

SELECTIVE HYDROGENATION PROCESS EMPLOYING A
SULPHURIZED CATALYST WITH A SPECIFIC COMPOSITION

Field of the invention

The production of gasoline satisfying new environmental standards necessitates that their sulphur content be reduced substantially, to values which generally do not exceed 50 ppm and are preferably less than 10 ppm.

5 It is also known that conversion gasolines, more particularly those from catalytic cracking, which may represent 30% to 50% of the gasoline pool, have high mono-olefin and sulphur contents.

For this reason, the sulphur present in the gasoline is more than 90% attributable to gasoline from catalytic cracking processes which will hereinafter be
10 termed FCC gasoline (fluid catalytic cracking). FCC gasolines thus constitute the preferred feed for the process of the present invention.

More generally, the process of the invention is applicable to any gasoline cut containing a certain proportion of diolefins, and which may also contain several lighter compounds from C₃ and C₄ cuts.

15 Gasoline from cracking units is generally rich in mono-olefins and in sulphur, but also in diolefins with a content, for gasoline from catalytic cracking, which can vary from 1% by weight to 5% by weight. The diolefins are unstable compounds which readily polymerize and generally have to be eliminated before any treatment of such gasoline such as hydrodesulphurization treatments intended
20 to satisfy specifications regarding the sulphur contents in the gasoline can be carried out. However, such hydrogenation must be applied selectively to diolefins in order to limit the hydrogenation of mono-olefins and to limit the consumption of hydrogen as well as the octane loss of the gasoline. Further, as described in patent application EP-01077247 A1, it is advantageous to transform saturated
25 light sulphur-containing compounds by weighting; these are sulphur-containing

compounds with a boiling point which is lower than the boiling point of thiophene, such as methane thiol, ethane thiol, dimethyl sulphide, before the desulphurization step as this means that a desulphurized gasoline fraction mainly composed of mono-olefins containing 5 carbon atoms can be produced with no
5 octane loss by simple distillation.

Further, dienic compounds present in the feed to be treated are unstable and have a tendency to form gums by polymerization. This gum formation results in progressive deactivation of the selective hydrogenation catalyst or progressive blockage of the reactor. For an industrial application, it is thus important to use
10 catalysts which limit the formation of polymers, i.e. catalysts with a low acidity or with an optimized porosity to facilitate continuous extraction of polymers or gum precursors by the hydrocarbons in the feed in order to ensure a maximum cycle time for the catalyst.

The present invention concerns the use of a novel catalyst in a process
15 which allows the joint hydrogenation of polyunsaturated compounds, more particularly diolefins, as well as weighting of light sulphur-containing compounds, more particularly mercaptans.

One advantage of the invention is to facilitate the elimination of sulphur by weighting the mercaptans in order to be able to separate them more easily and
20 thus to eliminate them in a subsequent hydrodesulphurization step.

Another advantage of the invention is the production of a gasoline with a high octane number.

A third advantage of the invention resides in the fact that the catalyst formulation is adjusted in order to provide high de-dienizing activity, better
25 catalyst stability as regards polymer formation, good selectivity as regards

diolefin hydrogenation and good activity for the conversion of mercaptans and other light sulphur-containing compounds.

Prior art

The literature describes catalytic formulations or processes which can
5 allow either the selective hydrogenation of diolefins into mono-olefins or the transformation of mercaptans by weighting, or both of these reaction types to be carried out in one or two steps.

The use of catalysts containing at least one noble metal is known. Thus, a number of patents propose palladium-containing selective hydrogenation
10 catalysts. Palladium is known for its hydrogenating activity and is widely used in selective hydrogenation processes. However, palladium is sensitive to poisons, in particular to the presence of sulphur. The present invention differs from such catalysts in that the catalyst of the invention contains no palladium, and more generally contains no noble metals.

15 European patent application EP-06 85552 B1 proposes a process for the hydrogenation of diolefins and for reducing the mercaptans content in a catalytic cracking gasoline based on a catalyst containing in the range 0.1% to 1% by weight of palladium.

US-6 469 223 concerns a process for the selective hydrogenation of
20 diolefins on a catalyst containing nickel and molybdenum on a support based on alumina. The process is characterized in that the metals nickel and molybdenum are employed in the oxide form. The present invention differs from this prior art in that the metals are employed in the form of the metal sulphides and not oxides.

The following patents and patent applications propose solutions for weighting mercaptans by thioetherification reactions and optional selective hydrogenation of diolefins.

Patent US-5 807 477 proposes a process which, in a first step, can transform mercaptans into sulphides by addition onto the diolefins over a catalyst comprising a metal from group VIII, preferably nickel in the oxide form, then in a second step of selectively hydrogenating the diolefins in a reactive distillation column in the presence of hydrogen. The present invention differs from that patent since the selective hydrogenation step and step for weighting the sulphur-containing compounds are carried out jointly over the same catalyst used in the sulphurized form.

Patent US-5 851 383 describes a process for selective hydrogenation and thioetherification of C_3 - C_5 cuts, characterized by a distillation device comprising two fractionation zones which can separately recover the light compounds and thioethers. The catalysts described are either catalysts based on a group VIII metal or resins containing a metal. A catalyst containing between 15% and 35% of nickel is preferred. The catalyst of the present invention differs from that patent in that the hydrogenation metal is a metal from group VIb and the nickel content is less than 15% by weight.

Patent application US-2007/7173674 proposes a selective hydrogenation process using a catalyst containing at least one metal from group VIb and a metal from group VIII supported on alumina. The molar ratio between the metal from group VIII and the metal from group VIb is in the range 0.2 to 0.5 mol/mol. The catalyst of the present invention differs from that prior art in that the molar ratio between the group VIII metal and the group VIb metal is in the range 0.6 to 3

mol/mol and also in the density of the group VIb element per unit surface area of catalyst.

In view of the solutions described in the literature, the present invention proposes a process employing a catalyst having a specific composition which can
5 be used to carry out joint hydrogenation of polyunsaturated compounds, more particularly diolefins, as well as weighting of light sulphur-containing compounds, more particularly mercaptans.

Brief description of the invention

The present invention describes a process for the selective hydrogenation
10 of polyunsaturated compounds, more particularly diolefins, which can jointly carry out weighting of saturated light sulphur-containing compounds, more particularly mercaptans, said process employing a catalyst containing at least one metal from group VIb and at least one non-noble metal from group VIII deposited on a porous support, and in which:

- 15 • the amount by weight of oxide of the element from group VIb is in the range 4% to 20% by weight;
- the amount by weight of oxide of the element from group VIII is less than 15% by weight;
- the degree of sulphurization of the constituent metals of
20 said catalyst is at least 60%;
- the molar ratio between the non-noble metal from group VIII and the metal from group VIb is in the range 0.6 to 3 mol/mol;

the density of the element from group VIb per unit surface area of catalyst is strictly less than 10^{-3} grams of the oxides of the group VIb element per m^2 of catalyst.

The process consists of passing over the catalyst a mixture constituted by
5 the gasoline to be treated and hydrogen.

The hydrogen is generally introduced in a slight excess, up to 5 moles per mole with respect to the stoichiometry of that which is necessary to hydrogenate the diolefins (one mole of hydrogen per mole of diolefin).

The mixture constituted by the gasoline and hydrogen is brought into
10 contact with the catalyst at a pressure in the range 0.5 to 5 MPa, a temperature in the range 80°C to 220°C , with a liquid hourly space velocity (LHSV) in the range 1 h^{-1} to 10 h^{-1} , the liquid hourly space velocity being expressed in litres of feed per litre of catalyst per hour (l/l.h).

Detailed description of the invention

15 The invention concerns a process for the treatment of gasoline comprising any type of chemical family, in particular diolefins, mono-olefins, and sulphur-containing compounds in the form of mercaptans and light sulphides. The present invention is of particular application in the transformation of conversion gasoline, in particular gasoline from catalytic cracking, fluid catalytic cracking (FCC), from
20 a cokefaction process, from a visbreaking process, or from a pyrolysis process. Feeds for which the invention is applicable have a boiling point in the range 0°C to 280°C , more precisely in the range 30°C to 250°C . The feeds may also contain hydrocarbons containing 3 or 4 carbon atoms.

As an example, the gasolines derived from catalytic cracking units (FCC)
25 contain, on average, in the range 0.5% to 5% by weight of diolefins, in the range

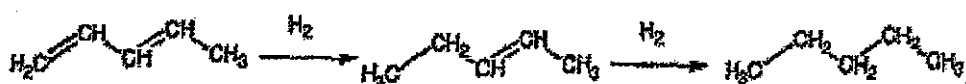
20% to 50% by weight of mono-olefins, in the range 10 ppm to 0.5% by weight of sulphur, generally with at least 300 ppm of mercaptans. The mercaptans are generally concentrated in the light fractions of the gasoline and more precisely in the fraction with a boiling point of less than 120°C.

5 Treatment of the gasoline described in the present process principally consists of:

- selectively hydrogenating the diolefins to mono-olefins;
 - transforming the light saturated sulphur-containing compounds, principally mercaptans, into sulphides or
- 10 heavier mercaptans by reaction with the mono-olefins.

Reactions for hydrogenating diolefins into mono-olefins are illustrated below by the transformation of 1,3-pentadiene, an unstable compound, which can readily be hydrogenated into pent-2-ene. However, secondary mono-olefin hydrogenation reactions should be limited since, as seen in the example below,

15 they would result in the formation of n-pentane:



The sulphur-containing compounds which are to be transformed are principally mercaptans and sulphides. The principal mercaptans transformation reaction consists of thioetherification of mono-olefins by the mercaptans. This

20 reaction is illustrated below by the addition of propane-2-thiol on pent-2-ene to form a propyl pentyl sulphide:

5 route under the preferred reaction conditions.

In addition to the mercaptans, compounds which can be transformed and weighted are sulphides and principally dimethyl sulphide, methyl ethyl sulphide and diethyl sulphide, CS_2 , COS, thiophane and methyl thiophane.

10 principally nitriles, pyrrole and derivatives thereof, may be observed.

15 edition, 1995-1996) and at least one metal from group VIII (groups 8, 9 and 10) of
said classification, deposited on a porous support.

In particular, it has been found that the performances of the catalysts are improved when the catalyst has the following characteristics:

oxide form is in the range 4% to 20% by weight, preferably in the range 5% to 15% by weight. The group VIb metal is preferably selected from molybdenum and tungsten. More preferably, the group VIb metal is molybdenum.

The catalyst also contains a non-noble metal from group VIII preferably selected from nickel, cobalt and iron. More preferably, the non-noble metal from group VIII is constituted by nickel. The quantity of non-noble metal from group VIII, expressed in the oxide form, is less than 15% by weight, preferably in the
5 range 1% by weight to 10% by weight.

The molar ratio between the non-noble metal from group VIII and the metal from group VIb is in the range 0.6 to 3 mol/mol, preferably in the range 1 to 2.5 mol/mol.

Beyond a Ni/Mo molar ratio of 3 and for molybdenum contents of more
10 than 4% by weight, dissolving the species to prepare the impregnation solution is difficult.

The density of molybdenum per unit surface area of catalyst is strictly less than 10^{-3} grams of MoO_3 per m^2 of catalyst, preferably strictly less than 7×10^{-4} grams of MoO_3 per m^2 of catalyst.

15 Preferably, a catalyst with a total pore volume, measured by mercury porosimetry, of more than $0.3 \text{ cm}^3/\text{g}$, preferably more than $0.4 \text{ cm}^3/\text{g}$ and less than $1.4 \text{ cm}^3/\text{g}$, is used. The mercury porosimetry is measured in accordance with the US standard ASTM D4284-92 with a wetting angle of 140° , using an Autopore III model from Micrometrics. The specific surface area of the catalyst is preferably
20 less than $300 \text{ m}^2/\text{g}$. Preferably, the catalyst of the invention contains no alkali metal, nor alkaline-earth metal.

The catalyst support is preferably a porous metallic oxide selected from alumina, nickel aluminate, silica, silicon carbide, and a mixture of these oxides. Preferably, alumina is used, more preferably pure alumina. Preferably, the
25 support used has a total pore volume, measured by mercury porosimetry, in the

range 0.4 to 1.4 cm³/g, preferably in the range 0.5 to 1.3 cm³/g. The specific surface area of the support is preferably less than 350 m²/g.

In a variation, the support is constituted by cubic gamma alumina or by delta alumina.

5 In a preferred implementation of the invention, a catalyst is used which contains a content by weight of nickel oxide in the NiO form in the range 1% to 15%, a content by weight of molybdenum oxide in the form MoO₃ of more than 5% and a nickel/molybdenum molar ratio in the range 1 to 2.5, the metals being deposited on a pure alumina support and the degree of sulphurization of the
10 metals constituting the catalyst being more than 80%.

The catalyst of the invention may be prepared using any technique which is known to the skilled person, in particular by impregnation of elements from groups VIII and VIb onto the selected support. This impregnation may, for example, be carried out using the mode which is known to the skilled person as
15 dry impregnation, in which exactly the quantity of the desired elements is introduced, in the form of salts which are soluble in the selected solvent, for example demineralized water, which can fill the pores of the support as exactly as possible. The support which has been filled with the solution is preferably dried. The preferred support is alumina which may be prepared from any type of
20 precursor and forming tool known to the skilled person.

After introducing the elements from groups VIII and VIb and optional forming of the catalyst, it undergoes an activation treatment. This treatment is generally intended to transform the molecular precursors of the elements into the oxide phase. In this case, it is an oxidizing treatment but simply drying of the
25 catalyst may also be carried out. In the case of an oxidizing treatment, also

known as calcining, this is generally carried out in air or in diluted oxygen, and the treatment temperature is generally in the range 200°C to 550°C, preferably in the range 300°C to 500°C. Examples of salts of metals from groups VIb and VIII for use in the catalyst preparation process are cobalt nitrate, nickel nitrate,
 5 ammonium heptamolybdate and ammonium metatungstate. Any other salt which is known to the skilled person with a sufficient solubility and which can be decomposed during the activation treatment may also be used.

After calcining, the metals deposited on the support are in the oxide form. In the case of nickel and molybdenum, the metals are principally in the form of
 10 MoO_3 and NiO . Before being brought into contact with the feed to be treated, the catalysts undergo a sulphurization step. Sulphurization is preferably carried out in a sulpho-reducing medium, i.e. in the presence of H_2S and hydrogen, to transform the metallic oxides into sulphides such as MoS_2 or Ni_3S_2 . Sulphurization is carried out by injecting onto the catalyst a stream containing H_2S and hydrogen,
 15 or a sulphur-containing compound which can decompose into H_2S in the presence of catalyst and hydrogen. Polysulphides such as dimethyldisulphide are H_2S precursors which are routinely used to sulphurize catalysts. The temperature is adjusted so that the H_2S reacts with the metallic oxides to form metallic sulphides. This sulphurization may be carried out in situ or ex situ (inside or outside the
 20 reactor) of the hydrodesulphurization reactor at temperatures in the range 200°C to 600°C, more preferably in the range 300°C to 500°C.

In order to be active, the metals must be substantially sulphurized. An element is considered to be substantially sulphurized when the molar ratio between the sulphur (S) present in the catalyst and said element is at least 60% of

the theoretical molar ratio corresponding to total sulphurization of the element under consideration:

$$(S/\text{element})_{\text{catalyst}} \geq 0.6 \times (S/\text{element})_{\text{theoretical}}$$

in which:

5 $(S/\text{element})_{\text{catalyst}}$ is the molar ratio between the sulphur (S) and the element present in the catalyst;

$(S/\text{element})_{\text{theoretical}}$ is the molar ratio between the sulphur and the element corresponding to total sulphurization of the element to the sulphide.

This theoretical molar ratio varies as a function of the element under
10 consideration:

- $(S/\text{Fe})_{\text{theoretical}} = 1$
- $(S/\text{Co})_{\text{theoretical}} = 8/9$
- $(S/\text{Ni})_{\text{theoretical}} = 2/3$
- $(S/\text{Mo})_{\text{theoretical}} = 2/1$
- 15 • $(S/\text{W})_{\text{theoretical}} = 2/1.$

For a catalyst comprising a plurality of metals, the molar ratio between the S present on the catalyst and the set of the elements must also be at least equal to 60% of the theoretical molar ratio corresponding to total sulphurization of each element to the sulphide, the calculation being carried out pro rata with the relative
20 molar fractions of each element.

As an example, for a catalyst comprising molybdenum and nickel with a respective molar fraction of 0.7 and 0.3, the minimum molar ratio $(S/\text{Mo} + \text{Ni})$ is given by the relationship:

$$(S/\text{Mo}+\text{Ni})_{\text{catalyst}} = 0.6 \times \{(0.7 \times 2) + (0.3 \times (2/3))\}$$

Highly preferably, the degree of sulphurization of the metals will be greater than 80%.

Sulphurization is carried out on the metals in the oxide form without carrying out a prior metal reduction step. It is in fact known that sulphurizing
5 reduced metals is more difficult than sulphurizing metals in the form of oxides.

In the selective hydrogenation process of the invention, the feed to be treated is mixed with hydrogen before being brought into contact with the catalyst. The quantity of hydrogen injected is such that the molar ratio between the hydrogen and the diolefins to be hydrogenated is more than 1 (stoichiometry)
10 and less than 10, preferably in the range 1 to 5 mol/mol. Too large an excess of hydrogen may result in intense hydrogenation of the mono-olefins and as a result a reduction in the octane number of the gasoline. The totality of the feed is generally injected into the reactor inlet. However, it may be advantageous in certain cases to inject a fraction or all of the feed between two consecutive
15 catalytic beds placed in the reactor. This implementation can in particular allow the reactor to continue to be operated if the reactor inlet is blocked by deposits of polymers, particles or gums present in the feed.

The mixture constituted by the gasoline and hydrogen is brought into contact with the catalyst at a temperature in the range 80°C to 220°C, preferably
20 in the range 90°C to 200°C, with a liquid hourly space velocity (LHSV) in the range 1 h^{-1} to 10 h^{-1} , the units for the liquid hourly space velocity being litres of feed per litre of catalyst per hour (l/l.h). The pressure is adjusted so that the reaction mixture is mainly in the liquid form in the reactor. The pressure is in the range 0.5 MPa to 5 MPa, preferably in the range 1 to 4 MPa.

The gasoline treated under the conditions defined above has a reduced diolefins and mercaptans content. In general, the gasoline produced contains less than 1% by weight of diolefins, preferably less than 0.5% by weight of diolefins. The light sulphur-containing compounds with a boiling point of less than that of thiophene (84°C) are generally more than 50% converted. Thus, it is possible to separate the light fraction from the gasoline by distillation and to send this fraction directly to the gasoline pool without supplemental treatment. The light fraction of the gasoline generally has an end point of less than 120°C, preferably less than 100°C and more preferably less than 80°C.

10 This novel catalyst is particularly suitable for use in the context of the process described in patent application EP-01077247 A1.

Example 1: Preparation of catalysts A and B (not in accordance) and C, D and E (in accordance with the invention)

Catalysts A, B, C, D and E were prepared by dry impregnation. The synthesis protocol consisted of carrying out dry impregnation of a solution of ammonium heptamolybdate and nickel nitrate, the volume of the aqueous solution containing the metallic precursors being equal to the water take-up volume corresponding to the mass of the support to be impregnated (total volume of water which can penetrate into the pores). The concentration of precursors in the solution was adjusted so as to deposit the desired weights of metal oxides onto the support.

The solid was then left to mature at ambient temperature for 12 hours, then dried at 120°C for 12 hours. Finally, the solid was calcined at 500°C for two hours in a stream of air (1 l/g.h).

The support used was an alumina with a pore volume of 0.7 ml/g. The characteristics of the catalysts which were prepared are provided in Table 1 below. The prepared catalysts differ in their active phase content.

Table 1: Characteristics of catalysts A, B, C, D, E, F in the oxide form

Catalyst	A	B	C	D	E
% by weight of MoO ₃	11	12	9	5	7
% by weight of NiO	0.6	1.9	4.7	5.2	5.5
Ni/Mo molar ratio	0.1	0.3	1	2	1.5
d MoO ₃ (10 ⁻⁴ g/m ² cat)	4.5	5.0	3.8	1.9	2.9
Specific surface area of support, m ² /g	280	280	280	280	280

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Catalysts C, D and E were in accordance with the invention; in contrast, catalysts A and B had a Ni/Mo ratio which was too small and thus were not in accordance with the invention.

Beyond a molar ratio Ni/Mo of 3 and for molybdenum contents of more than 4% by weight, dissolving the species to prepare the impregnation solution is difficult.

Catalyst evaluation

The activity of catalysts A, B, C, D and E was evaluated by a selective hydrogenation test for a mixture of model molecules carried out in a 500 ml stirred autoclave reactor. Between 2 and 6 grams of catalyst were sulphurized at atmospheric pressure in a sulphurization bench under a H₂S/H₂ mixture constituted by 15% by volume of H₂S for 1 l/g.h of catalyst and at 400°C for two hours. This protocol produced sulphurization ratios of more than 80% for all of the catalysts of the invention. The sulphurized catalyst was then transferred into

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the reactor in the absence of air and brought into contact with 250 ml of model feed at a total pressure of 1.5 MPa and at a temperature of 160°C. The pressure was kept constant during the test by adding hydrogen.

The feed used for the activity test had the following composition: 1000
5 ppm by weight of sulphur in the form of methyl-3-thiophene, 100 ppm by weight of sulphur in the form of propane-2-thiol, 10% by weight of olefin in the form of hexene-1, in n-heptane.

The time $t=0$ of the test corresponded to bringing the catalyst into contact with the feed. The test period was fixed at 45 minutes and gas chromatographic
10 analysis of the liquid effluent obtained allowed the activities of the various catalysts to be evaluated for the hydrogenation of isoprene (methylbutene formation), the hydrogenation of hexene-1 (formation of n-hexane) and for weighting of light mercaptans (conversion of propane-2-thiol).

The activity of the catalyst for each reaction is defined with respect to the
15 normalized rate constant obtained for each reaction per gram of catalyst. The rate constant is calculated by assuming first order for the reaction:

$$A(X) = k(X)/m$$

in which:

$A(X)$: activity of catalyst for reaction X, in min^{-1} per gram of catalyst;

20 k : rate constant for the reaction under consideration, in min^{-1} , being calculated in accordance with the formula:

$$k(X) = (1/45) * \ln(100/(100 - \text{conv}(X)))$$

where:

45: test duration in minutes;

conv(X): conversion of compound X; X = isoprene or propane-2-thiol
or hexene-1;

5 m: mass of catalyst (oxide form) engaged in the test;

X: reaction under consideration:

X = isoprene: hydrogenation of isoprene;

X = hexene-1: hydrogenation of hexene-1;

X = propane-2-thiol: conversion of propane-2-thiol.

10 The selectivity of the catalyst towards the hydrogenation of isoprene is equal to the ratio of the activities of the catalyst in hydrogenating isoprene and hexene-1:

$$A(\text{isoprene})/A(\text{hexene-1}).$$

The results obtained for the various catalysts are shown in Table 2 below.

15 **Table 2: Performances of catalysts in model molecule test**

Catalyst	A	B	C	D	E
$A(\text{isoprene}) \cdot 10^4$	6.1	8.3	25.2	28.3	23
$A(\text{hexene-1}) \cdot 10^3$	0.23	0.26	0.25	0.26	0.23
$A(\text{isoprene})/A(\text{hexene-1})$	27	32	102	109	98

Catalysts C, D and E, in accordance with the invention, have high activity compared with catalysts A and B, not in accordance with the invention, for the hydrogenation of isoprene without significantly hydrogenating the hex-1-ene.

20 **Example 2: Influence of surface density of Mo**

In this example, catalysts G and H were prepared using the operating protocol described in Example 1.

Table 3: Characteristics of catalysts G and H in the oxide form

Catalyst	G	H
% by weight of MoO ₃	12	8
% by weight of NiO	8	8
Ni/Mo molar ratio	1.3	1.9
d MoO ₃ (10 ⁻⁴ g/m ² cat)	11.5	7.2
specific surface area of support, m ² /g	130	130

Catalysts G and H were evaluated in the model molecule test described in Example 1.

5 Table 4: Performances of catalysts G and H in model molecule test

Catalyst	G	H
A(isoprene)*10 ³	6.9	13.6
A(hexene-1)*10 ³	0.14	0.13
A(isoprene)/A(hexene-1)	48	104

Catalyst G, not in accordance with the invention ($d \text{ MoO}_3 > 10^{-3} \text{ g/m}^2_{\text{cat}}$) exhibited a deficient isoprene hydrogenation activity compared with catalyst H, which was in accordance with the invention.

CLAIMS

1. A process for the selective hydrogenation of polyunsaturated compounds into mono-unsaturated compounds which can jointly carry out weighting of saturated light sulphur-containing compounds by reaction with the unsaturated compounds contained in gasoline, said process employing a catalyst containing at least one metal from group VIb and at least one non-noble metal from group VIII deposited on a support, and in which:
 - the amount by weight of oxide of the element from group VIb is in the range 4% to 20%;
 - the amount by weight of oxide of the element from group VIII is less than 15% by weight;
 - the degree of sulphurization of the constituent metals of said catalyst is at least 60%;
 - the molar ratio between the non-noble metal from group VIII and the metal from group VIb is in the range 0.6 to 3 mol/mol;
 - the density of the element from group VIb per unit surface area of catalyst is strictly less than 10^{-3} grams of the oxides of the group VIb element per m^2 of catalyst.
2. A process according to claim 1, in which the catalyst comprises a metal from group VIb selected from molybdenum and tungsten.
3. A process according to claim 2, in which the metal from group VIb is molybdenum.
4. A process according to claim 1, in which the catalyst comprises a non-noble metal from group VIII selected from nickel, cobalt and iron.

5. A process according to claim 4, in which the non-noble metal from group VIII is nickel.
6. A process according to one of the preceding claims, in which the catalyst comprises a weight content of the oxide of the element from group VIII in the range 1% to 10% by weight.
7. A process according to claim 1, in which the degree of sulphurization of the constituent metals of said catalyst is more than 80%.
8. A process according to claim 1, in which the molar ratio between the non-noble metal from group VIII and the metal from group VIb is in the range 1 to 2 mol/mol.
9. A process according to one of the preceding claims, in which the catalyst has a total pore volume of more than $0.3 \text{ cm}^3/\text{g}$.
10. A process according to claim 9, in which the catalyst has a total pore volume in the range $0.4 \text{ cm}^3/\text{g}$ to $1.4 \text{ cm}^3/\text{g}$.
11. A process according to one of the preceding claims, in which the specific surface area of the catalyst is less than $300 \text{ m}^2/\text{g}$.
12. A process according to claim 1, in which the catalyst support is a porous metal oxide selected from alumina, silica, silicon carbide and a mixture of said oxides.
13. A process according to claim 12, in which the catalyst support is constituted by pure alumina.
14. A process according to claim 12 or claim 13, in which the support is constituted by cubic gamma alumina or delta alumina.
15. A process according to one of claims 12 to 14, in which the catalyst support has a pore volume in the range 0.4 to $1.4 \text{ cm}^3/\text{g}$.

16. A process according to claim 15, in which the catalyst support has a pore volume in the range 0.5 to 1.3 cm³/g.
17. A selective hydrogenation process according to one of the preceding claims, in which the feed is brought into contact with the catalyst at a temperature in the range 80°C to 220°C at a liquid hourly space velocity in the range 1 h⁻¹ to 10 h⁻¹ and at a pressure in the range 0.5 to 5 MPa.