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(54) Benævnelse: **KATALYSATOR PÅ BASIS AF GAMMA-VALEROLACTON OG/ELLER HYDROLYSEPRODUKTER HERAF OG ANVENDELSE HERAF I EN FREMGANGSMÅDE TIL HYDROGENBEHANDLING OG/ELLER HYDROKRAKNING**

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**EP-A1- 0 482 817**  
**WO-A1-2005/035691**  
**US-A1- 2014 305 842**

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## Description

The invention relates to a catalyst impregnated with  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid, to the method for preparing same and to the use thereof in the field of hydrotreating and/or hydrocracking.

Usually, a catalyst for the hydrotreating of hydrocarbon cuts has the function of removing the sulfur-based or nitrogen-based compounds contained therein in order, for example, to make a petroleum product meet the required specifications (sulfur content, aromatic content, etc.) for a given application (motor vehicle fuel, gasoline or gas oil, domestic fuel oil, jet fuel). It may also be a matter of pretreating this feedstock so as to remove impurities therefrom or of hydrogenating it before subjecting it to various transformation processes to modify its physicochemical properties, for instance reforming, vacuum distillate hydrocracking, catalytic cracking, atmospheric or vacuum residue hydroconversion processes. The composition and use of hydrotreating catalysts is particularly well described in the article by B.S. Clausen, H.T. Topsøe and F.E. Massoth, taken from the publication *Catalysis Science and Technology*, volume 11 (1996), Springer-Verlag.

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The tightening of the motor vehicle pollution standards in the European Community (Official Journal of the European Union, L76, March 22, 2003, Directive 2003/70/EC, pages L76/10-L76/19) obliged refiners to drastically reduce the sulfur content of diesel and gasoline fuels (to a maximum 10 parts per million by weight (ppm) of sulfur as of January 1, 2009, as opposed to 50 ppm as of January 1, 2005). Moreover, refiners are obliged to use feedstocks that are increasingly resistant to hydrotreating processes, partly because crude oils are increasingly heavy and consequently contain more and more impurities, and partly because of the increase in conversion processes in refineries. This is because they generate cuts that are more difficult to hydrotreat than the cuts obtained directly from atmospheric

distillation. The expression "more difficult to hydrotreat" usually means higher operating temperatures to achieve the same sulfur content in the effluent, and consequently cycle times that can be reduced. These feedstocks require catalysts which 5 have greatly improved hydrodesulfurizing and hydrogenating functions relative to conventional catalysts.

In addition, conversion processes such as catalytic cracking or hydrocracking use catalysts bearing an acidic function, which 10 makes them particularly sensitive to the presence of nitrogen-based impurities, and particularly basic nitrogen compounds. It is thus necessary to use pretreatment catalysts for these feedstocks in order to remove these compounds.

15 Conventional hydrotreating catalysts generally comprise an oxide support and an active phase based on group VIB and VIII metals in the oxide forms thereof and also phosphorus. The preparation of these catalysts generally comprises a step of impregnating the metals and the phosphorus on the support, followed by drying 20 and calcining enabling the active phase to be obtained in the oxide forms thereof. Before the use thereof in a hydrotreating and/or hydrocracking reaction, these catalysts are generally subjected to sulfurization in order to form the active species.

25 The addition of an organic compound to the hydrotreating catalysts to improve their activity has been recommended by those skilled in the art, notably for catalysts which have been prepared by impregnation followed by drying without subsequent calcination. These catalysts are often referred to as 30 "impregnated dried catalysts".

Many documents describe the use of various ranges of organic compounds as additives, such as organic compounds containing nitrogen and/or organic compounds containing oxygen.

35 A family of compounds that is now well known in the literature concerns chelating nitrogen compounds (EP 0 181 035, EP 1 043 069 and US 6 540 908) with, for example,

ethylenediaminetetraacetic acid (EDTA), ethylenediamine, diethylenetriamine or nitrilotriacetic acid (NTA)

In the family of organic compounds containing oxygen, the use  
5 of monoalcohols, diols or polyols which are optionally  
etherified is described in WO 96/41848, WO 01/76741, US 4 012  
340, US 3 954 673, EP 601 722 and WO 2005/035691. The prior art  
less frequently mentions additives including ester functions (EP  
1 046 424, WO 2006/077 326).

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Several patents are also found which claim the use of carboxylic  
acids (EP 1 402 948, EP 0 482 817). In particular, in EP 0482  
817, citric acid, and also tartaric, butyric, hydroxyhexanoic,  
15 malic, gluconic, glyceric, glycolic and hydroxybutyric acids  
have been described. The specificity lies in the drying  
operation, which must be performed at a temperature below 200°C.

US 2014/0 305 842 describes the use of heterocyclic compounds,  
containing oxygen or nitrogen in the ring, such as lactams,  
20 oxacycloalkanes or lactones. With regard notably to lactones,  
said document cites  $\beta$ -propiolactone,  $\gamma$ -butyrolactone and  $\delta$ -  
valerolactone.

However, none of the documents relating to additives describes  
25 the use of  $\gamma$ -valerolactone, or even 4-hydroxyvaleric acid or 2-  
pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, which may  
be obtained directly or indirectly by hydrolysis of  $\gamma$ -  
valerolactone.

30 Irrespective of the compounds chosen, the modifications induced  
do not always make it possible to sufficiently increase the  
performance of the catalyst in order to meet the specifications  
concerning the sulfur and/or nitrogen contents of fuels.  
Furthermore, it is often very difficult to deploy them  
35 industrially since the methods are so complex to implement.

Consequently, it appears essential, for catalyst manufacturers, to find novel hydrotreating and/or hydrocracking catalysts with improved performance.

5 **Summary**

The invention relates to a catalyst comprising a support based on alumina or silica or silica-alumina, at least one group VIII element, at least one group VIB element and at least one additive 10 chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.

The Applicant has, in point of fact, found that the use of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid as 15 organic additive(s) on a catalyst containing at least one group VIII element and at least one group VIB element makes it possible to obtain a hydrotreating and/or hydrocracking catalyst which shows improved catalytic performance.

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Specifically, the catalyst according to the invention shows increased activity relative to the known catalysts that are not impregnated and the known impregnated dried catalysts. Typically, by means of increasing the activity, the temperature required 25 to achieve a desired sulfur or nitrogen content (for example 10 ppm of sulfur in the case of a gas oil feedstock, in ULSD or ultra-low sulfur diesel mode) may be lowered. Similarly, the stability is increased, since the cycle time is prolonged by means of reducing the required temperature.

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The catalyst according to the present invention is, in addition, easy to prepare due to the high solubility of  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and 4-pentenoic acid in water or any other polar protic solvent. In 35 addition, the catalyst according to the invention may be prepared from a biomass starting material preferably predominantly containing  $\gamma$ -valerolactone (J-C. Serrano-Ruiz in Green Chem, 2010, 12, 574-577 or W.R.H. Wright and R. Palkovits

in ChemSusChem 2012, 5, 9, 1657-1667) while at the same time remaining at an acceptable cost price.

The content of group VIB element is between 5% and 40% by weight expressed as group VIB metal oxide relative to the total weight of the catalyst, and the content of group VIII element is between 1% and 10% by weight expressed as group VIII metal oxide relative to the total weight of the catalyst.

According to one variant, the mole ratio of group VIII element to group VIB element in the catalyst is between 0.1 and 0.8.

According to one variant, the catalyst also contains phosphorus, the phosphorus content being between 0.1% and 20% by weight expressed as P<sub>2</sub>O<sub>5</sub> relative to the total weight of the catalyst, and the ratio of phosphorus to the group VIB element in the catalyst is greater than or equal to 0.05.

The total content of additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid is between 1% and 35% by weight relative to the total weight of the catalyst.

According to one variant, the catalyst also contains an organic compound other than the additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, said organic compound containing oxygen and/or nitrogen and/or sulfur. According to this variant, the organic compound is preferably chosen from a compound including one or more chemical functions chosen from carboxylic, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide functions. Preferably, it is chosen from triethylene glycol, diethylene glycol, ethylenediaminetetraacetic acid (EDTA), maleic acid, citric acid, dimethylformamide, bixin, or tricin.

According to one variant, the support contains from 0.1% to 50% by weight of zeolite.

According to one variant, the catalyst is at least partially sulfurized.

5 The invention also relates to the process for preparing said catalyst, comprising the following steps:

a) at least one component of a group VIB element, at least one component of a group VIII element, at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid,

10 3-pentenoic acid or 4-pentenoic acid and optionally phosphorus are placed in contact with a support based on alumina or silica or silica-alumina, or a regenerated catalyst containing a support based on alumina or silica or silica-alumina, at least one component of a group VIB element, at least one component of

15 a group VIII element and optionally phosphorus are placed in contact with at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, so as to obtain a catalyst precursor,

b) said catalyst precursor derived from step a) is dried at a

20 temperature below 200°C, without subsequently calcining it.

According to one variant, step a) is the following step:

a') a support based on alumina or silica or silica-alumina is impregnated with at least one solution containing at least one group VIB element, at least one group VIII element, at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, and optionally phosphorus, so as to obtain a catalyst precursor.

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

a1) a support based on alumina or silica or silica-alumina is impregnated with at least one solution containing at least one group VIB element, at least one group VIII element and optionally phosphorus, to obtain an impregnated support,

a2) the impregnated support obtained in step a1) is dried at a temperature below 200°C to obtain a dried impregnated support,

and optionally the dried impregnated support is calcined to obtain a calcined impregnated support,

5 a3) the dried and optionally calcined impregnated support obtained in step a2) is impregnated with an impregnating solution comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid so as to obtain a catalyst precursor,

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

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

15 a1') a support is prepared comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid and optionally at least part of the phosphorus,

20 a2') the support obtained in step a1') is impregnated with an impregnating solution comprising at least one group VIB element, at least one group VIII element and optionally phosphorus so as to obtain a catalyst precursor,

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

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

30 a1'') a solution containing at least one group VIB element, at least one group VIII element, at least one organic compound containing oxygen and/or nitrogen and/or sulfur, and optionally phosphorus is placed in contact by co-impregnation with a support based on alumina or silica or silica-alumina so as to obtain an impregnated support,

35 a2'') the impregnated support from step a1'') is dried at a temperature below 200°C, without subsequently calcining it, to obtain a dried impregnated support,

a3'') the dried impregnated support from step a2'') is placed in contact with a solution of an organic compound containing oxygen and/or nitrogen and/or sulfur which is

identical to or different from the one used in step a1''), so as to obtain a catalyst precursor,

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

5 and at least one of the organic compounds of step a1'') or of step a3'') is chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.

According to one variant, when it is desired to prepare the 10 catalyst according to the invention from a regenerated catalyst, step a) of the preparation process comprises the following steps:

a1''') a regenerated catalyst containing a support based on alumina or silica or silica-alumina, at least one component of a group VIB element, at least one component of a group VIII 15 element and optionally phosphorus is impregnated with an impregnating solution comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid so as to obtain a catalyst precursor,

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

According to one variant, the total mole ratio of the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic 25 acid, 3-pentenoic acid or 4-pentenoic acid to the group VIII element(s) is between 0.1 and 5.0 mol/mol.

The invention also relates to the use of the catalyst according to the invention or prepared according to the preparation 30 process according to the invention in a process for the hydrotreating and/or hydrocracking of hydrocarbon cuts.

In the text hereinbelow, the groups of chemical elements are given according to the CAS classification (CRC Handbook of 35 Chemistry and Physics, published by CRC Press, editor-in-chief D.R. Lide, 81st edition, 2000-2001). For 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 "hydrotreating" refers to reactions notably encompassing hydrodesulfurization (HDS), hydrodeazotization (HDA) and hydrogenation of aromatics (HOA).

5

#### Detailed description of the invention

##### Catalyst

10 The catalyst according to the invention is a catalyst impregnated with at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid. More particularly, the catalyst according to the invention comprises a support based 15 on alumina or silica or silica-alumina, at least one group VIII element, at least one group VIB element and at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, and in which the content of the group VIB element is between 5% and 40% by weight 20 expressed as group VIB metal oxide relative to the total weight of the catalyst and the content of the group VIII element is between 1% and 10% by weight expressed as group VIII metal oxide relative to the total weight of the catalyst, and the total content of additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid is between 1% and 35% by weight relative to the 25 total weight of the catalyst.

30 The catalyst according to the invention may be a fresh catalyst, i.e. a catalyst that has not been used beforehand as catalyst in a catalytic unit and notably in hydrotreating and/or hydrocracking.

35 The catalyst according to the invention may also be a rejuvenated catalyst. The term "rejuvenated catalyst" means a catalyst which has been used as catalyst in a catalytic unit and notably in hydrotreating and/or hydrocracking and which has been subjected to at least one step of calcination in order to burn off the

coke (regeneration). This rejuvenated catalyst is then impregnated with at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid 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) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.

10

The hydrogenating function of said catalyst, also known as the active phase, is provided by at least one group VIB element and by at least one group VIII element.

15 The preferred group VIB elements are molybdenum and tungsten. The preferred group VIII elements are non-noble elements and in particular cobalt and nickel. Advantageously, the hydrogenating function is chosen from the group formed by the combinations of the elements cobalt-molybdenum, nickel-molybdenum, nickel-20 tungsten or nickel-cobalt-molybdenum, or nickel-molybdenum-tungsten.

25 In the case where substantial hydrodesulfurization or hydrodeazotization activity or substantial hydrogenation activity on aromatics is desired, the hydrogenating function is advantageously provided 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 such as vacuum distillates or heavier distillates, combinations 30 of cobalt-nickel-molybdenum type may be advantageously used.

The total content of group VIB and group VIII elements is advantageously greater than 6% by weight expressed as oxide relative to the total weight of the catalyst.

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The content of group VIB element is between 5% and 40% by weight, preferably between 8% and 35% by weight, and more preferably

between 10% and 30% by weight expressed as group VIB metal oxide relative to the total weight of the catalyst.

5 The content of group VIII element is between 1% and 10% by weight, preferably between 1.5% and 9% by weight, and more preferably between 2% and 8% by weight expressed as group VIII metal oxide relative to the total weight of the catalyst.

10 The mole ratio of group VIII element to group VIB element in the catalyst is preferentially between 0.1 and 0.8, preferably between 0.15 and 0.6 and even more preferably between 0.2 and 0.5.

15 The catalyst according to the invention advantageously also comprises phosphorus as dopant. The dopant is an added element which in itself has no catalytic nature but which increases the catalytic activity of the active phase.

20 The phosphorus content in said catalyst is preferably between 0.1% and 20% by weight expressed as  $P_2O_5$ , preferably between 0.2% and 15% by weight expressed as  $P_2O_5$ , and very preferably between 0.3% and 10% by weight expressed as  $P_2O_5$ .

25 The mole ratio of phosphorus to the group VIB element 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 0.08 and 0.7 and very preferably between 0.08 and 0.5.

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

35 When the catalyst contains boron, the boron content is preferably between 0.1% and 10% by weight expressed as boron oxide, preferably between 0.2% and 7% by weight, and very preferably 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 as fluorine, preferably between

0.2% and 7% by weight, and very preferably 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 as boron oxide and fluorine, preferably between 0.2% and 7% by weight and very preferably between 0.2% and 5% by weight.

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

When the support for said catalyst is based on alumina, it contains more than 50% of alumina and, in general, it contains 15 only alumina or silica-alumina as defined below.

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

20 The alumina support advantageously has a total pore volume of between 0.1 and 1.5  $\text{cm}^3 \cdot \text{g}^{-1}$ , preferably between 0.4 and 1.1  $\text{cm}^3 \cdot \text{g}^{-1}$ . 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 book by Rouquerol F., Rouquerol J., 25 Singh K., "Adsorption by Powders & Porous Solids: Principle, Methodology and Applications", Academic Press, 1999, for example by means of a Micromeritics™ brand Autopore III™ model machine.

30 The specific surface area of the alumina support is advantageously between 5 and 400  $\text{m}^2 \cdot \text{g}^{-1}$ , preferably between 10 and 350  $\text{m}^2 \cdot \text{g}^{-1}$ , more preferably between 40 and 350  $\text{m}^2 \cdot \text{g}^{-1}$ . The specific surface area is determined in the present invention by the BET method according to the standard ASTM D3663, method described in the same book cited above.

35

In another preferred case, the support for said catalyst is a silica-alumina containing at least 50% by weight of alumina. The silica content in the support is at most 50% by weight, usually

less than or equal to 45% by weight, preferably less than or equal to 40% by weight.

Sources of silicon are well known to those skilled in the art.

5 Examples that may be mentioned include silicic acid, silica in powder form or in colloidal form (silica sol) and tetraethyl orthosilicate  $\text{Si(OEt)}_4$ .

When the support for said catalyst is based on silica, it 10 contains more than 50% by weight of silica and, generally, it contains only silica.

According to a particularly preferred variant, the support consists of alumina, silica or silica-alumina.

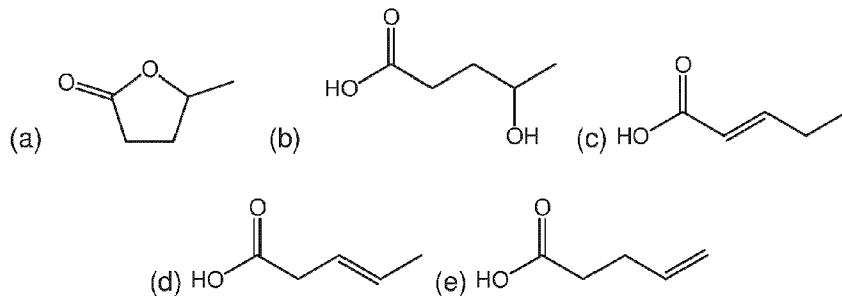
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The support may also advantageously further contain from 0.1% to 50% by weight of zeolite. In this case, any source of zeolite and any associated preparation method known to those skilled in the art may be incorporated. Preferably, the zeolite is chosen 20 from the group FAU, BEA, ISV, IWR, IWW, MEI, UWY and preferably, the zeolite is chosen from the group FAU and BEA, such as Y and/or beta zeolite.

In certain particular cases, the support may also contain at 25 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 chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid or 30 another additive containing oxygen) and/or nitrogen and/or sulfur which have been introduced independently of the impregnations (for example introduced during the preparation of the support).

35 The support is advantageously in the form of beads, extrudates, pellets or irregular and nonspherical agglomerates, the specific shape of which may result from a crushing step.

The catalyst according to the invention also comprises at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.  $\gamma$ -Valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and 4-pentenoic acid correspond, respectively, to the following formulae (a), (b), (c), (d) and (e) described below:



20 2-Pentenoic acid and 3-pentenoic acid may be in the form of the E or Z isomer or a mixture of the two isomers.

The presence of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid on the catalyst makes it possible to observe increased activity relative to known non-impregnated catalysts and impregnated dried catalysts.

Without being bound by any theory, it will be noted that 4-hydroxyvaleric acid or 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid may be obtained directly or indirectly by hydrolysis of  $\gamma$ -valerolactone. Indeed,  $\gamma$ -valerolactone can generate 4-hydroxyvaleric acid by hydrolysis as suggested by the work of Raghunath V. Chaudhari in Top Catal. (2012) 55:439-445 or by William N. Fishbein and Samuel P. Bessman in The Journal of Biological Chemistry, Vol. 241, No. 21, Issue of November 10, pages 4842-4847, 1966. Said acid can then be dehydrated in an acidic medium (Langmuir, 2010, 26 (21), pages 16291-16298 by J.Q. Bond, D.M. Alonso, R.M. West and J.A. Dumesic) leading to a mixture between 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid.

According to one variant, the presence of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid on the catalyst may be due to the addition as such of the additive(s), alone or 5 as a mixture.

According to another variant, the presence of at least one additive chosen from 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid on the catalyst may be 10 due to the hydrolysis of the  $\gamma$ -valerolactone contained in the impregnating solution added to said catalytic precursor or support and optionally to a subsequent dehydration step.

The total content of additive(s) chosen from  $\gamma$ -valerolactone, 15 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid on the catalyst according to the invention is between 1% and 35% by weight, preferably between 2% and 30% by weight and more preferably between 3% and 25% by weight relative to the total weight of the catalyst. During the preparation of 20 the catalyst, the drying step(s) subsequent to the introduction of the additive(s) are performed at a temperature below 200°C so as preferably to retain at least 30%, preferably at least 50% and very preferably at least 70% of the amount of additive(s) introduced calculated on the basis of the carbon remaining on 25 the catalyst.

The catalyst according to the invention may comprise, in addition to the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 30 4-pentenoic acid, another organic compound or group of organic compounds known for their role as additives. The function of the additives is to increase the catalytic activity relative to catalysts not impregnated with additives.

35 In the text hereinbelow, the term "said additives" will mean at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.

More particularly, the catalyst according to the invention may also comprise one or more organic compounds containing oxygen other than said additives and/or one or more organic compounds containing nitrogen and/or one or more organic compounds containing sulfur. Preferably, the catalyst according to the invention may also comprise one or more organic compounds containing oxygen other than said additives, and/or one or more organic compounds containing nitrogen. Preferably, the organic compound contains at least two carbon atoms and at least one oxygen and/or nitrogen atom.

Generally, the organic compound is chosen from a compound including one or more chemical functions chosen from carboxylic, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide functions. Preferably, the organic compound is chosen from a compound including two alcohol functions and/or two carboxylic functions and/or two ester functions and/or at least one amide function.

20

The organic compound containing oxygen may be one or more chosen from compounds including one or more chemical functions chosen from carboxylic, alcohol, ether, aldehyde, ketone, ester and carbonate functions. By way of example, the organic compound containing oxygen may be one or more chosen from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, 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, oxalic acid, gluconic acid, tartaric acid, citric acid,  $\gamma$ -ketovaleric acid, a C1-C4 dialkyl succinate, methyl acetoacetate, a lactone, dibenzofuran, a crown ether, orthophthalic acid, glucose and propylene carbonate.

The organic compound containing nitrogen may be one or more chosen from compounds including one or more chemical functions

chosen from amine and nitrile functions. By way of example, the organic compound containing nitrogen may be one or more chosen from the group consisting of ethylenediamine, diethylenetriamine, hexamethylenediamine, triethylenetetramine,

5 tetraethylenepentamine, pentaethylenhexamine, acetonitrile, octylamine, guanidine or a carbazole.

The organic compound containing oxygen and nitrogen may be one or more chosen from compounds including one or more chemical

10 functions chosen from carboxylic, alcohol, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, amide, urea and oxime functions. By way of example, the organic compound containing oxygen and nitrogen may be one or more chosen from the group consisting of 1,2-cyclohexanediaminetetraacetic acid,

15 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), tetramethylurea, glutamic acid, dimethylglyoxime,

20 bicine or tricine, or a lactam.

The organic compound containing sulfur may be one or more chosen from compounds including one or more chemical functions chosen from thiol, thioether, sulfone and sulfoxide functions. By way

25 of example, the organic compound containing sulfur may be one or more chosen from the group consisting of thioglycolic acid, 2-hydroxy-4-methylthiobutanoic acid, a sulfone derivative of a benzothiophene or a sulfoxide derivative of a benzothiophene.

30 Preferably, the organic compound containing oxygen is preferably chosen from triethylene glycol, diethylene glycol, ethylenediaminetetraacetic acid (EDTA), maleic acid, citric acid, dimethylformamide, bicine, or tricine.

35 When it is/they are present, the total content of impregnated functionalized organic compound(s) (other than said additives) containing oxygen and/or nitrogen and/or sulfur on the catalyst according to the invention is between 1% and 30% by weight,

preferably between 1.5% and 25% by weight and more preferably between 2% and 20% by weight relative to the total weight of the catalyst.

5 **Preparation process**

The catalyst according to the invention may be prepared according to a preparation process comprising the following steps:

10 a) at least one component of a group VIB element, at least one component of a group VIII element, at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid and optionally phosphorus are placed in contact with a support based on alumina or silica or silica-alumina, or a regenerated catalyst containing a support based on alumina or silica or silica-alumina, at least one component of a group VIB element, at least one component of a group VIII element and optionally phosphorus are placed in contact with at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, so as to obtain a catalyst precursor,

15 b) said catalyst precursor derived from step a) is dried at a temperature below 200°C, without subsequently calcining it.

20

25 The process for preparing a fresh catalyst will be described first, and the process for preparing a rejuvenated catalyst will then be described thereafter.

**Process for preparing a fresh catalyst**

30 Step a) of placing in contact includes several embodiments which differ notably by the moment of introduction of the additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, which may be

35 performed either at the same time as the impregnation of the metals (co-impregnation) or after the impregnation of the metals (post-impregnation), or, finally, before the impregnation of the metals (pre-impregnation). Furthermore, the step of placing in

contact may combine at least two embodiments, for example co-impregnation and post-impregnation. These various embodiments will be described hereinbelow. Each embodiment, taken alone or in combination, may proceed in one or more steps.

5

It is important to point out that the catalyst according to the invention, during its preparation process, does not undergo any calcination after the introduction of the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 10 3-pentenoic acid or 4-pentenoic acid or any other organic compound containing oxygen and/or nitrogen and/or sulfur so as to at least partly preserve additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid or any other organic compound 15 in the catalyst. The term "calcination" means herein a thermal treatment under a gas containing air or oxygen at a temperature of greater than or equal to 200°C.

However, the catalyst precursor may undergo a calcination step 20 before the introduction of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid or of any other organic compound containing oxygen and/or nitrogen and/or sulfur, notably after the impregnation of the group VIB and VIII elements 25 (post-impregnation) optionally in the presence of phosphorus and/or of another dopant or during regeneration of an already-used catalyst. The hydrogenating function comprising the group VIB and group VIII elements of the catalyst according to the invention, also known as the active phase, is then in an oxide 30 form.

According to another variant, the catalyst precursor does not undergo any calcination step after the impregnation of the group VIB and VIII elements (post-impregnation), it is simply dried. 35 The hydrogenating function comprising the group VIB and group VIII elements of the catalyst according to the invention, also known as the active phase, is then not in an oxide form.

Irrespective of the embodiment, step a) of placing in contact generally involves at least one impregnation step, preferably a dry impregnation step, in which the support is impregnated with an impregnating solution comprising at least one group VIB element, at least one group VIII element and optionally phosphorus. In the case of the co-impregnation described in detail below, this impregnating solution also comprises at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid. The group VIB and group VIII elements are generally introduced by impregnation, preferentially by dry impregnation or by impregnation in an excess of solution. Preferably, the total amount of the group VIB and group VIII elements is introduced by impregnation, preferably by dry impregnation, irrespective of the embodiment.

The group VIB and group VIII elements may also be partly introduced during the forming of said support at the moment of blending with at least one alumina gel chosen as matrix, the rest of the hydrogenating elements then being introduced subsequently by impregnation. Preferably, when the group VIB and group VIII elements are partly introduced at the moment of blending, the proportion of group VIB element introduced during this step is less than 5% by weight of the total amount of group VIB element introduced onto the final catalyst.

Preferably, the group VIB element is introduced at the same time as the group VIII element, irrespective of the introduction method.

30

The molybdenum precursors that may be used are well known to those skilled in the art. For example, among the sources of molybdenum, use may be made of oxides and hydroxides, molybdic acids and salts thereof, in particular the ammonium salts such as ammonium molybdate, ammonium heptmolybdate, phosphomolybdc acid ( $H_3PMo_{12}O_{40}$ ) and salts thereof, and optionally silicomolybdc acid ( $H_4SiMo_{12}O_{40}$ ) and salts thereof. The sources of molybdenum may also be heteropolycompounds of Keggin, lacunar Keggin,

substituted Keggin, Dawson, Anderson or Strandberg type, for example. Molybdenum trioxide and heteropolyanions of Strandberg, Keggin, lacunar Keggin or substituted Keggin type are preferably used.

5

The tungsten precursors that may be used are also well known to those skilled in the art. For example, among the sources of tungsten, use may be made of oxides and hydroxides, tungstic acids and salts thereof, in particular ammonium salts such as 10 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 heteropolycompounds of Keggin, lacunar Keggin, substituted Keggin or Dawson type, for example. Oxides and ammonium salts 15 such as ammonium metatungstate or heteropolyanions of Keggin, lacunar Keggin or substituted Keggin type are preferably used.

The precursors of the group VIII elements that may be used are advantageously chosen from oxides, hydroxides, 20 hydroxycarbonates, carbonates and nitrates of group VIII elements. For example, nickel hydroxycarbonate or cobalt carbonate or hydroxide are preferably used.

Phosphorus, when it is present, may be totally or partially 25 introduced by impregnation. Preferably, it is introduced by impregnation, preferably dry impregnation, by means of a solution containing the precursors of the group VIB and group VIII elements.

30 Said phosphorus may be advantageously introduced alone or as a mixture with at least one of the group VIB and group VIII elements, and this may be done in any of the steps of impregnation of the hydrogenating function if said function is introduced in several portions. Said phosphorus may also be 35 introduced, totally or partly, during the impregnation of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid 3-pentenoic acid or 4-pentenoic acid if the latter is introduced separately from the hydrogenating

function (in the case of the post- and pre-impregnation described later), said introduction being in the presence or absence of an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives. It may also be 5 introduced at the stage of synthesis of the support, at any step in the synthesis thereof. It may thus be introduced before, during or after the blending of the chosen alumina gel matrix, for instance and preferably aluminum oxyhydroxide (boehmite) which is the alumina precursor.

10

The preferred phosphorus precursor is orthophosphoric acid  $H_3PO_4$ , but its salts and esters, such as ammonium phosphates, are also suitable for use. The phosphorus may also be introduced at the same time as the group VIB element(s) in the form of Keggin, 15 lacunar Keggin, substituted Keggin or Strandberg heteropolyanions.

The additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid are 20 advantageously introduced into an impregnating solution which, depending on the preparation method, may be the same solution or a different solution from the one containing the group VIB and VIII elements, in a total amount corresponding to:

- a total mole ratio of the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid to the group VIB element(s) of the catalyst precursor of between 0.2 and 2.0 mol/mol, preferably between 0.3 and 1.7 mol/mol, preferably between 0.5 and 1.5 mol/mol and very preferably between 0.8 and 1.2 mol/mol, 30 calculated on the basis of the components introduced into the impregnating solution(s), and
- a total mole ratio of the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid to the group VIII element(s) of the catalyst precursor of between 0.1 and 5.0 mol/mol, 35 preferably between 0.5 and 4.0 mol/mol, preferably between 1.0 and 3.0 mol/mol and very preferably between 1.5 and 3.0 mol/mol,

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

Any impregnating solution described in the present invention may 5 include any polar solvent known to those skilled in the art. Said polar solvent used is advantageously chosen from the group formed by methanol, ethanol, water, phenol and cyclohexanol, taken alone or as a mixture. Said polar solvent may also be advantageously chosen from the group formed by propylene 10 carbonate, DMSO (dimethyl sulfoxide), N-methylpyrrolidone (NMP) and sulfolane, taken alone or as a mixture. Preferably, a polar protic solvent is used. A list of common polar solvents and also their dielectric constant can be found in the book "Solvents and Solvent Effects in Organic Chemistry" C. Reichardt, Wiley-VCH, 15 3rd edition, 2003, pages 472-474. Very preferably, the solvent used is water or ethanol, and particularly preferably, the solvent is water. In one possible embodiment, the solvent may be absent from the impregnating solution.

20 When the catalyst also comprises a dopant chosen from boron, fluorine or a mixture of boron and fluorine, the introduction of this (these) dopant(s) may be performed in the same manner as the introduction of phosphorus in various steps of the preparation and in various ways. Said dopant may be 25 advantageously introduced alone or as a mixture with at least one of the group VIB and group VIII elements, and this may be done in any of the steps of impregnation of the hydrogenating function if said function is introduced in several portions. Said dopant may also be introduced, totally or partly, during 30 the impregnation of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid 3-pentenoic acid or 4-pentenoic acid if the latter is introduced 35 separately from the hydrogenating function (in the case of the post- and pre-impregnation described later), said introduction being in the presence or absence of an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives. It may also be introduced at the stage of synthesis of the support, at any step in the synthesis thereof. It may

thus be introduced before, during or after the blending of the chosen alumina gel matrix, for instance and preferably aluminum oxyhydroxide (boehmite) which is the alumina precursor.

5 Said dopant, when it is present, is advantageously introduced as a mixture with the precursor(s) of the group VIB and group VIII elements, totally or partly, onto the formed support by dry impregnation of said support with a solution, preferably an aqueous solution, containing the precursors of the metals, the 10 phosphorus precursor and the precursor(s) of the dopant(s), (and also containing at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid in the co-impregnation mode).

15 The boron precursors may be boric acid, orthoboric acid  $H_3BO_3$ , ammonium diborate or pentaborate, boron oxide or boric esters. The boron may be introduced, for example, by a solution of boric acid in a water/alcohol mixture or in a water/ethanolamine mixture. Preferably, the boron precursor, if boron is introduced, 20 is orthoboric acid.

The fluorine precursors that may be used are well known to those skilled in the art. For example, the fluoride anions may be introduced in the form of hydrofluoric acid or salts thereof. 25 These salts are formed with alkali metals, ammonium or an organic compound. In the latter case, the salt is advantageously formed in the reaction mixture by reaction between the organic compound and hydrofluoric acid. The fluorine may be introduced, for example, by impregnation of an aqueous solution of hydrofluoric acid, or of ammonium fluoride or of ammonium difluoride.

When the catalyst also comprises an additional additive (in addition to the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid) or a group of additional additives chosen from an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives, the additional additive may 35 be introduced into the impregnating solution of step a).

The total mole ratio of organic compound(s) containing oxygen and/or nitrogen and/or sulfur, other than said additives, to the group VIB element(s) on the catalyst is between 0.05 and 5 mol/mol, preferably between 0.1 and 4 mol/mol, preferably between 0.2 and 3 mol/mol, calculated on the basis of the components introduced into the impregnating solution(s).

The total mole ratio of organic compound(s) containing oxygen and/or nitrogen and/or sulfur, other than said additives, relative to the sum of  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid is between 0.05 and 6 mol/mol, preferably between 0.1 and 5 mol/mol, preferably between 0.2 and 4 mol/mol, calculated on the basis of the components introduced into the impregnating solution(s).

Advantageously, after each impregnation step, the impregnated support is left to mature. Maturation allows the impregnating solution to become homogeneously dispersed within the support.

Any maturation step described in the present invention is advantageously performed at atmospheric pressure, in a water-saturated atmosphere and at a temperature of between 17°C and 50°C, and preferably at room temperature. Generally, a maturation time of between ten minutes and forty-eight hours, and preferably of between thirty minutes and five hours, is sufficient. Longer periods of time are not ruled out, but do not necessarily afford any improvement.

In accordance with step b) of the preparation process according to the invention, the optionally matured catalyst precursor obtained in step a) is subjected to a step of drying at a temperature below 200°C without a subsequent calcination step.

Any drying step subsequent to the introduction of said additives described in the present invention is performed at a temperature below 200°C, preferably between 50 and 180°C, preferably between 70 and 150°C and very preferably between 75 and 130°C.

The drying step is advantageously performed via any technique known to those skilled in the art. It is advantageously performed at atmospheric pressure or at reduced pressure. Preferably, this 5 step is performed at atmospheric pressure. It is advantageously performed in a crossed bed using hot air or any other hot gas. Preferably, when the drying is performed in a fixed bed, the gas used is either air, or an inert gas such as argon or nitrogen. Very preferably, the drying is performed in a crossed bed in the 10 presence of nitrogen and/or air. Preferably, the drying step has a short duration of between 5 minutes and 4 hours, preferably between 30 minutes and 4 hours and very preferably between 1 hour and 3 hours. The drying is then conducted so as preferentially to keep at least 30% of the additive(s) chosen 15 from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid introduced during an impregnation step; preferably, this amount is greater than 50% and even more preferably greater than 70%, calculated on the basis of the carbon remaining on the catalyst. When an organic 20 compound containing oxygen and/or nitrogen and/or sulfur other than said additives is present, the drying step is performed so as preferably to keep at least 30%, preferably at least 50%, and very preferably at least 70% of the amount introduced, calculated on the basis of the carbon remaining on the catalyst.

25

On conclusion of the drying step b), a dried catalyst is obtained, which is not subjected to any subsequent calcination step.

#### Co-impregnation

30

According to a first embodiment of step a) of the process for preparing the (fresh) catalyst, said components of the group VIB elements, of the group VIII elements, of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid and optionally phosphorus are deposited on said support by one or more co-impregnation steps, i.e. said components of the group VIB elements, of the group VIII elements, at least one additive 35

chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid and optionally phosphorus are simultaneously introduced into said support ("co-impregnation"). According to one variant, step a) is the

5 following step:

a') a support based on alumina or silica or silica-alumina is impregnated with at least one solution containing at least one group VIB element, at least one group VIII element, at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-  
10 pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, and optionally phosphorus, so as to obtain a catalyst precursor.

The co-impregnation step(s) are preferentially performed by dry impregnation or by impregnation in an excess of solution. When  
15 this first mode involves performing several co-impregnation steps, each co-impregnation step is preferably followed by an intermediate drying step at a temperature below 200°C, advantageously between 50 and 180°C, preferably between 70 and 150°C, very preferably between 75 and 130°C, and optionally a  
20 maturation period has been observed between the impregnation and the drying.

Very preferably, during the preparation via co-impregnation, the group VIB and group VIII elements, at least one additive chosen  
25 from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, optionally phosphorus, optionally another dopant chosen from boron and/or fluorine and optionally an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives are introduced in step  
30 a) in their entirety after the forming of said support by dry impregnation of said support with an aqueous impregnating solution containing the precursors of the group VIB and group VIII elements, at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid 3-pentenoic acid or 4-  
35 pentenoic acid, optionally the phosphorus precursor, optionally the dopant precursor chosen from boron and/or fluorine and optionally the organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives.

**Post-impregnation**

According to a second embodiment of step a) of the process for  
5 preparing the (fresh) catalyst according to the invention, at  
least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric  
acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid is  
placed in contact with a dried and optionally calcined  
10 impregnated support comprising at least one component of a group  
VIB element, at least one component of a group VIII element and  
optionally phosphorus, said support being based on alumina or  
silica or silica-alumina, so as to obtain a catalyst precursor.

This second embodiment is a preparation by "post-impregnation"  
15 of at least one additive chosen from  $\gamma$ -valerolactone, 4-  
hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-  
pentenoic acid. This preparation is performed, for example, by  
dry impregnation.

20 According to this second embodiment, the placing in contact  
according to step a) comprises the following successive steps  
which will be detailed later:

25 a1) a support based on alumina or silica or silica-alumina is  
impregnated with at least one solution containing at least one  
group VIB element, at least one group VIII element and optionally  
phosphorus, to obtain an impregnated support,

a2) the impregnated support obtained in step a1) is dried at a  
temperature below 200°C to obtain a dried impregnated support,  
and optionally the dried impregnated support is calcined to  
30 obtain a calcined impregnated support,

a3) the dried and optionally calcined impregnated support  
obtained in step a2) is impregnated with an impregnating  
solution comprising at least one additive chosen from  $\gamma$ -  
valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-  
35 pentenoic acid or 4-pentenoic acid so as to obtain a catalyst  
precursor,

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

In step a1) of the post-impregnation process, the introduction of the group VIB and group VIII elements and optionally of phosphorus onto the support may be advantageously performed via 5 one or more impregnations with an excess of solution on the support, or preferably via one or more dry impregnations, and, preferably, via only one dry impregnation of said support, using solution(s), preferably aqueous solution(s), containing the metal precursor(s) and preferably the phosphorus precursor.

10

When several impregnation steps are performed, each impregnation step is preferably followed by an intermediate drying step at a temperature below 200°C, advantageously between 50 and 180°C, preferably between 70 and 150°C, very preferably between 75 and 15 130°C, and optionally a maturation period has been observed between the impregnation and the drying. Each intermediate drying step, prior to the introduction of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid may be followed by a 20 calcination step under the conditions described below for step a2).

Very preferably, during the preparation via post-impregnation, the group VIB and group VIII elements and optionally phosphorus, 25 optionally another dopant chosen from boron and/or fluorine and optionally an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives are introduced in step a1) in their entirety after forming said support, by dry impregnation of said support with an aqueous impregnating 30 solution containing the precursors of the group VIB and group VIII elements, the phosphorus precursor, and optionally the dopant precursor chosen from boron and/or fluorine and optionally the organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives.

35

According to another variant, the group VIB and group VIII elements and optionally the phosphorus, optionally another dopant chosen from boron and/or fluorine and optionally an

organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives may be introduced in step a1) successively by several impregnating solutions containing one or more of the components.

5

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

10 According to step a2), the impregnated support obtained in step a1) is dried at a temperature below 200°C to obtain a dried impregnated support under the conditions described above for drying.

15 Optionally, the dried impregnated support may then undergo calcination. The calcination is generally performed at a temperature of between 200°C and 900°C, preferably between 250°C and 750°C. The calcination time is generally between 30 minutes and 16 hours, preferably between 1 hour and 5 hours. It is 20 generally performed in air. Calcination enables the precursors of the group VIB and VIII metals to be converted into oxides.

According to step a3), the dried impregnated support obtained in step a2) is impregnated with an impregnating solution 25 comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid so as to obtain a catalyst precursor.

30 The additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid may advantageously be deposited in one or more steps either by excess impregnation, or by dry impregnation, or by any other means known to those skilled in the art. Preferably, said additive(s) are introduced by dry impregnation, in the presence or absence 35 of a solvent as described above.

Preferably, the solvent in the impregnating solution used in step a3) is water, which facilitates implementation at the industrial scale.

5 The additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid are advantageously introduced into the impregnating solution of step a3) in the mole ratios per group VIB or group VIII element described above.

10

When it is desired also to introduce an additional additive (in addition to the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid) or a group of additional additives chosen from 15 an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives, this additive may be introduced into the impregnating solution of step a1) and/or into the impregnating solution of step a3) or via an additional impregnation step at any time in the preparation process before 20 the final drying of step b), it being understood that no calcination step is performed after its introduction. This compound is introduced in the proportions described above.

According to step a4), the catalyst precursor obtained in step 25 a3) is optionally allowed to mature under the maturation conditions described above.

In accordance with step b) of the preparation process according to the invention, the catalyst precursor which was optionally matured in step a4) is subjected to a step of drying at a 30 temperature below 200°C without a subsequent calcination step, as described above.

#### Pre-impregnation

35

According to a third embodiment of step a) of the process for preparing the (fresh) catalyst according to the invention, at least one component of a group VIB element, at least one

component of a group VIII element, and optionally phosphorus are placed in contact with the support based on alumina or silica or silica-alumina which contains at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid,  
5 3-pentenoic acid or 4-pentenoic acid so as to obtain a catalyst precursor.

This third embodiment is a preparation by "pre-impregnation" of at least one additive chosen from  $\gamma$ -valerolactone, 4-  
10 hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid. It is performed, for example, by dry impregnation.

According to this third embodiment, the placing in contact  
15 according to step a) comprises the following successive steps which will be detailed later:

a1') a support is prepared comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid and optionally at  
20 least part of the phosphorus,  
a2') the support obtained in step a1') is impregnated with an impregnating solution comprising at least one group VIB element, at least one group VIII element and optionally phosphorus so as to obtain a catalyst precursor,  
25 a3') optionally, the catalyst precursor obtained in step a2') is allowed to mature.

In step a1') of the implementation by pre-impregnation, a support is prepared comprising at least one additive chosen from  
30  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid and optionally at least part of the phosphorus. The additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid may be introduced at any time during the  
35 preparation of the support, and preferentially during the forming or by impregnation on an already-formed support.

If the introduction of at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid onto the previously formed support is chosen, then it may be performed as indicated for 5 step a3) of the post-impregnation. It will then be followed by an optional step of maturation and drying at a temperature below 200°C under the maturation and drying conditions as described above.

10 If introduction during the forming is chosen, preferably, said forming is performed by extrusion blending, by pelletizing, by the drop coagulation (oil-drop) method, by spinning-plate granulation or via any other method that is well known to those skilled in the art. Very preferably, said forming is performed 15 by extrusion blending, it being possible for  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid and/or 4-pentenoic acid to be introduced at any time during the extrusion blending. The formed material obtained on conclusion 20 of the forming step then advantageously undergoes a step of heat treatment at a temperature such that at least a portion of said additive(s) remains present.

This is likewise the case for any phosphorus present in said support in step a1'). The phosphorus may be introduced at any 25 moment in the preparation of the support, and preferentially during the forming or by impregnation on an already-formed support as described above. If phosphorus is introduced alone during forming, i.e. without an additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid, which is itself then 30 introduced by impregnation, the calcination following its introduction may then advantageously be performed at a temperature below 1000°C.

35 In step a2') of the implementation by pre-impregnation, the introduction of the group VI B and group VIII elements and optionally of phosphorus may be advantageously performed via one or more impregnations with an excess of solution on the support,

or preferably via one or more dry impregnations, and, preferably, via only one dry impregnation of said support, using solution(s), preferably aqueous solution(s), containing the metal precursor(s) and optionally the phosphorus precursor.

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

10 When it is desired also to introduce an additional additive (in addition to the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid) or a group of additional additives chosen from an organic compound containing oxygen and/or nitrogen and/or 15 sulfur other than said additives, this additive may be introduced into the support of step a1') during the forming or by impregnation, and/or into the impregnating solution of step a2') or via an additional impregnation step at any time in the preparation process before the final drying of step b), it being 20 understood that no calcination step is performed after its introduction.

The three modes described above may be performed alone as described or combined to give rise to other hybrid preparation 25 modes as a function of the technical and practical constraints.

According to another alternative embodiment, the placing in contact according to step a) combines at least two modes of placing in contact, for example co-impregnation of an organic 30 compound and post-impregnation of an organic compound which may be identical to or different from the one used for the co-impregnation, given that at least one of the organic compounds is chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.

35

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

a1'') a solution containing at least one group VIB element, at least one group VIII element, at least one organic compound containing oxygen and/or nitrogen and/or sulfur, and optionally phosphorus is placed in contact by co-impregnation with a support based on alumina or silica or silica-alumina so as to obtain an impregnated support,

a2'') the impregnated support from step a1'') is dried at a temperature below 200°C, without subsequently calcining it, to obtain a dried impregnated support,

a3'') the dried impregnated support from step a2'') is placed in contact with a solution of an organic compound containing oxygen and/or nitrogen and/or sulfur which is identical to or different from the one used in step a1''), so as to obtain a catalyst precursor,

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

and at least one of the organic compounds of step a1'') or of step a3'') is chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid.

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The operating conditions described above may, needless to say, be applied in the context of the latter embodiment.

#### Process for preparing a rejuvenated catalyst

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

a) a regenerated catalyst containing a support based on alumina or silica or silica-alumina, at least one component of a group VIB element, at least one component of a group VIII element and optionally phosphorus is placed in contact with at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid in order to obtain a catalyst precursor,

b) said catalyst precursor derived from step a) is dried at a temperature below 200°C, without subsequently calcining it.

According to step a), a regenerated catalyst is placed in contact with at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid in order to obtain a catalyst precursor. The 5 rejuvenated catalyst is a catalyst which has been used as catalyst in a catalytic unit and notably in hydrotreating and/or hydrocracking and which has been subjected to at least one step of calcination so as to burn off the coke (regeneration). Regeneration allows the combustion of the carbon deposited on 10 the catalyst during its industrial use.

It may be performed via any method known to those skilled in the art. The regeneration is generally performed at temperatures of between 350 and 550°C, and usually between 400 and 520°C, or 15 between 420 and 520°C, or between 450 and 520°C, temperatures below 500°C often being advantageous.

The regenerated catalyst contains a support based on alumina or silica or silica-alumina, at least one component of a group VIB 20 element, at least one component of a group VIII element and optionally phosphorus in the respective proportions indicated above. Following the regeneration (calcination step), the hydrogenating function comprising the group VIB and group VIII elements of the regenerated catalyst is in an oxide form. It may 25 also contain dopants other than phosphorus, as described above.

According to this embodiment, the placing in contact according to step a) comprises the following successive steps:

a1'') a regenerated catalyst containing a support based on 30 alumina or silica or silica-alumina, at least one component of a group VIB element, at least one component of a group VIII element and optionally phosphorus is impregnated with an impregnating solution comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 35 3-pentenoic acid or 4-pentenoic acid so as to obtain a catalyst precursor,

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

Preferably, the placing in contact of step a) is performed by impregnation of the regenerated catalyst with an impregnating solution comprising at least one additive chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid in order to obtain a catalyst precursor.

The additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid may advantageously be deposited in one or more steps either by excess impregnation, or by dry impregnation, or by any other means known to those skilled in the art. Preferably, the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid are introduced by dry impregnation, in the presence or absence of a solvent as described above.

Preferably, the solvent in the impregnating solution used is water, which facilitates the implementation at the industrial scale.

The additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid are advantageously introduced into the impregnating solution in the mole ratios per group VIB or group VIII element described above.

When it is desired also to introduce an additional additive (in addition to the additive(s) chosen from  $\gamma$ -valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid or 4-pentenoic acid) or a group of additional additives chosen from an organic compound containing oxygen and/or nitrogen and/or sulfur other than said additives, this additive may be introduced into the impregnating solution of step a1'''') or via an additional impregnation step at any time in the preparation process before the final drying of step b), it being understood that no calcination step is performed after its introduction. This compound is introduced in the proportions described above.

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

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In accordance with step b) of the preparation process according to the invention, the catalyst precursor which has been optionally matured in step a2''') is subjected to a step of drying at a temperature below 200°C without a subsequent 10 calcination step, as described above.

### Sulfurization

Before its use for the hydrotreating and/or hydrocracking 15 reaction, it is advantageous to transform the dried catalyst obtained according to any of the modes of introduction described in the present invention into a sulfurized catalyst in order to form its active species. This activation or sulfurization step is performed via the methods that are well known to those skilled 20 in the art, and advantageously under a sulfo-reductive atmosphere in the presence of hydrogen and hydrogen sulfide.

On conclusion of step b) according to the various modes of preparation of the process according to the invention, said 25 catalyst obtained is thus advantageously subjected to a sulfurization step, without an intermediate calcination step.

Said dried catalyst is advantageously sulfurized *ex situ* or *in situ*. The sulfurizing agents are H<sub>2</sub>S gas or any other sulfur-30 containing compound used for the activation of hydrocarbon feedstocks for the purpose of sulfurizing the catalyst. Said compounds containing sulfur are advantageously chosen from alkyl disulfides, for instance dimethyl disulfide (DMDS), alkyl sulfides, for instance dimethyl sulfide, thiols, for instance 35 n-butyl mercaptan (or 1-butanethiol), polysulfide compounds of tert-nonyl polysulfide type, or any other compound known to those skilled in the art which enables good sulfurization of the catalyst. Preferably, the catalyst is sulfurized *in situ* in the

presence of a sulfurizing agent and of a hydrocarbon feedstock. Very preferably, the catalyst is sulfurized *in situ* in the presence of a hydrocarbon feedstock impregnated with dimethyl disulfide.

5

#### Hydrotreating and/or hydrocracking process

Finally, another subject of the invention is the use of the catalyst according to the invention or prepared according to the 10 preparation process according to the invention in processes for the hydrotreating and/or hydrocracking of hydrocarbon cuts.

The catalyst according to the invention, which has preferably undergone a sulfurization step beforehand, is advantageously 15 used for the hydrotreating and/or hydrocracking reactions of hydrocarbon feedstocks such as petroleum cuts, cuts derived from coal or hydrocarbons produced from natural gas, optionally as mixtures or else from a hydrocarbon cut derived from biomass and more particularly for hydrogenation, hydrodeazotization, 20 hydrodearomatization, hydrodesulfurization, hydrodeoxygenation, hydrodemetallation or hydroconversion reactions of hydrocarbon feedstocks.

In these uses, the catalyst according to the invention, which 25 has preferably undergone a sulfurization step beforehand, has improved activity relative to the catalysts of the prior art. This catalyst may also advantageously be used in the pretreatment of catalytic cracking or hydrocracking feedstocks, or the hydrodesulfurization of residues or the forced 30 hydrodesulfurization of gas oils (ULSD: ultra-low-sulfur diesel).

The feedstocks used in the hydrotreating process are, for example, gasolines, gas oils, vacuum gas oils, atmospheric residues, vacuum residues, atmospheric distillates, vacuum 35 distillates, heavy fuel oils, oils, waxes and paraffins, used oils, deasphalting residues or crudes, feedstocks originating from thermal or catalytic conversion processes, lignocellulosic feedstocks, or, more generally, feedstocks derived from biomass,

taken alone or as a mixture. The feedstocks that are treated, and in particular those mentioned above, generally contain heteroatoms such as sulfur, oxygen and nitrogen and, for heavy feedstocks, they usually also contain metals.

5

The operating conditions used in the processes involving reactions for hydrotreating hydrocarbon feedstocks described above are generally the following: the temperature is advantageously between 180°C and 450°C, and preferably between 10 250°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<sup>-1</sup> and preferably between 0.2 and 5 h<sup>-1</sup>, and the hydrogen/feedstock ratio expressed as the volume of hydrogen, measured under normal temperature and 15 pressure conditions, per volume of liquid feedstock is advantageously between 50 l/l to 5000 l/l and preferably 80 to 2000 l/l.

According to a first mode of use, said hydrotreating process 20 according to the invention is a process for the hydrotreating, and notably for the hydrodesulfurization (HDS), of a gas oil cut performed in the presence of at least one catalyst according to the invention. Said hydrotreating process according to the invention is directed toward removing the sulfur-based compounds 25 present in said gas oil cut so as to meet the environmental standards in force, namely a permitted sulfur content of up to 10 ppm. It also makes it possible to reduce the contents of aromatics and of nitrogen of the gas oil cut to be hydrotreated.

30 Said gas oil cut to be hydrotreated according to the process of the invention contains from 0.02% to 5.0% by weight of sulfur. It is advantageously derived from the straight-run distillation (or the straight-run gas oil) of a coking unit, of a visbreaking unit, of a steam cracking unit, of a unit for hydrotreating 35 and/or hydrocracking heavier feedstocks and/or of a catalytic cracking unit (fluid catalytic cracking). Said gas oil cut preferentially contains at least 90% of compounds with a boiling point between 250°C and 400°C at atmospheric pressure.

The process for hydrotreating said gas oil cut according to the invention is performed under the following operating conditions: a temperature of between 200 and 400°C, preferentially between 5 300 and 380°C, a total pressure of between 2 MPa and 10 MPa and more preferentially between 3 MPa and 8 MPa with a ratio of the volume of hydrogen to the volume of hydrocarbon feedstock, expressed as volume of hydrogen, measured under normal 10 temperature and pressure conditions, to the volume of liquid feedstock, of between 100 and 600 liters per liter and more preferentially between 200 and 400 liters per liter, and an hourly space velocity of between 1 and 10 h<sup>-1</sup>, preferentially between 2 and 8 h<sup>-1</sup>. The HSV corresponds to the inverse of the contact time expressed in hours and is defined by the ratio of 15 the volume flow rate of liquid hydrocarbon feedstock to the volume of catalyst loaded into the reaction unit performing the hydrotreating process according to the invention. The reaction unit performing the process for hydrotreating said gas oil cut according to the invention is preferentially operated in a fixed 20 bed, in a moving bed or in a boiling bed, preferably in a fixed bed.

According to a second mode of use, said hydrotreating and/or hydrocracking process according to the invention is a process 25 for the hydrotreating (notably hydrodesulfurization, hydrodeazotization, hydrogenation of aromatics) and/or hydrocracking of a vacuum distillate cut performed in the presence of at least one catalyst according to the invention. Said hydrotreating and/or hydrocracking process, also referred 30 to as a hydrocracking pretreatment or hydrocracking process according to the invention, is directed, depending on the case, toward removing the sulfur-based, nitrogen-based or aromatic compounds present in said distillate cut so as to perform a pretreatment before conversion in catalytic cracking or 35 hydroconversion processes, or toward hydrocracking the distillate cut which may optionally have been pretreated beforehand, if necessary.

Very varied feedstocks may be treated via the vacuum distillate hydrotreating and/or hydrocracking processes described above. Generally, they contain at least 20% by volume and often at least 80% by volume of compounds boiling above 340°C at 5 atmospheric pressure. The feedstock may be, for example, vacuum distillates and also feedstocks derived from units for extraction of aromatics from lubricant oil bases or derived from the solvent deparaffining of lubricant oil bases, and/or of deasphalting oils, or the feedstock may be a deasphalting oil or 10 paraffins derived from the Fischer-Tropsch process, or any mixture of the feedstocks mentioned previously. In general, the feedstocks have a T5 boiling point above 340°C at atmospheric pressure, and better still above 370°C at atmospheric pressure, i.e. 95% of the compounds present in the feedstock have a boiling 15 point above 340°C and better still above 370°C. The nitrogen content of the feedstocks treated in the processes according to the invention is usually greater than 200 ppm by weight, preferably between 500 and 10 000 ppm by weight. The sulfur content of the feedstocks treated in the processes according to 20 the invention is usually between 0.01% and 5.0% by weight. The feedstock may optionally contain metals (for example nickel and vanadium). The asphaltene content is generally less than 3000 ppm by weight.

25 The hydrotreating and/or hydrocracking catalyst is generally placed in contact, in the presence of hydrogen, with the feedstocks described previously, at a temperature above 200°C, usually between 250°C and 480°C, advantageously between 320°C and 450°C, preferably between 330°C and 435°C, at a pressure 30 above 1 MPa, usually between 2 and 25 MPa, preferably between 3 and 20 MPa, the space velocity being between 0.1 and 20.0  $\text{h}^{-1}$  and preferably 0.1-6.0  $\text{h}^{-1}$ , preferably 0.2-3.0  $\text{h}^{-1}$ , and the amount of hydrogen introduced is such that the volume ratio of a liter of hydrogen/liter of hydrocarbon, expressed as volume of 35 hydrogen, measured under normal temperature and pressure conditions, to the volume of liquid feedstock, is between 80 and 5000 l/l and usually between 100 and 2000 l/l. These operating conditions used in the processes according to the invention

generally make it possible to obtain conversions per pass, into products having boiling points of less than 340°C at atmospheric pressure, and better still less than 370°C at atmospheric pressure, of greater than 15% and even more preferably between 5 20% and 95%.

The vacuum distillate hydrotreating and/or hydrocracking processes using the catalysts according to the invention cover pressure ranges and conversion ranges extending from mild 10 hydrocracking to high-pressure hydrocracking. The term "mild hydrocracking" refers to hydrocracking which leads to moderate conversions, generally of less than 40%, and which operates at low pressure, preferably between 2 MPa and 6 MPa.

15 The catalyst according to the invention may be used alone, in one or more fixed-bed catalytic beds, in one or more reactors, in a "one-step" hydrocracking scheme, with or without liquid recycling of the unconverted fraction, or in a "two-step" hydrocracking scheme, optionally in combination with a 20 hydrorefining catalyst located upstream of the catalyst of the present invention.

According to a third mode of use, said hydrotreating and/or hydrocracking process according to the invention is 25 advantageously performed as a pretreatment in a fluidized-bed catalytic cracking (or FCC: fluid catalytic cracking) process. The operating conditions of the pretreatment in terms of temperature range, pressure, hydrogen recycling rate and hourly 30 space velocity are generally identical to those described above for the vacuum distillate hydrotreating and/or hydrocracking processes. The FCC process may be conducted in a conventional manner known to those skilled in the art under suitable cracking conditions for the purpose of producing hydrocarbon-based products of smaller molecular weight. A summary description of 35 catalytic cracking will be found, for example, in Ullmann's Encyclopedia of Industrial Chemistry volume A18, 1991, pages 61 to 64.

According to a fourth mode of use, said hydrotreating and/or hydrocracking process according to the invention is a process for the hydrotreating (notably for the hydrodesulfurization) of a gasoline cut in the presence of at least one catalyst according 5 to the invention.

Unlike other hydrotreating processes, the hydrotreating (notably the hydrodesulfurization) of gasolines must make it possible to address a twofold conflicting constraint: ensuring in-depth 10 hydrodesulfurization of the gasolines and limiting the hydrogenation of the unsaturated compounds present so as to limit the loss of octane number.

The feedstock is generally a hydrocarbon cut with a distillation 15 range of between 30 and 260°C. Preferably, this hydrocarbon cut is a cut of the gasoline type. Very preferably, the gasoline cut is an olefinic gasoline cut derived, for example, from a catalytic cracking unit (fluid catalytic cracking).

20 The hydrotreating process consists in placing the hydrocarbon cut in contact with the catalyst according to the invention and hydrogen under the following conditions: at a temperature of between 200 and 400°C, preferably between 230 and 330°C, at a total pressure of between 1 and 3 MPa, preferably between 1.5 25 and 2.5 MPa, at an hourly space velocity (HSV), defined as being the volume flow rate of feedstock relative to the volume of catalyst, of between 1 and 10 h<sup>-1</sup>, preferably between 2 and 6 h<sup>-1</sup>, and at a hydrogen/gasoline feedstock volume ratio of between 100 and 600 Nl/l, preferably between 200 and 400 Nl/l.

30

The gasoline hydrotreating process may be performed in one or more reactors in series of the fixed-bed type or of the boiling-bed type. If the process is performed using at least two reactors in series, it is possible to provide a device for removing the 35 H<sub>2</sub>S from the effluent derived from the first hydrodesulfurization reactor before treating said effluent in the second hydrodesulfurization reactor.

The examples that follow demonstrate the substantial gain in activity on the catalysts prepared according to the process of the invention relative to the catalysts of the prior art and specify the invention without, however, limiting the scope 5 thereof.

### Examples

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

To an alumina support having a BET specific surface area of 230 m<sup>2</sup>/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 volume median 15 diameter by mercury porosimetry and which is in "extrudate" form, are added cobalt, molybdenum and phosphorus. The impregnating solution is prepared by dissolving, at 90°C, molybdenum oxide (24.34 g) and cobalt hydroxide (5.34 g) in 7.47 g of aqueous 85% phosphoric acid solution. After dry impregnation, the extrudates 20 are left to mature in a water-saturated atmosphere for 12 hours at room temperature, and are then dried at 90°C for 16 hours. The dried catalytic precursor thus obtained is denoted C1. Calcination of the catalytic precursor C1 at 450°C for 2 hours 25 leads to the calcined catalyst C2. The final composition of catalysts C1 and C2, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.5 ± 0.2 wt%, CoO = 4.1 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 4.0 ± 0.1 wt%.

30 **Example 2: Preparation of CoMoP catalysts on alumina C3 and C4 (not in accordance with the invention), C5 and C6 (in accordance with the invention) by co-impregnation.**

To the alumina support described previously in example 1 and which is in the "extrudate" form are added cobalt, molybdenum 35 and phosphorus. The impregnating solution is prepared by dissolving, at 90°C, molybdenum oxide (28.13 g) and cobalt hydroxide (6.62 g) in 7.88 g of aqueous 85% phosphoric acid solution. After homogenization of the preceding mixture, 37.79

g of citric acid were added before adjusting the volume of solution to the pore volume of the support by addition of water. The (citric acid)/Mo mole ratio is equal to 1 mol/mol and the (citric acid)/Co mole ratio is equal to 2.8 mol/mol. After dry 5 impregnation, the extrudates are left to mature in a water-saturated atmosphere for 12 hours at room temperature, and are then dried at 120°C for 16 hours. The dried catalytic precursor thus obtained is denoted C3. The final composition of catalyst 10 C3, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.7 ± 0.2 wt%, CoO = 4.2 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 3.8 ± 0.1 wt%.

Catalyst C4 is prepared in a similar manner to that of catalyst 15 C3, but, after homogenization of the metal solution containing cobalt, molybdenum and phosphorus, triethylene glycol (TEG) is added, once again in a proportion of 1 mol per mole of molybdenum or 2.8 mol per mole of cobalt. Catalyst C4 was allowed to mature 20 in a water-saturated atmosphere for 12 hours at room temperature, and then dried at 120°C for 16 hours. The final composition of catalyst C4, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.6 ± 0.2 wt%, CoO = 4.1 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 3.9 ± 0.1 wt%.

Catalysts C5 and C6 according to the invention are prepared as 25 follows. To the alumina support described in example 1 and which is in the "extrudate" form were added cobalt, molybdenum and phosphorus. An impregnating solution was prepared by dissolving, at 90°C, molybdenum oxide (78.75 g) and cobalt hydroxide (18.54 g) in 22.08 g of aqueous 85% phosphoric acid solution. After 30 homogenization of the preceding mixture, γ-valerolactone was added to the solution, in equimolar proportion relative to the molybdenum, i.e. 2.8 mol per mole of cobalt, to give catalyst C5. Similarly, 4-hydroxyvaleric acid was added to the solution, in equimolar proportion relative to the molybdenum, i.e. 2.8 mol 35 per mole of cobalt, to give catalyst C6. The volume of the solution was adjusted to the pore volume of the support by adding water before each impregnation. After dry impregnation, the extrudates of the two catalysts were left to mature in a water-

saturated atmosphere for 12 hours at room temperature, and then dried at 120°C for 16 hours. The final composition of catalyst C5, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.4 ± 0.2 wt%, CoO = 5 4.0 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 4.0 ± 0.1 wt%. The final composition of catalyst C6, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.3 ± 0.2 wt%, CoO = 3.8 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 4.2 ± 0.1 wt%.

10 Example 3: Preparation of the CoMoP catalyst on alumina C7 (according to the invention) by pre-impregnation.

On the alumina support described previously in Example 1 and which is in the "extrudate" form, 24.7 g of γ-valerolactone 15 diluted in water are added so as to obtain a solution with a total volume equal to the pore volume of the support. The solution thus formed is then dry-impregnated on the support, followed by observing a maturation time of 3 hours in a water-saturated atmosphere and at room temperature, followed by drying 20 at 120°C for 2 hours. The modified support is then impregnated with a new impregnating solution prepared by hot dissolution of molybdenum oxide (27.00 g) and cobalt hydroxide (6.36 g) in 7.57 g of aqueous 85% phosphoric acid solution, taking care to adjust the volume of said solution to the pore volume of the preceding 25 modified support by adding water. After dry impregnation, the extrudates were left to mature in a water-saturated atmosphere for 3 hours at room temperature, and were then dried at 120°C for 16 hours to give catalyst C7. The final composition of catalyst C7, expressed in the form of oxides and relative to the 30 mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.5 ± 0.2 wt%, CoO = 4.1 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 4.0 ± 0.1 wt%. The amounts engaged are such that the amount of γ-valerolactone is 1 mol per mole of molybdenum and 2.8 mol per mole of cobalt.

35 Example 4: Preparation of CoMoP catalysts on alumina C8 (not in accordance with the invention) and C9 (in accordance with the invention) by co-impregnation (low organic compound/Mo ratio)

To the alumina support described previously in example 1 and which is in the "extrudate" form are added cobalt, molybdenum and phosphorus as for the preparation of catalyst C3. However, during the preparation of the impregnating solution, the mole ratio of citric acid to molybdenum here is equal to 0.25 mol/mol, i.e. 0.70 mol of citric acid per mole of cobalt. After dry impregnation, the extrudates are left to mature in a water-saturated atmosphere for 12 hours at room temperature, and are then dried at 120°C for 16 hours. The dried catalytic precursor thus obtained is denoted C8. The final composition of catalyst C8, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.5 ± 0.2 wt%, CoO = 4.0 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 3.9 ± 0.1 wt%.

To the alumina support described previously in example 1 and which is in the "extrudate" form are added cobalt, molybdenum and phosphorus as for the preparation of catalyst C5. However, during the preparation of the impregnating solution, the mole ratio of γ-valerolactone to molybdenum was set at 0.25 mol/mol, i.e. 0.70 mol of γ-valerolactone per mole of cobalt. After dry impregnation, the extrudates were left to mature in a water-saturated atmosphere for 12 hours at room temperature, and then dried at 120°C for 16 hours. The dried catalytic precursor thus obtained is denoted C9. The final composition of catalyst C9, expressed in the form of oxides and relative to the mass of dry catalyst, is then the following: MoO<sub>3</sub> = 22.3 ± 0.2 wt%, CoO = 4.1 ± 0.1 wt% and P<sub>2</sub>O<sub>5</sub> = 4.3 ± 0.1 wt%.

Example 5: Evaluation in the HDS of gas oil of catalysts C1, C2, C3, C4 and C8 (not in accordance with the invention) and C5, C6, C7 and C9 (in accordance with the invention)

Catalysts C1, C2, C3, C4 and C8 (not in accordance with the invention) and C5, C6, C7 and C9 (in accordance with the invention) were tested in the HDS of gas oil.

Characteristics of the gas oil feedstock used: density at 15°C: 0.8522 g/cm<sup>3</sup>, sulfur: 1.44% by weight.

## · Simulated distillation:

- SP: 155°C
- 10%: 247°C
- 50%: 315°C
- 5 ○ 90%: 392°C
- EP: 444°C

The test is conducted in an isothermal crossed fixed-bed pilot reactor, the fluids circulating from the bottom upward. After 10 *in situ* sulfurization at 350°C in the pressurized unit using the test gas oil supplemented with 2% by weight of dimethyl disulfide, the hydrodesulfurization test was conducted under the following operating conditions: a total pressure of 7 MPa, a catalyst volume of 30 cm<sup>3</sup>, a temperature of 330-360°C, a hydrogen flow 15 rate of 24 l/h and a feedstock flow rate of 60 cm<sup>3</sup>/h.

The catalytic performances of the catalysts tested are given in table 1. They are expressed in degrees Celsius relative to a comparative catalyst chosen as reference (C2): they correspond 20 to the temperature difference to be applied in order to attain 50 ppm of sulfur in the effluent. A negative value means that the target sulfur content is attained for a lower temperature and that there is therefore a gain in activity. A positive value means that the target sulfur content is attained for a higher 25 temperature and that there is therefore a loss of activity. The results obtained are collated in table 1.

Table 1 clearly shows the gain on the catalytic effect afforded by  $\gamma$ -valerolactone, but also by 4-hydroxyvaleric acid. 30 Specifically, catalysts C5, C6 and C7 (according to the invention) have higher activities than those obtained for all the other catalysts evaluated at the same molar proportions of organic compound (1 mol/mol<sub>Mo</sub>).

35 The gain is also maximized, for the same amount of additive, catalysts C5 and C6 are more active than catalysts C3 and C4 obtained, respectively, with citric acid or TEG and which are less active.

The activity of catalyst C7 remains very much higher than that of the base catalyst C2 or of a dried catalyst C1 without  $\gamma$ -valerolactone or 4-hydroxyvaleric acid.

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The advantage of the catalyst according to the invention remains significant at a lower proportion of organic compound, as shown by catalyst C9, thus with an intrinsic efficacy of  $\gamma$ -valerolactone which is higher than that of the other compounds, 10 for which it is necessary to introduce a larger proportion of compound to observe a substantial catalytic effect.

Table 1: Isovolumic relative activity in the hydrodesulfurization of gas oil for catalysts C1, C2, C3, C4 and 15 C8 (not in accordance with the invention) and C5, C6, C7 and C9 (in accordance with the invention) relative to catalyst C2 (not in accordance).

Catalyst ( <u>comparative</u> or according to the invention)	Organic compound used and mole ratio / Mo	Method of introduction of the organic compound (post-/co- /pre- impregnation)	Heat treatment	HDS activity
C1 (comp)	None	No object	Dried 120°C	Base + 1.1°C
C2 (comp)	None	No object	Calcined	Base
C3 (comp)	Citric acid - 1.0	CO	Dried 120°C	Base - 3.1°C
C4 (comp)	TEG - 1.0	CO	Dried 120°C	Base - 5.3°C
C5 (inv)	$\gamma$ - Valerolactone - 1.0	CO	Dried 120°C	Base - 7.3°C

Catalyst ( <u>comparative</u> or according to the <u>invention</u> )	Organic compound used and mole ratio / Mo	Method of introduction of the organic compound (post-/co- /pre- impregnation)	Heat treatment	HDS activity
C6 (inv)	4- Hydroxyvaleric acid -1.0	CO	Dried 120°C	Base - 6.8°C
C7 (inv)	γ- Valerolactone - 1.0	PRE	Dried 120°C	Base - 6.2°C
C8 (comp)	Citric acid - 0.25	CO	Dried 120°C	Base - 2.2°C
C9 (inv)	γ- Valerolactone - 0.25	CO	Dried 120°C	Base - 4.4°C

## Patentkrav

1. Katalysator, der omfatter en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid, mindst 5 ét grundstof fra gruppe VIII, mindst ét grundstof fra gruppe VIB og mindst ét additiv, der er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, og hvor indholdet af grundstof fra gruppe VIB, udtrykt som oxid af metal fra gruppe VIB i forhold til katalysatorens samlede 10 vægt, ligger mellem 5 og 40 vægt-%, og indholdet af grundstof fra gruppe VIII, udtrykt som oxid af metal fra gruppe VIII i forhold til katalysatorens samlede vægt, ligger mellem 1 og 10 vægt-%, og det samlede indhold af additiv(er), der er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3- 15 pentensyre og 4-pentensyre, ligger mellem 1 og 35 vægt-% i forhold til katalysatorens samlede vægt.

2. Katalysator ifølge krav 1, hvor molforholdet mellem grundstof fra gruppe VIII og grundstof fra gruppe VIB i 20 katalysatoren ligger mellem 0,1 og 0,8.

3. Katalysator ifølge et af kravene 1 til 2, som i øvrigt indeholder phosphor, idet phosphorindholdet, udtrykt som  $P_2O_5$  i forhold til katalysatorens samlede vægt, ligger mellem 0,1 og 25 20 vægt-%, og forholdet mellem phosphor og grundstoffet fra gruppe VIB i katalysatoren er større end eller lig med 0,05.

4. Katalysator ifølge et af kravene 1 til 3, som i øvrigt indeholder en anden organisk forbindelse ud over additivet valgt 30 blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, hvilken organiske forbindelse indeholder oxygen og/eller nitrogen og/eller svovl.

5. Katalysator ifølge krav 4, hvor den organiske forbindelse 35 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.

6. Katalysator ifølge krav 5, hvor den organiske forbindelse  
er valgt blandt triethylenglycol, diethylenglycol,  
ethylendiamintetraeddikesyre, maleinsyre, citronsyre,  
5 dimethylformamid, bicin eller tricin.

7. Katalysator ifølge et af kravene 1 til 6, hvor bæreren  
indeholder fra 0,1 til 50 vægt-% zeolit.

10 8. Katalysator ifølge et af kravene 1 til 7, kendetegnet ved,  
at den i det mindste delvist er svovlholdig.

9. Fremgangsmåde til fremstilling af en katalysator ifølge et  
af kravene 1 til 8, hvilken fremgangsmåde omfatter de følgende  
15 trin:

a. mindst én komponent af et grundstof fra gruppe VIB, mindst  
én komponent af et grundstof fra gruppe VIII, mindst ét additiv,  
der er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-  
20 pentensyre, 3-pentensyre og 4-pentensyre, og eventuelt phosphor,  
bringes i kontakt med en bærer på basis af aluminiumoxid eller  
silica eller silica-aluminiumoxid, eller en regenereret  
katalysator, der indeholder en bærer på basis af aluminiumoxid  
eller silica eller silica-aluminiumdioxid, mindst én komponent  
af et grundstof fra gruppe VIB, mindst én komponent af et  
25 grundstof fra gruppe VIII og eventuelt phosphor, bringes i  
kontakt med mindst ét additiv, der er valgt blandt  $\gamma$ -  
valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre  
og 4-pentensyre, for at opnå en katalysatorforløber  
b. den katalysatorforløber, der er et resultat af trin a), tørres  
30 ved en temperatur på under 200 °C, uden at den yderligere  
kalcineres.

10. Fremgangsmåde ifølge krav 9, hvorved trin a) er det  
følgende trin:

35 a') en bærer på basis af aluminiumoxid eller silica eller silica-  
aluminiumoxid imprægneres med mindst én opløsning, der  
indeholder mindst ét grundstof fra gruppe VIB, mindst ét  
grundstof fra gruppe VIII, mindst ét additiv, der er valgt blandt

$\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, og eventuelt phosphor for at opnå en katalysatorforløber.

5 11. Fremgangsmåde ifølge krav 9, hvorved trin a) omfatter de følgende trin:

a1) en bærer på basis af aluminiumoxid eller silica eller silica-aluminiumoxid imprægneres med mindst én opløsning, der indeholder mindst ét grundstof fra gruppe VIB, mindst ét 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 ét additiv, som er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, for at opnå en katalysatorforløber

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

12. Fremgangsmåde ifølge krav 9, hvorved trin a) omfatter de følgende trin:

a1') der fremstilles en bærer, der omfatter mindst ét additiv, som er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, og eventuelt mindst en del af phosphoret

a2') den i trin a1') opnåede bærer imprægneres med en imprægneringsopløsning, der omfatter mindst ét grundstof fra gruppe VIB, mindst ét 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.

13. Fremgangsmåde ifølge krav 9, hvorved trin a) omfatter de følgende trin:

a1") en opløsning, der indeholder mindst ét grundstof fra gruppe VIB, mindst ét grundstof fra gruppe VIII, mindst én organisk forbindelse, der indeholder 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

5 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

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

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

og mindst én af de organiske forbindelser fra trin a1") eller fra trin a3") er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre.

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14. Fremgangsmåde ifølge krav 9, 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 én komponent af et grundstof fra gruppe VIB, mindst én komponent af et grundstof fra gruppe VIII og eventuelt phosphor, imprægneres med en imprægneringsopløsning, der omfatter mindst ét additiv, som er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, for at opnå en katalysatorforløber

30 a2'') den i trin a1'') opnåede katalysatorforløber får eventuelt lov til at modne.

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15. Fremgangsmåde ifølge et af kravene 9 til 14, hvorved det samlede molforhold mellem additiv(er), der er valgt blandt  $\gamma$ -valerolacton, 4-hydroxyvaleriansyre, 2-pentensyre, 3-pentensyre og 4-pentensyre, og grundstof(fer) i gruppe VIII ligger mellem 0,1 og 5,0 mol/mol.

16. Anvendelse af katalysatoren ifølge et af kravene 1 til 8,  
eller som er fremstillet ifølge et af kravene 9 til 15, i en  
fremgangsmåde til hydrogenbehandling og/eller hydrokrakning af  
5 carbonhydridfraktioner.