METHOD FOR THE PREPARATION OF A CATALYST BY SELECTIVE EXTRACTION FROM A CONTAMINATED CATALYST

Technical field

The present invention relates to the recycling of catalyst metals notably originating from hydrocarbon hydrotreatment or hydroconversion units, for the re-manufacture of catalysts. More particularly, the present invention relates to a process for preparing a catalyst involving a step of extracting the desired metals contained in a contaminated catalyst. It relates in particular to a process for preparing a catalyst involving a step of extracting the desired metals contained in a catalyst contaminated with arsenic while limiting the extraction of arsenic. The extraction solution is then used as an impregnation solution to prepare a catalyst. The resulting catalyst is intended, notably, to be used in units for the hydrotreating or hydroconversion of hydrocarbons.

Prior art

Most of the technological innovations necessary for the energy transition (electric vehicle, wind power, fuel cell, batteries, etc.) require the massive use of metals. In order to meet this demand while ensuring sustainable development, metal recycling is becoming a major issue for the next century.

In particular, the spent catalysts originating from hydrocarbon hydrotreatment or hydroconversion units contain metals of interest, namely at least one metal from group VIB and/or at least one metal from group VIII. Once spent, the metals contained in these catalysts are not currently recycled for the manufacture of new catalysts: they are essentially reused in the manufacture of special alloys, requiring complex purification operations, notably to rid the recovered metals of compounds regarded as contaminants, such as arsenic, or as problematic in view of the targeted applications, such as phosphorus, the presence of which disturbs, for example, the properties of chromium steel alloys.

However, processes have been developed to recover metals from catalysts, in order to recycle them for the manufacture of new catalysts.

For example, patent application US 2007/0167321 proposes the recovery of molybdenum from spent catalysts in order to make new catalysts. To do this, according to this process, the spent catalyst is dispersed in a basic solution and a contaminant/compound contained in the spent catalyst which it is desired to remove (arsenic, phosphorus) is withdrawn from the solution by causing it to precipitate, and the solution is then filtered. The molybdenum is then precipitated

by modifying the pH of the solution toward an acidic pH. The molybdenum precipitate is filtered off so that it can be reused by dispersion in an impregnation solution furthermore containing precursors of other metals, such as precursors of cesium, antimony or vanadium, and of other components necessary in order to constitute the new catalyst by impregnation of a support.

Patent application FR3117381 proposes the production of a recycled hydrocarbon hydrotreatment or hydroconversion catalyst. The metal from group VIII and the metal from group VIB are extracted using an aqueous solution containing at least one organic compound having complexing properties, and optionally also acidic properties. The solution obtained is then used directly for impregnation on an oxide support to produce a recycled catalyst, i.e. the extracted metals remain in the liquid phase during the entirety of this process. Unlike the prior techniques, this process does not seek to recover the metal in solid and monometallic form, thus sparing itself a number of operations of the precipitation/filtration type. The process is thus easy to implement on the industrial scale.

During its operation in a hydrotreating or hydroconversion process, a catalyst becomes deactivated by accumulation of coke and/or sulfur-containing compounds and/or other contaminants at the surface of the catalyst. The contaminants originate, among other things, from the feedstock. The most common contaminants are metals such as nickel, vanadium, iron and titanium, but also silicon, calcium, sodium, potassium, chlorine and arsenic. While poisoning by coke, for example, is reversible, poisoning by metals can, conversely, lead to a modification of the structure and an irreversible deactivation of the catalyst. The metals most commonly found in crude oils and heavy feedstocks are vanadium and nickel. These metals are generally less present in lighter feedstocks. However, several studies have shown the harmful influence of a small amount of arsenic on the lifetime of hydrotreating and/or hydroconversion catalysts. Arsenic-based organic compounds in fact react rapidly under hydrotreating conditions to be decomposed and adsorbed on the surface of the catalyst. The most problematic contaminant in a hydrotreating and/or hydroconversion catalyst is thus often arsenic.

When an extraction of metals from a contaminated catalyst is carried out so that the solution obtained can be used directly for the impregnation on a support in order to produce a catalyst as described in document FR3117381, it would thus be advantageous to extract the metals of interest, notably a metal from group VIII and/or a metal from group VIB, while avoiding extracting contaminants, and notably arsenic, to avoid “polluting” the future impregnation solution. The present invention thus targets a selective extraction of metals from group VIII and/or from group VIB with respect to contaminants, and notably arsenic. However, when extracting the desired metals, the extraction of at least part of one or more contaminants is

often inevitable. The treatment of contaminated catalysts is not trivial because the extraction of contaminants depends on their nature and content. The contaminants will not all be distributed in the same way between the solution and the leached catalyst depending on their nature and on the leaching agent.

Document FR3117381 proposes removing arsenic by heat treatment under a gas stream containing hydrogen sulfide before extraction. The present invention presents notably an improvement to the process described in document FR3117381 making it possible to eliminate the heat treatment under a gas stream containing hydrogen sulfide in order to remove arsenic.

In addition, the choice of certain organic compounds, combined with a high concentration of these organic compounds in the extraction solution, makes it possible to observe a high selectivity of extraction of the metal from group VIB and the metal from group VIII compared to arsenic, which remains largely in the leached catalyst.

Summary of the invention

The invention relates to a process for producing a catalyst comprising at least one metal from group VIB, and/or at least one metal from group VIII, optionally phosphorus and/or sulfur, and a support based on oxide(s), characterized in that said process comprises the recycling of at least a part of the metal(s) from group VIB and/or from group VIII from a source catalyst comprising at least one metal from group VIB and/or at least one metal from group VIII common with the catalyst to be produced, said source catalyst being contaminated, the process comprising:

- an extraction of the metal from group VIB and/or of the metal from group VIII from said source catalyst using an extraction solution comprising at least one organic compound having complexing properties, in order to obtain a solution of extracted metal/metals, then

- an impregnation of the support with an impregnation solution resulting from said solution of extracted metal/metals, in order to obtain an impregnated substrate, said extracted metal(s) remaining in the liquid phase from the extraction to the impregnation.

The process according to the invention makes it possible to ensure a high degree of extraction of the metals from group VIII and/or VIB while limiting the extraction of contaminants, and notably arsenic.

Furthermore, the invention provides a process, where the metal originating from the source catalyst is dissolved and remains in solution until it is re-employed as impregnation solution makeup for producing the fresh/new catalyst. Unlike the prior techniques, the invention does

not seek to recover the metal from the source catalyst in solid and monometallic form, thus sparing itself a number of operations of the precipitation/filtration type. The process of the invention is thus easier to implement on the industrial scale. It is even more simplified thereby when the extraction solution and the impregnation solution have a solvent (or mixture of solvents) in common, notably when the solvents of the two solutions are identical (or similar, except for the proportion of solvents, for example, in the case of a mixture of solvents).

According to one variant, the source catalyst is contaminated with nickel and/or vanadium and/or iron and/or titanium and/or silicon and/or calcium and/or sodium and/or potassium and/or chlorine and/or arsenic.

According to one variant, the organic compound is chosen from one at least of the following compounds: dimethylglyoxime, methyl acetoacetate, ethyl acetoacetate, ethyl lactate, methyl glycolate, ethyl glycolate, dimethyl malate, diethyl malate, dimethyl tartrate, diethyl tartrate, ethyl 3-hydroxybutanoate, ethyl 3-ethoxypropanoate, methyl 3-methoxypropanoate, methyl 3-(methylthio)propanoate, ethyl 3-(methylthio)propanoate, ethylene glycol, diethylene glycol, triethylene glycol, a polyethylene glycol (with a molecular weight of between 200 and 1500 g/mol), propylene glycol, glycerol, 2-butoxyethanol, 2-(2-butoxyethoxy)ethanol, 2-(2-methoxyethoxy)ethanol, triethylene glycol dimethyl ether, a crown ether, acetophenone, 2,4-pentanedione, pentanone, glucose, fructose, sucrose, sorbitol, xylitol, mannitol, γ-valerolactone, propylene carbonate, octylamine, N,N-diethylformamide, N,N-dimethylformamide, N-methylformamide, N,N-dimethylacetamide, propanamide, 1-methyl-2-pyrrolidinone, tetramethylurea, N,N′-dimethylurea, acetonitrile, lactamide, furfurol, 2-furaldehyde, 5-hydroxymethylfurfural, ethyl 3-hydroxybutanoate, 2-hydroxyethyl acrylate, 1-vinyl-2-pyrrolidinone, N,N,N',N'-tetramethyltartramide, 3-hydroxypropionitrile and N,N'-bis(2-hydroxyethyl)ethylenediamine.

According to one variant, the extraction solution comprises at least one organic compound having complexing and also acidic properties.

According to one variant, the organic compound is chosen from at least one of the following compounds: formic acid, acetic acid, oxalic acid, malonic acid, glutaric acid, glycolic acid, lactic acid, tartronic acid, citric acid, tartaric acid, pyruvic acid, γ-ketovaleric acid, succinic acid, acetoacetic acid, gluconic acid, ascorbic acid, phthalic acid, salicylic acid, maleic acid, malic acid, fumaric acid, acrylic acid, thioglycolic acid, 2-hydroxy-4-methylthiobutanoic acid, glutamic acid, N-acetylglutamic acid, alanine, glycine, cysteine, histidine, aspartic acid, N-acetylaspartic acid, 4-aminobutanoic acid, 1,2-cyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetic acid (HEDTA),

diethylenetriaminepentaacetic acid (DTPA), bicine, tricine, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP or etidronic acid), nitrilotris(methylenephosphonic acid), diethylenetriaminepentakis(methylenephosphonic acid), 4-sulfophthalic acid, 3-(N-morpholino)-2-hydroxy-1-propanesulfonic acid (MOPSO), 2-(4-pyridinyl)ethanesulfonic acid, phenol-4-sulfonic acid, thiodiacetic acid and diglycolic acid.

According to one variant, the organic compound is chosen from formic acid, acetic acid, oxalic acid, citric acid, γ-ketovaleric acid, fructose, ethylene glycol, diethylene glycol and triethylene glycol.

According to one variant, the source catalyst is a spent catalyst regenerated and/or rejuvenated beforehand.

According to one variant, the extraction solution comprises a mineral acid chosen from phosphoric acid, nitric acid or boric acid.

According to one variant, the concentration of each organic compound in the extraction solution is between 0.03 and 2 mol/l.

According to one variant, the source catalyst is subjected to at least one pretreatment step before the extraction step chosen from deoiling, regeneration, grinding or washing with water.

According to one variant, the solution of extracted metal/metals is subjected to at least one treatment step before impregnation of the support, said treatment step being chosen from concentration, dilution and/or modification of the composition of the solution by total or partial addition or removal of at least one compound of said solution.

According to one variant, the impregnation of the support with an impregnation solution is carried out starting from the solution of extracted metal/metals and from a makeup of at least one of the metals from group VIII/VIB, and optionally of phosphorus and/or of organic additive(s).

According to one variant, a part at least of the impregnation solution after impregnation of the support is reused as makeup for the extraction solution.

According to one variant, the support on which the impregnation is carried out with the impregnation solution derived from the solution of the extracted metal/metals is pre-impregnated or post-impregnated with an impregnation solution or is a metal-depleted catalyst.

According to one variant, said impregnated substrate obtained after impregnation is subjected to a drying step, optionally to a calcination step and optionally to a sulfidation step.

According to one variant, the source catalyst is contaminated with arsenic and the degree of extraction of the metal from group VIII or from group VIB is respectively greater than 50% by weight and the degree of extraction of the arsenic is less than 30% by weight, the degree of extraction corresponding to the mass of the extracted metal/metals and of the extracted arsenic in the extraction solution relative to the mass of metal/metals present and of the arsenic present initially on the source catalyst.

Definitions

For the purposes of the present invention, the various embodiments presented can be used alone or in combination with each other, without any limit to the combinations.

For the purposes of the present invention, the various ranges of parameters for a given step, such as the pressure ranges and the temperature ranges, can be used alone or in combination. For example, for the purposes of the present invention, a preferred range of pressure values may be combined with a preferred range of temperature values.

In the continuation of the text, the expressions “of between ... and ...” and “between ... and ...” are equivalent and mean that the limiting values of the range are included in the range of values described. If such were not the case and if the limiting values were not included in the range described, such a clarification will be introduced by the present invention.

In the present description, the term "to comprise" is synonymous with (means the same thing as) "to include" and "to contain", and is inclusive or open-ended and does not exclude other elements which might not be mentioned. It is understood that the verb “to comprise” includes the exclusive and closed term "to consist of".

According to the present invention, it is understood that the impregnation solution "results" from the extraction solution means that there is no intermediate treatment where the extracted metal(s) would be in the solid phase, nor a liquid/liquid extraction treatment of this/these.

In the present description, the term "extraction" is synonymous with the term "leaching", unless otherwise indicated. The term “leaching” or “extraction” in the present description means extracting one or more metals from a solid (source catalyst) by dissolving it in a liquid (leaching solution or extraction solution).

In the present description, the term "extracted metal/metals" refers to the metals sought, that is to say the metals from group VIII and/or VIB. Other metals are considered contaminants.

In the present description, the term "contaminants" refers to unwanted elements in the source catalyst and in the extraction solution that it is not desired to extract. The contaminants are notably nickel and/or vanadium and/or iron and/or titanium and/or silicon and/or calcium and/or sodium and/or potassium and/or chlorine and/or arsenic.

For the purposes of the present invention, it is necessary to distinguish the nickel possibly contained in the active phase of the source catalyst (and which it is desired to extract) from the contaminating nickel provided by the feedstock. Unlike the nickel of the active phase, which is distributed uniformly throughout the catalyst, the contaminating nickel is generally more concentrated at the periphery of the catalyst grain (beads, extrudates, etc.), and forms more or less well distributed clumps. Its presence in MoS_2 decoration is also very limited.

According to the present invention, the pressures are absolute pressures, also denoted abs., and are given in MPa absolute (or MPa abs.), unless otherwise indicated.

In the remainder of the text, the groups of chemical elements are given according to the CAS classification (CRC Handbook of Chemistry and Physics, published by CRC Press, editor-in-chief D.R. Lide, 81st edition, 2000-2001). For example, group VIII (or VIIIB) according to the CAS classification corresponds to the metals from columns 8, 9 and 10 according to the new IUPAC classification, and group VIB corresponds to the metals from column 6.

Elemental analyses, typically by inductively coupled plasma (ICP) spectrometry, or by X-ray fluorescence spectrometry, more commonly known as X-ray fluorescence (XRF), quantify the content of the different elements of the catalyst pretreated at 550°C in air and of the extraction solution.

Detailed description

The present invention relates to the recycling of catalyst metals notably originating from hydrocarbon hydrotreating or hydroconversion units.

The term “hydrotreating” denotes all of the purification processes which make it possible to remove, by the action of hydrogen, the various impurities contained in hydrocarbon feedstocks. Hydrotreating processes make it possible to remove, by the action of hydrogen, impurities present in feedstocks, such as nitrogen (hydrodenitrogenation), sulfur (hydrodesulfidation), oxygen (hydrodeoxygenation) and compounds containing metals which can poison the catalyst and cause operational problems downstream (hydrodemetallization). Hydrotreating can thus make it possible to bring the hydrocarbon to the required specifications (sulfur content,

aromatics content, and the like) for a given application (motor vehicle fuel, gasoline or diesel fuel, domestic fuel oil, and the like). Automotive standards, notably, have imposed a very strong reduction in the sulfur in diesel and gasoline fuels, hydrotreating thus making it possible to bring these products to the required specifications.

Hydrotreating will thus improve the quality of hydrocarbons, by reducing the content of certain compounds, elements regarded as impurities, but it can also make it possible to reduce the content of aromatic hydrocarbons, by hydrogenation, and thus to improve the cetane number of the hydrocarbons. During hydrotreating processes, small amounts of fuel gas and light cuts, such as LPG (acronym for Liquefied Petroleum Gas) and naphtha, can also be produced.

It is recalled that the hydrocracking (also denoted under the term “hydroconversion”) of heavy hydrocarbon cuts is a key process in refining which makes it possible to produce, from surplus and sparingly upgradable heavy feedstocks, lighter fractions, such as gasolines, jet fuels and light gas oils, which the refiner desires in order to adapt its production to demand. Some hydrocracking processes make it possible to also obtain a highly purified residue which can constitute excellent bases for oils.

The hydrocarbon feedstock targeted for hydrotreatment and/or hydroconversion may be of a different nature. The feedstock may notably be of fossil origin or derived from the conversion of biomass or waste, taken alone or as a mixture. The feedstocks that are treated, and in particular those mentioned below, generally contain heteroatoms such as sulfur, oxygen and nitrogen and may contain other contaminants such as iron, titanium, silicon, calcium, sodium, potassium, chlorine and arsenic, but also, notably for heavier feedstocks, nickel and vanadium.

The feedstock of fossil origin may be notably a cut derived from coal or hydrocarbons produced from natural gas, optionally as mixtures. They can also be heavy synthetic or petroleum cuts, for example kerosenes, gas oils or distillates resulting from atmospheric and vacuum distillation in order to produce kerosene, gas oil or vacuum distillate which can be upgraded, either in the storage unit receiving products of the same type (pool), or to a downstream unit, such as a catalytic cracking unit, where the feedstocks are "cracked" in order to produce hydrocarbons having shorter chains. Frequently, the hydrotreating process is in fact a preliminary step of treatment of a feedstock via a process of hydroconversion/hydrocracking type.
The feedstocks of fossil origin employed in a hydrotreating process, in greater detail, are, for example, gasolines, gas oils, vacuum gas oils, atmospheric residues, vacuum residues, atmospheric distillates, vacuum distillates, heavy fuel oils, oils, waxes and paraffins, spent

oils, deasphalted residues or crudes, feedstocks originating from thermal or catalytic conversion processes, taken alone or as a mixture.

The feedstock resulting from the conversion of biomass may advantageously be chosen from plant oils, oils from algae or algal oils, fish oils, waste edible oils, and fats of plant or animal origin, or mixtures of such feedstocks. Said plant oils may advantageously be crude or completely or partly refined, and may result from plants chosen from rape, sunflower, soya, palm, olive, coconut, coconut kernel, castor oil plant, cotton, peanut, flax and sea kale, and all the oils derived, for example, from sunflower or rape by genetic modification or hybridization, this list not being limiting. Said animal fats are advantageously chosen from lard and fats composed of residues from the food industry or resulting from the catering industries. Frying oils, various animal oils, such as fish oils, tallow and lard, may also be used. The feedstock derived from biomass conversion can also advantageously be chosen from fatty acid methyl esters of plant and/or animal origin or else fatty acid methyl esters from waste edible plant oils.

The feedstock derived from biomass conversion can also be chosen from feedstocks originating from processes for thermal or catalytic conversions of biomass, such as oils which are produced from biomass, in particular from lignocellulosic biomass, with various liquefaction methods, such as hydrothermal liquefaction or pyrolysis. The term "biomass" refers to a material derived from recently living organisms, which includes plants, animals and their by-products. The term "lignocellulosic biomass" denotes biomass derived from plants or from their by-products. The lignocellulosic biomass is composed of carbohydrate polymers (cellulose, hemicellulose) and of an aromatic polymer (lignin).

The feedstock obtained from the conversion of biomass can also advantageously be chosen from feedstocks obtained from the papermaking industry.

The feedstock obtained from waste conversion can be a pyrolysis oil resulting from plastics, tires or also solid recovered fuels (SRF). These oils are obtained via a thermal or catalytic pyrolysis treatment or else can be prepared by hydropyrolysis (pyrolysis in the presence of a catalyst and of hydrogen).

Conventional hydrotreating catalysts generally comprise an oxide support and an active phase based on metals from groups VIB and VIII in their oxide forms and also phosphorus. The preparation of these catalysts generally comprises a step of impregnation of the metals and the phosphorus on the support, followed by a drying operation and a calcination making it possible to obtain the active phase in their oxide forms. Before their use in a hydrotreating and/or hydroconversion reaction, these catalysts are generally also subjected to a sulfidation.

The addition of an organic additive to the hydrotreating catalysts in order to improve their activity is also known, notably for catalysts which have been prepared by impregnation followed by drying without subsequent calcination. These catalysts are often referred to as "additive-impregnated dried catalysts".

The catalysts used in hydrocracking are of bifunctional type, that is to say combining an acid function with a hydrogenating function. The acid function is provided by supports with large surface areas (generally 150 to 800 $m^2.g^{-1}$) having high acidity, such as halogenated (notably chlorinated or fluorinated) aluminas, combinations of boron and aluminum oxides, amorphous silica/aluminas and zeolites. The hydrogenating function is contributed either by one or more metals from group VIII, or by a combination of at least one metal from group VIB and at least one metal from group VIII, employed in the presence of sulfur. The equilibrium between the two acid and hydrogenating functions governs the activity and the selectivity of the catalyst.

During its operation in a hydrotreating or hydroconversion process, the catalyst is deactivated by accumulation on the catalyst surface of coke and/or sulfur-containing compounds and/or other contaminants such as nickel, vanadium, iron, titanium, but also silicon, calcium, sodium, potassium, chlorine and arsenic. Beyond a certain period of time, it thus needs to be replaced.

In order to combat these disadvantages, the regeneration (also called mild calcination) of hydrotreating/hydroconversion catalysts is an economically and ecologically advantageous process because it makes it possible to use these catalysts again in industrial units rather than to landfill them or to recycle them (recovery of the metals). The regeneration consists of a heat treatment, generally between 350°C and 550°C, in the presence of pure or diluted oxygen, the purpose of which is to remove at least a part of the coke present on the spent catalyst by combustion. This regeneration makes it possible for the “regenerated” catalyst to recover hydrotreating/hydroconversion activity. However, the regenerated catalysts are generally less active than the starting catalysts, also called “fresh” catalysts. Consequently, their cycle time in the hydrotreating/hydroconversion unit is thus reduced in comparison with that of a fresh catalyst. Optionally, it can be reused in less demanding applications.

In order to overcome the shortfall in hydrotreating/hydroconversion activity of the regenerated catalyst, it is possible to apply an additional treatment called "rejuvenation" treatment. The rejuvenation process consists in reimpregnating the already regenerated catalyst with a solution containing organic or inorganic additives and/or metal precursors. These rejuvenation processes are well known, notably in the field of middle distillates. Although more effective than a simple regeneration, the rejuvenation of the catalysts results, however, in most cases in a catalyst having a lower activity than the fresh catalyst. Finally, some spent catalysts cannot

undergo reuse via regeneration or rejuvenation, either because their integrity is impaired (excessively low size or mechanical strength) or because they contain an excessively large amount of contaminants rendering the performance of the regenerated or rejuvenated product insufficient.

Although the present invention relates to the recycling of the metals of catalysts originating notably from hydrocarbon hydrotreating or hydroconversion units, it is clearly understood that the process according to the invention applies to any catalyst comprising at least one metal from group VIII and/or at least one metal from group VIB, and an oxide support, for instance selective hydrogenation catalysts, hydrotreating catalysts for residues (for example performed in an ebullated bed) or alternatively Fischer-Tropsch catalysts.

The source catalyst

According to the present invention, the term "source" catalyst means the catalyst from which it is desired to extract the metals. The “source” catalyst is generally an at least partially spent catalyst, that is to say a catalyst which has already been used in production, notably in facilities for hydrotreating or hydroconversion, for example of the hydrocracking type. This catalyst may optionally have already been regenerated and/or rejuvenated prior to its recycling. This term is also understood to mean a catalyst which has not already been used in production but which is outside specification, for example because it contains an insufficient content of metal/metals or has too low a mechanical strength, or else smaller dimensioning than that sought, resulting from the various unitary operations of new-catalyst manufacture (“fines” of catalyst particles, for example). This term also includes an at least partially spent capture mass.

The source catalyst comprises at least one metal from group VIII and/or at least one metal from group VIB, an oxide support and optionally phosphorus. The source catalyst is contaminated. It may be contaminated with nickel and/or vanadium and/or iron and/or titanium and/or silicon and/or calcium and/or sodium and/or potassium and/or chlorine and/or arsenic. Preferably, it comprises as contaminant at least arsenic. It may also, without limitation, comprise coke and/or sulfur.

The oxide support of said source catalyst is usually a porous solid chosen from the group consisting of: aluminas, silica, silica-aluminas and also titanium and magnesium oxides, used alone or as a mixture with alumina or silica-alumina. Preferably, the oxide support essentially consists of at least one transition alumina, that is to say that it comprises at least 51% by weight, preferably at least 60% by weight, very preferably at least 80% by weight, or even at least 90% by weight, of transition alumina. It preferably consists solely of a transition alumina. Preferably, the oxide support of said catalyst is a γ-phase alumina.

In another preferred case, the oxide present in the support of said source catalyst is a silica-alumina containing at least 50% by weight of alumina, relative to the total weight of the composite support. The silica content in the support is at most 50% by weight relative to the total weight of the support, usually less than or equal to 45% by weight, preferably less than or equal to 40% by weight.

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

The oxide support can also advantageously additionally contain from 0.1% to 80% by weight, preferably from 0.1% to 50% by weight, of zeolite, relative to the total weight of the support. In this case, all sources of zeolite and all associated preparation methods which are known can be incorporated. Preferably, the zeolite is chosen from the group FAU, BEA, ISV, IWR, IWW, MEI and UWY, and preferably the zeolite is chosen from the group FAU and BEA, such as Y and/or beta zeolite, and particularly preferably such as USY and/or beta zeolite.

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

The oxide support advantageously has a total pore volume of between 0.1 and 1.5 ml/g, preferably between 0.4 and 1.1 ml/g. The total pore volume is measured by mercury porosimetry according to the standard ASTM D4284-92 with a wetting angle of 140°, for example using an Autopore III™ model device of the Micromeritics™ brand.

The specific surface area of the oxide support is advantageously between 5 and 400 $m^2.g^{-1}$, preferably between 10 and 350 $m^2.g^{-1}$, more preferably between 40 and 350 $m^2.g^{-1}$. The specific surface area is determined in the present invention via the BET method according to the standard ASTM D3663.

The active phase of the source catalyst comprises at least one metal from group VIB and/or at least one metal from group VIII. The metal from group VIB present in the active phase of the catalyst is preferentially chosen from molybdenum and tungsten, or the mixture of these two elements. The metal from group VIII present in the active phase of the catalyst is preferentially chosen from cobalt, nickel and the mixture of these two elements. The active phase of the catalyst is preferably chosen from the group formed by the combination of the elements nickel-molybdenum, cobalt-molybdenum, nickel-cobalt-molybdenum, nickel-tungsten, nickel-molybdenum-tungsten and nickel-cobalt-tungsten.

The content of metal from group VIII is between 1% and 50% by weight of oxide of the metal from group VIII, relative to the total weight of the source catalyst, preferably between 1% and

10% by weight, preferably between 1.5% and 9% by weight, and preferably between 2% and 8% by weight. When the metal is cobalt or nickel, the metal content is expressed as CoO and NiO respectively.

The content of metal from group VIB is of between 5% and 40% by weight of oxide of the metal from group VIB, relative to the total weight of the source catalyst, preferably of between 8% and 35% by weight, very preferably of between 10% and 30% by weight. When the metal is molybdenum or tungsten, the metal content is expressed as MoO_3 and WO_3, respectively.

The mole ratio of metal from group VIII to metal from group VIB in the catalyst, when the latter contains both types of metals, is preferentially between 0.1 and 0.8, preferably between 0.15 and 0.6 and even more preferably between 0.2 and 0.6 or between 0.3 and 0.5.

The source catalyst may also comprise phosphorus as dopant. The dopant is an added element which, in itself, does not have any catalytic nature but which increases the catalytic activity of the active phase.

The phosphorus content in said source catalyst is then preferably of between 0.1% and 20% by weight, expressed as P_2O_5 relative to the total weight of the source catalyst, preferably between 0.2% and 15% by weight, expressed as P_2O_5, and very preferably between 0.3% and 8% by weight, expressed as P_2O_5.

The mole ratio of phosphorus to the element from group VIB in the catalyst is greater than or equal to 0.05, preferably greater than or equal to 0.07, preferably between 0.08 and 1, preferably between 0.01 and 0.9 and very preferably between 0.15 and 0.6.

The source catalyst may comprise sulfur. The sulfur content in said source catalyst is then preferably of between 1% and 15% by weight, expressed as element relative to the total weight of the source catalyst, preferably between 2% and 12% and very preferably between 4% and 10% by weight. The sulfur content is measured by elemental analysis according to ASTM D5373.

The source catalyst may comprise coke, notably when it has not been regenerated. It should be noted that the term “coke” in the present patent application denotes a substance based on hydrocarbons which is deposited on the surface of the catalyst during its use, which is highly cyclized and condensed and which has an appearance similar to graphite.

The coke content, expressed as % by weight of the carbon element, can be of between 2% and 20% by weight, preferably between 3% and 16% by weight and notably between 4% and

14% by weight, relative to the total weight of the source catalyst. The coke content is determined according to the ASTM D5373 method.

The source catalyst is contaminated with at least one contaminant chosen from nickel, vanadium, iron, titanium, silicon, calcium, sodium, potassium, chlorine and arsenic. Preferably, it comprises as contaminant at least arsenic.

The arsenic content of the source catalyst is generally less than or equal to 25 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 25 000 ppm by weight, preferably between 1500 and 25 000 ppm by weight, and preferably between 2500 and 20 000 ppm by weight relative to the total weight of the source catalyst.

The (contaminating) nickel content of the source catalyst (besides that optionally present as active phase on the fresh catalyst) is generally less than or equal to 30 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 30 000 ppm by weight, preferably between 1000 and 30 000 ppm by weight, and preferably between 4000 and 10 000 ppm by weight relative to the total weight of the source catalyst.

The vanadium content of the source catalyst is generally less than or equal to 50 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 50 000 ppm by weight, preferably between 1000 and 50 000 ppm by weight, and preferably between 4000 and 30 000 ppm by weight relative to the total weight of the source catalyst.

The iron content of the source catalyst is generally less than or equal to 50 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 50 000 ppm by weight, preferably between 1500 and 50 000 ppm by weight, and very preferably between 2000 and 10 000 ppm by weight relative to the total weight of the source catalyst.

The titanium content of the source catalyst is generally less than or equal to 5000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 5000 ppm by weight, preferably between 100 and 5000 ppm by weight, and very preferably between 200 and 2000 ppm by weight relative to the total weight of the source catalyst.

The silicon content of the source catalyst (besides that optionally present on the fresh catalyst) is generally less than or equal to 100 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 100 000 ppm by weight, preferably between 1000 and 100 000 ppm by weight, and very preferably between 2000 and 50 000 ppm by weight relative to the total weight of the source catalyst.

The calcium content of the source catalyst is generally less than or equal to 10 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 10 000 ppm by weight, preferably between 100 and 10 000 ppm by weight, and preferably between 500 and 5000 ppm by weight relative to the total weight of the source catalyst.

The sodium content of the source catalyst (besides that optionally present on the fresh catalyst) is generally less than or equal to 10 000 ppm by weight, relative to the total weight of the source catalyst. It is preferably between 0 and 10 000 ppm by weight, preferably between 100 and 10 000 ppm by weight, and preferably between 500 and 5000 ppm by weight relative to the total weight of the source catalyst.

The potassium content of the source catalyst is generally less than or equal to 20 000 ppm by weight relative to the total weight of the source catalyst. It is preferably between 0 and 20 000 ppm by weight, preferably between 100 and 20 000 ppm by weight, and preferably between 500 and 10 000 ppm by weight relative to the total weight of the source catalyst.

The chlorine content of the source catalyst is generally less than or equal to 5000 ppm by weight relative to the total weight of the source catalyst. It is preferably between 0 and 5000 ppm by weight, preferably between 100 and 5000 ppm by weight, and very preferably between 200 and 2000 ppm by weight relative to the total weight of the source catalyst.

The source catalyst resulting from a process for hydrotreating a middle distillate feedstock (diesel, kerosene) or a naphtha feedstock is distinguished by contents of vanadium and nickel (besides the active phase) that are lower than that of a catalyst resulting from a process for hydroconversion of a heavier feedstock. The vanadium and nickel contents of a source catalyst resulting from a process for hydrotreating a middle distillate feedstock (diesel, kerosene) or a naphtha feedstock are generally less than or equal to 10 000 ppm by weight for nickel (besides the active phase), and less than or equal to 50 000 ppm by weight for vanadium, relative to the weight of the source catalyst.

Pretreatments (optional)

The source catalyst may be subjected to at least one pretreatment step prior to extraction according to the process according to the invention. The optional pretreatment step consists in withdrawing all or part of one or more of the impurities possibly contained in said source catalyst before the step of extracting the metals, by any method known to a person skilled in the art. The pretreatment step may be chosen from deoiling, regeneration, grinding or washing with water. The aim of these preliminary treatments is to make the extraction more efficient, by mechanical, physical or chemical treatments: grinding reduces the particle size of the particles

of the source catalyst and increases the particles/extraction solution contact surface area. Removing or reducing the amount of coke and other contaminants proceeds in the same direction, by improving/increasing the contact between the extraction solution and the metals to be extracted contained in the source catalyst. Preferably, the pretreatment step comprises a regeneration step to remove all or part of the coke, sulfur and/or chlorine, as detailed below.

- Deoiling

The discharging of the source catalyst from a hydrotreating and/or hydroconversion process is preferably preceded by a deoiling step. The deoiling step generally comprises bringing the source catalyst into contact with a stream of inert gas (that is to say essentially devoid of oxygen), for example in an atmosphere of nitrogen or the like, at a temperature of between 300°C and 400°C, preferably between 300°C and 350°C. The inert gas flow rate in terms of flow rate per unit volume of the catalyst is from 5 to 150 $NL.h^{-1}$ for 3 to 7 hours. As a variant, the deoiling step may be performed with light hydrocarbons, by steam treatment or any other analogous process.
The deoiling step is generally followed by a drying step and/or a heating step, preferably at a temperature of between 50°C and 200°C.
The drying gas is preferably an inert gas such as nitrogen.

- Regeneration

The optionally deoiled source catalyst may be subjected to a step of removal of the coke and of the sulfur: a regeneration step, which makes it possible to remove all or part of the coke, of the sulfur and/or of the chlorine possibly deposited on the catalyst.

Even if this is possible, the regeneration is preferably not performed by keeping the loaded catalyst in the hydrotreating reactor (*in situ* regeneration). Preferably, the source catalyst is thus extracted from the reactor and sent to a regeneration facility in order to perform the regeneration in said facility (*ex situ* regeneration).

The regeneration step is generally performed in a gas stream containing oxygen, generally air. The water content in the gas is generally between 0% and 50% by weight. The gas flow rate in terms of flow rate per unit volume of the source catalyst is preferably from 20 to 2000 $NL.h^{-1}$, more preferably from 30 to 1000 $NL.h^{-1}$ and particularly preferably from 40 to 500 $NL.h^{-1}$. The duration of the regeneration is preferably 2 hours or more, more preferably 2.5 hours or more and particularly preferably 3 hours or more. The regeneration of the source catalyst is generally performed at a temperature of between 320°C and 550°C, preferably between 360°C and 500°C.

The regenerated catalyst is composed of the oxide support and of the active phase formed of at least one metal from group VIB and/or of at least one metal from group VIII and optionally of phosphorus from the source catalyst. The regenerated catalyst contains substantially the same content of metal from group VIB and/or group VIII as the source catalyst. The regenerated catalyst contains substantially the same content of contaminants with the exception of coke, sulfur and chlorine.

The regenerated catalyst is characterized by a specific surface area of between 20 and 300 m^2/g, preferably between 30 and 280 m^2/g, preferably between 40 and 260 m^2/g, very preferably between 80 and 250 m^2/g.

The pore volume of the regenerated catalyst is generally between 0.1 cm^3/g and 1.3 cm^3/g, preferably between 0.2 cm^3/g and 1.1 cm^3/g.

The regenerated catalyst obtained in the regeneration step contains residual carbon in a content of less than 3% by weight, relative to the total weight of the regenerated catalyst, preferably between 0% and 2.9% by weight, relative to the total weight of the regenerated catalyst, preferentially between 0% and 2.0% by weight and particularly preferably between 0% and 1.0% by weight. It should be noted that the term "residual carbon" in the present patent application means carbon (coke) remaining in the regenerated catalyst after regeneration of the source catalyst. This residual carbon content in the regenerated catalyst is measured according to the ASTM D5373 method. The sulfur content after regeneration is preferably of between 0% and 4% by weight, expressed as element relative to the weight of the catalyst, preferably between 0% and 2% by weight. The chlorine content after regeneration is preferably between 0% and 0.2% by weight expressed as element relative to the weight of the catalyst, preferably between 0% and 0.1% by weight.

- Grinding

The optionally deoiled and/or regenerated source catalyst can advantageously undergo, before the extraction, an optional grinding step in order to promote the kinetics of extraction of the metals during the process according to the invention. In this case, the step includes a first optional phase of conditioning the source catalyst with at least one grinding operation so as to obtain catalyst particles having a size of at most 1 mm. It is of course possible to perform several successive grinding steps in order to reach the target particle size. Any method known to a person skilled in the art can be employed to perform this crushing or grinding step, for instance the use of a ball mill or a rotary cutter mill. Preferentially, 90% of the volume distribution of the particles of the source catalyst have an equivalent diameter of between 1 and 1000 micrometers, preferably between 5 and 500 micrometers, preferably between 10 and

300 micrometers and particularly preferably between 15 and 150 micrometers. The equivalent diameter denoted "de" is defined according to the following relationship: de = 6×V/S with V the volume of the particle and S the surface area of the sphere having the same volume as the particle.

Most often, the ground source catalyst is conveyed into the extraction zone by any means known to a person skilled in the art, in particular by a screw conveyor or by pneumatic transfer.

- Washing with water

The optionally deoiled and/or regenerated and/or ground source catalyst can be subjected to a step of washing with water.

The volume of water employed in this washing step is advantageously greater than the total pore volume of the source catalyst. This volume may notably lie in a range extending from 2 to 20 times the total pore volume of the source catalyst, preferably between 5 and 10 times said pore volume.

The washing step can be performed at any appropriate temperature, for example between 5°C and 150°C, preferably between ambient temperature (20°C) and 70°C.

During the washing step, it is advantageous to stir the source catalyst so as to ensure efficient washing. The washing step can be performed in continuous mode or in batch mode, batch mode being preferred, all the more so since it makes it possible to limit the amount of water used. The washing step can be performed in any solid/liquid extractor type unit or industrial mixer.

Extraction step

According to the process according to the invention, an extraction of the metal from group VIB and/or of the metal from group VIII from said source catalyst, optionally pretreated, is carried out with an extraction solution comprising at least one organic compound having complexing properties in order to obtain a solution of extracted metal/metals.

The extraction solution according to the present invention can comprise any polar protic solvent known to a person skilled in the art. Preferably, a polar protic solvent, for example chosen from the group formed by methanol, ethanol and water, or else a water-ethanol or water-methanol mixture, is used. Very preferably, the solvent used in the impregnation solution consists of water. In the case of an aqueous solution, it would be possible to modify the pH of

said solution by the optional addition of an acid or of a base. The extraction solution has a pH generally between 0.1 and 8.5, preferably between 0.5 and 6, preferably between 1 and 4.

Preferably, the extraction solution and the impregnation solution of the next step have at least one solvent in common. They can have a solvent or a mixture of solvents which are identical, or varying in the proportion of solvents in the case of a mixture. It can concern, for example, water, or a mixture of solvents comprising predominantly, or essentially, an aqueous solvent.

Preferably, the metal extraction is performed with a solution comprising a solvent, notably an aqueous solvent, and at least one organic compound having complexing and optionally also acidic properties (either at least one compound having both properties, or the combination of at least one acidic compound and at least one complexing compound, or only at least one complexing compound, for example).

This is because it turns out that adding an organic compound to the (generally aqueous) solution was very effective in extracting the metals of interest which it is desired to recycle, by passing them into the liquid phase, while the support of the source catalyst and optional other components, including arsenic, of the source catalyst remain largely in the solid phase and are thus easily removable.

It should be emphasized that the organic compounds which give the most advantageous results are often compounds having acidic and complexing properties. This is because an organic acid makes it possible to protonate the metal oxide, thus limiting its interaction with the support and promoting its dissolution in the extraction solution. A complexing agent for its part makes it possible to form a metal complex which is soluble in the extraction solution. The combination of the acidic and complexing properties is thus particularly advantageous: the use of an organic compound having these two properties or the combination of an acidic organic compound and of a complexing organic compound is thus particularly recommended.

This organic compound, or at least one of them when there are several of them, can comprise one or more chemical functions chosen from a carboxylic acid, phosphoric acid, sulfonic acid, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function, or compounds including a furan ring or sugars.

The organic compound (or at least one of them when there are several of them) having both acidic and complexing properties can be chosen from one at least of the following compounds: formic acid, acetic acid, oxalic acid, malonic acid, glutaric acid, glycolic acid, lactic acid, tartronic acid, citric acid, tartaric acid, pyruvic acid, γ-ketovaleric acid, succinic acid, acetoacetic acid, gluconic acid, ascorbic acid, phthalic acid, salicylic acid, maleic acid, malic

acid, fumaric acid, acrylic acid, thioglycolic acid, 2-hydroxy-4-methylthiobutanoic acid, glutamic acid, N-acetylglutamic acid, alanine, glycine, cysteine, histidine, aspartic acid, N-acetylaspartic acid, 4-aminobutanoic acid, 1,2-cyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), bicine, tricine, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP or etidronic acid), nitrilotris(methylenephosphonic acid), diethylenetriaminepentakis(methylenephosphonic acid), 4-sulfophthalic acid, 3-(N-morpholino)-2-hydroxy-1-propanesulfonic acid (MOPSO), 2-(4-pyridinyl)ethanesulfonic acid, phenol-4-sulfonic acid, thiodiacetic acid and diglycolic acid.

The organic compound (or at least one of them when there are several) having complexing properties may be chosen from at least one of the following compounds: dimethylglyoxime, methyl acetoacetate, ethyl acetoacetate, ethyl lactate, methyl glycolate, ethyl glycolate, dimethyl malate, diethyl malate, dimethyl tartrate, diethyl tartrate, ethyl 3-hydroxybutanoate, ethyl 3-ethoxypropanoate, methyl 3-methoxypropanoate, methyl 3-(methylthio)propanoate, ethyl 3-(methylthio)propanoate, ethylene glycol, diethylene glycol, triethylene glycol, a polyethylene glycol (with a molecular weight of between 200 and 1500 g/mol), propylene glycol, glycerol, 2-butoxyethanol, 2-(2-butoxyethoxy)ethanol, 2-(2-methoxyethoxy)ethanol, triethylene glycol dimethyl ether, a crown ether, acetophenone, 2,4-pentanedione, pentanone, glucose, fructose, sucrose, sorbitol, xylitol, mannitol, γ-valerolactone, propylene carbonate, octylamine, N,N-diethylformamide, N,N-dimethylformamide, N-methylformamide, N,N-dimethylacetamide, propanamide, 1-methyl-2-pyrrolidinone, tetramethylurea, N,N′-dimethylurea, acetonitrile, lactamide, furfurol, 2-furaldehyde, 5-hydroxymethylfurfural, ethyl 3-hydroxybutanoate, 2-hydroxyethyl acrylate, 1-vinyl-2-pyrrolidinone, N,N,N',N'-tetramethyltartramide, 3-hydroxypropionitrile and N,N'-bis(2-hydroxyethyl)ethylenediamine.

The concentration of each organic compound in the extraction solution is defined so that the organic compound/extracted metals mole ratio is of between 0.1 and 25, preferably between 0.2 and 11, preferably between 0.2 and 5, preferably between 0.3 and 3 and preferably between 0.4 and 2.

When several organic compounds are present, the different mole ratios apply for each of the organic compounds present.

The concentration of each organic compound in the extraction solution is generally between 0.03 and 2 mol/l, preferably between 0.1 and 1.3 mol/l and particularly preferably between 0.5 and 1 mol/l.

The extraction solution comprising at least one organic compound having complexing and optionally acidic properties is chosen so as to maximize the degree of extraction of the metal from group VIII and/or VIB while limiting the extraction of contaminants, notably arsenic.

The choice of certain organic compounds makes it possible to observe a high selectivity of extraction of the metal from group VIII and the metal from group VIIB compared to arsenic, which itself remains largely in the leached catalyst.

According to a preferred variant, the organic compound is chosen from a carboxylic acid which preferably comprises between 1 and 8 carbon atoms and which may be a mono-acid, di-acid or tri-acid. Preferably, the organic compound is chosen from acetic acid, glutaric acid, oxalic acid, glycolic acid, lactic acid, citric acid, γ-ketovaleric acid, acetoacetic acid and gluconic acid.

According to another preferred variant, the organic compound is chosen from fructose, ethylene glycol, diethylene glycol and triethylene glycol.

According to a very preferred variant, the organic compound is chosen from formic acid, acetic acid, oxalic acid, citric acid, γ-ketovaleric acid, fructose, ethylene glycol, diethylene glycol and triethylene glycol.

In addition, for the same organic compound it is observed that the degree of extraction of the metal from group VIII and/or group VIB can be improved by using a higher concentration of this organic compound in the extraction solution. It is generally observed that the degree of extraction of metal from group VIII and/or VIB can be increased by using an extraction solution with a higher concentration of organic compound, but that the degree of arsenic extraction remains stable. The concentration of organic compound of the extraction solution is preferably of between 0.5 and 1 mol/l.

The choice of certain organic compounds, combined with a high concentration of this organic compound in the extraction solution, thus makes it possible to significantly increase the degree of extraction of the metal from group VIII and/or group VIB while observing a stable degree of arsenic extraction. This is particularly the case when the organic compound is chosen from acetic acid, oxalic acid, citric acid, γ-ketovaleric acid, fructose, ethylene glycol, diethylene glycol and triethylene glycol, combined with an organic compound concentration in the extraction solution of between 0.5 and 1 mol/l.

In one embodiment according to the invention, the extraction solution can also contain phosphorus. The presence of phosphorus promotes the extraction of the metals and in particular of molybdenum, by virtue of the high stability of the heteropolyanions which this metal forms with phosphorus. The addition of phosphorus in the form of phosphoric acid H_3PO_4

also makes it possible to lower the pH of the solution, which is also generally beneficial for the extraction of the metals contained in the source catalyst. It is also possible to use mineral acids other than phosphoric acid, notably nitric acid or boric acid. It should be noted that the use of sulfuric acid, a conventional metal extraction agent, is not recommended. This is because sulfuric acid is not a selective extraction agent and extracts a lot of arsenic at the same time as the metals from group VIII and/or VIB. The extraction solution therefore preferably does not comprise sulfuric acid.

In one embodiment according to the invention, the extraction solution can also contain an oxidizing agent for promoting the extraction of the metals. Preferably, the oxidizing agent contained in the extraction solution is hydrogen peroxide. When an oxidizing agent is present, the concentration is generally between 0.1 and 5.0 mol/l.

In general, the operating conditions of the extraction step according to the invention are chosen so as to maximize the extraction of the metals from group VIII and/or VIB contained in the source catalyst, while minimizing the dissolution of the contaminants, and notably arsenic, of said source catalyst, while limiting as much as possible the amount of organic compound in order for the latter not to be in too great an excess with respect to the optimum amount of organic compound necessary in the impregnation step in order to obtain high-performance catalysts. It is also sought to minimize the amount of extraction solution to be used, in order to obtain a metal solution which is as concentrated as possible at the end of the extraction: the need to concentrate the solution before using it in the impregnation solution or as impregnation solution is thus limited.

The contacting operation is performed with the extraction solution under the following conditions:

the temperature is generally between 0°C and 300°C, preferably between 10°C and 100°C and more preferably between 15°C and 40°C. Particularly preferably, the temperature is ambient temperature;

the pressure is generally between atmospheric pressure and 20 bar (2 MPa), notably between atmospheric pressure and 10 bar (1 MPa);

the duration of the contacting operation per extraction step is generally between 1 minute and 20 hours, preferably between 5 and 300 minutes, and in a preferred manner between 5 and 120 minutes.

The amount of extraction solution used for this step is preferably as low as possible in order to obtain the desired effect, as indicated above. Preferably, this step is carried out by bringing the source catalyst into contact with a volume of said solution of between 1.5 and 60 times the

volume of the source catalyst. Preferably, the volume of said solution is of between 2 and 30 times the volume of the source catalyst and more preferentially between 2 and 20 times the volume of the source catalyst, and particularly preferably between 2 and 10 times the volume of the source catalyst.

When the device(s) in which the contacting operation is performed do not have any heating equipment incorporated, the temperature of the contacting operation is regulated by the temperature of the extraction solution. It may therefore be at ambient temperature, or may have been heated, for this specific contacting step. It can also be at a given temperature, notably above ambient temperature, because it originates, at least in part, from the recycling of liquid effluents produced during its use as an impregnation solution and which are already in this temperature range.

According to the present invention, “extraction” is understood to mean the fact that there is an extraction step but that the extraction can be carried out by one extraction operation or a plurality of successive extraction operations.

All the modes of bringing into contact in a single step or in several steps according to a cocurrent, countercurrent or crosscurrent mode are possible for the implementation of the extraction step in continuous mode. The extraction step includes bringing the extraction solution into contact with the source catalyst, then a solid/liquid separation step making it possible to obtain, on the one hand, a leached catalyst depleted in metal/metals from group VIII and/or VIB but containing most of the arsenic, and, on the other hand, the extraction solution enriched in at least one metal from group VIB and/or at least one metal from group VIII and containing as little arsenic as possible.

The extraction solution can be brought into contact with the source catalyst by any method known to a person skilled in the art, for example by suspending the source catalyst in the extraction solution by means of a rotary stirrer or by fluidization, or else by percolation of the leaching solution through a fixed bed containing the source catalyst.

The liquid/solid separation can be performed by any method known to a person skilled in the art, for example by sedimentation, by filtration, by draining, for example gravitational draining, and/or by centrifugation. The remaining solid residue may be washed with the extraction solvent and/or with water. It can also be dried.

According to one embodiment, when the source catalyst contains only one metal from group VIB or one metal from group VIII respectively, then all the more so only one metal from group VIB or one metal from group VIII is extracted from the catalyst. According to another

embodiment, when the source catalyst contains both at least one metal from group VIB and at least one metal from group VIII, either only the metal from group VIB or the metal from group VIII is extracted, respectively, or both the metal from group VIB and the metal from group VIII are extracted.

At the end of the extraction step, what is obtained is, on the one hand, a leached catalyst depleted in metal/metals but containing the majority of the arsenic, and, on the other hand, the extraction solution enriched in at least one metal from group VIB and/or at least one metal from group VIII and containing as little arsenic as possible.

Preferably, the residual content of metals from group VIII and/or VIB of the metal-depleted catalyst (sum of the contents of the different metals contained in the leached catalyst, expressed as oxide) is less than 10% by weight, preferentially less than 5% by weight and very preferably less than 2% by weight relative to the weight of the metal-depleted catalyst.

The degree of extraction of the metal from group VIII is generally greater than 50%, preferably greater than 60%, preferably greater than 70%. Preferably, the degree of extraction of the metal from group VIII is between 50% and 100%, preferably between 60% and 100% and in a preferred way between 70% and 100%.
The degree of extraction of the metal from group VIB is generally greater than 50%, preferably greater than 60%, preferably greater than 70%. Preferably, the degree of extraction of the metal from group VIB is between 50% and 100%, preferably between 60% and 100%, and preferably between 70% and 100%.

The degree of extraction corresponds to the mass of the metal/metals extracted in the extraction solution, relative to the mass of metal/metals initially present on the source catalyst.

The degree of arsenic extraction is preferably less than 30%, preferably less than 20%, preferably less than 15% and even more preferably less than 10%.

The titanium and iron contaminants are generally, just like arsenic, extracted to a limited extent, and remain largely in the leached catalyst. Similarly, a low content of phosphorus (from the source catalyst when present) and aluminum (from the source catalyst support) can be observed in the extraction solution. The degree of extraction of phosphorus, aluminum, titanium and iron is respectively preferably less than 30%, preferably less than 20%, preferably less than 15% and even more preferably less than 10%.

The vanadium, nickel (contaminant from the feedstock and not from the active phase), silicon, sodium, calcium and potassium contaminants are distributed between the extraction solution and the leached catalyst. The degree of extraction of vanadium, nickel (contaminant), silicon,

sodium, calcium and potassium is respectively generally between 20% and 70%, preferably between 25% and 65%, preferably between 25% and 60%.

The degree of extraction corresponds to the mass of the contaminant in the extraction solution relative to the mass of the contaminant initially present on the source catalyst.

The vanadium, nickel (contaminant from the feedstock and not from the active phase), silicon, sodium, calcium and potassium contaminants are distributed between the extraction solution and the leached catalyst, so they can be found in not insignificant amounts in the extraction solution.

In this case, their contents in the impregnation solution can be reduced by dilution (for example with another extraction solution containing no or fewer contaminants). According to another variant, it is also possible to envision adding a metal from group VIII and/or VIB to the extraction/impregnation solution containing too many contaminants.

(Optional) extraction solution treatment step(s) before impregnation

Prior its to use as an impregnation solution, the solution of extracted metal/metals may be subjected to at least one treatment step chosen from at least one of the following treatments: purification, concentration, dilution, modification of the composition of the solution by adding or removing, in whole or in part, at least one compound. The extracted metal(s) remain in the liquid phase during these treatments.

- Purification

The solution of extracted metal/metals may be subjected to a purification step. The purpose of purification is to remove all or some of the impurities possibly contained in the metal solution, resulting in particular from the impurities potentially present on the source catalyst or linked to a partial dissolution of the support of said catalyst. The purification can take place in a single step or in several successive steps.

In the case where the solution of extracted metal/metals contains suspended solids after the last liquid/solid separation step, any known method for removing these suspended materials may be used. Preferably, this removal is performed by filtration (for example, microfiltration and ultrafiltration on a cross-flow filter). Other methods are centrifugation, coagulation or sedimentation.

For the dissolved impurities, for instance arsenates or arsenites, all the known methods can be used, notably and preferably, sorption on solid, precipitation and extraction with solvent, care being taken not to remove, at the same time, the metals of interest which have been extracted.

- Concentration

The optionally purified solution of extracted metal/metals can be subjected to a concentration step. This step consists in concentrating the solution of extracted metal/metals by removal of some of the solvent, and optionally of all or some of the organic compound contained in the metal solution. This step may be necessary if the metal concentrations are too low with respect to the concentrations necessary to carry out an impregnation. Any known method for removing a portion of a solvent from a solution is envisioned. The concentration operation can take place in a single step or in several successive steps. All or some of the solvent optionally containing organic compound, extracted from the metal solution, may be recycled into the process according to the invention as extraction solution.

Preferably, and in particular in the case where the metal solution is an aqueous solution, the concentration operation is performed by evaporative concentration. In this case, neutralization will preferentially be performed, so that the effluent enters the evaporator in a pH range from 5 to 7. This regulation of the pH makes it possible to limit the phenomena of codistillation, unless the latter is sought for the co-removal of the solvent and of part of the organic compound and, moreover, in order to avoid as much as possible the precipitation of metal oxides. Preferably, all or some of the distillate may be recycled into the process according to the invention as extraction solution.

When only the removal of some of the solvent is desired, besides evaporative concentration, the preferred techniques are membrane techniques and very preferably nanofiltration, reverse osmosis and pervaporation, solvent extraction or cryoconcentration.

When it is desired to remove solvent and organic compound(s) when they are used, a preferred technique is evaporative concentration.

- Adjustment of the composition of the metal solution

The optionally purified and/or concentrated solution of extracted metal/metals may be subjected to a composition adjustment step. This step consists in modifying the metal solution by addition(s) and/or removal(s) of certain constituents. Metal precursors and/or phosphorus precursors and/or organic additives can be added. Organic compounds used for the extraction of the metals can also be removed, in all or part, if necessary. The objective is to obtain a metal

solution, the composition of which corresponds to that desired for the impregnation solution used for the synthesis of a new catalyst.

Even if it is desired for the catalyst obtained according to the invention to have a formulation identical to that of the source catalyst, the ratios between metals of the metal solution are potentially to be adjusted, on the one hand because the purification of the catalyst can modify the initial contents of metals of the source catalyst and, on the other hand, because the extraction step can bring about different degrees of extraction for each of the metals.

The adjustment of the ratios between metals is made either by addition of a makeup solution containing one or more of said metals, or by direct dissolution of one or more metal precursors in the solution of extracted metal/metals, the latter alternative being preferred. The mole ratio of metal from group VIII to metal from group VIB in the metal solution resulting from this adjustment step is generally between 0.1 and 0.8, preferably between 0.15 and 0.6.

By way of example for the metal precursors, among the sources of molybdenum, use may be made of the oxides and hydroxides, molybdic acids and salts thereof, in particular the ammonium salts, such as ammonium molybdate or ammonium heptamolybdate, phosphomolybdic acid ($H_3PMo_{12}O_{40}$) and salts thereof, and optionally silicomolybdic acid ($H_4SiMo_{12}O_{40}$) and salts thereof. The sources of molybdenum can also be any heteropolycompound of Keggin, lacunary Keggin, substituted Keggin, Dawson, Anderson or Strandberg type, for example. Use is preferably made of molybdenum trioxide and the heteropolycompounds of Keggin, lacunary Keggin, substituted Keggin and Strandberg type.

The tungsten precursors which can be used are also well known to a person skilled in the art. For example, among the sources of tungsten, use may be made of the oxides and hydroxides, tungstic acids and salts thereof, in particular the ammonium salts, such as ammonium tungstate or ammonium metatungstate, phosphotungstic acid and salts thereof, and optionally silicotungstic acid ($H_4SiW_{12}O_{40}$) and salts thereof. The sources of tungsten can also be any heteropolycompound of Keggin, lacunary Keggin, substituted Keggin or Dawson type, for example. Use is preferably made of the ammonium oxides and salts, such as ammonium metatungstate, or the heteropolyanions of Keggin, lacunary Keggin or substituted Keggin type.

The cobalt precursors which can be used are advantageously chosen from the oxides, hydroxides, hydroxycarbonates, carbonates and nitrates, for example. Use is preferably made of cobalt hydroxide and cobalt carbonate. Cobalt acetoacetate may also be used.

The nickel precursors that may be used are advantageously chosen from the oxides, hydroxides, hydroxycarbonates, carbonates and nitrates, for example. Nickel acetoacetate may also be used.

If the phosphorus/metal ratio of the solution of extracted metal/metals is lower than that desired for the impregnation solution, a phosphorus precursor, identical to or different from that optionally used in the extraction step, can be added to the solution of extracted metal/metals. This will notably be the case when no phosphorus compound/precursor has been added to the extraction solution, or when it has been consumed, at least partly, by the support, when it contains alumina, to form aluminophosphates. In this case, the mole ratio of the phosphorus to the metal from group VIB is between 0.1 and 2.5 mol/mol, preferably between 0.1 and 2.0 mol/mol, and even more preferably between 0.1 and 1.0 mol/mol or between 0.15 and 0.8 mol/mol, or else between 0.2 and 0.6 mol/mol.

The preferred phosphorus precursor is phosphoric acid H_3PO_4 but the esters thereof and the salts thereof, such as ammonium phosphates, are also suitable, just like the polyphosphates. The phosphorus can also be introduced at the same time as the element(s) from group VIB in the form of Keggin, lacunary Keggin, substituted Keggin or Strandberg-type heteropolyanions.

The addition of an organic additive to the hydrotreating/hydroconversion catalysts has been recommended by a person skilled in the art in order to improve their activity. They are known to improve the dispersion of metals at the surface of the support and/or to play a beneficial role during the sulfidation of the catalysts. Thus, one or more organic additives well known to a person skilled in the art can advantageously be added in this step. Generally, the amount of each organic additive added is defined so that the mole ratio of additive/metals is between 0.1 and 1 in the impregnation solution.

Patent FR3083134 describes examples of organic additives which may be suitable and which can be used in aqueous form, and which can thus be added to the impregnation solution. Patent FR3083131 also describes examples of organic additives which may be suitable but which will instead be added separately, in pre-impregnation or in post-impregnation of the support.

The solution of extracted metal/metals may contain an excess of organic compound, relative to the desired impregnation solution. The ratios of organic compound to metals can be adjusted in two ways. The first way consists in adding a concentrated solution of metal precursors or in directly dissolving these metal precursors, in order to achieve the desired ratios. In this case, the final catalyst obtained will comprise a mixture of recycled metals and new metals.

If the excess of organic compound is too high to use the first way (i.e., the amount of recycled metals incorporated in the final catalyst is not significant, for example less than 5% by weight of the total amount of metals), the second way then consists in removing, from the metal solution, all or part of the excess organic compound. In this case, the organic compound can be recycled to the extraction step. For this, any method known to a person skilled in the art for separating an organic molecule from a metal solution is envisioned. The concentration of excess organic compound can be reduced, for example, by evaporation, by liquid-liquid extraction, by adsorption or by membrane separation.

Impregnation step

The solution of extracted metal/metals, optionally previously subjected to one or more of the treatments described below, can be used for the preparation of a new catalyst. According to the process according to the invention, an impregnation of the support is carried out with an impregnation solution resulting from said solution of extracted metal/metals, in order to obtain an impregnated substrate, said extracted metal(s) remaining in the liquid phase from the extraction until the impregnation.

According to the present invention, “support” (which will be impregnated with the impregnation solution resulting from the solution of extracted metal/metals) is understood to mean a “new” support of oxides but also a support which has already been impregnated with another impregnation solution (reference is made to pre-impregnated support) or a support which is in fact a catalyst (a support provided with metals) but which contains an insufficient amount of metals, such as a spent or regenerated catalyst.

The impregnation may be performed via any known method, for instance ion exchange, dry impregnation, excess impregnation, vapor deposition, etc. The impregnation can take place in one step or in several successive steps.

According to a preferred embodiment, said support is impregnated with the impregnation solution by excess impregnation or by dry impregnation. Equilibrium or excess impregnation consists in immersing the support or the catalyst in a volume of solution (often considerably) greater than the pore volume of the support or of the catalyst. Dry impregnation consists, for its part, in introducing a volume of impregnation solution equal to or slightly less than the pore volume of the support or of the catalyst. Dry impregnation makes it possible to deposit, on a given support or a given catalyst, all of the constituents of the impregnation solution. The impregnation step can advantageously be carried out by one or more excess impregnations of solution or preferably by one or more dry impregnation(s), and, for example, by a single excess impregnation, using the impregnation solution. According to the present invention,

“impregnation” is understood to mean the fact that there is an impregnation step but that the impregnation can be carried out by one impregnation or a plurality of successive impregnation operations.

The impregnation is performed at a temperature generally of between 10°C and 95°C, at a pressure of between atmospheric pressure and 20 bar (2 MPa), preferably at atmospheric pressure, and for a period of time preferentially between 1 minute and 20 hours, preferably between 1 and 300 minutes. The impregnation is preferably performed at a temperature of between 10°C and 60°C, preferably at ambient temperature.

Advantageously, after each impregnation step, the impregnated support or catalyst is left to mature. Maturation enables the impregnation solution to disperse homogeneously within the support or the catalyst.

Any maturation step 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 ambient temperature. Generally, a maturation time of between 10 minutes and 48 hours and preferably of between 30 minutes and 6 hours is sufficient.

Advantageously, the contact impregnation step is followed by a step of drying at a temperature of less than 200°C, preferably between 50 and 180°C, more preferentially between 70 and 150°C and very preferably between 75 and 130°C. The drying step is preferentially performed for a period of time of between 10 minutes and 24 hours. Longer periods of time are not ruled out, but do not necessarily afford any improvement. The drying step can be performed via any known technique. It is advantageously performed at atmospheric pressure or at reduced pressure. Preferably, this step is performed at atmospheric pressure. It is advantageously performed using hot air or any other hot gas. Preferably, the gas used is either air or an inert gas, such as argon or nitrogen. Very preferably, the drying is performed in the presence of nitrogen and/or air and is advantageously performed in a flow-through bed.

According to one variant, the drying is advantageously performed so as to preferably retain at least 30% by weight of the organic additive introduced during an optional organic compound adjustment after the extraction step and/or introduced during the impregnation step. This amount is preferably greater than 50% by weight and even more preferably greater than 70% by weight, calculated on the basis of the carbon remaining on the catalyst.

According to one variant, the drying is advantageously performed so as to preferably retain at least 30% by weight of the organic extraction compound introduced during the extraction step;

this amount is preferably greater than 50% by weight and even more preferably greater than 70% by weight, calculated on the basis of the carbon remaining on the catalyst.

Optionally, the drying can be followed by a calcination step. This may be the case, for example, if it is desired to remove all or part of one or more organic extraction compounds. According to this variant, on conclusion of the drying step, a calcination step is performed at a temperature of between 200°C and 600°C, preferably between 250°C and 550°C, under an inert atmosphere (for example nitrogen) or under an atmosphere containing oxygen (for example air). The duration of this heat treatment is generally of between 0.5 hour and 16 hours, preferably between 1 hour and 5 hours. After this treatment, the active phase is thus found generally in the oxide form; the heteropolyanions are thus converted into oxides. Similarly, the catalyst contains very little, or no longer contains any, organic extraction compound and organic additive. However, the introduction of the organic additive during its preparation made it possible to increase the dispersion of the active phase, thus leading to a more active catalyst.

Preferably, the catalyst is not subjected to a calcination.

In the embodiment wherein the impregnation step is performed via at least two impregnation cycles, each impregnation is advantageously followed by drying and optionally calcination.

The "new" oxide support which will be impregnated with the impregnation solution resulting from the solution of extracted metal/metals may be of the same nature as the support for the source catalyst, a description of which has already been given above.

The support can also contain at least a part of the group VIB and VIII metal(s) and/or at least a part of the phosphorus and/or at least a part of the sulfur and/or at least a part of the organic additive(s), apart from those which can be introduced during the step of adjusting the composition of the metal solution and/or the impregnation step. They are introduced, for example, during the preparation of the support. This is then referred to as a “pre-impregnated” support.

It is also possible to add one or more metals to the support already impregnated with the impregnation solution according to the invention. This is then referred to as a “post-impregnated” support.

In both cases, "pre-impregnated" or "post-impregnated" support, the aim is the same: it is a question of adjusting the metal content of the final catalyst, either by adding a certain amount of the metal(s) present in the impregnation solution according to the invention or by adding one or more other metals in a separate step, with another impregnation solution notably, before and/or after the step of impregnation with the impregnation solution of the invention.

A catalyst already containing one or more metals can also be contacted with the solution of extracted metal/metals. It may be a catalyst which has been depleted in metals, and may notably be a spent catalyst itself optionally regenerated and then optionally rejuvenated.

The active phase of the recycled catalyst targeted by the process according to the invention is generally of the type of that already described above for the “source” catalyst.

It should be pointed out that the new catalyst can have a different formulation from that of the source catalyst used to recover the metals and different amounts of metal and different ratios between metals: thus, a spent catalyst comprising a high charge of metals can, according to the invention, be used to produce a catalyst comprising a lower charge of metals (or *vice versa*). This makes it possible, if appropriate, to avoid a step of concentrating the solution after extraction or at the very least to reduce the intensity/duration thereof. The recycled catalyst can then be used differently (on different hydrocarbon feedstocks) from the source catalyst from which it is derived (for example a catalyst having 20% weight of Mo expressed as MoO_3, relative to the weight of the dry catalyst, can be used for the hydrotreating of distillates, whereas a catalyst containing a lower charge of Mo, 10% by weight of Mo expressed as MoO_3, can be used for the hydrotreating of naphtha). Thus, it is possible to use a source catalyst which does not have the same function as the recycled catalyst to be produced, as long as they have at least one metal in common (hydrotreating catalyst, hydrocracking catalyst, Fischer-Tropsch catalyst), or which has the same function (hydrotreating catalyst in both cases, for example).

It should also be noted that the new catalyst can be post-additivated, that is to say that it is possible to carry out an additional step of impregnation with one or more organic additives, the function of which is to increase the catalytic activity relative to the non-additivated catalysts, before the final optional sulfidation, it being understood that, preferably, no calcination step is performed after its introduction.

The amount of recycled metals contained in the new catalyst is between 1% and 100% by weight of the metals contained in the new catalyst, preferably between 10% and 100% by weight, in a preferred manner between 20% and 100% by weight and even more preferably between 50% and 100% by weight relative to the weight of the new catalyst.

Before its use, the new catalyst may undergo an optional sulfidation step. The sulfidation is preferably performed in a sulforeducing medium, that is to say in the presence of H_2S and hydrogen, in order to convert the metal oxides into sulfides, for instance MoS_2 and Co_9S_8. The sulfidation is performed by injecting, onto the catalyst, a stream containing H_2S and hydrogen, or a sulfur-containing compound that is capable of decomposing to give H_2S in the presence

of the catalyst and hydrogen. Polysulfides, such as dimethyl disulfide (DMDS), are H_2S precursors commonly used to sulfide catalysts. The sulfur can also originate from the feedstock. The temperature is adjusted in order for H_2S to react with the metal oxides to form metal sulfides. This sulfidation can be performed *in situ* or *ex situ* (inside or outside the reactor) of the reactor of the hydrotreating or hydroconversion process according to the invention at temperatures of between 200 and 600°C and more preferentially between 300 and 500°C.

According to one variant, it is possible to reuse a part at least of the impregnation solution after impregnation of the support, notably as makeup for the extraction solution. This thus limits the consumption of the process in terms of solvent and in terms of (optional) organic compound.

Examples

The starting material is a spent “CoMoP” catalyst, containing molybdenum, cobalt and phosphorus, which are deposited on an alumina support which is used in a hydrotreating process and which has been contaminated with arsenic. It was regenerated beforehand under a stream of dry air at 450°C for 4 hours.

The regenerated catalyst contains molybdenum, phosphorus and cobalt. The composition of the catalyst is expressed in the form of oxides and with respect to the weight of dry catalyst: 20.3% by weight of MoO_3 (13.5% by weight of molybdenum), 4.1% by weight of CoO (3.2% by weight of cobalt, i.e. a Co/Mo mole ratio equal to 0.39) and 3.4% by weight of P_2O_5 (1.5% by weight of phosphorus, i.e. a P/Mo mole ratio equal to 0.34). It also contains 8400 ppm by weight of arsenic.

<u>Extraction with an aqueous solution containing 0.15 mol/l citric acid:</u>

A step of extraction of the metals molybdenum and cobalt from this regenerated catalyst is carried out on the laboratory scale: 30 g of this contaminated regenerated catalyst (known as source catalyst), ground beforehand to a particle size of between 100 and 300 microns, and 75 ml of extraction solution are introduced into a round-bottomed flask. The extraction solution is an aqueous solution containing 0.15 mol/l of citric acid. The mixture is stirred at ambient temperature at 200 rpm via a magnetic bar for 6 hours. The mixture is subsequently filtered on a sintered glass of porosity 5, in order to recover a multimetal solution, on the one hand, and a solid residue, on the other hand. The analysis of the solution shows that it contains 30.5 g/l of molybdenum, 7.2 g/l of cobalt and 0.57 g/l of arsenic. The calculated degrees of extraction of the Mo and Co are thus 56% and 55% respectively, and the degree of extraction of arsenic is 17%.

7.6 ml of leaching solution is withdrawn and 2.58 g of molybdenum oxide (MoO_3), 0.63 g of cobalt hydroxide ($Co(OH)_2$), 0.60 g of phosphoric acid (100% pure H_3PO_4) and 1.42 g of citric acid (100%) are added thereto. 8 ml of impregnation solution are obtained and said solution is impregnated on 10 g of alumina (dry impregnation). After 16 hours of maturation at ambient temperature in a humid atmosphere and 2 hours of drying at 120°C, the recycled catalyst A obtained contains 21% by weight of MoO_3 and the mole ratios Co/Mo 0.38, P/Mo 0.3 and AC/Mo 0.4.

Extraction with an aqueous solution containing 1 mol/l citric acid:

A step of extraction of the metals molybdenum and cobalt from this regenerated catalyst is carried out on the laboratory scale: 30 g of this contaminated regenerated catalyst (known as source catalyst), ground beforehand to a particle size of between 100 and 300 microns, and 75 ml of extraction solution are introduced into a round-bottomed flask. The extraction solution is an aqueous solution containing 1 mol/l of citric acid. The mixture is stirred at ambient temperature at 200 rpm via a magnetic bar for 6 hours. The mixture is subsequently filtered on a sintered glass of porosity 5, in order to recover a multimetal solution, on the one hand, and a solid residue, on the other hand. The analysis of the solution shows that it contains 48.2 g/l of molybdenum, 11.3 g/l of cobalt and 0.64 g/l of arsenic. The calculated degrees of extraction of the Mo and Co are thus 88% and 87% respectively, and the degree of extraction of arsenic is 19%.

7.6 ml of leaching solution is withdrawn and 2.38 g of molybdenum oxide (MoO_3), 0.58 g of cobalt hydroxide ($Co(OH)_2$), 0.60 g of phosphoric acid (100% pure H_3PO_4) and 0.19 g of citric acid (100%) are added thereto. 8 ml of impregnation solution are obtained and said solution is impregnated on 10 g of alumina (dry impregnation). After 16 hours of maturation at ambient temperature in a humid atmosphere and 2 hours of drying at 120°C, the recycled catalyst B obtained contains 21% by weight of MoO_3 and the mole ratios Co/Mo 0.38, P/Mo 0.3 and AC/Mo 0.4.

The increase in the citric acid concentration thus makes it possible to increase the degree of extraction of the metals Mo and Co without significantly increasing that of arsenic.

The catalyst B, which contains less arsenic, has a higher performance level than the catalyst A, which contains more arsenic.

Claims

1. A process for producing a catalyst comprising at least one metal from group VIB, and/or at least one metal from group VIII, optionally phosphorus and/or sulfur, and a support based on oxide(s), characterized in that said process comprises the recycling of at least a part of the metal(s) from group VIB and/or from group VIII from a source catalyst comprising at least one metal from group VIB and/or at least one metal from group VIII common with the catalyst to be produced, said source catalyst being contaminated, the process comprising:

- an extraction of the metal from group VIB and/or of the metal from group VIII from said source catalyst using an extraction solution comprising at least one organic compound having complexing properties, in order to obtain a solution of extracted metal/metals, then

- an impregnation of the support with an impregnation solution resulting from said solution of extracted metal/metals, in order to obtain an impregnated substrate, said extracted metal(s) remaining in the liquid phase from the extraction to the impregnation.

2. The process as claimed in claim 1, wherein the source catalyst is contaminated with nickel and/or vanadium and/or iron and/or titanium and/or silicon and/or calcium and/or sodium and/or potassium and/or chlorine and/or arsenic.

3. The process as claimed in either of the preceding claims, wherein the organic compound is chosen from one at least of the following compounds: dimethylglyoxime, methyl acetoacetate, ethyl acetoacetate, ethyl lactate, methyl glycolate, ethyl glycolate, dimethyl malate, diethyl malate, dimethyl tartrate, diethyl tartrate, ethyl 3-hydroxybutanoate, ethyl 3-ethoxypropanoate, methyl 3-methoxypropanoate, methyl 3-(methylthio)propanoate, ethyl 3-(methylthio)propanoate, ethylene glycol, diethylene glycol, triethylene glycol, a polyethylene glycol (with a molecular weight of between 200 and 1500 g/mol), propylene glycol, glycerol, 2-butoxyethanol, 2-(2-butoxyethoxy)ethanol, 2-(2-methoxyethoxy)ethanol, triethylene glycol dimethyl ether, a crown ether, acetophenone, 2,4-pentanedione, pentanone, glucose, fructose, sucrose, sorbitol, xylitol, mannitol, γ-valerolactone, propylene carbonate, octylamine, N,N-diethylformamide, N,N-dimethylformamide, N-methylformamide, N,N-dimethylacetamide, propanamide, 1-methyl-2-pyrrolidinone, tetramethylurea, N,N′-dimethylurea, acetonitrile, lactamide, furfurol, 2-furaldehyde, 5-hydroxymethylfurfural, ethyl 3-hydroxybutanoate, 2-hydroxyethyl acrylate, 1-vinyl-2-pyrrolidinone, N,N,N',N'-tetramethyltartramide, 3-hydroxypropionitrile and N,N'-bis(2-hydroxyethyl)ethylenediamine.

4. The process as claimed in claims 1 to 2, wherein the extraction solution comprises at least one organic compound having complexing and also acidic properties.

5. The process as claimed in the preceding claim, wherein the organic compound is chosen from at least one of the following compounds: formic acid, acetic acid, oxalic acid, malonic acid, glutaric acid, glycolic acid, lactic acid, tartronic acid, citric acid, tartaric acid, pyruvic acid, γ-ketovaleric acid, succinic acid, acetoacetic acid, gluconic acid, ascorbic acid, phthalic acid, salicylic acid, maleic acid, malic acid, fumaric acid, acrylic acid, thioglycolic acid, 2-hydroxy-4-methylthiobutanoic acid, glutamic acid, N-acetylglutamic acid, alanine, glycine, cysteine, histidine, aspartic acid, N-acetylaspartic acid, 4-aminobutanoic acid, 1,2-cyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), bicine, tricine, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP or etidronic acid), nitrilotris(methylenephosphonic acid), diethylenetriaminepentakis(methylenephosphonic acid), 4-sulfophthalic acid, 3-(N-morpholino)-2-hydroxy-1-propanesulfonic acid (MOPSO), 2-(4-pyridinyl)ethanesulfonic acid, phenol-4-sulfonic acid, thiodiacetic acid and diglycolic acid.

6. The process as claimed in one of the preceding claims, wherein the organic compound is chosen from formic acid, acetic acid, oxalic acid, citric acid, γ-ketovaleric acid, fructose, ethylene glycol, diethylene glycol and triethylene glycol.

7. The process as claimed in one of the preceding claims, wherein the source catalyst is a spent catalyst regenerated and/or rejuvenated beforehand.

8. The process as claimed in one of the preceding claims, wherein the extraction solution comprises a mineral acid chosen from phosphoric acid, nitric acid or boric acid.

9. The process as claimed in one of the preceding claims, characterized in that the concentration of each organic compound in the extraction solution is between 0.03 and 2 mol/l.

10. The process as claimed in one of the preceding claims, wherein the source catalyst is subjected to at least one pretreatment step before the extraction step chosen from deoiling, regeneration, grinding or washing with water.

11. The process as claimed in one of the preceding claims, wherein the solution of extracted metal/metals is subjected to at least one treatment step before impregnation of the support, said treatment step being chosen from concentration, dilution and/or modification of the composition of the solution by total or partial addition or removal of at least one compound of said solution.

12. The process as claimed in one of the preceding claims, wherein the impregnation of the support with an impregnation solution is carried out starting from the solution of extracted

metal/metals and from a makeup of at least one of the metals from group VIII/VIB, and optionally of phosphorus and/or of organic additive(s).

13. The process as claimed in one of the preceding claims, wherein a part at least of the impregnation solution is reused after impregnation of the support, as makeup for the extraction solution.

14. The process as claimed in one of the preceding claims, wherein the support on which the impregnation is carried out with the impregnation solution derived from the solution of extracted metal/metals is pre-impregnated or post-impregnated with an impregnation solution or is a metal-depleted catalyst.

15. The process as claimed in one of the preceding claims, wherein said impregnated substrate obtained after impregnation is subjected to a drying step, optionally to a calcination step and optionally to a sulfidation step.

16. The process as claimed in one of the preceding claims, wherein the source catalyst is contaminated with arsenic and the degree of extraction of the metal from group VIII or from group VIB is respectively greater than 50% by weight and the degree of extraction of the arsenic is less than 30% by weight, the degree of extraction corresponding to the mass of the extracted metal/metals and of the extracted arsenic in the extraction solution relative to the mass of metal/metals present and of the arsenic present initially on the source catalyst.