(19) DANMARK

(10) **DK/EP 3490708 T3**

Patent- og Varemærkestyrelsen

(12) Oversættelse af europæisk patentskrift

(51) Int.Cl.: ***B 01 J 31/04 (2006.01)*** ***B 01 J 23/85 (2006.01)*** ***B 01 J 23/882 (2006.01)***
***B 01 J 23/94 (2006.01)*** ***B 01 J 27/051 (2006.01)*** ***B 01 J 27/128 (2006.01)***
***B 01 J 27/19 (2006.01)*** ***B 01 J 27/28 (2006.01)*** ***B 01 J 35/10 (2006.01)***
***B 01 J 37/02 (2006.01)*** ***B 01 J 37/08 (2006.01)*** ***B 01 J 37/20 (2006.01)***
***B 01 J 38/52 (2006.01)*** ***B 01 J 38/62 (2006.01)*** ***C 10 G 11/05 (2006.01)***
***C 10 G 45/08 (2006.01)*** ***C 10 G 45/12 (2006.01)***

(45) Oversættelsen bekendtgjort den: **2021-07-05**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2021-04-14**

(86) Europæisk ansøgning nr.: **17730827.7**

(86) Europæisk indleveringsdag: **2017-06-22**

(87) Den europæiske ansøgnings publiceringsdag: **2019-06-05**

(86) International ansøgning nr.: **EP2017065384**

(87) Internationalt publikationsnr.: **WO2018019491**

(30) Prioritet: **2016-07-28 FR 1657307**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **IFP Energies nouvelles, 1 & 4 Avenue de Bois-Préau, 92852 Rueil-Malmaison, Frankrig**

(72) Opfinder: **CARRETTE, Pierre-Louis, 0010 Rue Soeur Janin, 69005 Lyon, Frankrig**

(74) Fuldmægtig i Danmark: **RWS Group, Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Bucks SL9 9FG, Storbritannien**

(54) Benævnelse: **KATALYSATOR PÅ BASIS AF 2-ACETYLBUTYROLACTON OG/ELLER DENS HYDROLYSEPRODUKTER OG DENS ANVENDELSE I EN FREMGANGSMÅDE TIL HYDROGENBEHANDLING OG/ELLER HYDROKRAKNING**

(56) Fremdragne publikationer:
**EP-A1- 2 174 711**
**WO-A1-2013/093229**
**US-A1- 2014 305 842**
**PASHIGREVA A V ET AL: "Activity and sulfidation behavior of the CoMo/Al"2O"3 hydrotreating catalyst: The effect of drying conditions", CATALYSIS TODAY, ELSEVIER, AMSTERDAM, NL, vol. 149, no. 1-2, 15 janvier 2010 (2010-01-15), pages 19-27, XP026815655, ISSN: 0920-5861 [extrait le 2009-08-28]**

## DESCRIPTION

The invention relates to a catalyst containing 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid as an additive, its preparation method, and its use in the field of hydrotreatment and/or hydrocracking.

Usually, a catalyst for the hydrotreatment of hydrocarbon fractions is intended to eliminate the sulphur-containing or nitrogen-containing compounds contained therein so as to bring a petroleum product, for example, up to the required specifications (sulphur content, aromatic compound content, etc.) for a given application (automotive fuel, gasoline or diesel fuel, domestic fuel oil, jet fuel). It may also involve pre-treating this feedstock so as to eliminate impurities from it or to hydrogenate it before it undergoes various transformation processes in order to modify its physico-chemical properties such as, for example, processes for reforming, hydrocracking of vacuum distillates, catalytic cracking, hydroconversion of atmospheric or vacuum residues. The composition and the use of hydrotreatment catalysts are particularly well described in the article by B. S. Clausen, H. T. Topsøe and F. E. Massoth, obtained from the work Catalysis Science and Technology, Volume 11 (1996), Springer-Verlag.

The tightening of automobile pollution standards in the European Community (Journal Officiel de L'Union Européenne [Official Journal of the European Union], L76, March 22, 2003, Directive 2003/70/CE, pages L76/10-L76/19) has constrained refiners to very substantially reduce the sulphur content in diesel fuels and gasolines (to a maximum of 10 parts per million (ppm) by weight of sulphur on January 1, 2009, as opposed to 50 ppm on January 1, 2005). Furthermore, the refiners are now constrained to use feedstocks which are increasingly refractory to hydrotreatment processes, on the one hand because crudes are becoming heavier and heavier and consequently contain more and more impurities, and on the other hand because of the increase

in conversion processes in the refineries. In fact, the latter generate fractions which are more difficult to hydrotreat than the fractions which are obtained directly from atmospheric distillation. The term “more difficult to hydrotreat” usually means higher operating temperatures to reach the same sulphur content in the effluent, and consequently service lives which may be reduced. These feedstocks require catalysts which have hydrodesulphurizing and hydrogenating functions which are greatly improved in relation to traditional catalysts.

In addition, conversion processes such as catalytic cracking or hydrocracking use catalysts which have an acid function, which makes them particularly sensitive to the presence of nitrogen-containing impurities and particularly basic nitrogen-containing compounds. It is therefore necessary to use catalysts for the pre-treatment of these feedstocks so as to remove these compounds.

Conventional hydrotreatment catalysts generally comprise an oxide substrate and an active phase based on metals from groups VIB and VIII in their oxide forms, as well as phosphorus. The preparation of these catalysts generally comprises a step for impregnation of metals and phosphorus onto the substrate, followed by drying and calcining, making it possible to obtain the active phase in the oxide forms thereof. Before using them in a hydrotreatment and/or hydrocracking reaction, these catalysts generally undergo sulphurization so as to form the active species.

The addition of an organic compound to the hydrotreatment catalysts to improve their activity has been recommended by the person skilled in the art, in particular for catalysts which have been prepared by impregnation followed by drying without subsequent calcining. These catalysts are often called “additive-containing dried catalysts.”

Numerous documents describe the use of different ranges of organic compounds as additives, such as organic compounds which

contain nitrogen and/or organic compounds which contain oxygen.

A family of compounds which is now well known in literature relates to chelating nitrogen-containing compounds (EP 0 181 035, EP 1 043 069, and US 6 540 908) with, by way of example, ethylenediaminetetraacetic acid (EDTA), ethylenediamine, diethylenetriamine or nitrilotriacetic acid (NTA).

Within the family of organic compounds which contain oxygen, the use of mono-, di-, or polyalcohols which are optionally etherified is described in the documents WO 96/41848, WO 01/76741, US 4 012 340, US 3 954 673, EP 0 601 722, and WO 2005/035691. The prior art mentions additives which comprise ester groups (EP 1 046 424, WO 2006/077326) more rarely.

There are also many patents which claim the use of carboxylic acids (EP 1 402 948, EP 0 482 817). In particular, in the document EP 0 482 817, citric acid, but also tartaric acid, butyric acid, hydroxyhexanoic acid, malic acid, gluconic acid, glyceric acid, glycolic acid, hydroxybutyric acid have been described. The specificity resides in the drying which is to be carried out at a temperature which is lower than 200°C.

The documents US 2014/353213 and US 2014/305482 describe the use of heterocyclic compounds containing oxygen or nitrogen in the cycle, such as lactams, oxacycloalkanes or lactones. Regarding lactones in particular, these documents cite β-propriolactone, γ-butyrolactone, and δ-valerolactone.

However, none of the documents which relate to the additives describes the use of 2-acetylbutyrolactone, or even of 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid which may be obtained directly or indirectly by the hydrolysis of 2-acetylbutyrolactone.

Irrespective of the compounds which are selected, the modifications which are made do not always make it possible to increase the performance of the catalyst enough to meet the

specifications relating to the sulphur and/or nitrogen contents of fuels. In addition, it is often very difficult to proceed to their industrial scale deployment because the process is complicated to carry out.

Consequently, it is becoming essential for the manufacturers of catalysts to find new hydrotreatment and/or hydrocracking catalysts with improved performance.

## Summary

The invention concerns a catalyst comprising a substrate based on alumina or silica or silica-alumina, at least one element from group VIII, at least one element from group VIB, and at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, 2-(2-hydroxyethyl)-3-oxobutanoic acid, and 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid.

In the remainder of the text, the term "hydrolysis products of 2-acetylbutyrolactone" is defined as 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid.

The applicant has in fact established that the use of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products as (an) organic additive(s) on a catalyst containing at least one element from group VIII and at least one element from group VIB means that it is possible to obtain a hydrotreatment and/or hydrocracking catalyst exhibiting improved catalytic performance.

In fact, the catalyst according to the invention exhibits an activity which is increased with respect to catalysts not containing additives and to dried additive-containing catalysts which are known. Typically, because of the increase in activity, the temperature which is necessary for reaching a desired sulphur or nitrogen content (for example, 10 ppm of sulphur in

the case of a diesel fuel fraction, in ULSD or Ultra Low Sulphur Diesel) may be reduced. Similarly, stability is increased since the service life is extended because of the necessary reduction in temperature.

In addition, the catalyst according to the present invention is easy to prepare because of a high solubility of 2-acetylbutyrolactone and/or its hydrolysis products in water or any other protic polar solvent.

According to a variation, the content of the element from group VIB is between 5 and 40% by weight, expressed in terms of oxide of metal from group VIB with respect to the total weight of the catalyst; the content of the element from group VIII is between 1 and 10% by weight, expressed in terms of oxide of metal from group VIII with respect to the total weight of the catalyst.

According to a variation, the molar ratio of the element from group VIII to the element from group VIB in the catalyst is between 0.1 and 0.8.

According to a variation, the catalyst also contains phosphorus, with the phosphorus content being between 0.1 and 20% by weight, expressed in terms of $P_2O_5$ with respect to the total weight of the catalyst, and the molar ratio of phosphorus to the element from group VIB in the catalyst is greater than or equal to 0.05.

According to a variation, the total content of additive(s) selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid is between 1 and 45% by weight with respect to the total weight of the catalyst.

According to a variation, the catalyst furthermore contains an organic compound in addition to the additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, said organic compound containing oxygen and/or nitrogen and/or sulphur. According to this variation, the organic compound is

preferably selected from a compound comprising one or more chemical functions selected from a carboxyl, alcohol, thiol, thioether, sulphone, sulphoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function. Preferably, it is selected from triethylene glycol, diethylene glycol, ethylene glycol, ethylenediaminetetraacetic acid (EDTA), maleic acid, malonic acid, citric acid, dimethylformamide, N-methylpyrrolidone, propylene carbonate, bicine or tricine.

According to a variation, the substrate contains from 0.1 to 50% by weight of zeolite.

According to a variation, the catalyst is at least partially sulphurized.

The invention also concerns the method for the preparation of said catalyst, comprising the following steps:

a) at least one component of an element from group VIB, at least one component of an element from group VIII, at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid, and optionally phosphorus are brought into contact with a substrate based on alumina or silica or silica-alumina, or a regenerated catalyst containing a substrate based on alumina or silica or silica-alumina, at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus is brought into contact with at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid in such a way as to obtain a catalyst precursor,

b) said catalyst precursor which is obtained from step a) is dried at a temperature which is lower than 200°C, without being calcined subsequently.

According to a variation, step a) is the following step:

a') a substrate based on alumina or silica or silica-alumina is impregnated by at least one solution which contains at least one element from group VIB, at least one element from group VIII, at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid, and optionally phosphorus in such a manner as to obtain a catalyst precursor.

According to another variation, step a) comprises the following steps:

a1) a substrate based on alumina or silica or silica-alumina is impregnated by at least one solution which contains at least one element from group VIB, at least one element from group VIII and optionally phosphorus, to obtain an impregnated substrate,

a2) the impregnated substrate which is obtained in step a1) is dried at a temperature which is lower than 200°C to obtain a dried impregnated substrate, and optionally the dried impregnated substrate is calcined to obtain a calcined impregnated substrate,

a3) the dried and optionally calcined impregnated substrate which is obtained in step a2) is impregnated by an impregnation solution comprising at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid in a manner such as to obtain a catalyst precursor,

a4) optionally, the catalyst precursor which is obtained in step a3) is allowed to mature.

According to another variation, step a) comprises the following steps:

a1') a substrate which comprises at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid and optionally at least one part of phosphorus is prepared,

a2') the substrate which is obtained in step a1') is impregnated by an impregnation solution comprising at least one element from group VIB, at least one element from group VIII and optionally phosphorus, in a manner such as to obtain a catalyst precursor,

a3') optionally, the catalyst precursor which is obtained in step a2') is allowed to mature.

According to another variation, step a) comprises the following steps:

a1'') a solution which contains at least one element from group VIB, at least one element from group VIII, at least one organic compound containing oxygen and/or nitrogen and/or sulphur, and optionally phosphorus is brought into contact by co-impregnation with a substrate based on alumina or silica or silica-alumina in such a manner as to obtain an impregnated substrate,

a2'') the impregnated substrate which is obtained from step a1'') is dried at a temperature which is lower than 200°C, without being calcined subsequently, to obtain a dried impregnated substrate,

a3'') the dried impregnated substrate which is obtained from step a2'') is brought into contact with a solution of at least one organic compound containing oxygen and/or nitrogen and/or sulphur which is identical to or different from that used in step a1'') in a manner such as to obtain a catalyst precursor,

a4'') optionally, the catalyst precursor which is obtained in step a3'') is allowed to mature,

and at least one of the organic compounds of step a1'') or of step a3'') is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid.

According to a variation, when the catalyst according to the invention is to be prepared starting from a regenerated catalyst, step a) of the preparation method comprises the following steps:

a1''') a regenerated catalyst containing a substrate based on alumina or silica or silica-alumina, at least one component of an element from group VIB, at least one omponent of an element from group VIII and optionally phosphorus, is impregnated by an impregnation solution comprising at least one additive which is selected from among 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid in such a manner as to obtain a catalyst precursor,

a2''') optionally, the catalyst precursor which is obtained in step a1''') is allowed to mature.

According to a variation, the total molar ratio of the additive(s) selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid to element(s) from group VIII is between 0.1 and 5.0 mol/mol.

The invention also concerns the use of the catalyst according to the invention or prepared in accordance with the preparation method according to the invention in a method for the hydrotreatment and/or hydrocracking of hydrocarbon fractions.

Below, the groups of chemical elements are provided according to the CAS classification (CRC Handbook of Chemistry and Physics, published by CRC Press, Editor-in-Chief D. R. Lide, 81st Edition, 2000-2001). As an example, group VIII according to the CAS classification corresponds to the metals of columns 8,

9 and 10 according to the new IUPAC classification.

The term “hydrotreatment” is defined as reactions which in particular encompass hydrodesulphurization (HDS), hydrodenitrification (HDN) and the hydrogenation of aromatic compounds (HDA).

## Detailed Description of the Invention

### Catalyst

The catalyst according to the invention is an additive-containing catalyst with at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products. More particularly, the catalyst according to the invention comprises a substrate based on alumina or silica or silica-alumina, at least one element from group VIII, at least one element from group VIB, and at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid.

The catalyst according to the invention may be a fresh catalyst, i.e., a catalyst which has not previously been used as a catalyst in a catalytic unit, and in particular in hydrotreatment and/or hydrocracking.

The catalyst according to the invention may also be a rejuvenated catalyst. The term “rejuvenated catalyst” means a catalyst which has been used as a catalyst in a catalytic unit and in particular in hydrotreatment and/or hydrocracking and which has undergone at least one calcining step so as to burn the coke (regeneration). This regenerated catalyst is then supplemented at least with an additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products to obtain the rejuvenated catalyst. This rejuvenated catalyst may contain one or more other organic additive(s) which may be added before, after, or at the same time as the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products.

The hydrogenating function of said catalyst, also termed the active phase, is ensured by at least one element from group VIB and by at least one element from group VIII.

Preferred elements from group VIB are molybdenum and tungsten. Preferred elements from group VIII are non-noble elements, and in particular cobalt and nickel. Advantageously, the hydrogenating function is selected from the group which is formed by the following combinations of elements: cobalt-molybdenum, nickel-molybdenum, nickel-tungsten or nickel-cobalt-molybdenum, or nickel-molybdenum-tungsten.

In the case in which significant hydrodesulphurization or hydrodenitrification and hydrogenation activity of the aromatic compounds is desired, the hydrogenating function is advantageously ensured by the combination of nickel and molybdenum; a combination of nickel and tungsten in the presence of molybdenum may also be advantageous. In the case of feedstocks of the vacuum distillate type or heavier type, combinations of the cobalt-nickel-molybdenum type may advantageously be used.

The total content of elements from group VIB and from group VIII is advantageously greater than 6% by weight, expressed in terms of the oxide with respect to the total weight of the catalyst.

The content of the element from group VIB is between 5 and 40% by weight, preferably between 8 and 35% by weight, and in a more preferred manner between 10 and 30% by weight, expressed in terms of the oxide of the metal from group VIB with respect to the total weight of the catalyst.

The content of the element from group VIII is between 1 and 10% by weight, preferably between 1.5 and 9% by weight, and in a more preferred manner between 2 and 8% by weight, expressed in terms of the oxide of the metal from group VIII with respect to the total weight of the catalyst.

The molar ratio of the element from group VIII to the element from group VIB in the catalyst is preferably between 0.1 and 0.8, preferably between 0.15 and 0.6, and in an even more preferred manner between 0.2 and 0.5.

The catalyst according to the invention advantageously also comprises phosphorus as dopant. The dopant is an added element which in itself does not have any catalytic nature, but which increases the catalytic activity of the active phase.

The phosphorus content in said catalyst is preferably between 0.1 and 20% by weight, expressed in terms of $P_2O_5$, preferably between 0.2 and 15% by weight, expressed in terms of $P_2O_5$, and in a very preferred manner between 0.3 and 11% by weight, expressed in terms of $P_2O_5$.

The molar ratio of phosphorus to the element from group VIB in the catalyst is greater than or equal to 0.05, preferably greater than or equal to 0.07, preferably between 0.08 and 1, preferably between 0.1 and 0.9, and in a very preferred manner between 0.15 and 0.8.

The catalyst according to the invention may advantageously also contain at least one dopant which is selected from boron, fluorine and a mixture of boron and fluorine.

When the catalyst contains boron, the boron content is preferably between 0.1 and 10% by weight, expressed in terms of boron oxide, preferably between 0.2 and 7% by weight, and in a very preferred manner between 0.2 and 5% by weight.

When the catalyst contains fluorine, the fluorine content is preferably between 0.1 and 10% by weight, expressed in terms of fluorine, preferably between 0.2 and 7% by weight, and in a very preferred manner between 0.2 and 5% by weight.

When the catalyst contains boron and fluorine, the total content of boron and fluorine is preferably between 0.1 and 10% by

weight, expressed in terms of boron oxide and fluorine, preferably between 0.2 and 7% by weight, and in a very preferred manner between 0.2 and 5% by weight.

The catalyst according to the invention comprises a substrate based on alumina or silica or silica-alumina.

When the substrate of said catalyst is based on alumina, it contains more than 50% alumina, and in general, it contains only alumina or silica-alumina as defined below.

Preferably, the substrate comprises alumina, and preferably extruded alumina. Preferably, the alumina is gamma alumina.

The alumina substrate advantageously has a total pore volume of between 0.1 and 1.5 $cm^3.g^{-1}$, preferably between 0.4 and 1.1 $cm^3.g^{-1}$. The total pore volume is measured by mercury porosimetry according to the Standard ASTM D4284 with a wetting angle of 140°, as described in the publication by Rouquerol, F.; Rouquerol, J.; Singh, K. "Adsorption by Powders & Porous Solids: Principle, Methodology and Applications," Academic Press, 1999, for example by means of an Autopore III™ model instrument from the Micromeritics™ brand.

The specific surface area of the alumina substrate is advantageously between 5 and 400 $m^2.g^{-1}$, preferably between 10 and 350 $m^2.g^{-1}$, in a more preferred manner between 40 and 350 $m^2.g^{-1}$·. The specific surface area is determined in the present invention by the B.E.T. method according to the Standard ASTM D3663, a method which is described in the same publication cited above.

In another preferred case, the substrate for said catalyst is a silica-alumina containing at least 50% by weight of alumina. The silica content in the substrate is at most 50% by weight, most often less than or equal to 45% by weight, preferably less than or equal to 40% by weight.

The silicon sources are well known to the person skilled in the art. Examples which may be cited are silicic acid, silica in powder form or in colloidal form (silica sol), tetraethyl orthosilicate $Si(OEt)_4$.

When the substrate of said catalyst is based on silica, it contains more than 50% by weight of silica and in general, it contains only silica.

According to a particularly preferred variation, the substrate is constituted by alumina, silica or silica-alumina.

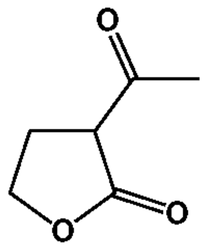
The substrate may also advantageously additionally contain 0.1 to 50% by weight of zeolite. In this case, any of the zeolite sources and any of the associated preparation methods which are known to the person skilled in the art may be incorporated. Preferably, the zeolite is selected from the groups FAU, BEA, ISV, IWR, IWW, MEI, UWY, and in a preferred manner, the zeolite is selected from the groups FAU and BEA, such as Y zeolite and/or beta zeolite.

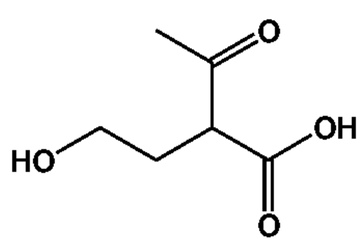
In certain particular cases, the substrate may also contain at least a portion of the VIB and VIII metal(s), and/or at least a portion of the dopant(s), including phosphorus, and/or at least a portion of the organic compound(s) containing oxygen (at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products or another additive which contains oxygen), and/or nitrogen and/or sulphur, which have been introduced outside of the impregnations (for example, introduced during the preparation of the substrate).

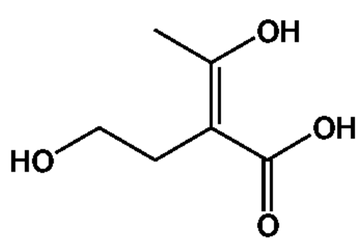
The substrate is advantageously in the form of beads, extrudates, pellets, or agglomerates which are irregular and non-spherical, the specific shape possibly resulting from a crushing step.

The catalyst according to the invention also comprises at least one additive which is selected from 2-acetylbutyrolactone and/or

its hydrolysis products, 2-(2-hydroxyethyl)-3-oxobutanoic acid and 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid. 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid respectively correspond to the following formulae (a) and (b) and (c) which are described below:

(a) 

(b) 

(c) 

The presence of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products on the catalyst makes it possible to observe an increased activity compared with the catalysts which do not contain additive and with known dried additive-containing catalysts.

Without wishing to be bound by any particular theory, it should be noted which 2-(2-hydroxyethyl)-3-oxobutanoic acid and 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid may be obtained directly or indirectly by hydrolysis of 2-acetylbutyrolactone.

According to a variation, the presence of at least one additive which is selected from 2-acetylbutyrolactone, 2-(2-hydroxyethyl)-3-oxobutanoic acid and 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid on the catalyst may be due to the addition per se as additive(s), alone or in a mixture.

According to another variation, the presence of the additive 2-(2-hydroxyethyl)-3-oxobutanoic acid and/or 3-hydroxy-2-(2-hydroxyethyl)-2-butenoic acid on the catalyst may be due to hydrolysis of the 2-acetylbutyrolactone which is contained in the impregnation solution which is added to said catalytic precursor or substrate and optionally to a consecutive dehydration step.

The total content of additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products on the

catalyst according to the invention is between 1 and 45% by weight, preferably between 2 and 30% by weight, and in a more preferred manner between 3 and 25% by weight with respect to the total weight of the catalyst. During the preparation of the catalyst, the drying step(s) following the introduction of the additive(s) is (are) carried out at a temperature which is lower than 200°C in a manner such as to preferably preserve at least 30%, preferably at least 50%, and in a very preferred manner at least 70% of the quantity of additive(s) introduced, calculated on the basis of the carbon remaining on the catalyst.

In addition to the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products, the catalyst according to the invention may comprise another organic compound or a group of organic compounds known to act as additives. The function of additives is to increase the catalytic activity with respect to catalysts without additives.

In the remainder of the text, the term “said additives” should be understood to mean at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products.

More particularly, the catalyst according to the invention may furthermore comprise one or more organic compounds which contain oxygen in addition to said additives and/or one or more organic compounds which contain nitrogen and/or one or more organic compounds which contain sulphur. Preferably, the catalyst according to the invention may comprise one or more organic compounds which contain oxygen in addition to said additives, and/or one or more organic compounds which contain nitrogen. Preferably, the organic compound contains at least 2 carbon atoms and at least one oxygen and/or nitrogen atom.

Generally, the organic compound is selected from a compound comprising one or more chemical functions selected from a carboxyl, alcohol, thiol, thioether, sulphone, sulphoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function. Preferably, the organic compound is

selected from a compound comprising two alcohol functions and/or two carboxyl functions and/or two ester functions and/or at least one amide function.

The organic compound containing oxygen may be one or more selected from compounds which comprise one or more chemical functions selected from a carboxyl, alcohol, ether, aldehyde, ketone, ester, or carbonate function. By way of example, the organic compound containing oxygen may be one or more selected from the group constituted by ethylene glycol, diethylene glycol, triethylene glycol, a polyethylene glycol (with a molecular weight of between 200 and 1500 g/mol), propylene glycol, 2-butoxyethanol, 2-(2-butoxyethoxy)ethanol, 2-(2-methoxyethoxy)ethanol, triethylene glycol dimethyl ether, glycerol, acetophenone, 2,4-pentanedione, pentanone, acetic acid, maleic acid, malic acid, malonic acid, malic acid, oxalic acid, gluconic acid, tartaric acid, citric acid, a C1-C4 dialkyl succinate, methyl acetoacetate, ethyl acetoacetate, dibenzofuran, a crown ether, orthophthalic acid, glucose, and propylene carbonate.

The organic compound which contains nitrogen may be one or more selected from the compounds which comprise one or more chemical functions selected from an amine or nitrile function. By way of example, the organic compound which contains nitrogen may be one or more selected from the group constituted by ethylenediamine, diethylenetriamine, hexamethylenediamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, acetonitrile, octylamine, guanidine or a carbazole.

The organic compound containing oxygen and nitrogen may be one or more which are selected from compounds which comprise one or more chemical functions which are selected from a carboxylic acid, alcohol, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, amide, urea or oxime function. By way of example, the organic compound containing oxygen and nitrogen may be one or more selected from the group constituted by 1,2-cyclohexanediaminetetraacetic acid, monoethanolamine (MEA), N-

methylpyrrolidone, dimethylformamide, ethylenediaminetetraacetic acid (EDTA), alanine, glycine, nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), tetramethyl urea, glutamic acid, dimethylglyoxime, bicine or tricine, or in fact a lactam.

The organic compound which contains sulphur may be one or more selected from compounds which comprise one or more chemical functions selected from a thiol, thioether, sulphone or sulphoxide function. By way of example, the organic compound which contains sulphur may be one or more selected from the group constituted by thioglycolic acid, 2-hydroxy-4-methylthiobutanoic acid, a sulphonated derivative of a benzothiophene or a sulphoxidized derivative of a benzothiophene.

Preferably, the organic compound contains oxygen; in a preferred manner, it is selected from triethylene glycol, diethylene glycol, ethylene glycol, ethylenediaminetetraacetic acid (EDTA), maleic acid, malonic acid, citric acid, dimethylformamide, N-methylpyrrolidone, propylene carbonate, bicine or tricine.

When it/they is/are present, the total content of organic compound(s) with an additive group (in addition to said additives) containing oxygen and/or nitrogen and/or sulphur on the catalyst according to the invention is between 1 and 30% by weight, preferably between 1.5 and 25% by weight, and in a more preferred manner between 2 and 20% by weight with respect to the total weight of the catalyst.

**Preparation Method**

The catalyst according to the invention may be prepared in accordance with a preparation method comprising the following steps:

a) at least one component of an element from group VIB, at

least one component of an element from group VIII, at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, and optionally phosphorus are brought into contact with a substrate based on alumina or silica or silica-alumina, or a regenerated catalyst containing a substrate based on alumina or silica or silica-alumina, at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus is brought into contact with at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, in such a manner as to obtain a catalyst precursor,

b) said catalyst precursor which is obtained from step a) is dried at a temperature which is lower than 200°C, without subsequently calcining it.

Firstly, the method for the preparation of a fresh catalyst will be described, and then subsequently, the method for the preparation of a rejuvenated catalyst will be described.

**Method for the Preparation of a Fresh Catalyst**

Contact step a) comprises several implementations which are primarily distinguished by the time when the additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products is introduced, which may be either at the same time as the impregnation of the metals (co-impregnation), or after impregnation of the metals (post-impregnation), or, finally, before the impregnation of the metals (pre-impregnation). In addition, the contact step may combine at least two implementations, for example co-impregnation and post-impregnation. These different implementations will be described below. Each method, taken by itself or in combination, may be carried out in one or more steps.

It is important to emphasize that during the method for its preparation, the catalyst according to the invention does not undergo calcining after the introduction of the additive(s)

selected from 2-acetylbutyrolactone and/or its hydrolysis products, or of any other organic compound containing oxygen and/or nitrogen and/or sulphur, so as to at least in part preserve the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products, or any other organic compound in the catalyst. Here, the term "calcining" is defined as a heat treatment under a gas containing air or oxygen at a temperature of 200°C or higher.

However, the catalyst precursor may undergo a calcining step before the introduction of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, or of any other organic compound containing oxygen and/or nitrogen and/or sulphur, in particular after the impregnation of elements from groups VIB and VIII (post-impregnation), optionally in the presence of phosphorus and/or another dopant or during a regeneration of a catalyst which has already been used. The hydrogenating function comprising the elements from group VIB and from group VIII of the catalyst according to the invention, also called the active phase, is then present in an oxide form.

According to another variation, the catalyst precursor does not undergo a calcining step after impregnation of the elements from groups VIB and VIII (post-impregnation); it is simply dried. The hydrogenating function comprising the elements from group VIB and from group VIII of the catalyst according to the invention, also called the active phase, is not then present in an oxide form.

Irrespective of the implementation, contact step a) generally comprises at least one impregnation step, preferably a dry impregnation step, in which the substrate is impregnated by an impregnation solution comprising at least one element from group VIB, at least one element from group VIII, and optionally phosphorus. In the case of the co-impregnation which is described in detail below, this impregnation solution additionally comprises at least one additive which is selected

from 2-acetylbutyrolactone and/or its hydrolysis products. The elements from group VIB and from group VIII are generally introduced by impregnation, preferably by dry impregnation, or by excess solution impregnation. Preferably, all of the elements from group VIB and from group VIII are introduced by impregnation, preferably by dry impregnation, irrespective of the implementation.

A portion of the elements from group VIB and from group VIII may also be introduced during shaping of said substrate at the time of mixing with at least one alumina gel selected as a matrix, with the rest of the hydrogenating elements then subsequently being introduced by impregnation. In a preferred manner, when a portion of the elements from group VIB and from group VIII are introduced at the time of mixing, the proportion of the element from group VIB which is introduced during this step is less than 5% by weight of the total quantity of the element from group VIB which is introduced onto the final catalyst.

In a preferred manner, the element from group VIB is introduced at the same time as the element from group VIII, irrespective of the method of introduction.

The molybdenum precursors which may be used are well known to the person skilled in the art. Examples of sources of molybdenum which may be used are oxides and hydroxides, molybdic acids and salts thereof, in particular ammonium salts such as ammonium molybdate, ammonium heptamolybdate, phosphomolybdic acid ($H_3PMo_{12}O_{40}$) and salts thereof, and optionally silicomolybdic acid ($H_4SiMo_{12}O_{40}$) and salts thereof. The sources of molybdenum may also be heteropoly compounds of the Keggin, lacunary Keggin, substituted Keggin, Dawson, Anderson, Strandberg types, for example. Preferably, molybdenum trioxide and heteropolyanions of the Strandberg, Keggin, lacunary Keggin or substituted Keggin type are used.

Precursors of tungsten which may be used are also well known to the person skilled in the art. Examples of sources of tungsten

which may be used are oxides and hydroxides, tungstic acids and salts thereof, in particular ammonium salts such as ammonium tungstate, ammonium metatungstate, phosphotungstic acid and salts thereof, and optionally silicotungstic acid ($H_4SiW_{12}O_{40}$) and salts thereof. The sources of tungsten may also be heteropoly compounds of the Keggin, lacunary Keggin, substituted Keggin, Dawson type, for example. Preferably, oxides and salts of ammonium such as ammonium metatungstate or heteropolyanions of the Keggin, lacunary Keggin or substituted Keggin type are used.

The precursors of the elements from group VIII which may be used are advantageously selected from oxides, hydroxides, hydroxycarbonates, carbonates and nitrates of elements from group VIII; as an example, nickel hydroxycarbonate, cobalt carbonate or hydroxide are preferably used.

Phosphorus, when it is present, may be introduced in its entirety or in part by impregnation. Preferably, it is introduced by impregnation, preferably dry, using a solution which contains the precursors of the elements from group VIB and from group VIII.

Said phosphorus may advantageously be introduced by itself or as a mixture with at least one of the elements from group VIB and from group VIII, during any of the steps for impregnation of the hydrogenating function if the latter is introduced several times. Some or all of said phosphorus may also be introduced during the impregnation of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products if the latter is introduced separately from the hydrogenating function (case of post-and pre-impregnation, described below) in the presence or absence of an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives. It may also be introduced upon synthesis of the substrate, at any step of the synthesis thereof. It may thus be introduced before, during, or after mixing the selected alumina gel matrix such as, for example and preferably, the aluminium oxyhydroxide (boehmite) precursor of alumina.

The preferred phosphorus precursor is orthophosphoric acid $H_3PO_4$, but its salts and esters such as ammonium phosphates are also suitable. Phosphorus may also be introduced at the same time as the element(s) from group VIB in the form of Keggin, lacunary Keggin, substituted Keggin or Strandberg type heteropolyanions.

The additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products is/are advantageously introduced into an impregnation solution which, depending on the preparation method, may be the same solution or a solution which is different from that which contains the elements from groups VIB and VIII, in a total quantity which corresponds:

- to a total molar ratio of the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products to the element(s) from group VIB of the catalyst precursor in the range 0.01 to 5 mol/mol, preferably in the range 0.05 to 3 mol/mol, in a preferred manner between 0.1 and 1.5 mol/mol, and in a very preferred manner between 0.2 and 1 mol/mol, calculated on the basis of components introduced into the impregnation solution(s), and

- to a total molar ratio of the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products to the element(s) from group VIII of the catalyst precursor in the range 0.02 to 17 mol/mol, preferably in the range 0.1 to 10 mol/mol, in a preferred manner between 0.2 and 5 mol/mol, and in a very preferred manner between 0.4 and 3.5 mol/mol, calculated on the basis of the components introduced into the impregnation solution(s).

Any impregnation solution which is described in this invention may comprise any polar solvent which is known to the person skilled in the art. Said polar solvent which is used is advantageously selected from the group which is formed by methanol, ethanol, water, phenol, cyclohexanol, alone or as a mixture. Said polar solvent may also advantageously be selected

from the group which is formed by propylene carbonate, DMSO (dimethyl sulphoxide), N-methylpyrrolidone (NMP) or sulpholane, alone or as a mixture. In a preferred manner, a polar protic solvent is used. A list of customary polar solvents as well as their dielectric constant can be found in the book "Solvents and Solvent Effects in Organic Chemistry," C. Reichardt, Wiley-VCH, 3rd Edition, 2003, pages 472-474. In a very preferred manner, the solvent which is used is water or ethanol, and in a particularly preferred manner, the solvent is water. In one possible embodiment, the solvent may be absent from the impregnation solution, in particular during a pre- or post-impregnation preparation.

When the catalyst furthermore comprises a dopant which is selected from boron, fluorine, or a mixture of boron and fluorine, this/these dopant(s) may be introduced in the same manner as the introduction of phosphorus in various steps of the preparation and in various ways. Said dopant may advantageously be introduced alone or as a mixture with at least one of the elements from group VIB and from group VIII during any of the steps for impregnation of the hydrogenating function if the latter is introduced a number of times. Some or all of said dopant may also be introduced during the impregnation of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products if the latter is introduced separately from the hydrogenating function (case of post- and pre-impregnation, described below) in the presence or absence of an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives. It may also be introduced upon the synthesis of the substrate at any step of the synthesis thereof. It may thus be introduced before, during, or after mixing the selected alumina gel matrix such as, for example and preferably, the aluminium oxyhydroxide (boehmite) precursor of alumina.

Said dopant, when present, is advantageously introduced as a mixture with the precursor(s) of the elements from group VIB and from group VIII, in its entirety or in part onto the substrate

shaped by dry impregnation of said substrate using a solution, preferably aqueous, containing the precursors of the metals, the precursor of phosphorus and the precursor(s) of the dopant(s) (and also containing at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in the co-impregnation mode).

The boron precursors may be boric acid, orthoboric acid $H_3BO_3$, ammonium biborate or pentaborate , boron oxide, boric esters. The boron may be introduced by means of, for example, a boric acid solution in a water/alcohol mixture, or in fact in a water/ethanolamine mixture. Preferably, the boron precursor , if boron is introduced, is orthoboric acid.

The fluorine precursors which may be used are well known to the person skilled in the art. As an example, the fluoride anions may be introduced in the form of hydrofluoric acid or its salts. These salts are formed with alkaline metals, ammonium, or an organic compound. In this latter case, the salt is advantageously formed in the reaction mixture by reaction between the organic compound and hydrofluoric acid. The fluorine may, for example, be introduced by impregnation with an aqueous solution of hydrofluoric acid or ammonium fluoride, or in fact ammonium bifluoride.

When the catalyst also comprises a supplementary additive (in addition to the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products) or a group of supplementary additives selected from an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives, the latter may be introduced into the impregnation solution of step a).

The total molar ratio of (an) organic compound(s) containing oxygen and/or nitrogen and/or sulphur in addition to said additives to the element(s) from group VIB on the catalyst is in the range 0.05 to 5 mol/mol, preferably in the range 0.1 to 4 mol/mol, in a preferred manner between 0.2 and 3 mol/mol,

calculated on the basis of the components introduced into the impregnation solution(s).

The total molar ratio of (an) organic compound(s) containing oxygen and/or nitrogen and/or sulphur in addition to said additives with respect to the sum of the 2-acetylbutyrolactone and/or its hydrolysis products is between 0.05 and 6 mol/mol, preferably between 0.1 and 5 mol/mol, in a preferred manner between 0.2 and 4 mol/mol, calculated on the basis of the components introduced into the impregnation solution(s).

Advantageously, after each impregnation step, the impregnated substrate is allowed to mature. Maturation makes it possible for the impregnation solution to become dispersed in a homogeneous manner within the substrate.

Any maturation step which is described in this invention is advantageously carried out at atmospheric pressure, in a water-saturated atmosphere and at a temperature of between 17°C and 50°C, and preferably at ambient temperature. Generally, a maturation period of between 10 minutes and 48 hours, and preferably of between 30 minutes and 5 hours, is adequate. Longer periods are not ruled out, but do not necessarily provide an improvement.

In accordance with step b) of the preparation method according to the invention, the catalyst precursor which is obtained in step a) and which is optionally matured undergoes a drying step at a temperature which is lower than 200°C, without a subsequent calcining step.

Any drying step following the introduction of said additives which is described in the present invention is carried out at a temperature which is lower than 200°C, preferably of between 50°C and 180°C, in a preferred manner of between 70°C and 150°C, and in a very preferred manner of between 75°C and 130°C.

The drying step is advantageously carried out using any

technique which is known to the person skilled in the art. It is advantageously carried out at atmospheric pressure or at reduced pressure. In a preferred manner, this step is carried out at atmospheric pressure. It is advantageously carried out in a flushed bed using air or any other hot gas. In a preferred manner, when the drying is carried out in a fixed bed, the gas which is used is either air or an inert gas such as argon or nitrogen. In a very preferred manner, the drying is carried out in a flushed bed in the presence of nitrogen and/or air. Preferably, the drying step is of a short duration of between 5 minutes and 4 hours, preferably between 30 minutes and 4 hours, and in a very preferred manner between 1 hour and 3 hours. Drying is then carried out in such a manner as to preferably preserve at least 30% of the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products introduced during an impregnation step; preferably, this quantity is greater than 50%, and in an even more preferred manner greater than 70%, calculated on the basis of the carbon remaining on the catalyst. When an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives is present, the drying step is carried out in such a manner as to preferably preserve at least 30%, preferably at least 50%, and in a very preferred manner at least 70% of the quantity which is introduced, calculated on the basis of the carbon remaining on the catalyst.

At the end of the drying step b), a dried catalyst which has not undergone any subsequent calcining step is obtained.

**Co-Impregnation**

According to a first implementation of step a) of the method for the preparation of the (fresh) catalyst, said components of the elements from group VIB, from group VIII, at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products and optionally phosphorus are deposited onto said substrate, by one or more co-impregnation steps; i.e., said components of the elements from group VIB, from group VIII, at least one additive which is selected from 2-acetylbutyrolactone

and/or its hydrolysis products and optionally phosphorus are introduced simultaneously into said substrate ("co-impregnation"). According to a variation, step a) is the following step:

a') a substrate based on alumina or silica or silica-alumina is impregnated by at least one solution which contains at least one element from group VIB, at least one element from group VIII, at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products and optionally phosphorus in a manner such as to obtain a catalyst precursor.

The co-impregnation step(s) is (are) preferably carried out by dry impregnation or by excess solution impregnation. When this first embodiment comprises the implementation of several co-impregnation steps, each co-impregnation step is preferably followed by a step for intermediate drying at a temperature which is lower than 200°C, advantageously between 50°C and 180°C, preferably between 70°C and 150°C, in a very preferred manner between 75°C and 130°C, and optionally a maturation period has been observed between impregnation and drying.

In a very preferred manner, during preparation via co-impregnation, the elements from group VIB and from group VIII, at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, optionally phosphorus, optionally another dopant which is selected from boron and/or fluorine, and optionally an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives are introduced into step a) in their entirety after shaping said substrate, by dry impregnation of said substrate using an aqueous impregnation solution which contains the precursors of the elements from group VIB and from group VIII, at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, the optional phosphorus precursor, the optional dopant precursor which is selected from boron and/or fluorine, and optionally the organic

compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives.

**Post-Impregnation**

According to a second implementation of step a) of the method for the preparation of (fresh) catalyst according to the invention, at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products is brought into contact with a dried and optionally calcined impregnated substrate which comprises at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus, said substrate being based on alumina or silica or silica-alumina, in a manner such as to obtain a catalyst precursor.

This second implementation is a preparation by "post-impregnation" of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products. The latter is carried out by dry impregnation, for example.

According to this second implementation, contact according to step a) comprises the following successive steps which will be presented in detail below:

a1) a substrate based on alumina or silica or silica-alumina is impregnated by at least one solution which contains at least one element from group VIB, at least one element from group VIII, and optionally phosphorus in order to obtain an impregnated substrate,

a2) the impregnated substrate which is obtained in step a1) is dried at a temperature which is lower than 200°C to obtain a dried impregnated substrate and, optionally, the dried impregnated substrate is calcined to obtain a calcined impregnated substrate,

a3) the dried and optionally calcined impregnated substrate

which is obtained in step a2) is impregnated by an impregnation solution comprising at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in such a manner as to obtain a catalyst precursor,

a4) optionally, the catalyst precursor which is obtained in step a3) is allowed to mature.

In step a1) of the implementation by post-impregnation, the introduction of the elements from group VIB and from group VIII and optionally phosphorus onto the substrate may advantageously be carried out by one or more excess solution impregnations onto the substrate, or preferably by one or more dry impregnations, and in a preferred manner by a single dry impregnation of said substrate, using (a) preferably aqueous solution(s) containing the precursor(s) of the metals and preferably the phosphorus precursor.

When several impregnation steps are carried out, each impregnation step is preferably followed by an intermediate drying step at a temperature which is lower than 200°C, advantageously between 50°C and 180°C, preferably between 70°C and 150°C, in a very preferred manner between 75°C and 130°C; and optionally a maturation period has been observed between impregnation and drying. Prior to the introduction of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products each intermediate drying step may be followed by a calcining step under the conditions which are described below for step a2).

In a very preferred manner, during the preparation via post-impregnation, the elements from group VIB and from group VIII, and optionally phosphorus, optionally another dopant which is selected from boron and/or fluorine, and optionally an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives are introduced in step a1) in their entirety after shaping said substrate, by dry impregnation of said substrate using an aqueous impregnation solution which

contains the precursors of the elements from group VIB and from group VIII, the phosphorus precursor, and optionally the dopant precursor which is selected from between boron and/or fluorine, and optionally the organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives.

According to another variation, the elements from group VIB and from group VIII and optionally phosphorus, optionally another dopant which is selected from boron and/or fluorine, and optionally an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives may be introduced in step a1) in a sequential manner by several impregnation solutions which contain one or more of the components.

Advantageously, the impregnated substrate which is obtained in step a1) is allowed to mature under the conditions which described above for maturation.

According to step a2), the impregnated substrate which is obtained in step a1) is dried at a temperature which is lower than 200°C in order to obtain a dried impregnated substrate under the conditions which are described above for drying.

Optionally, the dried impregnated substrate may then undergo calcining. Calcining is generally carried out at a temperature of between 200°C and 900°C, preferably between 250°C and 750°C. The calcining period is generally between 0.5 hour and 16 hours, preferably between 1 hour and 5 hours. It is generally carried out in air. Calcining makes it possible to transform the precursors of the metals from groups VIB and VIII into oxides.

According to step a3), the dried impregnated substrate which is obtained in step a2) is impregnated with an impregnation solution comprising at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in a manner such as to obtain a catalyst precursor.

The additive(s) selected from 2-acetylbutyrolactone and/or its

hydrolysis products may advantageously be deposited in one or more steps either by excess impregnation or by dry impregnation, or by any other means which is known to the person skilled in the art. Preferably, said additive(s) is/are introduced by dry impregnation, in the presence or absence of a solvent, as described above.

Preferably, the solvent in the impregnation solution which is used in step a3) is water, which facilitates implementation on an industrial scale.

The additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products is/are advantageously introduced into the impregnation solution of step a3) with the molar ratios for the element from group VIB or from group VIII which are described above.

When an additional additive (in addition to the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products) or a group of supplemental additives selected from an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives is to be introduced, it may be introduced into the impregnation solution of step a1) and/or into the impregnation solution of step a3), or in fact by an additional impregnation step at any time during the preparation method before the final drying of step b), it being understood no calcining steps are carried out after its introduction. This compound is introduced in the proportions described above.

According to step a4), the catalyst precursor which is obtained in step a3) is optionally allowed to mature under the maturation conditions described above.

In accordance with step b) of the preparation method according to the invention, the catalyst precursor which has optionally been matured during step a4) undergoes a drying step at a temperature which is lower than 200°C without a subsequent

calcining step, as described above.

**Pre-Impregnation**

According to a third implementation of step a) of the method for the preparation of the (fresh) catalyst according to the invention, at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus are brought into contact with the substrate based on alumina or silica or silica-alumina which contains at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in such a manner as to obtain a catalyst precursor.

This third implementation is a preparation by “pre-impregnation” of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products. This is carried out by dry impregnation, for example.

According to this third implementation, contact according to step a) comprises the following successive steps which will be presented in detail below:

a1’) a substrate which comprises at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products and optionally at least one part of phosphorus is prepared,

a2’) the substrate which is obtained in step a1’) is impregnated by an impregnation solution comprising at least one element from group VIB, at least one element from group VIII and optionally phosphorus in a manner such as to obtain a catalyst precursor,

a3’) optionally, the catalyst precursor which is obtained in step a2’) is allowed to mature.

In step a1’) of the implementation by pre-impregnation, a substrate comprising at least one additive which is selected

from 2-acetylbutyrolactone and/or its hydrolysis products and optionally at least a portion of phosphorus is prepared. The additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products may be introduced at any time in the preparation of the substrate, and in a preferred manner during shaping or by impregnation onto a ready-shaped substrate.

If the introduction of at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products onto the ready-shaped substrate is selected, then it can be carried out as is indicated for step a3) of the post-impregnation. It will then be followed by an optional step for maturation and for drying at a temperature which is lower than 200°C under the maturation and drying conditions as described above.

If introduction during shaping is selected, preferably, said shaping is carried out by mixing-extrusion, by pelletization, by the drop coagulation method (oil-drop method), by rotary plate granulation or by any other method which is well known to the person skilled in the art. In a very preferred manner, said shaping is carried out by mixing-extrusion, with the 2-acetylbutyrolactone and/or its hydrolysis products being able to be introduced at any time in the mixing-extrusion. The shaped material obtained at the end of the shaping step then advantageously undergoes a heat treatment step at a temperature such that at least a portion of said additive(s) remains present.

This is also the case for the phosphorus which is optionally present in said substrate of step a1'). The phosphorus may be introduced at any time in the preparation of the substrate, and in a preferred manner during shaping or by impregnation onto a ready-shaped substrate as described above. If the phosphorus is introduced by itself during shaping, i.e., without an additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, itself then introduced by impregnation, the calcining temperature following its introduction may then advantageously be produced at a temperature which is lower than 1000°C.

In step a2') of the implementation by pre-impregnation, the introduction of the elements from group VIB and from group VIII and optionally phosphorus may advantageously be carried out by one or more excess solution impregnations onto the substrate, or preferably by one or more dry impregnations and, in a preferred manner, by a single dry impregnation of said substrate, using (a) preferably aqueous solution(s) containing the metal precursor(s) and optionally the phosphorus precursor.

Advantageously, the catalyst precursor which is obtained in step a2') is allowed to mature under the maturation conditions described above.

When it is also desired to introduce an additional additive (in addition to the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products) or a group of additional additives which is selected from an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives, the latter may be introduced into the substrate of step a1') during shaping or by impregnation, and/or into the impregnation solution of step a2'), or in fact by an additional impregnation step at any time in the preparation method before the final drying of step b), it being understood which the calcining step is not carried out after its introduction.

The three embodiments described above may be implemented by themselves as described or mixed in order to produce other hybrid preparation modes, depending on technical and practical constraints.

According to another alternative embodiment, contact according to step a) combines at least two embodiments for contact, for example co-impregnation of an organic compound and post-impregnation of an organic compound which may be identical to or different from that used for co-impregnation, given that at least one of the organic compounds is selected from 2-acetylbutyrolactone and/or its hydrolysis products.

According to this alternative implementation, the contact according to step a) comprises the following successive steps:

a1'') a solution which contains at least one element from group VIB, at least one element from group VIII, at least one organic compound containing oxygen and/or nitrogen and/or sulphur and optionally phosphorus is brought into contact by co-impregnation with a substrate based on alumina or silica or silica-alumina in such a manner as to obtain an impregnated substrate,

a2'') the impregnated substrate which is obtained from step a1'') is dried at a temperature which is lower than 200°C, without being calcined subsequently, in order to obtain a dried impregnated substrate,

a3'') the dried impregnated substrate which is obtained from step a2'') is brought into contact with a solution of at least one organic compound containing oxygen and/or nitrogen and/or sulphur which is identical to or different from that used in step a1'') in such a manner as to obtain a catalyst precursor,

a4'') optionally, the catalyst precursor which is obtained in step a3'') is allowed to mature,

and at least one of the organic compounds of step a1'') or of step a3'') is selected from 2-acetylbutyrolactone and/or its hydrolysis products.

The operating conditions described above are, of course, applicable in the context of this last embodiment.

**Method for the Preparation of a Rejuvenated Catalyst**

The catalyst according to the invention may be a rejuvenated catalyst. This catalyst may be prepared according to the preparation method comprising the following steps:

a) a regenerated catalyst containing a substrate based on alumina or silica or silica-alumina, at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus is brought into contact with at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in a manner such as to obtain a catalyst precursor,

b) said catalyst precursor which is obtained from step a) is dried at a temperature which is lower than 200°C, without being calcined subsequently.

According to step a), a regenerated catalyst is brought into contact with at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in a manner such as to obtain a catalyst precursor. The regenerated catalyst is a catalyst which has been used as a catalyst in a catalytic unit and in particular in hydrotreatment and/or hydrocracking and which has undergone at least one calcining step, so as to burn the coke (regeneration). Regeneration enables the combustion of carbon which is deposited on the catalyst during its industrial use. It may be carried out by any means known to the person skilled in the art. Regeneration is in general carried out at temperatures of between 350°C and 550°C, and most often between 400°C and 520°C, or between 420°C and 520°C, or in fact between 450°C and 520°C, with temperatures which are lower than 500°C often being advantageous.

The regenerated catalyst contains a substrate based on alumina or silica or silica-alumina, at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus in the respective proportions indicated above. Following regeneration (calcining step), the hydrogenating function which comprises the elements from group VIB and from group VIII of the regenerated catalyst is in an oxide form. It may also contain dopants other than phosphorus, as described above.

According to this implementation, contact according to step a) comprises the following successive steps:

a1''') a regenerated catalyst containing a substrate based on alumina or silica or silica-alumina, at least one component of an element from group VIB, at least one component of an element from group VIII, and optionally phosphorus is impregnated by an impregnation solution comprising at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products, in a manner such as to obtain a catalyst precursor,

a2''') optionally, the catalyst precursor which is obtained in step a1''') is allowed to mature.

Preferably, the contact of step a) is carried out by impregnation of the regenerated catalyst by an impregnation solution comprising at least one additive which is selected from 2-acetylbutyrolactone and/or its hydrolysis products in a manner such as to obtain a catalyst precursor.

The additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products may advantageously be deposited in one or more steps either by excess impregnation, or by dry impregnation, or by any other means which is known to the person skilled in the art. Preferably, the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products is/are introduced by dry impregnation, in the presence or absence of a solvent as described above.

Preferably, the solvent in the impregnation solution which is used is water, which facilitates implementation on the industrial scale.

The additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products is/are advantageously introduced into the impregnation solution with the molar ratios for the element from

group VIB or from group VIII described above.

When an additional additive (in addition to the additive(s) selected from 2-acetylbutyrolactone and/or its hydrolysis products) or a group of supplemental additives selected from an organic compound containing oxygen and/or nitrogen and/or sulphur in addition to said additives, the latter may be introduced into the impregnation solution of step a1'''), or in fact by an additional impregnation step at any time of the preparation method before the final drying of step b), it being understood which a calcining step is not carried out after it has been introduced. This compound is introduced in the proportions described above.

According to step a2'''), the catalyst precursor which is obtained in step a1''') is optionally allowed to mature under the maturation conditions described above.

In accordance with step b) of the preparation method according to the invention, the catalyst precursor which has optionally been matured during step a2''') undergoes a drying step at a temperature which is lower than 200°C without a subsequent calcining step, as described above.

**Sulphurization**

Before it is used for the hydrotreatment and/or hydrocracking reaction, it is advantageous to transform the dried catalyst which is obtained according to any one of the introduction methods described in this invention into a sulphurized catalyst so as to form its active species. This step of activation or sulphurization is carried out by methods which are well known to the person skilled in the art and advantageously under a sulpho-reducing atmosphere in the presence of hydrogen and hydrogen sulphide.

At the end of step b) according to the various preparation embodiments of the method according to the invention, said

catalyst which is obtained therefore advantageously undergoes a sulphurization step, without an intermediate calcining step.

Said dried catalyst is advantageously sulphurized in an *ex situ* or *in situ* manner. The sulphurizing agents are $H_2S$ gas or any other compound which contains sulphur and which is used for the activation of hydrocarbon feedstocks for the purposes of sulphurizing the catalyst. Said compounds which contain sulphur are advantageously selected from alkyl disulphides such as, for example, dimethyl disulphide (DMDS); alkyl sulphides such as, for example, dimethyl sulphide; thiols such as, for example, n-butylmercaptan (or 1-butanethiol); polysulphide compounds of the tert-nonyl polysulphide type; or any other compound which is known to the person skilled in the art which makes it possible to obtain good sulphurization of the catalyst. In a preferred manner, the catalyst is sulphurized *in situ* in the presence of a sulphurizing agent and a hydrocarbon feedstock. In a very preferred manner, the catalyst is sulphurized *in situ* in the presence of an additive-containing hydrocarbon feedstock of dimethyl disulphide.

**Method for Hydrotreatment and/or Hydrocracking**

Finally, another object of the invention concerns the use of the catalyst according to the invention or prepared according to the preparation method of the invention in methods for hydrotreating and/or hydrocracking hydrocarbon fractions.

The catalyst according to the invention and which has preferably previously undergone a sulphurization step is advantageously used for reactions for the hydrotreatment and/or hydrocracking of hydrocarbon feedstocks such as petroleum fractions, fractions obtained from coal, or hydrocarbons produced from natural gas, optionally as mixtures , or in fact from a hydrocarbon fraction obtained from biomass and more particularly for the reactions of hydrogenation, hydrodenitrification, hydrodearomatization, hydrodesulphurization, hydrodeoxygenation, hydrodemetallization or hydroconversion of hydrocarbon feedstocks.

In these uses, the catalyst according to the invention and which has preferably previously undergone a sulphurization step has improved activity with respect to the catalysts of the prior art. This catalyst may also advantageously be used during the pre-treatment of feedstocks for catalytic cracking or hydrocracking, or the hydrodesulphurization of residues or the intense hydrodesulphurization of diesel fuels (ULSD, Ultra Low Sulphur Diesel).

Examples of the feedstocks which are used in the hydrotreatment method are gasolines, diesel fuels, vacuum diesel fuels, atmospheric residues, vacuum residues, atmospheric distillates, vacuum distillates, heavy fuels, oils, waxes and paraffins, spent oils, deasphalted crudes or residues, feedstocks obtained from thermal or catalytic conversion methods, lignocellulosic feedstocks or, more generally, feedstocks obtained from biomass, alone or as a mixture. The feedstocks which are treated, and in particular those cited above, generally contain heteroatoms such as sulphur, oxygen, and nitrogen, and for the heavy feedstocks, they most often also contain metals.

The operating conditions which are used in the methods implementing reactions for the hydrotreatment of hydrocarbon feedstocks described above are generally as follows: the temperature is advantageously between 180°C and 450°C, and preferably between 250°C and 440°C; the pressure is advantageously between 0.5 and 30 MPa, and preferably between 1 and 18 MPa; the hourly space velocity is advantageously between 0.1 and 20 $h^{-1}$, and preferably between 0.2 and 5 $h^{-1}$; and the hydrogen/feedstock ratio, expressed in terms of the volume of hydrogen, measured under normal conditions of temperature and pressure, per volume of liquid feedstock, is advantageously between 50 L/L to 5,000 L/L, and preferably 80 to 2,000 L/L.

According to a first embodiment, said hydrotreatment method according to the invention is a method for hydrotreatment, and in particular hydrodesulphurization (HDS), of a diesel fuel

fraction which is carried out in the presence of at least one catalyst according to the invention. The aim of said hydrotreatment method according to the invention is to eliminate the sulphur-containing compounds present in said diesel fuel fraction so as to comply with the environmental standards which are in force, namely an allowed sulphur content which of to 10 ppm. It also makes it possible to reduce the contents of aromatic compounds and nitrogen in the diesel fuel fraction which is to be hydrotreated.

Said diesel fuel fraction which is to be hydrotreated according to the method of the invention contains from 0.02% to 5.0% by weight of sulphur. It is advantageously obtained from straight run distillation (straight run diesel fuel), from a coking unit (coking), from a visbreaking unit , from a steam cracking unit , from a unit for hydrotreatment and/or hydrocracking of heavier feedstocks and/or a catalytic cracking unit (Fluid Catalytic Cracking). Preferably, at least 90% of the compounds in said diesel fuel fraction have a boiling point of between 250°C and 400°C at atmospheric pressure.

The method for the hydrotreatment of said diesel fuel fraction according to the invention is implemented under the following operating conditions: a temperature of between 200°C and 400°C, preferably between 300°C and 380°C; a total pressure of between 2 MPa and 10 MPa, and more preferably of between 3 MPa and 8 MPa; with a ratio of the volume of hydrogen per volume of hydrocarbon feedstock, expressed as the volume of hydrogen, measured under the normal conditions of temperature and pressure, to the volume of liquid feedstock, of between 100 and 600 litres per litre and more preferably between 200 and 400 litres per litre; and an hourly space velocity of between 1 and 10 $h^{-1}$, preferably between 2 and 8 $h^{-1}$. The HSV corresponds to the reciprocal of the contact time which is expressed in hours and is defined by the ratio of the space velocity of liquid hydrocarbon feedstock to the volume of catalyst charged into the reaction unit carrying out the hydrotreatment method according to the invention. The reaction unit carrying out the method for

the hydrotreatment of said diesel fuel fraction according to the invention is preferably operated in a fixed bed, in a moving bed, or in a boiling bed, preferably in a fixed bed.

According to a second mode of use, said method for hydrotreatment and/or hydrocracking according to the invention is a method for hydrotreatment (in particular hydrodesulphurization, hydrodenitrification, hydrogenation of aromatic compounds) and/or for hydrocracking a vacuum distillate fraction carried out in the presence of at least one catalyst according to the invention. Said hydrotreatment and/or hydrocracking method, otherwise known as a hydrocracking pre-treatment method or hydrocracking method according to the invention, is intended, depending on the case, to eliminate the sulphur-containing, nitrogen-containing or aromatic compounds present in said distillate fraction in a manner such as to carry out a pre-treatment before conversion in catalytic cracking or hydroconversion methods, or to hydrocrack the distillate fraction which would previously have been optionally pre-treated if necessary.

A very wide variety of feedstocks can be treated by the methods for hydrotreatment and/or hydrocracking of vacuum distillates described above. Generally, they contain at least 20% by volume and often at least 80% by volume of compounds boiling above 340°C at atmospheric pressure. The feedstock may, for example, be vacuum distillates as well as feedstocks deriving from units for the extraction of aromatic compounds from lubricating oil bases or obtained from solvent dewaxing of lubricating oil bases and/or of deasphalted oils, or in fact the feedstock may be a deasphalted oil or paraffins obtained from the Fischer-Tropsch process, or in fact any mixture of the feedstocks cited above. In general, the feedstocks have a boiling point T5 of more than 340°C at atmospheric pressure, and even better more than 370°C at atmospheric pressure; i.e., 95% of the compounds which are present in the feedstock have a boiling point higher than 340°C, and even better higher than 370°C. The nitrogen content of the feedstocks which are treated in the methods according to the

invention is usually more than 200 ppm by weight, preferably between 500 and 10000 ppm by weight. The sulphur content of the feedstocks which are treated in the methods according to the invention is usually between 0.01% and 5.0% by weight. The feedstock may optionally contain metals (for example, nickel and vanadium). The asphaltenes content is generally less than 3000 ppm by weight.

The hydrotreatment and/or hydrocracking catalyst is generally brought into contact, in the presence of hydrogen, with the feedstocks described above, at a temperature of more than 200°C, often between 250°C and 480°C, advantageously between 320°C and 450°C, preferably between 330°C and 435°C; under a pressure of more than 1 MPa, often between 2 and 25 MPa, in a preferred manner between 3 and 20 MPa; with the space velocity being between 0.1 and 20.0 $h^{-1}$ and preferably 0.1-6.0 $h^{-1}$, preferably 0.2-3.0 $h^{-1}$; and the quantity of hydrogen introduced is such that the volumetric ratio in litres of hydrogen/litre of hydrocarbon, expressed in terms of hydrogen volume, measured under the normal conditions of temperature and pressure, to the volume of liquid feedstock, is between 80 and 5000 L/L and most often between 100 and 2000 L/L. These operating conditions which are used in the methods according to the invention generally make it possible to reach conversions per pass into products with boiling points of lower than 340°C at atmospheric pressure, and even better, lower than 370°C at atmospheric pressure, of more than 15%, and in an even more preferred manner between 20% and 95%.

The methods for the hydrotreatment and/or hydrocracking of vacuum distillates which implement the catalysts according to the invention cover the fields of pressure and conversion ranging from mild hydrocracking to high-pressure hydrocracking. The term “mild hydrocracking” is defined as hydrocracking resulting in moderate conversions, generally less than 40%, and operating at low pressure, generally between 2 MPa and 6 MPa.

The catalyst according to the invention may be used alone, in one or more fixed bed catalytic beds, in one or more reactors,

in what is known as a once-through hydrocracking operation, with or without a liquid recycle of the unconverted fraction, or in fact in what is known as a two-step hydrocracking operation, optionally associated with a hydrorefining catalyst located upstream of the catalyst of the present invention.

According to a third mode of use, said hydrotreatment and/or hydrocracking method according to the invention is advantageously implemented as a pre-treatment in a fluidized bed catalytic cracking method (or FCC method, Fluid Catalytic Cracking). The operating conditions for the pre-treatment in terms of range of temperature, pressure, hydrogen recycle ratio, hourly space velocity are generally identical to those described above for the methods for the hydrotreatment and/or hydrocracking of vacuum distillates. The FCC method may be executed in a conventional manner which is known to the person skilled in the art under adequate cracking conditions for the purposes of producing hydrocarbon products with a lower molecular weight. A summary description of catalytic cracking will be found in, for example, ULLMANS ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY, VOLUME A 18, 1991, pages 61 to 64.

According to a fourth mode of use, said hydrotreatment and/or hydrocracking method according to the invention is a method for hydrotreatment (in particular hydrodesulphurization) of a gasoline fraction in the presence of at least one catalyst according to the invention.

In contrast to other hydrotreatment methods, the hydrotreatment (in particular the hydrodesulphurization) of gasolines is supposed to make it possible to meet two competing constraints: to ensure deep hydrodesulphurization of gasolines and to limit the hydrogenation of unsaturated compounds which are present so as to limit the loss of octane number.

The feedstock is generally a hydrocarbon fraction with a distillation range of between 30°C and 260°C. Preferably, this hydrocarbon fraction is a gasoline-type fraction. In a very

preferred manner, the gasoline fraction is an olefinic gasoline fraction obtained, for example, from a catalytic cracking unit (Fluid Catalytic Cracking).

The hydrotreatment method consists in bringing the hydrocarbon fraction into contact with the catalyst according to the invention and with hydrogen under the following conditions: at a temperature of between 200°C and 400°C, preferably between 230°C and 330°C; at a total pressure of between 1 and 3 MPa, preferably between 1.5 and 2.5 MPa; at an hourly space velocity (HSV), defined as the volumetric flow rate of feedstock with respect to the volume of catalyst, of between 1 and 10 $h^{-1}$, preferably between 2 and 6 $h^{-1}$, and with a hydrogen/gasoline feedstock volumetric ratio of between 100 and 600 NL/L, preferably between 200 and 400 NL/L.

The method for the hydrotreatment of gasolines may be carried out in one or more fixed bed type or boiling bed type reactors disposed in series. If the method is implemented by means of at least two reactors arranged in series, it is possible to provide a device for eliminating $H_2S$ from the effluent which is obtained from the first hydrodesulphurization reactor before treating said effluent in the second hydrodesulphurization reactor.

The following examples demonstrate the significant increase in activity on the catalysts prepared according to the method of the invention with respect to the catalysts of the prior art and clarify the invention without, however, limiting its scope.

**Examples**

Example 1: Preparation of CoMoP catalysts on alumina without C1 and C2 organic compounds (not in accordance with the invention).

Cobalt, molybdenum, and phosphorus are added to an alumina substrate which has a BET surface area of 230 $m^2/g$, a pore volume obtained by mercury porosimetry of 0.78 mL/g, and a mean pore diameter of 11.5 nm, defined as the median diameter by volume,

by mercury porosimetry and in the “extruded” form. The impregnation solution is prepared by dissolving molybdenum oxide (21.1 g) and cobalt hydroxide (5.04 g) in 11.8 g of an aqueous solution of 85% phosphoric acid and water at 90°C. After dry impregnation, the extrudates are allowed to mature in a water-saturated atmosphere for 24 hours at ambient temperature, and then they are dried at 90°C for 16 hours. The dried catalytic precursor obtained in this manner is denoted C1. Calcining of the catalytic precursor C1 at 450°C for 2 hours results in the calcined catalyst C2. The final composition of the catalysts C1 and C2 expressed in the form of oxides and with respect to the dry catalyst mass is then as follows: MoO3 = 19.5 ± 0.2% by weight, CoO = 3.8 ± 0.1% by weight, and $P_2O_5$ = 6.7 ± 0.1% by weight.

Example 2: Preparation of CoMoP on alumina catalysts C3 (not in accordance with the invention), C4 (in accordance with the invention) by co-impregnation.

Cobalt, molybdenum, and phosphorus are added to the alumina substrate described previously in Example 1 and in the “extruded” form. The impregnation solution is prepared dissolving molybdenum oxide (28.28 g) and cobalt hydroxide (6.57 g) in 15.85 g of an aqueous solution of 85% phosphoric acid and water at 90°C. After homogenization of the preceding mixture, 38 g of citric acid was added before adjustment of the volume of the solution to the pore volume of the substrate by the addition of water. The (citric acid)/Mo molar ratio is equal to 1 mol/mol and which of (citric acid)/Co is equal to 2.7 mol/mol. After dry impregnation, the extrudates are allowed to mature in a water-saturated atmosphere for 24 hours at ambient temperature, and then they are dried at 120°C for 16 hours. The dried catalytic precursor obtained in this manner is denoted C3. The final composition of the catalyst C3, expressed in the form of oxides and with respect to the dry catalyst mass, is then as follows: MoO3 = 19.6 ± 0.2% by weight, CoO = 3.7 ± 0.1% by weight, and $P_2O_5$ = 6.7 ± 0.1% by weight.

The catalyst C4 according to the invention is prepared as follows. Cobalt, molybdenum, and phosphorus are added to the alumina substrate described in Example 1 and in the "extruded" form. An impregnation solution has been prepared by dissolving molybdenum oxide (58.5 g) and cobalt hydroxide (13.6 g) in 32.8 g of an aqueous solution of 85% phosphoric acid and water at 90°C. After homogenization of the preceding mixture, 2-acetylbutyrolactone was added to the solution at 0.5 mole per mole of molybdenum or 1.4 mole per mole of cobalt to produce the catalyst C4. The volume of the solution was adjusted to the pore volume of the substrate by the addition of water before each impregnation. After dry impregnation, the extrudates of the two catalysts were allowed to mature in a water-saturated atmosphere for 24 hours at ambient temperature, and then dried at 120°C for 16 hours. The final composition of the catalyst C4 which is expressed in the form of oxides and with respect to the dry catalyst mass is then as follows: MoO3 = 19.4 ± 0.2% by weight, CoO = 3.6 ± 0.1% by weight, and $P_2O_5$ = 6.8 ± 0.1% by weight.

Example 3: Preparation of CoMoP on alumina catalyst C5 (in accordance with the invention) by pre-impregnation.

13 g of 2-acetylbutyrolactone diluted in water is added to the alumina substrate previously described in Example 1 and in the "extruded" form in a manner such as to obtain a solution with a total volume equal to the pore volume of the substrate. The solution obtained in this manner is then dry impregnated onto the substrate before observing a maturation period of 3 hours in a water-saturated atmosphere and at ambient temperature, followed by drying at 120°C for 2 hours. The modified substrate is then impregnated by a new impregnation solution which is prepared by dissolving molybdenum oxide (29.25 g) and cobalt hydroxide (6.80 g) in 16.4 g of a hot aqueous solution of 85% phosphoric acid and water, taking care to adjust - by adding water - the volume of this latter solution to the pore volume of the preceding modified substrate. After dry impregnation, the extrudates were allowed to mature in a water-saturated atmosphere for 24 hours at ambient temperature, then dried at

120°C for 16 hours to produce the catalyst C5. The final composition of the catalyst C5 expressed in the form of oxides and with respect to the dry catalyst mass is then as follows: MoO3 = 19.3 ± 0.2% by weight, CoO = 3.5 ± 0.1% by weight, and $P_2O_5$ = 6.6 ± 0.1% by weight. The quantities involved are such which the quantity of 2-acetylbutyrolactone is 0.5 mole per mole of molybdenum or 1.4 mole per mole of cobalt.

Example 4: Diesel fuel HDS evaluation of catalysts C1, C2 and C3 (not in accordance with the invention) and catalysts C4 and C5 (in accordance with the invention)

The catalysts C1, C2 and C3 (not in accordance with the invention) and catalysts C4 and C5 (in accordance with the invention) underwent diesel fuel HDS testing.

Characteristics of the diesel fuel feedstock used: density at 15°C: 0.8522 g/cm³, sulphur: 1.44% by weight.

Simulated Distillation:

- IP: 155°C
- 10%: 247°C
- 50%: 315°C
- 90%: 392°C
- EP: 444°C

The test is carried out in an isothermal pilot reactor with a fixed flushed bed, with the fluids circulating from bottom to top. After sulphurization in situ at 350°C in the pressurized unit by means of the diesel fuel of the test to which 2% by weight of dimethyl disulphide is added, the hydrodesulphurization test was carried out under the following operating conditions: a total pressure of 7 MPa, a catalyst

volume of 30 $cm^3$, a temperature of 330°C to 360°C, a hydrogen flow rate of 24 L/h, and a feedstock flow rate of 60 $cm^3/h$.

The catalytic performances of the tested catalysts are provided in Table 1. They are expressed in degrees Celsius starting from a comparative catalyst selected as a reference (C2): they correspond to the temperature difference to be applied in order to reach 50 ppm of sulphur in the effluent. A negative value means that the target sulphur content is reached for a lower temperature, and there is therefore an increase in activity. A positive value means that the sulphur content target is reached for a higher temperature, and there is therefore a loss of activity. The results obtained are recorded in Table 1.

Table 1 clearly shows the increase in the catalytic effect provided by 2-acetylbutyrolactone. In fact, the C4 and C5 catalysts (according to the invention) have higher activities than those obtained for all of the other catalysts which were evaluated. 2-acetylbutyrolactone therefore provides an increase in catalytic activity irrespective of its method of introduction.

The advantage of the catalyst according to the invention is significant even though it has a smaller proportion of organic compound than the catalyst C3, and thus the inherent effectiveness of 2-acetylbutyrolactone is greater than that of the other compounds for which it is necessary to introduce a larger proportion of compound in order to observe a significant catalytic effect.

*Table 1: Iso-Volume Relative Activity for Diesel-Fuel Hydrodesulphurization of C1, C2 and C3 Catalysts (Not in accordance with the Invention) and Catalysts C4 and C5 (In accordance with the Invention) with respect to the Catalyst C2 (Not in accordance)*

| Catalyst (for comparison or according to the invention) | Organic compound used and molar ratio/Mo | Method for introduction of organic compound (post-/co-/pre-impregnation) | Heat treatment | HDS activity |
|---|---|---|---|---|
| C1 (comp) | None | Not applicable | Dried 120°C | Base + 1.0°C |
| C2 (comp) | None | Not applicable | Calcined | Base |
| C3 (comp) | Citric acid - 1.0 | CO | Dried 120°C | Base - 2.9°C |
| **C4 (inv)** | 2-acetylbutyrolactone **- 0.5** | **CO** | **Dried 120°C** | **Base - 4.9°C** |
| **C5 (inv)** | 2-acetylbutyrolactone **- 0.5** | **PRE** | **Dried 120°C** | **Base - 5.1°C** |

Patentkrav

1. Katalysator, der omfatter en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid, mindst et grundstof fra gruppe VIII, mindst et grundstof fra gruppe VIB og mindst et additiv, der er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre.

2. Katalysator ifølge krav 1, hvor indholdet af grundstof fra gruppe VIB ligger mellem 5 og 40 vægt-%, udtrykt som oxid af metal fra gruppe VIB i forhold til katalysatorens samlede vægt, og indholdet af grundstof fra gruppe VIII ligger mellem 1 og 10 vægt-%, udtrykt som oxid af metal fra gruppe VIII i forhold til katalysatorens samlede vægt.

3. Katalysator ifølge krav 1 eller 2, hvor molforholdet mellem grundstof fra gruppe VIII og grundstof fra gruppe VIB i katalysatoren ligger mellem 0,1 og 0,8.

4. Katalysator ifølge et af kravene 1 til 3, som i øvrigt indeholder phosphor, idet phosphorindholdet ligger mellem 0,1 og 20 vægt-%, udtrykt som $P_2O_5$ i forhold til katalysatorens samlede vægt, og molforholdet mellem phosphor og grundstof fra gruppe VIB i katalysatoren er større end eller lig med 0,05.

5. Katalysator ifølge et af kravene 1 til 4, hvor det samlede indhold af additiv(er), der er valgt blandt 2-acetylbutyrolacton, 2- (2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre, ligger mellem 1 og 45 vægt-% i forhold til katalysatorens samlede vægt.

6. Katalysator ifølge et af kravene 1 til 5, som i øvrigt indeholder en anden organisk forbindelse ud over additivet valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre, hvilken organiske forbindelse indeholder oxygen og/eller nitrogen og/eller svovl.

7. Katalysator ifølge krav 6, hvor den organiske forbindelse er valgt blandt en forbindelse, der omfatter en eller flere kemiske grupper, som er valgt blandt en gruppe af typen carboxyl, alkohol, thiol, thioether, sulfon, sulfoxid, ether, aldehyd, keton, ester, carbonat, amin, nitril, imid, oxim, urea og amid.

8. Katalysator ifølge krav 7, hvor den organiske forbindelse er valgt blandt triethylenglycol, diethylenglycol, ethylenglycol, ethylendiamintetraeddikesyre (EDTA), maleinsyre, malonsyre, citronsyre, dimethylformamid, N-methylpyrrolidon, propylencarbonat, bicin eller tricin.

9. Katalysator ifølge et af kravene 1 til 8, hvor bæreren indeholder fra 0,1 til 50 vægt-% zeolit.

10. Katalysator ifølge et af kravene 1 til 9, kendetegnet ved, at den i det mindste delvist er svovlholdig.

11. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 10, hvilken fremgangsmåde omfatter de følgende trin:

a) mindst en komponent af et grundstof fra gruppe VIB, mindst en komponent af et grundstof fra gruppe VIII, mindst et additiv, der er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethylsyre)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre og eventuelt phosphor bringes i kontakt med en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid, eller en regenereret katalysator indeholdende en bærer på basis af aluminiumoxid eller silica-aluminiumdioxid, mindst en komponent af et grundstof fra gruppe VIB, mindst en komponent af et grundstof fra gruppe VIII og eventuelt phosphor bringes i kontakt med mindst et additiv, der er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre, for at opnå en katalysatorforløber

b) den katalysatorforløber, der er et resultat af trin a), tørres ved en temperatur på under 200 °C, uden at den yderligere

kalcineres.

12. Fremgangsmåde ifølge krav 11, hvorved trin a) er det følgende trin:

a') en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid imprægneres med mindst et grundstof fra gruppe VIB, mindst et grundstof fra gruppe VIII, mindst et additiv, der er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre og eventuelt phosphor, for at opnå en katalysatorforløber.

13. Fremgangsmåde ifølge krav 11, hvorved trin a) omfatter de følgende trin:

a1) en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid imprægneres med mindst en opløsning, der indeholder mindst et grundstof fra gruppe VIB, mindst et grundstof fra gruppe VIII og eventuelt phosphor for at opnå en imprægneret bærer

a2) den i trin a1) opnåede imprægnerede bærer tørres ved en temperatur på under 200 °C for at opnå en tørret, imprægneret bærer, og eventuelt kalcineres den tørrede, imprægnerede bærer for at opnå en kalcineret, imprægneret bærer

a3) den i trin a2) opnåede imprægnerede, tørrede og eventuelt kalcinerede bærer imprægneres med en imprægneringsopløsning, der omfatter mindst et additiv, som er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre, for at opnå en katalysatorforløber

a4) den i trin a3) opnåede katalysatorforløber får eventuelt lov til at modne.

14. Fremgangsmåde ifølge krav 11, hvorved trin a) omfatter de følgende trin:

a1') der fremstilles en bærer, der omfatter mindst et additiv, som er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre og eventuelt mindst en del af phosphoret

a2') den i trin a1') opnåede bærer imprægneres med en

imprægneringsopløsning, der omfatter mindst et grundstof fra gruppe VIB, mindst et grundstof fra gruppe VIII og eventuelt phosphor, for at opnå en katalysatorforløber

a3') den i trin a2') opnåede katalysatorforløber får eventuelt lov til at modne.

15. Fremgangsmåde ifølge krav 11, hvorved trin a) omfatter de følgende trin:

a1") en opløsning, der indeholder mindst et grundstof fra gruppe VIB, mindst et grundstof fra gruppe VIII, mindst en organisk forbindelse indeholdende oxygen og/eller nitrogen og/eller svovl, og eventuelt phosphor bringes i kontakt med en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid for at opnå en imprægneret bærer

a2") den imprægnerede bærer, der er et resultat af trin a1"), tørres ved en temperatur på under 200 °C, uden at den yderligere kalcineres, for at opnå en tørret, imprægneret bærer

a3") den tørrede, imprægnerede bærer, der er et resultat af trin a2"), bringes i kontakt med en opløsning af mindst en organisk forbindelse, der indeholder oxygen og/eller nitrogen og/eller svovl, og som kan være identisk med eller forskellig fra den, der er blevet anvendt i trin a1"), for at opnå en katalysatorforløber

a4") den i trin a3") opnåede katalysatorforløber får eventuelt lov til at modne

og mindst en af de organiske forbindelser fra trin a1") eller fra trin a3") er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre.

16. Fremgangsmåde ifølge krav 11, hvorved trin a) omfatter de følgende trin:

a1'") en regenereret katalysator, der indeholder en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid, mindst en komponent af et grundstof fra gruppe VIB, mindst en komponent af et grundstof fra gruppe VIII og eventuelt phosphor, imprægneres med en imprægneringsopløsning, der omfatter mindst et additiv, som er valgt blandt 2-acetylbutyrolacton, 2-(2-

hydroxyethyl)-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre for at opnå en katalysatorforløber a2"') den i trin a1"')opnåede katalysatorforløber får eventuelt lov til at modne.

17. Fremgangsmåde ifølge et af kravene 11 til 16, hvorved det samlede molforhold mellem additiv(er), der er valgt blandt 2-acetylbutyrolacton, 2-(2-hydroxyethyl-3-oxobutansyre og/eller 3-hydroxy-2-(2-hydroxyethyl)-2-butensyre, og grundstof(fer) i gruppe VIII ligger mellem 0,1 og 5,0 mol/mol.

18. Anvendelse af katalysatoren ifølge et af kravene 1 til 10, eller som er fremstillet ifølge et af kravene 11 til 17, i en fremgangsmåde til hydrogenbehandling og/eller hydrokrakning af carbonhydridfraktioner.