio of 80) and 20% by weight of an alumina binder was used. This carrier was impregnated with an aqueous uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution to reach 20% by weight U_3O_8 (corresponding with 17.0% by weight of U). The partially prepared catalyst was then dried and calcined for 2 hours at 400 °C, after which impregnation with an aqueous solution of H_2PdCl_4 took place to reach a PdO content of 5% by weight (corresponding with 4.3% by weight of Pd). Finally, the completed catalyst was dried and calcined for 2 hours at 350 °C in air.

Example 2

The catalyst obtained in Example 1 was presulphided according to the method disclosed in EP-A-0,181,254. This method involved impregnation with di-tertiary nonyl polysulphide diluted in n-heptane, followed by drying

- 15 -

for 2 hours at 150 °C under nitrogen at atmospheric pressure.

The presulphided catalyst was subsequently contacted with a hydrocarbon feed consisting of a blend of 25% by weight light cycle oil and 75% by weight straight-run gas oil. Feedstock characteristics are indicated in Table I (B.P. means boiling point).

Operating conditions were a total pressure of 50 bar, weight hourly space velocity (WHSV) of 1.0 kg/l/h, a gas rate of 500 Nl/kg and an operating temperature of 360 °C.

The product characteristics and conversion levels are indicated in Table I. Conversions (in %) are calculated by assuming that aromatics are hydrogenated through a sequential reaction pathway, i.e. it is assumed that tri+ aromatics are converted into diaromatics, diaromatics into monoaromatics and monoaromatics into naphthenics. Accordingly, the monoaromatics which are found in the product may come from three sources: (i) from the unconverted monoaromatics already present in the feed, (ii) from converted diaromatics which were originally present in the feed and (iii) from converted diaromatics which, in return, originate from converted tri+ aromatics present in the feed.

TABLE I Feedstock and product characteristics

	Feed	Product	Conversion (%)
Aromatics (mmol/100 g)			
Mono	77.3	77.3	46
Di	55.3	8.9	88
Tri+	20.4	2.4	88
Sulphur (% wt)	1.4	0.005	99.6
Nitrogen (ppmw)	230	6	97.4
B.P. distribution (°C)			
Initial B.P.	150	79	
50% by weight B.P.	287	273	
Final B.P.	424	420	



- 17 -

C L A I M S

THIS SHEET HAS BEEN REPLACED

1. Catalyst comprising from 0.1 to 15% by weight of platinum and/or palladium and from 2 to 40% by weight of at least one metal of the actinium series supported on an acidic carrier, said weight percentages indicating the amount of metal based on the total weight of carrier.
2. Catalyst according to claim 1 comprising from 3 to 10% by weight of platinum and/or palladium and from 5 to 30% by weight of at least one metal of the actinium series.
3. Catalyst according to any one of the preceding claims comprising one metal of the actinium series, preferably uranium.
4. Catalyst according to any one of the preceding claims comprising palladium.
5. Catalyst according to any one of the preceding claims, wherein the acidic carrier comprises aluminosilicate zeolite, silicoaluminophosphate, amorphous silica-alumina, alumina, fluorided alumina or a mixture of two or more of these.
6. Catalyst according to claim 5 wherein the acidic carrier comprises an aluminosilicate zeolite.
7. Catalyst according to claim 6, wherein the aluminosilicate zeolite is modified zeolite Y.
8. Catalyst according to claim 7, wherein the modified zeolite Y has a unit cell size below 24.60 Å, preferably from 24.20 to 24.45 Å, and a SiO₂/Al₂O₃ molar ratio in the range of from 10 to 150, preferably from 15 to 110.
9. Catalyst according to any one of the preceding claims, wherein the acidic carrier also comprises from 5 to 95% by weight of a binder.

This Sheet Has Been Replaced





- 18 -

THIS SHEET HAS BEEN
REPLACED

10. Catalyst according to claim 9, wherein the binder is silica or alumina.
11. Use of a catalyst according to any one of claims 1-10 in a process wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen.
12. Use according to claim 11, wherein the hydrocarbon feedstock also comprises sulphur and/or nitrogen containing compounds.
13. Use according to claim 11 or 12, wherein the process is a hydrotreating process.
14. Use according to claim 13, wherein the hydrocarbon feedstock is a gas oil, a light gas oil, a thermally and/or catalytically cracked distillate or a mixture of two or more of these.
15. Use according to claim 11 or 12, wherein the process is a lubricating base oil manufacture process.
16. Use according to claim 11 or 12, wherein the process is a hydrocracking process.
17. Process for the preparation of a catalyst according to any one of claims 1-10, which process comprises incorporating the catalytically active metals into the carrier followed by drying and calcining.
18. Process according to claim 17 comprising the subsequent steps of:
- 25 (a) impregnating the carrier with a solution containing a platinum and/or palladium compound and a solution containing at least one compound of a metal of the actinium series; and
- (b) drying and calcining the thus impregnated carrier at a temperature in the range of from 250 to 650 °C.
- 30 19. Process according to claim 18 comprising the subsequent step of

This Sheet Has Been Replaced





WO 97/05948

PCT/EP96/03555

- 19

THIS SHEET HAS BEEN
REPLACED

(c) presulphiding the calcined catalyst obtained in step
(b).

This Sheet Has Been Replaced



CATALYST, USE THEREOF AND PREPARATION PROCESS

The present invention relates to a ~~novel~~ catalyst and to its use in hydroconversion processes, wherein a hydrocarbon oil comprising aromatic compounds is contacted with hydrogen in the presence of such a catalyst. ~~Furthermore, the present invention relates to a process for the preparation of the novel catalyst.~~

Hydrotreating catalysts are well known in the art. Conventional hydrotreating catalysts comprise at least one Group VIII metal component and/or at least one Group VIB metal component supported on a refractory oxide support. The Group VIII metal component may be either based on a non-noble metal, such as nickel (Ni) and/or cobalt (Co), or may be based on a noble metal, such as platinum (Pt) and/or palladium (Pd). Useful Group VIB metal components include those based on molybdenum (Mo) and tungsten (W). The most commonly applied refractory oxide support materials are inorganic oxides such as silica, alumina and silica-alumina and aluminosilicates, such as modified zeolite Y. Specific examples of conventional hydrotreating catalysts are NiMo/alumina, CoMo/alumina, NiW/silica-alumina, Pt/silica-alumina, PtPd/silica-alumina, Pt/modified zeolite Y and PtPd/modified zeolite Y.

Hydrotreating catalysts are normally used in processes wherein a hydrocarbon oil feed is contacted with hydrogen to reduce its content of aromatic compounds, sulphur compounds and/or nitrogen compounds. Typically, hydrotreating processes wherein reduction of the aromatics content is the main purpose are referred to as hydrogenation processes, whilst processes predominantly focusing on reducing sulphur and/or

hydrotreating gas oils, whereby also mono-aromatic compounds are effectively hydrogenated which is more difficult with the traditional hydrotreating catalysts. In EP-A-0,653,242 it is furthermore described that the catalysts, due to their excellent hydrogenation activity and good desulphurisation and denitrogenation activity, could be very useful in the development of a single stage process for reducing the amount of aromatics and sulphur- and nitrogen-containing compounds. The conventional way for reducing the amounts of aromatics and sulphur- and nitrogen-containing compounds, namely, is via a two-stage process with in the first stage mainly hydrodesulphurisation and/or hydrodenitrogenation occurring and in the second stage mainly hydrogenation of the aromatic compounds still left. Such two-stage process is necessary, as conventional aromatics hydrogenation catalysts have a relatively low sulphur and/or nitrogen tolerance, so that they exhibit poor hydrogenation activity in the presence of substantial amounts of sulphur- and/or nitrogen-containing compounds. This applies in particular for the saturation of monoaromatics.

Like the invention which is the subject of EP-A-0,653,242, the present invention aims to provide a hydrotreating ^{process} ~~catalyst~~ having an excellent aromatics hydrogenation activity, even in the presence of substantial quantities of sulphur- and nitrogen-containing compounds. The present invention also aims to provide a hydrotreating ^{process} ~~catalyst~~ enabling an effective reduction of the contents of aromatics, sulphur-containing compounds and nitrogen-containing compounds in a single stage. The present invention moreover aims to provide ^{a process which achieves} ~~catalysts exhibiting~~ an excellent hydrogenation activity towards aromatics, which is at least equal to the hydrogenation activity of the

process disclosed in EP-A-0,653,242, and having an improved hydrodesulphurisation and/or hydrodenitrogenation activity. It will be understood that such a process offers an increased potential for meeting future low-content specifications for (mono)aromatics, sulphur and nitrogen.

Accordingly, the present invention in a first aspect provides use of a catalyst which comprises, as the sole catalytically active metal components, from 0.1 to 15% by weight of platinum and/or palladium and from 2 to 40% by weight of at least one metal of the actinium series supported on an acidic carrier, said weight percentages indicating the amount of metal based on the total weight of carrier, in a hydroconversion process, wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen.

The combination of a platinum group metal and an actinide in a catalyst has been proposed for a number of other treatments, and often one or more further components are required in the catalyst. US-A-5051392 concerns the treatment of exhaust gas, e.g. from diesel engines, utilising a three-metal containing catalyst; US-A-4886928 describes a steam dehydrogenation process utilising a three-metal, but four component, catalyst. US-A-3788977 and equivalent FR-A-2110236, US-A-3929624 and the Derwent abstract 75-47166W all disclose reforming processes to increase the aromatic content of a hydrocarbon feedstock utilising a platinum group component, and an uranium component.

In the present invention, the actinium series refers to those elements of the Periodic Table of Elements having an atomic number ranging from 89 (Actinium, Ac) to 103 (Lawrentium, Lr). These elements are also sometimes referred to as actinides. For the purpose of the present invention the enriched forms of the actinides, i.e. the radio-active isotopes, are not likely to be used in practice. The catalytically active metals, i.e. platinum and/or palladium and the actinium series metal component, may be present in elemental form, as an oxide, as a sulphide or as a mixture of two or more of these forms. As will be discussed in detail hereinafter, a suitable preparation method used to prepare the present catalyst includes a final step of calcination in air, which will cause the catalytically active metals to be at least partially converted into their oxides. Usually such final calcination step will cause substantially all catalytically active metals to be converted into their oxides. If the catalyst is subsequently contacted with a sulphur-containing feed, then at least a part of these oxides will be sulphided and hence converted into the corresponding sulphides ("in situ" sulphidation). Very

MCS14/TS5530PCT

AMENDED SHEET

good catalyst performance has been observed in this situation and therefore it is considered a preferred embodiment of the present invention to have the catalytically active metals at least partly present in the catalyst as sulphides. Accordingly, the catalyst may also be subjected to a separate presulphiding treatment prior to being contacted with the feed. The degree of sulphidation of the metal oxides can be controlled by relevant parameters such as temperature and partial pressures of hydrogen, hydrogen sulphide, water and/or oxygen. The metal oxides may be completely converted into the corresponding sulphides, but suitably an equilibrium state between the oxides and sulphides of the catalytically active metals will be formed, so that the catalytically active metals are present both as oxides and as sulphides.

As will be discussed in more detail below, the catalyst ^{utilised in} ~~according to~~ the present invention can suitably be used in a variety of hydroconversion processes. The catalyst has been found to be particularly useful in the hydrotreatment of gas oils, thermally and/or catalytically cracked distillates (such as light cycle oils and cracked cycle oils) and mixtures of two or more of these. These oils usually contain a relatively large amount of aromatic compounds, sulphur-containing compounds and nitrogen-containing compounds. The amounts of such compounds must usually be reduced in view of environmental regulations. Aromatic compounds reduction may also be desirable for reaching certain technical quality specifications, such as cetane number in the case of automotive gas oils, smoke point in the case of jet fuels and colour and stability in the case of lubeoil fractions. When using the catalyst ~~according to the present invention~~ in the hydrotreatment of gas oils, thermally and/or catalytically cracked distillates and

mixtures of two or more of these, the required reduction for e.g. meeting automotive gas oil specifications can be attained in a single stage. It has been found that the catalysts ~~of the present invention~~ are especially
5 active in reducing the amount of mono-aromatics in the final product, even in the presence of substantial amounts of sulphur_L containing compounds, such as hydrogen sulphide, and nitrogen_L containing compounds.

The catalyst ^{utilised in} ~~according to~~ the present invention
10 comprises as catalytically active metals from 0.1 to 15% by weight of platinum and/or palladium and from 2 to 40% by weight of at least one metal of the actinium series. It has been found that if lower amounts of catalytically active metals are applied, the activity of the catalyst
15 becomes too low to be commercially attractive. If, on the other hand, the amount of catalytically active metals is higher than the upper limits indicated, the further increase in catalytic activity does not warrant the costs of the extra amount of metal. This applies in
20 particular for platinum and palladium. Good results can be obtained with catalysts comprising from 3 to 10% by weight of platinum and/or palladium and from 5 to 30% by weight of at least one metal of the actinium series.

As has already been indicated above the actinium
25 series covers those elements of the Periodic Table of Elements which have an atomic number from 89 (actinium) to 103 (lawrentium). Suitably, the catalyst ^{utilised in} ~~according to~~
the present invention comprises one metal of the actinium series and preferred candidates are thorium and
30 uranium. Of these, uranium is most preferred. With respect to the noble metal component, it is preferred to use palladium only. A very much preferred catalyst, accordingly, is a catalyst comprising palladium and uranium as the catalytically active metals.

The carrier used to support the catalytically active metals is an acidic carrier. Acidic carriers are known in the art. Examples of suitable carriers for the purpose of the present invention, then, include acidic carriers comprising an aluminosilicate or silico-aluminophosphate zeolite, amorphous silica-alumina, alumina, fluorided alumina or a mixture of two or more of these. It will be appreciated that the type of acidic carrier to be used largely depends on the intended application of the catalyst. For most applications it is, however, preferred that the carrier comprises a zeolite. Examples of suitable zeolites are silico-aluminophosphates, such as SAPO-11, SAPO-31 and SAPO-41 and aluminosilicate zeolites like ferrierite, ZSM-5, ZSM-23, SSZ-32, mordenite, beta zeolite and zeolites of the faujasite type, such as faujasite and the synthetic zeolite Y. The use of silicoaluminophosphates may, for instance, be considered ~~when using the present catalyst,~~ in a process for producing lubricating base oils which involves a hydroconversion step. In general, however, the use of aluminosilicate zeolites is preferred. A particularly preferred aluminosilicate zeolite is zeolite Y, which is usually used in a modified, i.e. dealuminated, form. Particularly when using the catalyst ^{utilised in} ~~according to~~ the present invention as a hydrotreating catalyst for reducing the content of aromatics and sulphur- and nitrogen-containing compounds, the use of an acidic carrier comprising a modified zeolite Y is very much preferred. A particularly useful modified zeolite Y is one having a unit cell size below 24.60 Å, preferably from 24.20 to 24.45 Å and even more preferably from 24.20 to 24.35 Å, and a SiO₂/Al₂O₃ molar ratio in the range of from 10 to 150, preferably from 15 to 110 and more preferably from 30 to 90. Such carriers are known in the art and examples are, for instance,

described in EP-A-0,247,678; EP-A-0,303,332 and EP-A-0,512,652. Modified zeolite Y having an increased alkali(ne) metal -usually sodium- content, such as described in EP-A-0,519,573, can also be suitably applied.

In addition to any of the aforementioned carrier materials the carrier may also comprise a binder material. The use of binders in catalyst carriers is well known in the art and suitable binders, then, include inorganic oxides, such as silica, alumina, silica-alumina, boria, zirconia and titania, and clays. Of these, the use of silica and alumina is preferred for the purpose of the present invention, whereby the use of alumina is most preferred. If present, the binder content of the carrier may vary from 5 to 95% by weight based on total weight of carrier. In a preferred embodiment, the carrier comprises 10 to 60% by weight of binder. A binder content of from 10 to 40% by weight has been found particularly advantageous.

The catalyst ^{utilised in} ~~according to~~ the present invention can be used in a variety of hydroconversion processes, wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen. Specific examples of such processes are hydrocracking, luboil manufacture (hydrocracking/hydroisomerization) and hydrotreating.

~~Accordingly, the present invention also relates to the use of the catalyst described above in a process wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen.~~ Since the ~~present~~ catalysts are active not only in hydrogenating aromatic compounds, but also in removing sulphur and/or nitrogen compounds, hydrocarbon

feedstocks comprising sulphur_L and/or nitrogen_L containing compounds in addition to the aromatic compounds are particularly suitable.

5 If the catalyst is to be applied in a hydrocracking process, the carrier will usually comprise either an amorphous silica-alumina or an aluminosilicate zeolite with silica and/or alumina as a binder. A carrier which is preferably used comprises zeolite Y and alumina. A hydrocracking process typically comprises contacting a
10 hydrocarbon feedstock boiling between 100 and 500 °C in the presence of hydrogen with a suitable catalyst at a temperature of between 300 and 500 °C and a hydrogen partial pressure of up to 300 bar. The catalyst
~~utilised in~~
~~according to~~ the present invention is, due to its
15 excellent hydrotreating performance, particularly useful as the first stage catalyst in a two stage hydrocracking process.

In lubricating base oil manufacture processes at least one hydroconversion step may be included for
20 removal of sulphur_L and/or nitrogen_L containing contaminants from the feedstock and/or hydrogenation of aromatic compounds and/or hydroisomerisation of straight chain and slightly branched hydrocarbons into further branched hydrocarbons and/or hydrocracking of waxy
25 molecules (usually long chain paraffinic molecules or molecules containing tails of this type) into smaller molecules. For application in such lubricating base oil manufacture process, the catalyst ~~utilised in~~
~~according to~~ the present invention will preferably comprise a carrier
30 comprising amorphous silica-alumina, fluorided alumina or a zeolite with silica and/or alumina as binder. If the hydrotreating reactions are intended to occur predominantly, the use of carriers comprising modified zeolite Y is preferred. If cracking and/or hydro-
35 isomerisation of the waxy molecules is the main

objective, preferred carriers comprise fluorided alumina, amorphous silica-alumina or zeolites, such as ferrierite, ZSM-5, ZSM-23, SSZ-32 and SAPO-11. A hydroconversion step in a lubricating base oil manufacture process typically comprises contacting a luboil feedstock at a temperature of between 200 and 450 °C and a pressure up to 200 bar with a suitable catalyst in the presence of hydrogen. Examples of suitable lubricating base oil manufacturing processes/~~wherein/~~ ^{utilised in} ~~the catalyst according to the present invention may be used/~~ are disclosed in GB-A-1,546,504 and EP-A-0,178,710.

The catalyst ~~according to~~ ^{utilised in} the present invention has been found to be particularly suitable for use in a hydrotreating process. Suitable hydrotreating operating conditions are a temperature in the range of from 200 to 450 °C, preferably between 210 and 350 °C, and a total pressure in the range of from 10 to 200 bar, preferably between 25 and 100 bar. Examples of suitable hydro-treatment processes have been described in European patent applications 0,553,920 and 0,611,816. Suitable feedstocks for such a hydrotreating process are gas oils, light gas oils, gas oils, thermally and/or catalytically cracked distillates (such as light cycle oils and cracked cycle oils) and mixtures of two or more of these. All these feedstocks normally comprise at least 70% by weight of hydrocarbons boiling between 150 and 450 °C. When used in such a hydrotreating catalyst, it is preferred that the carrier comprises a binder in an amount as indicated above. The preferred acidic material in the carrier in case of hydrotreating is an aluminosilicate zeolite, most preferably modified zeolite Y. It has been found that the present catalyst exhibits an excellent hydrotreating activity and is particularly effective in hydrogenating mono-aromatics,

even in the presence of substantial amounts of sulphur-
and nitrogen-containing compounds. In addition, the
present catalyst is also very effective in the
hydrogenation of di-aromatics and higher aromatics (tri-
aromatics).

~~The present invention also relates to a process for~~
~~preparing the catalysts described above~~ ^{may be prepared by a process} ~~which process~~

comprises incorporating the catalytically active metals
into the refractory oxide carrier, suitably by means of
impregnation or ion-exchange techniques, followed by
drying and calcining and optionally presulphiding. In
order to obtain catalysts having a particularly good
catalytic activity, this process can be carried out by
the subsequent steps of:

(a) impregnating the carrier with a solution containing
at least one compound of a metal of the actinium series
and a solution containing a platinum and/or palladium
compound; and

(b) drying and calcining the thus impregnated carrier at
a temperature in the range of from 250 to 650 °C.

A preferred method of impregnating the carrier is
the so-called pore volume impregnation, which involves
the treatment of a carrier with a volume of impregnating
solution, whereby said volume of impregnating solution
is substantially equal to the pore volume of the
carrier. In this way, full use is made of the
impregnating solution. For the purpose of the present
invention this impregnation method has been found to be
particularly suitable as the resulting catalysts show a
particularly good performance. The impregnation step (a)
can be carried out using one impregnation solution
containing all metal components or can be carried out in
two separate impregnation steps, one step for
impregnation with platinum and/or palladium and one step

for impregnation with the actinide, possibly with an intermediate drying and/or calcining step.

5 Metal compounds which can be used in the impregnating solutions for preparing the catalysts ^{utilised in} ~~according to~~ the present invention, are known in the art. Typical actinide compounds are salts thereof which are soluble in water, such as chlorides, sulphates, nitrates and acetates. In case of uranium, uranyle nitrate, uranium sulphate, ammonium diuranate, uranyle
10 chloride and uranium acetate may conveniently be applied in a water-based impregnating solution. Additionally, uranium salts soluble in alcohol and/or hydrocarbon solvents may be used in impregnating solutions based on such solvents. An example of a suitable uranium salt in
15 this connection is uranyle acetylacetonate. Typical palladium compounds for use in impregnating solutions are tetrachloropalladium acid (H_2PdCl_4), palladium nitrate, palladium(II) chloride and its amine complex. The use of H_2PdCl_4 is preferred. Typical platinum
20 compounds for use in an impregnating solution are hexachloroplatinic acid, optionally in the presence of hydrochloric acid, platinum amine hydroxide and the appropriate platinum amine complexes.

25 It is common practice in catalyst preparation, to subject the catalysts in the final step to calcination in air, whereby the metals are brought in the form of their oxides. To convert the metals at least partially into their sulphides, the catalyst can be presulphided after the final calcination step and prior to contact
30 with the feedstock. Suitable presulphiding methods are known in the art, such as for instance from EP-A-0,181,254. Accordingly, ~~in a further embodiment of the present invention,~~ ^{may further} the process for preparing the catalyst ~~comprises~~ the ~~further~~ step of:

(c) subjecting the dried and calcined catalyst to a presulphiding treatment.

In stead of the aforementioned presulphiding methods, presulphiding can take place via in situ presulphidation, i.e. by contacting the calcined catalyst with a sulphur-containing hydrocarbon feedstock. In most cases, namely, the hydrocarbon feed to the hydroconversion process contains substantial amounts of sulphur-containing compounds and if not, it can be spiked with sulphur-containing compounds like di-tertiary nonyl polysulphide for presulphiding purposes, so that the metal oxides present on the calcined catalyst are at least partially converted into the corresponding sulphides when contacted with the said hydrocarbon feedstock. Suitably, such contact is conducted at conditions which are less severe than the actual hydroconversion operating conditions. For instance, in situ presulphidation can be carried out at a temperature which is gradually increased from ambient temperature to a temperature of between 150 and 250 °C. The catalyst is to be maintained at this temperature for between 10 and 20 hours. Subsequently, the temperature is to be raised gradually to the operating temperature for the actual hydroconversion process. In general, in situ presulphidation can take place, if the hydrocarbon feedstock has a sulphur content of at least 0.5% by weight, said weight percentage indicating the amount of elemental sulphur relative to the total amount of feedstock. It will be understood that in situ presulphidation of the catalyst may be advantageous for both process-efficiency and economic reasons.

The catalyst ^{utilised in} ~~according to~~ the present invention will usually slowly deactivate during use in a hydrocarbon conversion process. If the activity of the catalyst becomes too low, the catalyst can be regenerated.



TS 5530 PCT

C L A I M S

1. Use of a catalyst which comprises, as the sole catalytically active metal components, from 0.1 to 15% by weight of platinum and/or palladium and from 2 to 40% by weight of at least one metal of the actinium series supported on an acidic carrier, said weight percentages indicating the amount of metal based on the total weight of carrier, in a hydroconversion process, wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen.
2. Use according to claim 1, wherein the feedstock also comprises sulphur- and/or nitrogen-containing compounds.
3. Use according to claim 1 or claim 2, wherein the process is a hydrotreating process.
4. Use according to claim 3, wherein the feedstock is a gas oil, a light gas oil, a thermally and/or catalytically cracked distillate or a mixture of two or more of these.
5. Use according to any one of claims 1 to 4, wherein the catalyst comprises from 3 to 10% by weight of platinum and/or palladium and from 5 to 30% by weight of at least one metal of the actinium series.
6. Use according to any one of claims 1 to 5, wherein, in the catalyst, the metal of the actinium series is uranium.
7. Use according to any one of claims 1 to 6, wherein the catalyst contains palladium.

AMENDED SHEET



8. Use according to any one of claims 1 to 7, wherein the acidic carrier of the catalyst comprises modified zeolite Y having a unit cell size below 24.60 Å, preferably from 24.20 to 24.45 Å, and a SiO₂/Al₂O₃ molar ratio in the range of from 10 to 150, preferably from 15 to 110.
9. Use according to any one of claims 1 to 8, wherein the acidic carrier of the catalyst also comprises from 5 to 95% by weight of a binder.
10. Use according to any one of claims 1 to 9, wherein the catalyst is presulphided.

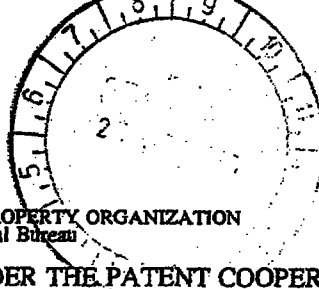
MCS14/TS5530PCT

AMENDED SHEET

9801886-4

1POS COPY

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 23/63, 29/08, C10G 35/09	A1	(11) International Publication Number: WO 97/05948 (43) International Publication Date: 20 February 1997 (20.02.97)
(21) International Application Number: PCT/EP96/03555 (22) International Filing Date: 7 August 1996 (07.08.96) (30) Priority Data: 95401850.8 8 August 1995 (08.08.95) EP (34) Countries for which the regional or international application was filed: FR et al. (71) Applicant (for all designated States except CA): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (72) Inventors: BARRE, Guy; Shell Recherche S.A., Route de Caen, F-76530 Grand-Couronne (FR). GRANDVALLET, Pierre; Shell Recherche S.A., Route de Caen, F-76530 Grand-Couronne (FR). LEBIGRE, Sylvie, Claude; Shell Recherche S.A., Route de Caen, F-76530 Grand-Couronne (FR).	(81) Designated States: AU, CA, CZ, HU, JP, KR, NO, <u>SG</u> , European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	
(54) Title: CATALYST, USE THEREOF AND PREPARATION PROCESS (57) Abstract Catalyst comprising from 0.1 to 15 % by weight of platinum and/or palladium and from 2 to 40 % by weight of at least one metal of the actinium series, said weight percentages indicating the amount of metal based on the total weight of carrier, supported on an acidic carrier. Use of this catalyst in a process wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature and pressure in the presence of hydrogen. Process for the preparation of the above catalyst, which process comprises incorporating the catalytically active metals into the carrier followed by drying and calcining.		