

CONTINUOUS COUNTER-CURRENT LEACHING METHOD FOR RECYCLING CATALYST METALS

Technical field

The present invention relates to the recycling of catalyst metals notably originating from hydrocarbon hydrotreatment or hydroconversion units. More particularly, the present invention relates to a continuous countercurrent leaching process for recycling metals from catalysts that provides a high rate of metal extraction and reduced leaching solution consumption.

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 group VIB metal and at least one group VIII metal. 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 in the manufacture of new catalysts.

For example, patent application US 2007/0167321 proposes to recover 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and a contaminant/compound contained in the spent catalyst which it is desired to remove (arsenic, phosphorus) is withdrawn from the solution by causing it to precipitate, and the solution is then filtered.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 in order to be able to 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. Cobalt and molybdenum are extracted with an aqueous solution containing at least one organic acid. The solution obtained is then used directly for impregnation on an aluminum support, to produce a recycled catalyst. The extracted metals remain in the liquid phase throughout this process.

Most processes for recovering metals operate in batch mode by proposing one or more contacts between the leaching solution and the solid, without displacement of the solid. On an industrial scale and in the case of high tonnages, these processes can be improved.

Indeed, it is often preferable to opt for a continuous process beyond a certain tonnage, with a multi-stage implementation ensuring greater extraction. Contact with the leaching solution takes place in cocurrent or countercurrent with the solid to be treated, the latter option being preferred because it makes it possible to significantly reduce the consumption of leaching solution.

Continuous countercurrent leaching processes are known in other fields. An example that may be mentioned is patent application WO 2021/133435A1, which describes a continuous countercurrent extraction process for purifying a solid biomass. The latter travels through a series of agitated tanks while an acidified aqueous solution circulates in the opposite direction to maximize the performance of the process. In this type of process, the solid is dispersed in the liquid in the form of a suspension (or slurry), requiring separation steps between each stage by means of an injection of air to fluidize the solid before separating it on a grate outside the tank.

Another way of proceeding is to move the solid rather than a slurry, making it possible to limit the amount of equipment to be used. Mobile baskets, a conveyor belt or a mobile grid can be used for this purpose. For example, patent application WO 2020/078811A1 describes a process for the production of a concentrate of plant proteins from a plant material, by extraction of soluble carbohydrates with an aqueous alcohol solvent. Solvent extraction is performed in a conveyor belt extractor equipped with means for cleaning the belt on its return path.

The present invention aims to improve the processes for recovering metals from catalysts by proposing a continuous countercurrent leaching process for recycling metals from catalysts.

Summary of the invention

The invention relates to a continuous process for the countercurrent leaching of a spent catalyst comprising at least one Group VIB metal, and/or at least one Group VIII metal, optionally phosphorus and/or sulfur, and an oxide-based support, characterized in that said process comprises N leaching steps, N being greater than or equal to 2, by countercurrent contact of the spent catalyst with a leaching solution comprising at least one organic

compound, the leaching solution being fed continuously and passing through each of the leaching steps in the opposite direction to the circulation of the spent catalyst, each leaching step being followed by a solid/liquid separation step to obtain a solution of extracted metal(s) and a metal-depleted catalyst.

The process according to the invention ensures a high metal extraction rate and a reduced consumption of leaching solution compared to a batch process.

In addition, according to one embodiment, the solution of extracted metal(s) can be used as an impregnation solution for preparing a new catalyst as described in FR3117381, i.e. without any intermediate treatment where the extracted metal(s) would be in the solid phase, nor any liquid/liquid extraction treatment of the latter.

According to a variant, the leaching solution/spent catalyst ratio, expressed as mass of leaching solution per mass of spent catalyst to be treated, is between 1 and 15.

According to a variant, the spent catalyst and the leaching solution are brought into contact by suspending, fluidizing or percolating the leaching solution through a fixed bed containing the spent catalyst.

According to a variant, the circulation of the spent catalyst is performed by moving baskets, a conveyor belt, a moving grate, an endless screw, or in suspension with the leaching solution, or is simulated by permutation of the injection point of the leaching solution.

According to a variant, the solid/liquid separation is performed by sedimentation, filtration, draining and/or centrifugation.

According to a variant, the leaching steps are performed in stirred tanks and the separation steps are performed with filters.

According to a variant, the process is performed with a belt filter on which the spent catalyst is conveyed on a perforated conveyor belt on which it is sprayed with leaching solution circulating in countercurrent to the spent catalyst.

According to this variant, the spent catalyst is fed with suspension on the belt by means of a device comprising at least two stirred tanks operating in a permutable mode: when the first tank feeds the belt with suspension, the suspension of the spent catalyst is prepared in the second tank with the leaching solution from the downstream leaching step and, when the first tank is empty, the suspension feed to the belt is performed by the second tank, and the suspension of the spent catalyst is prepared in the first tank with the leaching solution coming from the downstream leaching step.

According to a variant, the organic compound of the leaching solution has complexing properties, and optionally also acidic properties.

According to a variant, the organic compound comprises one or more chemical functions chosen from a carboxylic acid, phosphonic acid, sulfonic acid, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function or also compounds including a furan ring or also sugars.

According to a 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-acetylaspatic 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 a variant, the organic compound is 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, furfural, 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 concentration of organic compound(s) in the leaching solution is defined so that the mole ratio of organic compound/metal(s) extracted, for the organic compound or for each of the organic compounds, is between 0.2 and 25.

According to a variant, the spent catalyst is subjected to at least one pretreatment step before the first leaching/separation step chosen from deoiling, regeneration, separation of compounds of contaminant/impurity type, grinding or washing with water.

According to a variant, at least part of the solution of extracted metal(s) is used as an impregnation solution to prepare a new catalyst comprising an oxide-based support, said extracted metal(s) remaining in the liquid phase from extraction to impregnation.

According to this variant, the solution of extracted metal(s) is subjected to at least one treatment step before impregnation, 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 a variant, at least a portion of the impregnation solution is reused after impregnation of said support based on oxide(s) as a supplement of the leaching solution.

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 remainder of the text, the expressions "of between ... and ..." and "between ... and ..." are equivalent and mean that the limiting values of the interval are included in the range of values described. Should such not be the case and should the limiting values not be included in the range described, such a clarification will be provided by the present invention.

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

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

In the present description, the term "leaching step" is synonymous with the term "leaching stage", a term often used in the field of leaching.

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.

The content of metals is measured by X-ray fluorescence.

List of figures

Figure 1 shows a diagram of the principle of continuous countercurrent leaching.

Figure 2 shows a diagram of a first variant of implementation of the process according to the invention with stirred tanks and filters.

Figure 3 shows a first embodiment of a second variant embodiment of the process according to the invention with a belt filter.

Figure 4 shows a second embodiment of a second variant embodiment of the process according to the invention with a belt filter.

Figures 5 to 8 show a diagram of a third variant of implementation of the process according to the invention with simulated circulation of the solid.

The figures are highly diagrammatic and do not necessarily represent all the operations which may be involved in the process according to the invention. The references which are identical from one figure to the other relate to the same operation/to the same component/to the same device.

Detailed description

The present invention relates to the recycling of catalyst metals notably originating from hydrocarbon hydrotreatment 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 is then referred to), sulfur (hydrodesulfurization is then referred to), oxygen (hydrodeoxygenation is then referred to) and compounds containing metals which can poison the catalyst and cause operational problems downstream (hydrodemetallization is then referred to). 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, in particular, 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 to thus 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 of 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 which are treated, and in particular those mentioned below, generally contain heteroatoms, such as sulfur, oxygen and nitrogen, and, for heavy feedstocks, they usually also contain metals.

The feedstock of fossil origin is notably a cut derived from coal or hydrocarbons produced from natural gas, possibly 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 can advantageously be chosen from plant oils, oils from algae or algal oils, fish oils, waste food oils, and fats of plant or animal origin, or mixtures of such feedstocks. Said plant oils can advantageously be crude or completely or partly refined, and can result from plants chosen from rape, sunflower, soya, palm, olive, coconut, coconut kernel, castor oil plant, cotton, groundnut, flax and sea kale, and all the oils resulting, 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, can also be used. The feedstock obtained from the conversion of biomass can also advantageously be chosen from fatty acid methyl esters of vegetable and/or animal origin or else fatty acid methyl esters from waste edible vegetable oils.

The feedstock obtained from the conversion of biomass can also be chosen from feedstocks originating from thermal or catalytic biomass conversion processes, 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, comprising plants, animals and byproducts thereof. The term "lignocellulosic biomass" denotes biomass derived from plants or byproducts thereof. 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 hydrolysis (pyrolysis in the presence of a catalyst and of hydrogen).

Conventional hydrotreating catalysts generally comprise an oxide support and an active phase based on Group VIB and VIII metals in the oxide forms thereof and also phosphorus. The preparation of these catalysts generally comprises a step of impregnation of the metals and the phosphorus on the support, followed by drying and a calcination making it possible to obtain the active phase in their oxide forms. Before their use in a hydrotreating and/or hydrocracking 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, in particular 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 having large surface areas (generally 150 to 800 m².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 of the Periodic Table of the Elements, or by a combination of at least one metal from group VIB of the Periodic Table and at least one metal from group VIII, employed in the presence of sulfur. The balance between the two acid and hydrogenating functions governs the activity and the selectivity of the catalyst.

During its operation in a hydrotreating or hydrocracking process, the catalyst becomes deactivated by accumulation of coke and/or sulfur-based compounds or compounds containing other heteroelements at the surface of the catalyst. Beyond a certain period, its replacement is thus necessary.

In order to combat these disadvantages, the regeneration (also called gentle calcination) of hydrotreating/hydrocracking 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/hydrocracking activity. However, the regenerated catalysts are generally less active than the starting catalysts, also called "fresh" catalysts. Consequently, their cycle time in the hydrotreating/hydrocracking 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/hydrocracking activity of the regenerated catalyst, it is possible to apply an additional treatment called a "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, in particular 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 which has lower activity than the fresh catalyst. Finally, some spent catalysts cannot form the subject of reuse via a regeneration or a 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 hydrotreatment or hydroconversion units, it is understood that the process according to the invention applies to any catalyst comprising at least one group VIII metal and/or at least one group VIB metal, and an oxide support, for instance selective hydrogenation catalysts, hydrotreatment catalysts for residues (for example performed in an ebullated bed) or alternatively Fischer-Tropsch catalysts.

The spent catalyst

According to the present invention, the term "spent" catalyst means the catalyst from which it is desired to extract the metals. The "spent" 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 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(s), or by a smaller dimensioning than that sought ("fines" of catalyst particles, for example). This term also includes an at least partially spent capture mass.

The spent catalyst of the process according to the invention is a catalyst comprising at least one oxide support and at least one metal, preferentially several metals. The spent catalyst comprises at least one group VIII metal and/or at least one group VIB metal, an oxide support and optionally phosphorus. It can also, without limitation, comprise coke and/or sulfur as described below.

The oxide support of said spent catalyst is usually a porous solid chosen from the group consisting of: aluminas, silica, silica-aluminas and also titanium or magnesium oxides, used

alone or as a mixture with alumina or silica-alumina. Preferably, the oxide support is essentially constituted by 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 spent 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, generally 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 spent 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, 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 $\text{m}^2\cdot\text{g}^{-1}$, preferably between 10 and 350 $\text{m}^2\cdot\text{g}^{-1}$, more preferably between 40 and 350 $\text{m}^2\cdot\text{g}^{-1}$. The specific surface area is determined in the present invention via the BET method according to the standard ASTM D3663.

The active phase of the catalyst comprises at least one group VIB metal and at least one group VIII metal. The group VIB metal present in the active phase of the catalyst is preferentially chosen from molybdenum and tungsten, or the mixture of these two elements. The group VIII metal 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 group VIII metal is between 1% and 10% by weight of oxide of the group VIII metal, relative to the total weight of the spent catalyst, 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 group VIB metal is between 5% and 40% by weight of oxide of the group VIB metal, relative to the total weight of the spent catalyst, preferably between 8% and 35% by weight, very preferably between 10% and 30% by weight. When the metal is molybdenum or tungsten, the content of metal is expressed as MoO₃ and WO₃ respectively.

The mole ratio of group VIII metal to group VIB metal 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 spent 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 spent catalyst is then preferably between 0.1% and 20% by weight, expressed as P₂O₅ relative to the total weight of the spent catalyst, preferably between 0.2% and 15% by weight, expressed as P₂O₅, and very preferably between 0.3% and 8% by weight, expressed as P₂O₅.

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

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

The spent 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 weight percentage of the carbon element, may be 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 spent catalyst. The coke content is determined according to the ASTM D5373 method.

Optionally, the spent catalyst may also have a low content of contaminants resulting from the feedstock treated with the fresh catalyst from which it originates, such as silicon, arsenic, iron, sodium or chlorine or sulfur.

Preferably, the silicon content of the spent catalyst (besides that possibly present on the fresh catalyst) is less than 2% by weight and very preferably less than 2000 ppm by weight, relative to the total weight of the spent catalyst.

Preferably, the arsenic content is less than 2000 ppm by weight and very preferably less than 500 ppm by weight, relative to the total weight of the spent catalyst.

Preferably, the chlorine content is less than 2000 ppm by weight and very preferably less than 500 ppm by weight, relative to the total weight of the spent catalyst.

Very preferably, the spent catalyst, when it is a regenerated catalyst, is not contaminated, that is to say contains a content of less than 100 ppm by weight of silicon (besides that possibly present on the fresh catalyst), 100 ppm by weight of sodium (besides that possibly present on the fresh catalyst), 50 ppm by weight of arsenic, 50 ppm by weight of iron and 50 ppm by weight of chlorine.

According to one embodiment of the invention, the spent catalyst may comprise or consist of fines produced during the operation of discharging the spent catalyst from the industrial unit from which it is withdrawn, or during the regeneration.

According to another embodiment, the spent catalyst comprises or consists of fines and/or of products outside the specifications resulting from the various unit operations of the manufacture of new catalysts.

Pretreatments (optional)

The spent catalyst may be subjected to at least one pretreatment step prior to leaching 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 spent

catalyst before the metal extraction step, via any method known to a person skilled in the art. The pretreatment step may be chosen from de-oiling, regeneration, separation of compounds of contaminant/impurity type, grinding or washing with water. Preferably, the pretreatment step comprises a regeneration step in order to remove all or part of the coke, of the sulfur and/or of the chlorine, as described in detail below, and/or a step of heat treatment under a gas stream containing hydrogen sulfide, notably performed in order to remove the arsenic.

- De-oiling

The discharging of the spent catalyst from a hydrotreating and/or hydrocracking process is preferably preceded by a deoiling step. The deoiling step generally involves bringing the spent 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.

- Regeneration

The optionally deoiled spent 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 spent 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 at least partially spent 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 spent 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 group VIB metal and/or of at least one group VIII metal and optionally of phosphorus from the spent catalyst. The regenerated catalyst contains substantially the same

group VIB and/or group VIII metal content as the spent catalyst. The regenerated catalyst is characterized by a specific surface area of between 20 and 300 m²/g, preferably between 30 and 280 m²/g, preferably between 40 and 260 m²/g, very preferably between 80 and 250 m²/g.

The pore volume of the regenerated catalyst is generally between 0.1 cm³/g and 1.3 cm³/g, preferably between 0.2 cm³/g and 1.1 cm³/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 spent catalyst. This residual carbon content in the regenerated catalyst is measured according to the ASTM D5373 method.

- Heat treatment in a gaseous stream containing hydrogen sulfide

All or part of the elemental arsenic or of the arsenic compounds potentially contained in the spent catalyst can be removed by passing a stream of hydrogen sulfide and of steam or of inert gas through the solid at a temperature of between 300°C and 750°C. During this treatment, the arsenic contained in the spent catalyst forms arsenic sulfide (of formula As₂S₃) which is volatilized from the solid. The reaction is preferably performed by fluidizing the solid in the stream of hydrogen sulfide and of steam or of inert gas. When a mixture of hydrogen sulfide and inert gas is used, the latter is preferentially nitrogen, carbon dioxide or combustion gases.

This step of heat treatment under a gaseous stream containing hydrogen sulfide is preferably performed before regeneration.

- Grinding

The spent catalyst, optionally deoiled, regenerated and/or subjected to the H₂S treatment, may advantageously undergo, before 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 spent 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 spent catalyst have an equivalent diameter of between 1 and 1000 micrometres, preferably between 5 and 500 micrometres, preferably between 10 and 300 micrometres and particularly preferably between 15 and 150 micrometres. The equivalent diameter denoted "de" is defined according to the following relationship: $d_e = 6 \times V/S$ 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 spent 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 spent catalyst, optionally deoiled, regenerated, subjected to the H₂S treatment and/or ground, can undergo a water washing step.

The volume of water employed in this washing step is advantageously greater than the total pore volume of the spent catalyst. This volume may notably lie in a range extending from 2 to 20 times the total pore volume of the spent 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 spent 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.

Leaching process

The spent catalyst, optionally pretreated, is subjected to the continuous countercurrent leaching process according to the invention, which comprises N leaching steps, N being greater than or equal to 2, by bringing the spent catalyst into countercurrent contact with a leaching solution comprising at least one organic compound, each leaching step being followed by a solid/liquid separation step to obtain a solution of extracted metal(s) and a metal-depleted catalyst.

The process according to the invention is characterized in that the leaching solution is fed continuously and passes through the various steps in the opposite direction to the movement of the solid, that is to say the spent catalyst.

Figure 1 shows an illustration of the process according to the invention. Each numbered block (1, 2, ... N) represents a step (or stage) of leaching by bringing the solid into contact with the leaching solution, followed by solid/liquid separation. The spent catalyst circulates from step 1 to step N. The leaching solution circulates in the opposite direction, from step N to step 1.

In this way, the fresh solid C_R (i.e. the most heavily metal-laden spent catalyst) always encounters the most metal-enriched solution first, then come additional steps of leaching/separation of the catalyst increasingly leached of these metals with solutions less and less charged with extracted metals up to the last step (step N) using the leaching solution free of metals S_P . In this way, an enriched solution of extracted metal(s) S_R and a metal-depleted catalyst C_P are recovered. This principle ensures a higher concentration of metals in the final solution.

The process according to the invention comprises N leaching steps, N being greater than or equal to 2. Advantageously, it comprises between 2 and 20 leaching/separation steps, preferentially between 2 and 6 steps. Each step makes it possible to bring the liquid and the solid into contact and then to perform a liquid/solid separation.

The solid and liquid can be brought into contact via any method known to those skilled in the art, for example by suspending the spent catalyst in the leaching solution by means of a rotary stirrer or by fluidization, or else by percolation of the leaching solution through a fixed bed containing the spent catalyst.

The movement of the solid can be produced by any method known to those skilled in the art, for example by mobile baskets, a conveyor belt, a mobile grid, an endless screw or in suspension with the leaching solution (also called a "slurry"). The movement of the solid can also be simulated by switching around the injection point of the leaching solution. Specifically, if the injection point is periodically moved from step i to $i + 1$, the solid moves in the opposite direction to the liquid, relative to its injection point.

The liquid/solid separation can be performed via any method known to those skilled in the art, for example by sedimentation, by filtration, by draining, for example gravitational draining, and/or by centrifugation.

The process according to the invention can be performed according to numerous variants. These different variants are described hereinbelow.

According to a first variant, the method according to the invention can be implemented with stirred tanks and filters. Each leaching/separation step comprises a stirred tank and a filter. Figure 2 shows a diagram of the first implementation variant of the process according to the invention comprising 3 leaching/separation steps with stirred tanks and filters. In the figure, the arrows in solid lines represent the catalyst, the dotted lines represent the leaching solution and the dotdash lines represent the slurry.

The spent catalyst C_R is introduced, preferably in ground form, into the stirred tank R1 where it is suspended in the liquid S2. The formed slurry SR1 is sent to a filter F1 which separates the liquid and the solid. The catalyst cake C1 obtained is sent to the tank R2 where it is redispersed and suspended in the liquid S1. The slurry SR2 withdrawn from the bottom of the tank R2 sent to a filter F2, which separates a new catalyst cake C2 sent to the tank R3. The depleted catalyst C_P is finally recovered at the outlet of the filter F3 fed by the slurry SR3 withdrawn from the bottom of the tank R3. The catalyst therefore travels through the process in the direction R1 to R3.

Conversely, the leaching solution S_P continuously feeds the tank R3. The filtrate S1 recovered in the filter F3 is returned to the tank R2 forming a slurry SR2 feeding the filter F2 whose filtrate S2 is returned to the tank R1. The slurry SR1 formed in the tank R1 is separated in the filter F1 and the filtrate thus recovered constitutes the final enriched solution S_R . The leaching solution thus travels through the process in the direction R3 to R1.

According to a second variant, the process according to the invention can be performed with a belt filter. In this case, the catalyst is conveyed, preferably in ground form, on a perforated conveyor belt on which it is sprinkled with leaching solution circulating in countercurrent to the solid.

According to a first embodiment of this second variant, shown in Figure 3, the spent catalyst C_R (solid) is loaded onto the conveyor belt by means of a device ensuring a controlled and uniform height of solid over the width of the belt. Once loaded, the solid advances with the movement of the belt. As it travels, the solid passes through several (N) zones or extraction steps (3 zones in Figure 3) in which it is sprayed with leaching solution by a spray nozzle. The metal-free leaching solution S_P is introduced at the end of the conveyor belt. A vacuum is in place under the belt to force the liquid to percolate through the solid. The liquid is recovered in a tank located under the belt and constitutes a solution enriched in metallic species following contact with the solid. This solution is returned by a pump to the upstream extraction zone. In this way, the leaching solution is countercurrent to the solid circulation. The solution recovered as close as possible to the fresh solid feed constitutes the final solution enriched in metallic

species S_R . At the other end of the belt, the depleted solid C_P is discharged, for example by means of a scraper.

According to a second embodiment of this second variant, represented in Figure 4, the spent catalyst C_R (solid) is fed with slurry on the belt, by means of a device consisting of two stirred tanks operating in a permutable mode (also known as "swing" mode). A first tank R1 receives the solid and the leaching solution from the downstream extraction zone, the outlet of the tank being closed. During this time, the second tank R2 feeds slurry to the conveyor belt. When it is empty, the feed is provided via the first tank R1 and the second tank R2 receives the solid and the leaching solution. This device ensures a continuous slurry feed of the conveyor belt. The metal-free leaching solution S_P is introduced at the end of the conveyor belt. The first lengths of the belt see a cake formed as the liquid percolates through the solid. The solid advances with the movement of the belt and passes through several (N) extraction zones or extraction steps (3 zones in Figure 4). In the last N-1 zones, it is sprayed with leaching solution by a spray nozzle. The liquid is recovered in a tank located under the belt and constitutes a solution enriched in metallic species following contact with the solid. Said solution recovered under the belt in one of the last N-2 extraction zones is returned by a pump to the upstream extraction zone. In this way, the leaching solution is countercurrent to the solid circulation. The solution recovered at the level of the first zone or extraction step closest to the fresh solid feed constitutes the final solution S_R enriched in metallic species. The solution recovered in the second zone or extraction step is returned by a pump to the stirred tank, the outlet of which is closed to prepare the slurry. At the other end of the belt, the depleted solid C_P is discharged, for example by means of a scraper. This second embodiment is preferred because the stirring maintained in the slurry feed tank ensures sufficient suspension of the fines, which avoids forming a layer of fines on the belt, the latter possibly being problematic for the filtration properties.

According to a third variant, the process according to the invention can be performed with simulated circulation of the spent catalyst (solid). Figures 5 to 8 show a diagram of this third embodiment variant in which the circulation of the solid is effected by permutation of the injection of the fresh leaching solution, with three leaching/separation steps in four catalyst-containing columns including one for unloading leached catalyst/loading fresh spent catalyst. The dashed arrows represent the path of the leaching solution. The spent catalyst (solid) is introduced, preferably in the form of extrudates, into columns, named R1 to R4. The solid/liquid separation step is intrinsically performed in each of the columns by flow of the liquid.

During step 1 of this embodiment (Figure 5), the fresh leaching solution S_P is injected at the top of column R2 and percolates through the catalyst bed, before passing through column R3 and then column R4. The enriched solution S_R is withdrawn from the bottom of R4. During this

time, column R1 is off-line in order to discharge the depleted spent catalyst C_P and reload a spent catalyst to be treated C_R .

During step 2 of this embodiment (Figure 6), the leaching solution S_P is now injected at the top of column R3 and column R2 undergoes unloading C_P /reloading C_R . Relative to the injection point, the catalyst moved in the opposite direction to the liquid circulation, with a solid flow rate equal to the mass of catalyst contained in a column divided by the permutation time. The permutation time between each step is generally between 1 min and 24 h.

The reloaded spent catalyst C_R in step 1 thus first encounters the most enriched solution coming from column R4, making it possible to draw off a concentrated enriched solution S_R at the bottom of R1.

Similarly, during step 3 of this embodiment (Figure 7), the leaching solution S_P is injected at the top of column R4 and at the top of column C1 during step 4 of this embodiment (Figure 8). Then, the cycle starts again according to Figure 5.

According to the process according to the invention, the spent catalyst is brought into contact with a leaching solution containing at least one organic compound.

The leaching solution according to the present invention can comprise any polar protic solvent known to those skilled in the art. Preferably, a polar protic solvent, for example chosen from the group formed by methanol, ethanol and water, or also a water-ethanol or water-methanol mixture, is used. Very preferably, the solvent used 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, in a preferred manner between 0.5 and 6, preferably between 1 and 4.

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 for extracting the metals of interest which it is desired to recycle, by passing them into the liquid phase, while the support of the spent catalyst and optional other components of the spent catalyst remain in the solid phase and are thus easily removable.

It should be emphasized that the organic compounds which give the most advantageous results are 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 also compounds including a furan ring or also 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-acetylaspatic 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, 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, furfural, 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.

Preferably, 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 formic acid, acetic acid, glutaric acid, oxalic acid, glycolic acid, lactic acid, citric acid, γ -ketovaleric acid, acetoacetic acid, gluconic acid and ascorbic acid.

The concentration of each organic compound in the leaching solution is defined so that the mole ratio of organic compound/extracted metals is between 0.2 and 25, preferably between 0.2 and 11, preferably between 0.2 and 5, preferably between 0.4 and 2 and in a preferred manner between 0.4 and 1.2.

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

The organic compound concentration of the leaching solution is generally between 5 and 300 g/l, preferably between 15 and 200 g/l.

In one embodiment according to the invention, the leaching solution may 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 spent catalyst. It is also possible to use mineral acids other than phosphoric acid, notably nitric acid, sulfuric acid or boric acid.

In one embodiment according to the invention, the leaching solution can also contain an oxidizing agent for promoting the extraction of the metals. Preferably, the oxidizing agent contained in the leaching 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 process according to the invention are chosen so as to maximize the extraction of the metals contained in the spent catalyst, while minimizing the dissolution of the metal(s) contained in the support of said spent catalyst and while limiting the amount of organic compound in order for the latter not to be in too great excess relative to the optimum amount of organic compound optionally 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 optionally 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 is generally between 1 minute and 20 hours, preferably between 5 minutes and 300 minutes, and in a preferred manner between 5 minutes and 180 minutes.

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 optional use as an impregnation solution and which are already in this temperature range.

The amount of leaching solution used for the process according to the invention is preferably as low as possible in order to obtain the desired effect, as indicated above. Preferably, the liquid/solid ratio, expressed as mass of leaching solution per mass of spent catalyst to be treated, is between 1 and 15, preferably between 2 and 12, in a preferred manner between 3 and 10.

According to one embodiment, when the spent catalyst contains only one group VIB metal or one group VIII metal, respectively, only one group VIB metal or one group VIII metal is in principle extracted from the catalyst. According to another embodiment, when the spent

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

At the end of the leaching step, the solution is separated from the solid residue to obtain, on the one hand, a leached catalyst depleted in metal(s), and, on the other hand, the leaching solution enriched in at least one group VIB metal and/or at least one group VIII metal.

The liquid/solid separation can be performed via any method known to those skilled in the art, for example by sedimentation, by filtration, by draining, for example gravitational draining, and/or by centrifugation.

Preferably, the residual metal content 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 leaching is generally greater than 50%, preferably greater than 60%, in a preferred manner greater than 70%. The degree of leaching corresponds to the mass of the metal(s) extracted in the final solution, relative to the mass of metal(s) initially present on the spent catalyst.

Upgrading the leaching solution

According to one embodiment, the extracted metal(s) contained in the solution of extracted metal(s) can be recovered in solid form. Recovery in solid form can be performed via any method known to those skilled in the art, for example by precipitation/filtration, crystallization/filtration or a liquid/liquid extraction treatment followed by evaporation of the solvent, or else by adsorption on a capture mass.

According to another preferred embodiment, the solution of extracted metal(s) can be used as an impregnation solution for preparing a new catalyst as described in FR3117381, that is to say without intermediate treatment where the extracted metal(s) would be in the solid phase, nor liquid/liquid extraction treatment of the latter. In this case, the extracted metal(s) contained in the solution of extracted metal(s) remain in solution until they are re-used as supplemental impregnation solution to produce a new catalyst. This allows "direct" upgrading, thus avoiding a quantity of precipitation/filtration type operations allowing the production of a new catalyst which is easy to implement on an industrial scale. It is even more simplified thereby when the

leaching 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).

Prior to use as an impregnating solution, the solution of extracted metal(s) 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(s) 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 spent 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(s) contains suspended solids after the last liquid/solid separation step, any known method for removing these suspended solids 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(s) can be subjected to a concentration step. This step consists in concentrating the solution of extracted metal(s) 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 envisaged. The concentration can take place in a single step or in several successive steps. All or some of the solvent containing or not containing organic compound, extracted from the metal solution, can be recycled into the process according to the invention as a leaching solution.

Preferably, and in particular in the case where the metal solution is an aqueous solution, the concentration operation is performed by evapoconcentration. 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 coremoval of the solvent and of a 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 a leaching solution.

When only the removal of some of the solvent is desired, besides evapoconcentration, 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 evapoconcentration.

- Adjustment of the composition of the metal solution

The optionally purified and/or concentrated solution of extracted metal(s) 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.

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(s), the latter alternative being preferred. The mole ratio of group VIII metal to group VIB metal in the metal solution resulting from this adjustment step is generally between 0.1 and 0.8, preferably of between 0.15 and 0.6.

Use may be made, by way of example for the metal precursors, among the sources of molybdenum, of the oxides and hydroxides, molybdic acids and their salts, in particular the ammonium salts, such as ammonium molybdate or ammonium heptamolybdate, phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and their salts, and optionally silicomolybdic acid ($\text{H}_4\text{SiMo}_{12}\text{O}_{40}$) and its salts. 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 their salts, in particular the ammonium salts, such as ammonium tungstate or ammonium metatungstate, phosphotungstic acid and their salts, and optionally silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) and its salts. 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 oxides and the ammonium 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 concerned.

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 concerned.

A phosphorus precursor may be used for the leaching process according to the invention. If the phosphorus/metal ratio of the solution of extracted metal(s) is lower than that desired for the impregnation solution, a phosphorus precursor, identical to or different from that optionally used for leaching, can be added to the solution of extracted metal(s). This will notably be the case when no phosphorus compound/precursor has been added during leaching, 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 group VIB metal 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 its esters and its salts, such as ammonium phosphates, are also suitable, just like 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/hydrocracking catalysts has been recommended by those 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 those 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 FR 3 083 134 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. The patent FR 3 083 131 also describes examples of organic additives which may be suitable but which will instead be added separately, in preimpregnation or in postimpregnation of the support.

The solution of extracted metal(s) 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% 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 leaching process according to the invention. For this, any method known to a person skilled in the art for separating an organic molecule from a metal solution is envisaged. The concentration of excess organic compound can be reduced, for example, by evaporation, by liquid-liquid extraction, by adsorption or by membrane separation.

The solution of extracted metal(s), optionally previously subjected to one or more of the treatments described below, can be used for the preparation of a new catalyst. For this purpose, an oxide support, or a catalyst already containing one or more metals, is brought into contact with the solution of extracted metal(s). The contacting operation may be performed via any known method, for instance ion exchange, dry impregnation, excess impregnation, vapor deposition, etc. The contacting operation can take place in one step or in several successive steps.

The oxide support which will be impregnated with the impregnation solution resulting from the solution of extracted metal(s) may be of the same nature as the support for the spent catalyst, a description of which has already been given above.

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

According to a preferred embodiment, said support is brought into contact with the metal 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 contacting operation may advantageously be performed 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.

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 between 30 minutes and 6 hours is sufficient.

Advantageously, the contacting 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 traversed bed.

According to a 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 and/or during the impregnation step. Preferably this amount is 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 can 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. Likewise, the catalyst no longer contains or contains very little organic extraction compound and organic additive. However, the introduction of the organic additive during its preparation has 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 in which the impregnation step is performed via at least two impregnation cycles, each impregnation is advantageously followed by drying and optionally calcination.

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.

It should be pointed out that the new catalyst can have a different formulation from that of the spent 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.

It should also be noted that the new catalyst can be postadditivated, 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 operation, it being understood that, preferably, no calcination step is performed after its introduction.

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 transform 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 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.

Example

The solid to be treated is a previously ground regenerated CoMoP hydrotreatment catalyst, 90% of whose particle size distribution by volume has a size of less than 150 microns (μm) and contains 21% by weight of molybdenum (expressed as oxide MoO_3). The leaching solution is a solution of water and glutaric acid at a concentration equal to 180 g/l. Extraction is performed at 20°C and with a liquid/solid (or leaching solution/catalyst) ratio equal to 3 kg/kg.

In this example, the process according to the invention, called process B, is compared with a batch process with one extraction, called process A1, and with a batch process with two extractions, called A2.

In process A1 (comparative), the solid to be treated is introduced into a stirred tank filled with leaching solution and is kept stirred for 60 minutes. The slurry is then sent to a frontal filtration under a vacuum of 0.5 bar (0.05 MPa), with a cut-off threshold of 20 microns (μm). The filtrate recovered constitutes the final solution enriched in molybdenum and cobalt.

In process A2 (comparative), the solid to be treated is introduced into a stirred tank filled with leaching solution and is kept stirred for 60 minutes. The slurry is then sent to a frontal filtration under a vacuum of 0.5 bar (0.05 MPa), with a cut-off threshold of 20 microns (μm). The recovered filtrate is sent for product storage. The depleted cake is returned to the stirred tank and is once again brought into contact with a metal-free leaching solution for 60 min. The resulting slurry is sent to frontal filtration under a vacuum of 0.5 bar (0.05 MPa), with a cut-off

threshold of 20 microns (μm). The recovered filtrate is sent for product storage and is mixed with the filtrate obtained in the preceding step to form the final solution.

Process B is a process according to the invention with implementation on a conveyor belt fed with slurry. The vacuum under the belt is maintained at 0.5 bar (0.05 MPa) and the filtering medium has a cut-off threshold of 20 microns (μm). The cake formed has a thickness of 10 mm. The belt moves at a speed of 1 m/min and the residence time of the solid on the belt is 20 min. The process passes through two extraction zones arranged in countercurrent and spraying the liquid according to a liquid/solid (or leaching solution/catalyst) ratio equal to 3 kg/kg. The final solution is collected under the belt, on the slurry feed side.

The performance quality is considered in terms of molybdenum extraction rate and leaching solution consumption. The degree of extraction corresponds to the mass of molybdenum extracted in the final solution, relative to the mass of molybdenum initially present on the catalyst. The consumption of leaching solution is expressed in liters of solution required per kg of molybdenum extracted. The performance qualities of the processes are collated in Table 1.

TABLE 1

	Degree of extraction (%)	Leaching solution consumption (L/kg)
Process A1 (comparative)	54.5	39.3
Process A2 (comparative)	83.2	51.5
Process B (according to the invention)	76.7	27.9

Compared to process A1, process B according to the invention provides a higher degree of extraction and a reduced consumption of leaching solution.

Compared to process A2, process B according to the invention ensures a reduced consumption of leaching solution while ensuring a degree of extraction.

Claims

1. A continuous process for the countercurrent leaching of a spent catalyst comprising at least one Group VIB metal, and/or at least one Group VIII metal, optionally phosphorus and/or sulfur, and an oxide(s)-based support, characterized in that said process comprises N leaching steps, N being greater than or equal to 2, by countercurrent contact of the spent catalyst with a leaching solution comprising at least one organic compound, the leaching solution being fed continuously and passing through each of the leaching steps in the opposite direction to the circulation of the spent catalyst, each leaching step being followed by a solid/liquid separation step to obtain a solution of extracted metal(s) and a metal-depleted catalyst.
2. The process as claimed in claim 1, wherein the leaching solution/spent catalyst ratio, expressed as mass of leaching solution per mass of spent catalyst to be treated, is between 1 and 15.
3. The process as claimed in either of the preceding claims, wherein the spent catalyst and the leaching solution are brought into contact by suspending, fluidizing or percolating the leaching solution through a fixed bed containing the spent catalyst.
4. The process as claimed in one of the preceding claims, wherein the circulation of the spent catalyst is performed by moving baskets, a conveyor belt, a moving grate, an endless screw, or in suspension with the leaching solution, or is simulated by permutation of the injection point of the leaching solution.
5. The process as claimed in one of the preceding claims, wherein the solid/liquid separation is performed by sedimentation, filtration, draining and/or centrifugation.
6. The process as claimed in one of the preceding claims, wherein the leaching steps are performed in stirred tanks and the separation steps are performed with filters.
7. The process as claimed in one of the preceding claims, which is performed with a belt filter on which the spent catalyst is conveyed on a perforated conveyor belt on which it is sprayed with leaching solution circulating in countercurrent to the spent catalyst.
8. The process as claimed in the preceding claim, wherein the spent catalyst is fed with suspension on the belt by means of a device comprising at least two stirred tanks operating in a permutable mode: when the first tank feeds the belt with suspension, the suspension of the spent catalyst is prepared in the second tank with the leaching solution from the downstream leaching step and, when the first tank is empty, the suspension feed to the belt is performed by the second tank, and the suspension of the spent catalyst is prepared in the first tank with the leaching solution coming from the downstream leaching step.

9. The process as claimed in one of the preceding claims, characterized in that the organic compound of the leaching solution has complexing properties, and optionally also acidic properties.

10. The process as claimed in the preceding claim, characterized in that the organic compound comprises one or more chemical functions chosen from a carboxylic acid, phosphonic acid, sulfonic acid, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function or also compounds including a furan ring or also sugars.

11. The process as claimed in either of claims 9 and 10, characterized in that the organic compound is 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-acetylaspatic 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.

12. The process as claimed in either of claims 9 and 10, characterized in that 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, furfural, 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.

13. The process as claimed in one of the preceding claims, characterized in that the concentration of organic compound(s) in the leaching solution is defined so that the mole ratio of organic compound/metal(s) extracted, for the organic compound or for each of the organic compounds, is between 0.2 and 25.

14. The process as claimed in one of the preceding claims, wherein the spent catalyst is subjected to at least one pretreatment step before the first leaching/separation step chosen from deoiling, regeneration, separation of contaminants/impurities type compounds, grinding or washing with water.

15. The process as claimed in one of the preceding claims, wherein at least part of the solution of extracted metal(s) is used as an impregnation solution to prepare a new catalyst comprising an oxide-based support, said extracted metal(s) remaining in the liquid phase from extraction to impregnation.

16. The process as claimed in the preceding claim, wherein the solution of extracted metal(s) is subjected to at least one treatment step before impregnation, 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.

17. The process as claimed in claims 15 and 16, characterized in that at least a portion of the impregnation solution is reused after impregnation of said support based on oxide(s) as a supplement of the leaching solution.