

PROCESS FOR HYDROTREATMENT AND HYDROISOMERIZATION OF FEEDSTOCKS OBTAINED FROM A RENEWABLE SOURCE IMPLEMENTING A ZEOLITE THAT IS MODIFIED BY A BASIC TREATMENT

Technical Field

In an international context marked by the rapid growth of fuel requirements, in particular gas oil and kerosene bases in the European Community, the search for new sources of renewable energy that can be integrated into the traditional arrangement of the refining and production of fuels constitutes a major venture.

In this regard, there has been a very sharp resurgence, in recent years, of interest in integration into the process for refining new products of plant origin, obtained from the conversion of the lignocellulosic biomass or obtained from the production of vegetable oils or animal fats, due to the increase in the cost of fossil fuels. Likewise, the traditional biofuels (ethanol or methyl esters of vegetable oils, primarily) have acquired an actual status of a supplement to petroleum-type fuels in the fuel pools. In addition, the processes that are now known that use vegetable oils or animal fats are at the origin of CO₂ emissions, known for these negative effects on the environment. A better use of these bio resources, such as, for example, their integration into the fuel pool, would therefore offer a certain advantage.

The high demand for gas oil and kerosene fuels, coupled with the importance of concerns linked to the environment, reinforces the advantage of using feedstocks obtained from renewable sources. Among these feedstocks, it is possible to cite, for example, vegetable oils, animal fats that are raw or that have been pretreated, as well as mixtures of such feedstocks. These feedstocks contain chemical structures such as triglycerides or esters or fatty acids, whereby the structure and the length of the hydrocarbon chain of the latter are compatible with the hydrocarbons that are present in the gas oils and kerosene.

One possible method is the catalytic transformation of the feedstock that is obtained from the renewable source of paraffinic fuel from which oxygen is removed in the presence of hydrogen (hydrotreatment). Numerous metal or sulfur catalysts are known for being active for this type of reaction.

These processes for hydrotreatment of the feedstock obtained from a renewable source are already well known and are described in numerous patents. It is possible to cite, for example, the patents: US 4,992,605, US 5,705,722, EP 1,681,337 and EP 1,741,768.

The use of solids based on transition metal sulfides makes possible the production of paraffins from the ester-type molecule according to two reaction methods:

- The hydrodeoxygenation leading to the formation of water by consumption of hydrogen and to the formation of hydrocarbons of the carbon number (C_n) that is equal to that of the initial fatty acid chains,
- The decarboxylation/decarbonylation leading to the formation of carbon oxides (carbon monoxide and carbon dioxide: CO and CO₂) and to the formation of hydrocarbons, having one carbon less (C_{n-1}) relative to the initial fatty acid chains

The liquid effluent that is obtained from these hydrotreatment processes essentially consists of n-paraffins that can be incorporated in the gas oil and kerosene pool. So as to improve the properties under cold conditions of this hydrotreated liquid effluent, a hydroisomerization stage is necessary for transforming the n-paraffins into branched paraffins exhibiting better properties under cold conditions

The patent application EP 1 741 768 describes, for example, a process that comprises a hydrotreatment followed by a hydroisomerization stage so as to improve the properties under cold conditions of the linear paraffins that are obtained. The catalysts that are used in the hydroisomerization stage are bifunctional catalysts [and] consist of a metal active phase that comprises a metal of group VIII that is selected from among palladium, platinum and nickel, dispersed on a molecular sieve-type acid substrate that is selected from among SAPO-11, SAPO-41, ZSM-22, ferrierite or ZSM-23, whereby said process operates at a temperature of between 200 and 500°C and at a pressure of between 2 and 15 MPa. Nevertheless, the use of this type of solid brings about a loss in yield of middle distillates

The modification of zeolite by alkaline treatment is a process that has been studied in open literature. This process of modification by alkaline treatment makes it possible to create mesoporosity in a certain type of zeolite such as the ZSM-5 microporous zeolite in Ogura et al., *Applied Catal. A:General*, 219 (2001) 33, Groen et al., *Colloids and Surfaces A:Physicochem. Eng. Aspects* 241 (2004) 53, and Groen et al., *Microporous and Mesoporous Materials*, 69 (2004) 29, the FER in Groen et al., *Microporous and Mesoporous Materials*, 69 (2004) 29, the MOR in Groen et al.,

Microporous and Mesoporous Materials, 69 (2004) 29, and Groen et al, *J Catal* 243 (2006) 212 or the BEA Zeolite, Groen et al, *Microporous and Mesoporous Materials*, 69 (2004) 29, Groen et al, *J Catal* 243 (2006) 212 and Groen et al, *Microporous and Mesoporous Materials*, 114 (2008) 93, and the catalysts that are obtained have been used for different catalytic reactions. These studies show that the alkaline treatment makes it possible to remove silicon atoms from the structure, thus creating a mesoporosity. The creation of mesoporosity and maintaining crystallinity and acidic properties of zeolite are identified in these publications as being linked to the initial overall Si/Al molar ratio of the zeolites, whereby said optimal overall Si/Al ratio is to be between 20 and 50. Actually, beyond this range of the overall Si/Al ratio of between 20 and 50, and, for example, for an overall Si/Al ratio that is less than 20, the structure of the zeolite is very stable because of the presence of a large number of aluminum atoms that prevent the extraction of silicon atoms and therefore the creation of additional mesoporosity.

Advantage of the Invention

The dealuminified Y zeolite contains mesopores, created by extracting aluminum atoms from the framework of the zeolite. The presence of mesopores makes it possible to improve the selectivity of middle distillates of hydrocracking catalysts that implement such a zeolite by facilitating the diffusion of primary products of the reaction (jet fuels and gas oils) and thus by limiting the supercracking of light products. However, the extraction of aluminum atoms of the framework reduces the Brønsted acidity of said zeolite and therefore its catalytic activity. The gain in selectivity of middle distillates linked to the mesoporosity of the zeolite is therefore done to the detriment of the catalytic activity.

The research work carried out by the applicant on the modification of numerous zeolites and crystallized microporous solids and on the hydrogenating active phases has led to the discovery that, surprisingly enough, a catalyst for hydroisomerization of paraffinic hydrocarbon feedstocks and in particular obtained from the hydrotreatment of feedstocks obtained from a renewable source, comprising at least one hydrodehydrogenating metal that is selected from the group that is formed by the metals of group VIB and group VIII of the periodic table, taken by themselves or in a mixture, and

a substrate that comprises at least one dealuminified Y zeolite and that contains a specific fraction by weight of extra-network aluminum atoms, whereby said zeolite is modified by a) a basic treatment stage that consists in the mixing of said dealuminified Y zeolite with a basic aqueous solution that makes it possible to remove silicon atoms from the structure and to insert extra-network aluminum atoms into the framework of the zeolite, and at least one heat treatment stage c), made it possible to obtain an activity, i.e., a higher conversion level, and a higher selectivity of middle distillates (kerosene and gas oils), with the hydroisomerization stage being implemented in a process for treatment of feedstocks obtained from a renewable source comprising a hydrotreatment stage upstream from said hydroisomerization stage.

Without being linked by any theory, the basic treatment of the zeolite that is dealuminified and that contains an initial specific fraction by weight of extra-network aluminum atoms makes possible the creation of mesopores forming a network of mesopores that are interconnected up to the surface of the zeolite crystals, by desilication, i.e., by extraction of silicon atoms from the framework of the initial zeolite. The creation of mesopores that are accessible by the outer surface of the zeolite crystals promoting the intercrystalline diffusion of molecules makes it possible for a catalyst that implements said modified zeolite according to the invention, used in a process for the production of middle distillates, to obtain a higher selectivity of middle distillates. Furthermore, the basic treatment also makes possible the realuminification, i.e., the reintroduction of at least a portion of extra-network aluminum atoms that are present in the initial zeolite in the framework of the modified zeolite, whereby this realuminification makes possible an increase in the Brønsted acidity of the modified zeolite that is reflected for a catalyst that implements said modified zeolite according to the invention by improved catalytic properties, i.e., a better conversion.

One objective of the invention is therefore to provide a process for treatment of feedstocks that are obtained from a renewable source implementing – in one hydroisomerization stage downstream from a hydrotreatment stage – a hydroisomerization catalyst that comprises a modified zeolite-based substrate that makes it possible to obtain high yields of gas oil and kerosene bases.

Another objective of the invention is to provide a process for treatment of feedstocks obtained from a renewable source implementing – in one hydroisomerization stage downstream from a hydrotreatment stage – a catalyst that comprises as substrate a modified zeolite that makes it possible to reduce the 150°C- light fraction production.

Object of the Invention

More specifically, the invention relates to a process for treatment of feedstocks obtained from a renewable source and comprising the following stages:

a) Hydrotreatment in the presence of a fixed-bed catalyst, at a temperature of between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 h⁻¹ and 10 h⁻¹, and in the presence of a total quantity of hydrogen that is mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³ of hydrogen/m³ of feedstock,

b) Separation, starting from the effluent that is obtained from stage a), of hydrogen, gases, and at least one hydrocarbon base,

c) Hydroisomerization of at least a portion of said hydrocarbon base that is obtained from stage b) in the presence of a fixed-bed hydroisomerization catalyst, whereby said catalyst comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIB and group VIII of the periodic table, taken by itself or in a mixture, and a substrate that comprises at least one dealuminified Y zeolite that has an initial overall atomic ratio of silicon to aluminum of between 2.5 and 20, an initial extra-network aluminum atom fraction by weight that is greater than 10%, relative to the total weight of the aluminum that is present in the zeolite, an initial mesopore volume that is measured by nitrogen porosimetry that is greater than 0.07 ml g⁻¹, and an initial crystalline parameter a_0 of the elementary mesh that is between 24.38 Å and 24.30 Å, whereby said zeolite is modified by a) a basic treatment stage that consists in the mixing of said dealuminified Y zeolite with a basic aqueous solution, and at least one heat treatment stage c), whereby said hydroisomerization stage is carried out at a temperature of between 150 and 500°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 and 10 h⁻¹, and in the presence of a total quantity of hydrogen that is mixed with the

feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³/m³ of feedstock,

d) Separation, starting from the effluent that is obtained from stage c), of hydrogen, gases, and at least one gas oil base and one kerosene base.

Detailed Description of the Invention

This invention is particularly devoted to the preparation of gas oil and kerosene fuel bases corresponding to new environmental standards, starting from feedstocks obtained from renewable sources.

The feedstocks that are obtained from renewable sources used in this invention are advantageously selected from among the oils and fats of plant or animal origin, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters. The vegetable oils can advantageously be raw or refined, totally or partially, and obtained from the following plants: canola, sunflower, soybean, palm, palm-kernel, olive, coconut, and jatropha, whereby this list is not exhaustive. The oils of algae or fish are also relevant. Animal fats are advantageously selected from among lard or fats composed of waste from the food industry or obtained from catering industries.

These feedstocks essentially contain chemical structures of the triglyceride type that one skilled in the art also knows under the name fatty acid triesters as well as free fatty acids. A fatty acid triester is thus composed of three chains of fatty acids. These fatty acid chains in triester form or in free fatty acid form have a number of unsaturations per chain, also called a number of carbon-carbon double bonds per chain, generally encompassed between 0 and 3 but that can be higher in particular for the oils that are obtained from algae that generally have a number of unsaturations per chain of 5 to 6.

The molecules that are present in the feedstocks that are obtained from renewable sources used in this invention therefore have a number of unsaturations, expressed per triglyceride molecule, advantageously between 0 and 18. In these feedstocks, the unsaturation level, expressed in terms of the number of unsaturations per hydrocarbon fatty chain, is advantageously between 0 and 6.

The feedstocks that are obtained from renewable sources generally also comprise various impurities and in particular heteroatoms such as nitrogen. The nitrogen contents

in the vegetable oils are generally between approximately 1 ppm and 100 ppm by weight according to their nature. They can reach up to 1% by weight in particular feedstocks

Prior to stage a) of the process according to the invention, the feedstock can advantageously undergo a pretreatment or pre-refining stage so as to eliminate, by a suitable treatment, contaminants such as metals, like the alkaline compounds, for example on ion-exchange resins, alkaline-earths, and phosphorus. Suitable treatments can be, for example, heat treatments and/or chemical treatments that are well known to one skilled in the art

According to stage a) of the process according to the invention, the feedstock, optionally pretreated, is brought into contact with a fixed-bed catalyst at a temperature of between 200 and 450°C, preferably between 220 and 350°C, in a preferred manner between 220 and 320°C, and in an even more preferred manner between 220 and 310°C. The pressure is between 1 MPa and 10 MPa, in a preferred manner between 1 MPa and 6 MPa, and in an even more preferred manner between 1 MPa and 4 MPa. The hourly volumetric flow rate is between 0.1 h⁻¹ and 10 h⁻¹. The feedstock is brought into contact with the catalyst in the presence of hydrogen. The total quantity of hydrogen mixed with the feedstock is such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³ of hydrogen/m³ of feedstock, and in a preferred manner between 150 and 750 Nm³ of hydrogen/m³ of feedstock.

In stage a) of the process according to the invention, the fixed-bed catalyst is advantageously a hydrotreatment catalyst that comprises a hydro-dehydrogenating function that comprises at least one metal of group VIII and/or group VIB, taken by itself or in a mixture, and a substrate that is selected from the group that is formed by alumina, silica, silica-aluminas, magnesia, clays, and the mixtures of at least two of these minerals. This substrate can also advantageously contain other compounds and, for example, oxides that are selected from the group that is formed by boron oxide, zirconia, titanium oxide, and phosphoric anhydride. The preferred substrate is an alumina substrate, and, in a very preferred manner, it is η -, δ -, or γ -alumina.

Said catalyst is advantageously a catalyst that comprises metals of group VIII that are preferably selected from among nickel and cobalt, taken by itself or in a mixture,

preferably combined with at least one metal of group VIB, preferably selected from among molybdenum and tungsten, taken by itself or in a mixture

The content of metal oxides of group VIII and preferably of nickel oxide is advantageously between 0.5 and 10% by weight of nickel oxide (NiO) and preferably between 1 and 5% by weight of nickel oxide, and the content of metal oxides of group VIB and preferably of molybdenum trioxide is advantageously between 1 and 30% by weight of molybdenum oxide (MoO_3), preferably 5 to 25% by weight, the percentages being expressed in terms of % by weight relative to the total mass of the catalyst

The total content of oxides of metals of groups VIB and VIII in the catalyst that is used in stage a) is advantageously between 5 and 40% by weight and in a preferred manner between 6 and 30% by weight relative to the total mass of the catalyst

The ratio by weight that is expressed in terms of metal oxide between metal (or metals) of group VIB to metal (or metals) of group VIII is advantageously between 20 and 1 and in a preferred manner between 10 and 2.

Said catalyst that is used in stage a) of the process according to the invention is advantageously to be characterized by a strong hydrogenating power so as to orient as much as possible the selectivity of the reaction to a hydrogenation preserving the number of carbon atoms of the fatty chains, i.e., the hydrodeoxygenation method, so as to maximize the yield of hydrocarbons entering the field of distillation of kerosenes and/or gas oils. This is why the operation is performed in a preferred manner at a relatively low temperature. Maximizing the hydrogenating function also makes it possible to limit the reactions of polymerization and/or condensation leading to the formation of coke that would degrade the stability of the catalytic performances. Preferably, a catalyst of Ni or NiMo type is used.

Said catalyst that is used in the hydrotreatment stage a) of the process according to the invention can also advantageously contain a doping element that is selected from among phosphorus and boron, taken by themselves or in a mixture. Said doping element can be introduced into the matrix or preferably be deposited on the substrate. It is also possible to deposit silicon on the substrate by itself or with phosphorus and/or boron and/or fluorine

The content by weight of oxide of said doping element is advantageously less than 20% and in a preferred manner less than 10%, and it is advantageously at least 0.001%.

The metals of the catalysts that are used in stage a) for hydrotreatment of the process according to the invention are sulfurized metals or metal phases and preferably sulfurized metals.

The scope of this invention would not be exceeded by using a single catalyst or several different catalysts simultaneously or successively in stage a) of the process according to the invention. This stage can be carried out industrially in one or more reactors with one or more catalytic beds and preferably with liquid downflow.

According to stage b) of the process according to the invention, the hydrotreated effluent that is obtained from stage a) is subjected at least partially, and preferably completely, to one or more separations. The object of this stage is to separate the gases from the liquid and in particular to recover the hydrogen-rich gases that can also contain gases such as CO and CO₂, and at least one liquid hydrocarbon base with a sulfur content that is less than 10 ppm by weight. The separation is carried out according to all separation methods that are known to one skilled in the art. The separation stage can advantageously be implemented by any method that is known to one skilled in the art, such as, for example, the combination of one or more high- and/or low-pressure separators, and/or distillation stages and/or high- and/or low-pressure stripping stages.

The water that is optionally formed during the stage a) for hydrotreatment of the process according to the invention can also advantageously be separated at least partially from the liquid hydrocarbon base. The separation stage b) can therefore advantageously be followed by an optional stage for elimination of at least a portion of the water and preferably all of the water.

The optional stage for water removal has as its object to eliminate at least partially the water that is produced during hydrotreatment reactions. Elimination of water is defined as the elimination of the water that is produced by hydrodeoxygenation (HDO) reactions. The more or less complete elimination of the water can be based on the tolerance to water of the hydroisomerization catalyst that is used in the subsequent stage c) of the process according to the invention. The elimination of water can be carried out

by any of the methods and techniques known to one skilled in the art, for example by drying, running it over a desiccant, flash, decanting, . . .

According to stage c) of the process according to the invention, at least a portion and preferably all of the liquid hydrocarbon base that is obtained at the end of stage b) of the process according to the invention is hydroisomerized in the presence of a fixed-bed hydroisomerization catalyst, whereby said catalyst comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIB and of group VIII of the periodic table, taken by itself or in a mixture, and a substrate that comprises at least one dealuminified Y zeolite that has an initial overall atomic ratio of silicon to aluminum of between 2.5 and 20, an initial extra-network aluminum atom fraction by weight that is greater than 10%, relative to the total mass of the aluminum that is present in the zeolite, an initial mesopore volume that is measured by nitrogen porosimetry that is greater than 0.07 ml g⁻¹, and an initial crystalline parameter a_0 of the elementary mesh that is between 24.38 Å and 24.30 Å, whereby said zeolite is modified according to a particular process.

The Hydrogenating Phase

According to the invention, the catalyst that is implemented in stage c) for hydroisomerization of the process according to the invention comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIII and the metals of group VIB, taken by themselves or in a mixture

Preferably, the elements of group VIII are selected from among iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, or platinum, taken by themselves or in a mixture

In the case where the elements of group VIII are selected from among the noble metals of group VIII, the elements of group VIII are advantageously selected from among platinum and palladium, taken by themselves or in a mixture.

In the case where the elements of group VIII are selected from among the non-noble metals of group VIII, the elements of group VIII are advantageously selected from among iron, cobalt and nickel, taken by themselves or in a mixture

Preferably, the elements of group VIB of the catalyst according to this invention are selected from among tungsten and molybdenum, taken by themselves or in a mixture.

In the case where the hydrogenating function comprises an element of group VIII and an element of group VIB, the following combinations of metals are preferred: nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, cobalt-tungsten, and in a very preferred manner: nickel-molybdenum, cobalt-molybdenum, and nickel-tungsten. It is also possible to use combinations of three metals, such as, for example, nickel-cobalt-molybdenum.

When a combination of metals of group VIB and group VIII is used, the catalyst is then preferably used in a sulfurized form.

In the case where the catalyst comprises at least one metal of group VIB in combination with at least one non-noble metal of group VIII, the metal content of group VIB is advantageously encompassed, in oxide equivalent, between 5 and 40% by weight relative to the total mass of said catalyst, in a preferred manner between 10 and 35% by weight and in a very preferred manner between 15 and 30% by weight, and the non-noble metal content of group VIII is advantageously encompassed, in oxide equivalent, between 0.5 and 10% by weight relative to the total mass of said catalyst, in a preferred manner between 1 and 8% by weight, and in a very preferred manner between 1.5 and 6% by weight.

In the case where said catalyst comprises at least one metal of group VIB in combination with at least one non-noble metal of group VIII, said catalyst can also advantageously comprise at least one doping element that is selected from the group that consists of silicon, boron, and phosphorus, taken by itself or in a mixture, whereby the content of doping element is preferably between 0 and 20% by weight of oxide of the doping element, in a preferred manner between 0.1 and 15% by weight, in a very preferred manner between 0.1 and 10% by weight, and in an even more preferred manner between 0.5 and 6% by weight relative to the total mass of the catalyst.

When the hydro-dehydrogenating element is a noble metal of group VIII, the catalyst preferably contains a content of noble metal of between 0.01 and 10% by weight, in an even more preferred manner 0.02 to 5% by weight relative to the total mass of said catalyst. The noble metal is preferably used in its reduced and non-sulfurized form.

It is advantageously also possible to use a catalyst that is based on reduced and non-sulfurized nickel. In this case, the content of metal in its oxide form is advantageously between 0.5 and 25% by weight relative to the finished catalyst. Preferably, the catalyst also contains, in addition to the reduced nickel, a metal of group IB and preferably copper, or a metal of group IVB and preferably tin in proportions such that the ratio by mass of the metal of group IB or IVB and nickel to the catalyst is advantageously between 0.03 and 1.

Said hydroisomerization catalyst that is used in stage c) of the process according to the invention comprises a substrate that comprises at least one modified zeolite and advantageously an oxide-type porous mineral matrix, whereby said substrate comprises and preferably consists of, preferably:

- 0.1 to 99.8% by weight, preferably 0.1 to 80% by weight, and in an even more preferred manner 0.1 to 70% by weight, and in a very preferred manner 0.1 to 50% by weight, of modified zeolite according to the invention relative to the total mass of the catalyst,
- 0.2 to 99.9% by weight, preferably 20 to 99.9%, in a preferred manner 30 to 99.9% by weight, and in a very preferred manner 50 to 99.9% by weight relative to the total mass of catalyst, of at least one oxide-type porous mineral matrix.

The Zeolite According to the Invention

According to the invention, the initially used zeolite that is suitable for the implementation of the substrate of the catalyst implemented in the hydroisomerization stage c) of the process according to the invention is the dealuminified (USY) Y zeolite of the FAU-structural type.

According to the invention, the initial dealuminified Y zeolite that is suitable for the implementation of the substrate of the catalyst that is used in the hydroisomerization stage c) of the process according to the invention has, before being modified, an initial overall atomic ratio of silicon to aluminum of between 2.5 and 20.0, preferably between 2.6 and 12.0, and in a preferred manner between 2.7 and 10.0, an initial extra-network aluminum atom fraction by weight that is greater than 10%, preferably greater than 20%,

and in a preferred manner greater than 30% by weight relative to the total mass of the aluminum that is present in the zeolite, an initial mesopore volume measured by nitrogen porosimetry that is greater than 0.07 ml g^{-1} , preferably greater than 0.10 ml g^{-1} , and in a preferred manner greater than 0.13 ml g^{-1} , and an initial crystalline parameter a_0 of the elementary mesh that is between $24.38 \text{ \AA}$ and $24.30 \text{ \AA}$.

Preferably, the initial dealuminified Y zeolite that is suitable for the implementation of the substrate of the catalyst that is used in the hydroisomerization stage c) of the process according to the invention, has - before being modified - an initial micropore volume that is measured by nitrogen porosimetry that is greater than 0.20 ml g^{-1} and preferably greater than 0.25 ml g^{-1} .

According to the invention, said initial dealuminified Y zeolite that has an initial overall atomic ratio of silicon to Si/Al of between 2.5 and 20.0, preferably between 2.6 and 12.0, and in a preferred manner between 2.7 and 10.0 - said overall Si/Al atomic ratio that is measured by X-fluorescence (FX) and that has an initial extra-network aluminum atom fraction by weight that is measured by NMR of aluminum is greater than 10%, preferably greater than 20%, and in a preferred manner greater than 30% by weight relative to the total weight of the aluminum that is present in the zeolite - is obtained by dealuminification of a FAU-structural-type Y zeolite by any of the dealuminification methods that are known to one skilled in the art.

Preparation of the Initial Dealuminified Y Zeolite.

The FAU-structural-type Y zeolite that advantageously comes in NaY form after synthesis can advantageously undergo one or more ion exchanges before undergoing the dealuminification stage.

The dealuminification treatment of the FAU-structural-type Y zeolite that generally has an overall Si/Al atomic ratio after synthesis of between 2.3 and 2.8 can advantageously be implemented by any of the methods that are known to one skilled in the art. In a preferred manner, the dealuminification is carried out by a heat treatment in the presence of water vapor (or steaming according to English terminology) and/or by one or more acid attacks that are advantageously implemented by treatment with an aqueous solution of mineral or organic acid.

Preferably, the dealuminification is implemented by a heat treatment followed by one or more acid attacks or only by one or more acid attacks

Preferably, the heat treatment in the presence of water vapor to which the Y zeolite is subjected is implemented at a temperature of between 200 and 900°C, preferably between 300 and 900°C, and in an even more preferred manner between 400 and 750°C. The duration of said heat treatment is advantageously greater than or equal to 0.5 hour, preferably between 0.5 hour and 24 hours, and in a very preferred manner between 1 hour and 12 hours. The volumetric percentage of water vapor during the heat treatment is advantageously between 5 and 100%, preferably between 20 and 100%, in a manner between 40% and 100%. The volumetric fraction other than the optionally present water vapor is formed by air. The flow rate of gas formed by water vapor and optionally air is advantageously between 0.2 L/h/g and 10 L/h/g of the Y zeolite.

The heat treatment makes it possible to extract aluminum atoms from the framework of the Y zeolite while maintaining the overall Si/Al atomic ratio of the unchanged treated zeolite.

The heat treatment in the presence of water vapor is advantageously repeated as many times as it is necessary to obtain the initial dealuminified Y zeolite that is suitable for the implementation of the substrate of the catalyst used in the hydroisomerization stage c) of the process according to the invention that has the desired characteristics and in particular a fraction by weight of extra-network aluminum atoms representing more than 10% by weight relative to the total mass of aluminum present in said zeolite. The heat treatment number is advantageously less than 4, and preferably a heat treatment threshold is produced at the end of which the fraction by weight of initial extra-network aluminum atoms is measured by NMR of the aluminum.

So as to implement a dealuminification of said Y zeolite and to adjust the overall Si/Al atomic ratio of the dealuminified Y zeolite to a value of between 2.5 and 20 according to the invention, it is necessary to properly select and monitor the operating conditions of each stage of acid attack. In particular, the temperature at which the treatment by the aqueous solution of mineral or organic acid is implemented, the nature and the concentration of the acid that is used, the ratio between the quantity of acid solution and the weight of treated zeolite, the duration of acid attack treatment, and the

treatment number implemented are significant parameters for the implementation of each acid attack stage

The acid that is selected for the implementation of said acid attack stage is advantageously either a mineral acid or an organic acid; preferably, the acid is a mineral acid that is selected from among nitric acid HNO_3 , hydrochloric acid HCl , and sulfuric acid H_2SO_4 . In a very preferred manner, the acid is nitric acid. When an organic acid is used for the acid attack, the acetic acid $\text{CH}_3\text{CO}_2\text{H}$ is preferred

Preferably, the acid attack treatment of the Y zeolite by an aqueous solution of a mineral acid or an organic acid is implemented at a temperature of between 30°C and 120°C , preferably between 50°C and 120°C , and in a preferred manner between 60 and 100°C . The concentration of acid in the aqueous solution is advantageously between 0.05 and 20 mol L^{-1} , preferably between 0.1 and 10 mol L^{-1} , and in a very preferred manner between 0.5 and 5 mol L^{-1} . The ratio between the volume of acidic solution V in ml and the weight of treated Y zeolite P in grams is advantageously between 1 and 50 , and preferably between 2 and 20 . The duration of the acid attack is advantageously more than 1 hour, preferably between 2 hours and 10 hours, and in a preferred manner between 2 hours and 8 hours. The successive acid attack treatment number of the Y zeolite by an acidic aqueous solution is advantageously less than 4 . In the case where several successive acid attack treatments are implemented, aqueous solutions of mineral acid or organic acid of different acidic concentrations can be used.

So as to adjust the overall Si/Al atomic ratio of the dealuminified Y zeolite to a value of between 2.5 and 20 , said ratio is measured by X fluorescence at the end of each acid attack treatment that is implemented.

After having carried out the acid attack treatment(s), the zeolite is then advantageously washed with distilled water and then is dried at a temperature of between 80 and 140°C for a period of between 10 and 48 hours.

The treatment by acid attack makes it possible both to extract the aluminum atoms from the framework, and to extract the aluminum atoms from the pores of the zeolitic solid. Thus, the overall Si/Al atomic ratio of the dealuminified Y zeolite that is obtained increases up to a value of between 2.5 and 20 , whereby said zeolite is suitable for the

implementation of the substrate of the catalyst that is used in the process according to the invention

Likewise, said initial dealuminified Y zeolite that is obtained and that is suitable for the implementation of the substrate of the catalyst that is used in the hydroisomerization stage c) of the process according to the invention has, after dealuminification, an initial mesopore volume that is measured by nitrogen porosimetry that is greater than 0.07 ml g^{-1} , preferably greater than 0.10 ml g^{-1} , and in a preferred manner greater than 0.13 ml g^{-1} , the creation of mesoporosity resulting from the extraction of aluminum atoms outside of the pores of the zeolitic solid and an initial crystalline parameter a_0 of the elementary mesh that is between $24.38 \text{ \AA}$ and $24.30 \text{ \AA}$.

Said initial dealuminified Y zeolite that is obtained also advantageously has an initial micropore volume that is measured by nitrogen porosimetry that is greater than 0.20 ml g^{-1} , and preferably greater than 0.25 ml g^{-1} .

The micropore and mesopore volumes of the dealuminified Y zeolite are measured by adsorption/desorption of nitrogen, and the mesh parameter of the zeolite is measured by x-ray diffraction (XRD).

Process for Modification of the Initial Dealuminified Y Zeolite According to the Invention

According to the invention, the initial dealuminified Y zeolite that is suitable for the implementation of the substrate of the catalyst that is used in the process according to the invention is modified by a specific modification process that comprises a') a basic treatment stage that consists of the mixing of said dealuminified Y zeolite with a basic aqueous solution, whereby said basic aqueous solution is a solution of basic compounds that are selected from among the alkaline bases and the strong non-alkaline bases, whereby said stage a) is implemented at a temperature of between 40 and 100°C and for a duration of between 5 minutes and 5 hours, and at least one heat treatment stage c) that is implemented at a temperature of between 200 and 700°C .

The basic treatment stage a') makes it possible to remove silicon atoms from the structure and to insert extra-network aluminum atoms in the framework.

According to the invention, the process for modification of said initial dealuminified Y zeolite comprises a basic treatment stage a') that consists in the mixing of said USY dealuminified zeolite with a basic aqueous solution, whereby said basic aqueous solution is a solution of basic compounds that are selected from among the alkaline bases and the strong, non-alkaline bases, whereby said stage a) is implemented at a temperature of between 40 and 100°C and for a duration of between 5 minutes and 5 hours.

The basic compounds that are selected from among the alkaline bases are preferably selected from among the alkaline carbonates and the alkaline hydroxides, whereby the alkaline cations of the alkaline carbonates and the alkaline hydroxides advantageously belong to the groups IA and/or IIA of the periodic table, and the strong, non-alkaline bases are preferably selected from among the quaternary ammonium compounds, taken by themselves or in a mixture, and in a preferred manner, the strong non-alkaline base is the tetramethylammonium hydroxide.

Said alkaline cations of the alkaline carbonates and the alkaline hydroxides that advantageously belong to group IA or IIA of the periodic table are preferably selected from among the cations Na^+ , Li^+ , K^+ , Rb^+ , Cs^+ , Ba^{2+} , and Ca^{2+} , and in a very preferred manner, said cation is the cation Na^+ or K^+ .

Preferably, the aqueous solution is a sodium carbonate or sodium hydroxide solution, and in a preferred manner, the aqueous solution is a sodium hydroxide solution.

Said basic aqueous solution with a concentration of between 0.001 mol/L and 12 mol/L, in a preferred manner with a concentration of between 0.005 mol/L and 11 mol/L, and in an even more preferred manner with a concentration of between 0.01 mol/L and 9 mol/L.

According to the invention, the basic treatment stage a') of the process for modification of said initial dealuminified USY zeolite is implemented under temperature conditions of between 40 and 100°C (reflux), and in a preferred manner between 40 and 90°C, and for a duration of between 5 minutes and 5 hours, in a preferred manner between 15 minutes and 4 hours, and in an even more preferred manner between 15 minutes and 3 hours.

Once the basic treatment of said zeolite is ended, the solution is cooled quickly to ambient temperature, and then said zeolite is separated from the liquid by any of the techniques that are known to one skilled in the art. The separation can be implemented by filtration or by centrifuging, and in a preferred manner by centrifuging. The modified USY zeolite that is obtained is then washed with distilled water at a temperature of between 20 and 100°C and preferably at a temperature of between 40 and 80°C, and in a very preferred manner at 50°C and dried at a temperature of between 80 and 150°C, and preferably between 100 and 130°C, and in a very preferred manner at 120°C.

In the case where the basic treatment stage a') consists of the mixing of said initial dealuminified Y zeolite with a basic aqueous solution of compounds that are selected from among the alkaline bases, the zeolite that is contained in the substrate of the catalyst that is used in the process according to the invention contains, at the end of stage a) of the modification process, a partial or total fraction of alkaline ions in cationic position.

In the case where the basic treatment stage a') consists of the mixing of said initial dealuminified Y zeolite with a basic aqueous solution of compounds that are selected from among the non-alkaline bases, the zeolite that is contained in the substrate of the catalyst that is used in the process according to the invention contains, at the end of stage a') of the modification process, a partial or total fraction of quaternary ammonium ions in cationic position.

During the basic treatment stage a') of the process for modification of the initial dealuminified Y zeolite according to the invention, a portion of the silicon atoms contained in the framework of said zeolite are extracted; the phenomenon is called desilication, creating vacuums in the structure and the formation of a mesoporosity and/or making possible the reinsertion of at least a portion of the fraction of the extra-network aluminum atoms that are present in said initial dealuminified Y zeolite, instead of the silicon atoms that are extracted by desilication and thus making possible the formation of new Brønsted acid sites. This second phenomenon is called re-alumination.

In the case where the basic treatment stage a') consists of the mixing of said initial dealuminified USY zeolite with a basic aqueous solution of basic compounds that are selected from among the alkaline bases and preferably selected from among the

alkaline carbonates and the alkaline hydroxides, and in a very preferred manner with a sodium hydroxide (NaOH) solution, the process for modification of said initial dealuminified USY zeolite advantageously comprises a stage b') for at least one partial or total exchange of said alkaline cations that belong to the groups IA and IIA of the periodic table that are introduced during stage a') and are present in cationic position, by NH_4^+ cations, and preferably Na^+ cations by NH_4^+ cations.

Partial or total exchange of alkaline cations by NH_4^+ cations is defined as the exchange of 80 to 100%, in a preferred manner 85 to 99.5%, and in a more preferred manner 88 and 99%, of said alkaline cations by NH_4^+ cations. The remaining quantity of alkaline cations and, preferably, the remaining quantity of Na^+ cations in the modified zeolite, relative to the quantity of NH_4^+ cations that are initially present in the zeolite, at the end of stage b'), is advantageously between 0 and 20%, preferably between 0.5 and 15%, and in a preferred manner between 1 and 12%.

Preferably, for this stage, several ion exchange(s) are initiated with a solution that contains at least one ammonium salt that is selected from among the salts of chlorate, sulfate, nitrate, phosphate or acetate of ammonium, in such a way as to eliminate, at least partially, the alkaline cations and preferably the Na^+ cations that are present in the zeolite. Preferably, the ammonium salt is ammonium nitrate NH_4NO_3 .

Thus, the remaining content of alkaline cations and preferably Na^+ cations in the modified zeolite at the end of stage b') is preferably such that the alkaline cation/aluminum molar ratio and preferably the Na/Al molar ratio is between 0.2:1 and 0:1, preferably between 0.15:1 and 0.005:1, and in a more preferred manner between 0.12:1 and 0.01:1.

The desired Na/Al ratio is obtained by adjusting the NH_4^+ concentration of the cationic exchange solution, the temperature of the cationic exchange, and the cationic exchange number. The concentration of the NH_4^+ solution in the solution advantageously varies between 0.01 and 12 mol/L, and preferably between 1 and 10 mol/L. The temperature of the exchange stage is advantageously between 20 and 100°C, preferably between 60 and 95°C, in a preferred manner between 60 and 90°C, and in a more preferred manner between 60 and 85°C, and in an even more preferred manner between

60 and 80°C The cationic exchange number advantageously varies between 1 and 10 and preferably between 1 and 4

In the case where the basic treatment stage a') consists in mixing said initial dealuminified USY zeolite with an aqueous solution of basic compounds that are selected from among the strong non-alkaline bases that are preferably selected from among the quaternary ammonium compounds, taken by themselves or in a mixture, and in a preferred manner the strong non-alkaline base being tetramethylammonium hydroxide, the modified zeolite that is obtained from stage a') contains a partial or total fraction of quaternary ammonium ions in a cationic position.

In this case, the process for modification of said initial dealuminified USY zeolite advantageously does not comprise stage b') of at least one partial or total intermediate exchange; the modified zeolite that is obtained from stage a) directly undergoes the heat treatment stage c')

According to the invention, the process for modification of the initial dealuminified Y zeolite next comprises at least one heat treatment stage c')

In the case where the basic treatment stage a') consists in the mixing of said initial dealuminified USY zeolite with a basic aqueous solution of compounds that are selected from among the alkaline bases and preferably selected from among the alkaline carbonates and the alkaline hydroxides, and in a very preferred manner with a sodium hydroxide (NaOH) solution, the heat treatment stage c') makes possible both drying and the transformation of the NH_4^+ cations, exchanged during stage b'), into protons

In the case where the basic treatment stage a') consists in the mixing of said initial dealuminified USY zeolite with a basic aqueous solution of compounds that are selected from among the strong non-alkaline bases and preferably selected from among the quaternary ammonium compounds that are taken by themselves or in a mixture and in a preferred manner with a strong non-alkaline base being the tetramethylammonium hydroxide, the heat treatment stage c') makes possible both the drying and the decomposition of the quaternary ammonium cations in a position of counterions and the formation of protons

In any case, at the end of said heat treatment stage c'), the protons of the zeolite are partially or totally regenerated.

The heat treatment stage c') according to the invention is implemented at a temperature of between 200 and 700°C, more preferably between 300 and 500°C. Said heat treatment stage is advantageously implemented in air, under oxygen, under hydrogen, under nitrogen or under argon, or under a mixture of nitrogen and argon. The duration of said treatment is advantageously between 1 and 5 hours.

At the end of the modification process according to the invention, the final modified zeolite that is used in the substrate of the catalyst that is used in the process according to the invention advantageously has a final mesopore volume, measured by nitrogen porosimetry, that is greater by at least 10% relative to the initial mesopore volume and preferably greater by at least 20% relative to the initial mesopore volume of the initial dealuminified USY zeolite, a final micropore volume that is measured by nitrogen porosimetry that should not decrease by more than 40%, preferably more than 30%, and in a preferred manner more than 20% relative to the initial micropore volume of said initial dealuminified USY zeolite, a greater Brønsted acidity of more than 10% and preferably more than 20% relative to the Brønsted acidity of the initial dealuminified Y zeolite, and a final crystalline parameter a_0 of the elementary mesh that is greater than the initial crystalline parameter a_0 of the mesh of the initial dealuminified Y zeolite.

At the end of the process for modification of the dealuminified Y zeolite according to the invention, the resulting significant increase of the mesopore volume of the modified zeolite and the maintaining of a significant micropore volume relative to the initial dealuminified Y zeolite reflect the creation of an additional mesoporosity by desilication.

Furthermore, the increase of the Brønsted acidity of the final modified zeolite relative to the initial dealuminified Y zeolite demonstrates the reintroduction of extra-network aluminum atoms into the framework of the zeolite, i.e., the phenomenon of realumination.

The Amorphous or Poorly Crystallized Oxide-Type Porous Mineral Matrix

The substrate of the catalyst that is used in the hydroisomerization stage c) of the process according to the invention advantageously contains a porous mineral matrix, preferably amorphous, which advantageously consists of at least one refractory oxide.

Said matrix is advantageously selected from the group that is formed by alumina, silica, clays, titanium oxide, boron oxide, and zirconia, taken by itself or in a mixture. The matrix can consist of a mixture of at least two of the oxides cited above, and preferably silica-alumina. It is also possible to select the aluminates. It is preferred to use matrices that contain alumina in all of these forms that are known to one skilled in the art, for example gamma-alumina.

It is also advantageously possible to use mixtures of alumina and silica, and mixtures of alumina and silica-alumina.

Techniques of Characterization

The overall Si/Al atomic ratio of the initial and final dealuminified Y zeolite, i.e., after modification, is measured by X fluorescence. The X fluorescence is a comprehensive elementary analysis technique that allows the analysis of all of the elements of the periodic system starting from boron. It is possible to meter from several ppm up to 100%. In this invention, this technique is used to meter the silicon and the aluminum of the zeolites (by percentage by mass) and thus makes it possible to calculate the Si/Al atomic ratio.

The fraction by weight of tetracoordinated and hexacoordinated aluminum atoms that are present in the modified USY zeolite is determined by nuclear magnetic resonance of the solid of ^{27}Al . The NMR of aluminum is actually known for being used for the purpose of referencing and quantifying the different states of coordination of this core ("Analyse physico-chimiques des catalyseurs industriels [Physico-Chemical Analysis of Industrial Catalysts]," J. Lynch, Technip Editions (2001) Chap. 13, pages 290 and 291). The NMR spectrum of the aluminum of the initial USY zeolite and that of the modified USY zeolite according to the invention has two signals, one being characteristic of the resonance of the tetracoordinated aluminum atoms (i.e., aluminum atoms encompassed in the crystalline network of the zeolite), and the other being characteristic of the resonance of the hexacoordinated aluminum atoms (i.e., aluminum atoms outside of the crystalline network or extra-network aluminum atoms). The tetracoordinated aluminum Al_{IV} atoms

resonate with a chemical displacement of between +40 ppm and +75 ppm, and the hexacoordinated or extra-network aluminum Al_{VI} atoms resonate with a chemical displacement of between -15 ppm and +15 ppm. The fraction by weight of the two aluminum Al_{IV} and Al_{VI} radicals is quantified by integration of the signals that correspond to each of these radicals

More specifically, the modified USY zeolite according to the invention that is present in the substrate of the catalyst according to the invention has been analyzed by NMR-MAS of the ^{27}Al solid on a 400 MHz Avance-type Brücker spectrometer using a 4 mm probe that is optimized for ^{27}Al . The speed of rotation of the sample is close to 14 kHz. The aluminum atom is a quadrupolar core whose spin is equal to 5/2. Under these so-called selective analysis conditions - namely a field of low radiofrequency that is equal to 30 kHz, a low impulse angle that is equal to $\pi/2$ and in the presence of a water-saturated sample - the NMR technique with rotation at the magic angle (MAS), denoted NMR-MAS, is a quantitative technique. The decomposition of each NMR-MAS spectrum makes it possible to access directly the quantity of different aluminum radicals, namely the tetracoordinated aluminum Al_{IV} atoms and hexacoordinated or extra-network aluminum Al_{VI} atoms. Each spectrum is locked in chemical displacement relative to a 1 M solution of aluminum nitrate for which the aluminum signal is at zero ppm. The signals that characterize the tetracoordinated aluminum Al_{IV} atoms are integrated between +40 ppm and +75 ppm, which corresponds to the area 1, and the signals that characterize the hexacoordinated aluminum Al_{VI} atoms are integrated between -15 ppm and +15 ppm, which corresponds to the area 2. The fraction by weight of hexacoordinated aluminum Al_{VI} atoms is equal to the ratio of area 2/(area 1 + area 2).

The crystalline mesh parameter a_0 of the initial and final dealuminified Y zeolites, i.e., after modification, is measured by x-ray diffraction (XRD). For the FAU-type zeolite, the mesh parameter a_0 is calculated starting from the positions of the peaks corresponding to the Miller indices 533, 642 and 555 ("Théorie et technique de la radiocristallographie [Theory and Technology of Radiocrystallography]," A. Guinier, Dunod Edition, 1964). The length of the Al-O connection being larger than that of the Si-O bond, the greater the aluminum number in tetrahedral position in the framework of the zeolite, the larger the parameter a_0 . For the crystals that consist of cubic meshes such

as FAU-type Y zeolites, a linear relationship exists between the mesh parameter a_0 and the Si/Al ratio ("Hydrocracking Science and Technology," J. Scherzer, A. J. Gruia, Marcel Dekker, Inc., 1996)

The micropore and mesopore volumes of the initial and final dealuminified Y zeolite are measured by nitrogen adsorption/desorption. The analysis of the isothermal curves of nitrogen adsorption of microporous and mesoporous solids makes possible the calculation of pore volumes by the technique called volumetric technique. Different types of models can be used. The pore distribution that is measured by nitrogen adsorption has been determined by the Barrett-Joyner-Halenda (BJH) model. The nitrogen adsorption-desorption isotherm according to the BJH model is described in the periodical "The Journal of American Society," 73, 373 (1951) written by E. P. Barrett, L. G. Joyner and P. P. Halenda. In the following disclosure of the invention, nitrogen adsorption volume is defined as the volume that is measured for $P/P_0 = 0.95$. The micropore volume is obtained by the "t-plot" method or else by measuring the adsorbed volume with $P/P_0 = 0.35$ (P = adsorption pressure; P_0 = saturating vapor pressure of the adsorbate at the temperature of the test). The mesopore volume is obtained by subtracting the micropore volume from the total pore volume.

The Lewis and Brønsted acidity of the zeolites is measured by adsorption of pyridine followed by infra-red spectroscopy (FTIR). The integration of bands that are characteristic of the pyridine coordinated at $1,455\text{ cm}^{-1}$ and the protonated pyridine at $1,545\text{ cm}^{-1}$ makes it possible to compare the relative acidity of Lewis- and Brønsted-type catalysts, respectively. Before adsorption of pyridine, the zeolite is pretreated under secondary vacuum at 450°C for 10 hours with an intermediate plateau at 150°C for 1 hour. The pyridine is next adsorbed at 150°C and then desorbed under secondary vacuum at this same temperature before the spectra are taken.

Preparation of the Catalyst

The modified zeolite can be, without this being limiting, for example, in the form of powder, ground powder, suspension, and a suspension that has undergone a deagglomeration treatment. Thus, for example, the modified zeolite can advantageously be put into a suspension that may or may not be slightly acidic at a concentration that is

adjusted to the final zeolite content that is targeted in the substrate. This suspension, commonly called a slip, is then advantageously mixed with the precursors of the matrix.

According to a preferred preparation method, the modified zeolite can advantageously be introduced during the shaping of the substrate with the elements that constitute the matrix. For example, according to this preferred method of this invention, the modified zeolite according to the invention is added to a moist alumina gel during the stage for shaping the substrate.

One of the preferred methods for the shaping of the substrate in this invention consists in kneading at least one modified zeolite with a moist alumina gel for several tens of minutes, and then in passing the thus obtained paste through a die for forming extrudates with a diameter of between 0.4 and 4 mm.

According to another preferred preparation method, the modified zeolite can be introduced during the synthesis of the matrix. For example, according to this preferred method of this invention, the modified zeolite is added during the synthesis of the silico-aluminum matrix; the zeolite can be added to a mixture that consists of an alumina compound in an acidic medium with a completely soluble silica compound.

The substrate can be shaped by any technique that is known to one skilled in the art. The shaping can be carried out, for example, by extrusion, by pelletizing, by the drop (oil-drop) coagulation method, by turntable granulation, or by any other method that is well known to one skilled in the art.

At least one calcination cycle can be carried out after any of the stages of the preparation. The calcination treatment is usually carried out in air at a temperature of at least 150°C, preferably at least 300°C, and in a more preferred manner between about 350 and 1,000°C.

The elements of group VIB and/or the elements of group VIII, and optionally at least one doping element that is selected from among boron, silicon, and phosphorus, and optionally the elements of group IVB, or IB in the case where the active phase contains reduced nickel, optionally can be introduced, completely or partially, at any stage of the preparation, during the synthesis of the matrix, preferably during the shaping of the substrate, or in a very preferred manner after the shaping of the substrate by any method

that is known to one skilled in the art. They can be introduced after the shaping of the substrate and after or before the drying and the calcination of the substrate.

According to a preferred method of this invention, all or part of the elements of group VIB and/or the elements of group VIII, and optionally at least one doping element that is selected from among boron, silicon and phosphorus, and optionally the elements of group IVB, or IB in the case where the active phase contains reduced nickel, can be introduced during the shaping of the substrate, for example during the stage for kneading the modified zeolite with a moist alumina gel.

According to another preferred method of this invention, all or part of the elements of the group VIB and/or the elements of group VIII, and optionally at least one doping element that is selected from among boron, silicon, and phosphorus, and optionally the elements of group IVB, or IB in the case where the active phase contains reduced nickel, can be introduced by one or more operations for impregnation of the substrate that is shaped and calcined, by a solution that contains the precursors of these elements. In a preferred way, the substrate is impregnated by an aqueous solution. The impregnation of the substrate is preferably carried out by the so-called "dry" impregnation method that is well known to one skilled in the art.

In the case where the catalyst of this invention contains at least one non-noble metal of group VIII, the metals of group VIII are preferably introduced by one or more operations for impregnation of the substrate that is shaped and calcined, and after those of group VIB or at the same time as the latter.

In the case where the catalyst of this invention contains a noble metal of group VIII, the metals of group VIII are preferably introduced by one or more operations for impregnation of the substrate that is shaped and calcined.

According to another preferred method of this invention, the deposition of the elements of group IVB or group IB can also be implemented simultaneously by using, for example, a solution that contains a tin salt or a copper salt.

According to another preferred method of this invention, the deposition of boron and silicon can also be implemented simultaneously by using, for example, a solution that contains a boron salt and a silicone-type silicon compound.

When at least one doping element, P and/or B and/or Si, is introduced, its distribution and its location can be determined by techniques such as the Castaing microprobe (distribution profile of various elements), the transmission electron microscopy coupled to an EDX analysis (energy-dispersive analysis) of the components of the catalyst, or else by combining distribution mapping of the elements that are present in the catalyst by electronic microprobe

For example, among the sources of molybdenum and tungsten, it is possible to use oxides and hydroxides, molybdic and tungstic acids and their salts, in particular ammonium salts such as ammonium molybdate, ammonium heptamolybdate, ammonium tungstate, phosphomolybdic acid, phosphotungstic acid, and salts thereof, silicomolybdic acid, silicotungstic acid, and salts thereof. The oxides and salts of ammonium, such as ammonium molybdate, ammonium heptamolybdate, and ammonium tungstate, are preferably used

The sources of non-noble elements of group VIII that can be used are well known to one skilled in the art. For example, for the non-noble metals, nitrates, sulfates, hydroxides, phosphates, halides such as, for example, chlorides, bromides and fluorides, and carboxylates, such as, for example, acetates and carbonates, will be used.

The sources of noble elements of group VIII that can advantageously be used are well known to one skilled in the art. For the noble metals, halides, for example, chlorides, nitrates, acids such as hexachloroplatinic acid, hydroxides, and oxychlorides such as ammoniacal ruthenium oxychloride, are used. It is also possible advantageously to use the cationic complexes such as the ammonium salts when it is desired to deposit the metal on the Y-type zeolite by cationic exchange.

The noble metals of group VIII of the catalyst of this invention can advantageously be present completely or partially in metallic and/or oxide form.

The promoter element(s) selected from the group that is formed by silicon, boron and phosphorus can advantageously be introduced by one or more impregnation operations with excess solution on the calcined precursor.

The boron source can advantageously be boric acid, preferably orthoboric acid H_3BO_3 , ammonium biborate or pentaborate, boron oxide, and boric esters. Boron can be introduced, for example, in the form of a mixture of boric acid, hydrogen peroxide, and a

basic organic compound that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the family of pyridine, and quinolines, and the compounds of the pyrrole family. Boron can be introduced by, for example, a boric acid solution in a water/alcohol mixture. The preferred phosphorus source is the orthophosphoric acid H_3PO_4 , but its salts and esters, such as the ammonium phosphates, are also suitable. Phosphorus can be introduced, for example, in the form of a mixture of phosphoric acid and a basic organic compound that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the pyridine family, and quinolines, and compounds of the pyrrole family.

Numerous silicon sources can advantageously be used. Thus, it is possible to use ethyl orthosilicate $\text{Si}(\text{OEt})_4$, siloxanes, polysiloxanes, silicones, silicone emulsions, halide silicates such as ammonium fluorosilicate $(\text{NH}_4)_2\text{SiF}_6$ or sodium fluorosilicate Na_2SiF_6 . The silicomolybdic acid and its salts, and the silicotungstic acid and its salts can also advantageously be used. Silicon can advantageously be added by, for example, impregnation of ethyl silicate in solution in a water/alcohol mixture. The silicon can be added by, for example, impregnation of a silicone-type silicon compound or the silicic acid suspended in water.

The sources of elements of group IB that can be used are well known to one skilled in the art. For example, among the copper sources, it is possible to use copper nitrate $\text{Cu}(\text{NO}_3)_2$.

The element sources of group IVB that can be used are well known to one skilled in the art. For example, among tin sources, it is possible to use tin chloride SnCl_2 .

The catalysts that are used in the process according to the invention advantageously have the shapes of spheres or extrudates. It is advantageous, however, that the catalyst comes in the form of extrudates with a diameter of between 0.5 and 5 mm and more particularly between 0.7 and 2.5 mm. The shapes are cylindrical (which may or may not be hollow), braided cylindrical, multilobe (2, 3, 4 or 5 lobes, for example), or rings. The cylindrical shape is used in a preferred manner, but any other shape can be used. The catalysts according to the invention optionally can be manufactured and used in the form of crushed powder, tablets, rings, balls, and wheels.

In the case where the hydroisomerization catalyst contains at least one noble metal, the noble metal that is contained in said hydroisomerization catalyst is advantageously to be reduced. One of the preferred methods for conducting the reduction of metal is the treatment under hydrogen at a temperature of between 150°C and 650°C and a total pressure of between 1 and 250 bar. For example, a reduction consists of a plateau at 150°C for two hours and then an increase in temperature up to 450°C at the rate of 1°C/minute, and then a plateau for two hours at 450°C; during this entire reduction stage, the flow rate of hydrogen is 1,000 normal m³ of hydrogen/m³ of catalyst, and the total pressure is kept constant at 1 bar. Any ex-situ reduction method can advantageously be taken into consideration.

According to the hydroisomerization stage c) of the process according to the invention, at least a portion of the hydrocarbon base that is obtained from stage b) is brought into contact, in the presence of hydrogen, with said hydroisomerization catalyst, at temperatures and operating pressures that advantageously make it possible to carry out hydroisomerization of the non-converting feedstock. This means that the hydroisomerization is performed with a conversion of the 150°C+ fraction into the 150°C- fraction that is less than 20% by weight, in a preferred manner less than 10% by weight, and in a very preferred manner less than 5% by weight.

Thus, according to the invention, the hydroisomerization stage c) of the process according to the invention is performed at a temperature of between 150 and 500°C, preferably between 150°C and 450°C, and in a very preferred manner between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, preferably between 2 MPa and 10 MPa, and in a very preferred manner between 1 MPa and 9 MPa, at an hourly volumetric flow rate that is advantageously between 0.1 h⁻¹ and 10 h⁻¹, preferably between 0.2 and 7 h⁻¹, and in a very preferred manner between 0.5 and 5 h⁻¹, at a flow rate of hydrogen such that the hydrogen/hydrocarbon volumetric ratio is advantageously between 70 and 1,000 Nm³/m³ of feedstock, between 100 and 1,000 normal m³ of hydrogen per m³ of feedstock, and in a preferred manner between 150 and 1,000 normal m³ of hydrogen per m³ of feedstock.

In a preferred manner, the optional hydroisomerization stage operates in co-current.

The products, gas oil- and kerosene-based, obtained according to the process of the invention, and in particular after hydroisomerization, are endowed with excellent characteristics

The gas oil base that is obtained, after mixing with a petroleum gas oil that is obtained from renewable feedstock such as carbon or lignocellulosic biomass, and/or with an additive, is of excellent quality:

- Its sulfur content is less than 10 ppm by weight
- Its total aromatic compound content is less than 5% by weight, and the polyaromatic compound content is less than 2% by weight
- The cetane number is excellent, higher than 55.
- The density is less than 840 kg/m^3 , and most often greater than 820 kg/m^3
- Its kinematic viscosity at 40°C is 2 to $8 \text{ mm}^2/\text{s}$.
- Its cold strength properties are compatible with the standards in force, with a filterability boundary temperature at -15°C and a cloud point that is less than -5°C .

The kerosene fraction that is obtained, after mixing with a petroleum kerosene that is obtained from renewable feedstock such as carbon or lignocellulosic biomass and/or with an additive, has the following characteristics:

- A density of between 775 and 840 kg/m^3
- A viscosity at -20°C of less than $8 \text{ mm}^2/\text{s}$
- A crystal disappearance point of below -47°C
- A flash point of greater than 38°C
- A smoke point of greater than 25 mm.

Examples

Stage a): Hydrotreatment

170 g/h of pre-refined canola oil with a density of 920 kg/m^3 that has a sulfur content of less than 10 ppm by weight, with a cetane number of 35, and whose composition is presented in detail below, is introduced into a reactor that is temperature-regulated in such a way as to ensure an isothermal operation and that has a fixed bed

charged with 190 ml of hydrotreatment catalyst based on nickel and molybdenum, having a nickel oxide content that is equal to 3% by weight, and a molybdenum oxide content that is equal to 16% by weight and a P_2O_5 content that is equal to 6%, whereby the catalyst is sulfurized in advance:

Fatty Acid Glycerides	Nature of the Fatty Chain	% by Mass
Palmitic	C16:0	4
Palmitoleic	C16:1	< 0.5
Stearic	C18:0	2
Oleic	C18:1	61
Linoleic	C18:2	20
Linolenic	C18:3	9
Arachidic	C20:0	< 0.5
Gadoleic	C20:1	1
Behenic	C22:0	< 0.5
Erucic	C22:1	< 1

700 Nm³ of hydrogen/m³ of feedstock is introduced into the reactor that is kept at a temperature of 300°C and at a pressure of 5 MPa.

Stage b): Separation of the Effluent that is Obtained from Stage a).

The entire hydrotreated effluent that is obtained from stage a) is separated so as to recover the hydrogen-rich gases and a hydrocarbon base.

Stage c): Hydroisomerization of the Hydrotreated Effluent that is Obtained from Stage b) on a Catalyst According to the Invention

Preparation of the Initial Dealuminified Y Zeolite Z1 According to the Invention

100 g of the crude synthesis NaY zeolite is exchanged 3 times by a 1N solution of NH_4NO_3 at a temperature of 80°C to obtain the NH_4Y zeolite. The NH_4Y zeolite next undergoes a heat treatment at 700°C for 3 hours in the presence of 60% water vapor. The

heat treatment is done by using a flow of gas formed by water vapor and air of 2 L/h/g of zeolite. The zeolite next undergoes a treatment with a solution of 2 mol/L of HNO_3 ($V/P = 15$) for 3 hours at 80°C . The zeolite is finally filtered and dried for 12 hours at 120°C . The zeolite is then in the form of dealuminified HY.

The dealuminified HY zeolite Z1 that is obtained has an overall Si/Al atomic ratio = 6.2, measured by X fluorescence, a fraction by weight of initial extra-network aluminum atoms that is equal to 37% by weight relative to the total mass of the aluminum that is present in the zeolite and measured by NMR of the aluminum, an initial mesopore volume that is measured by nitrogen porosimetry that is equal to 0.15 ml g^{-1} , and an initial crystalline parameter a_0 of the elementary mesh that is equal to $24.35 \text{ \AA}$, measured by XRD.

Preparation of the Modified Zeolite Z2 In Accordance with the Invention Used in the Catalyst According to the Invention.

100 g of dealuminified HY zeolite Z1, with an overall Si/Al atomic ratio = 6.2 measured by FX that is prepared in Example 1, is mixed with 1 L of a 0.1N sodium hydroxide (NaOH) solution at 60°C for 30 minutes. After rapid cooling in ice water, the suspension is then filtered, and the zeolite is washed at 50°C and dried for one night at 120°C . The modified dealuminified Y zeolite is then exchanged 3 times by a 1N NH_4NO_3 solution at a temperature of 80°C to obtain the partially exchanged NH_4^+ form. The zeolite is finally calcined at 450°C for 2 hours under an air stream of 1 L/h/g of zeolite. The characterizations of the Z2 zeolite that are measured by nitrogen adsorption/desorption, by X fluorescence, by NMR of ^{27}Al and ^{29}Si , and by adsorption of pyridine followed by IR are provided in Table 1.

Table 1: Characterization of the Samples.

	Initial Unmodified Zeolite Z1	Modified Zeolite Z2 According to the Invention
Overall Si/Al (FX)	6.2	4.7

% Al _{VI} (NMR)	37	33
S _{BET} (m ² /g)	778	743
Mesopore Volume (ml/g)	0.15	0.28 (+86%)
Micropore Volume (ml/g)	0.28	0.25 (-11%)
Brønsted acidity (i a)	4.3	5.4 (+25%)

Preparation of the Catalysts

The catalyst substrates according to the invention containing the modified zeolite (Z2 according to the invention) or unmodified zeolite (Z1) are produced by using 19.5 g of zeolite mixed with 80.5 g of a matrix that consists of ultrafine tabular boehmite or alumina gel marketed under the name SB3 by the Condéa Chemie GmbH Company. This powder mixture is then mixed with an aqueous solution that contains nitric acid at 66% by weight (7% by weight of acid per gram of dry gel) and then kneaded for 15 minutes. The kneaded paste is then extruded through a die with a 1.2 mm diameter. The extrudates are next calcined at 500°C for 2 hours in air.

The thus prepared substrate extrudates are impregnated in the dry state by a solution of a mixture of ammonium heptamolybdate and nickel nitrate and calcined in air at 550°C in situ in the reactor. The contents by weight of oxides of the catalysts that are obtained are indicated in Table 2.

The catalysts C1 and C2 are thus prepared starting from the unmodified zeolites Z1 and modified according to the invention Z2. The contents by weight of oxides of the catalysts that are obtained are indicated in Table 2.

Table 2 : Characteristics of the Catalysts.

Reference of the Catalyst	C1 (Not According to the Invention)	C2 (According to the Invention)
Catalyst-Based Zeolite	Unmodified Z1	Modified Z2
MoO ₃ (% by Weight)	12.3	12.3

NiO (% by Weight)	3	3.1
Overall SiO ₂ (% by Weight)	14.3	13.9
Supplement to 100% (for the most part composed of Al ₂ O ₃ , % by weight)	70.4	70.4

The hydrotreated hydrocarbon effluent that is obtained at the end of stage b) is hydroisomerized with hydrogen that is lost in a hydroisomerization reactor under the operating conditions below:

- VVH (volume of feedstock/volume of catalyst/hour) = 1 h⁻¹
- Total working pressure: 5 MPa
- Temperature: 300°C
- Hydrogen/feedstock ratio: 700 normal liters/liter

The reaction temperature is set so as to achieve a crude conversion (denoted CB) that is equal to 70% by weight.

50 ppm by weight of dimethyl disulfide is added to the feedstock so as to simulate the partial pressures of H₂S and to keep the catalyst in sulfide form. The thus prepared feedstock is injected into the hydroisomerization test unit that comprises a fixed-bed reactor with upward circulation of the feedstock ("up-flow") into which 100 ml of catalyst is introduced. The catalyst is sulfurized by a direct distillation gas oil/DMDS and aniline mixture up to 320°C. We note that any in-situ or ex-situ sulfurization method is suitable. Once the sulfurization is carried out, the feedstock can be transformed. The operating conditions of the test unit are indicated above.

The jet fuel yield (kerosene, 150-250°C fraction, Kero yield hereinafter) is equal to the percentage by weight of compounds that have a boiling point of between 150 and 250°C in the effluents. The gas oil yield (250°C+ fraction) is equal to the percentage by weight of compounds that have a boiling point that is greater than 250°C in the effluents.

The temperature of 300°C is adjusted so as to have a conversion of the 150°C⁺ fraction into the 150°C⁻ fraction that is less than 5% by weight during the hydroisomerization in the case where the hydroisomerization catalyst that is used in stage

c) of the process according to the invention contains the modified zeolite according to the invention. In Table 3, we recorded the temperature of the yields in kerosene and gas oil for the catalysts described in the examples above.

Table 3: Catalytic Activities of the Hydroisomerization Catalysts.

	150°C- Yield	Kerosene Yield (% by Weight)	Gas Oil Yield (% by Weight)
C1 Not According to the Invention (Prepared from Unmodified Z1)	13	30	57
C2 According to the Invention (Prepared from Modified Z3 According to the Invention)	5	34	61

In the hydroisomerization stage c) and at a temperature of 300°C, the process that implements a catalyst containing an unmodified zeolite brings about the production of a 150°C- light fraction with a yield of 13% and therefore the production of middle distillates with a yield that is lower relative to the implementation of a catalyst that contains a modified zeolite according to the invention in the hydroisomerization stage c) of the process according to the invention. The process according to the invention therefore demonstrates that the catalyst that contains a zeolite that is modified according to the invention and that is used in said process according to the invention is more active than the catalysts, not according to the invention, for obtaining a level of conversion of the 150°C+ fraction that is less than 5% by weight, while making it possible to obtain higher middle distillate yields, and therefore a better selectivity of middle distillates, relative to a hydroisomerization process that implements a catalyst, not according to the invention, that contains a zeolite that is unmodified or that is modified in a manner that is not in accordance with the invention.

CLAIMS

1 Process for treatment of feedstocks obtained from a renewable source and comprising the following stages:

a) Hydrotreatment of said feedstock in the presence of a fixed-bed catalyst that comprises a hydro-dehydrogenating function comprising at least one metal of group VIII and/or group VIB, taken by itself or in a mixture, and a substrate that is selected from the group that is formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals, whereby said hydrotreatment stage operates at a temperature of between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 h⁻¹ and 10 h⁻¹, and in the presence of a total quantity of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³ of hydrogen/m³ of feedstock,

b) Separation, starting from the effluent that is obtained from stage a), of hydrogen, gases, and at least one hydrocarbon base,

c) Hydroisomerization of at least a portion of said hydrocarbon base that is obtained from stage b) in the presence of a fixed-bed hydroisomerization catalyst, whereby said catalyst comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIB and group VIII of the periodic table and a substrate that comprises at least one dealuminified Y zeolite that has an initial overall atomic ratio of silicon to aluminum of between 2.5 and 20, an initial extra-network aluminum atom fraction by weight that is greater than 10%, relative to the total mass of the aluminum that is present in the zeolite, an initial mesopore volume that is measured by nitrogen porosimetry that is greater than 0.07 ml.g⁻¹, and an initial crystalline parameter a_0 of the elementary mesh that is between 24.38 Å and 24.30 Å, whereby said zeolite is modified by a') a basic treatment stage that consists in the mixing of said dealuminified Y zeolite with a basic aqueous solution, whereby said basic aqueous solution is a solution of basic compounds that are selected from among the alkaline bases and the strong non-alkaline bases, and at least one heat treatment stage c') that is implemented at a temperature of between 200 and 700°C, whereby said hydroisomerization stage is carried out at a temperature of between 150 and 500°C, at a

pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 and 10 h⁻¹, and in the presence of a total quantity of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³/m³ of feedstock,

d) Separation, starting from the effluent that is obtained from stage c), of hydrogen, gases, and at least one gas oil base and one kerosene base.

2 Process according to Claim 1, in which the metals of group VIII of said catalyst that is used in the hydroisomerization stage c) are selected from among the noble metals of group VIII and are selected from among platinum and palladium, taken by themselves or in a mixture

3 Process according to one of Claims 1 or 2, in which the content of noble metal of said catalyst that is used in the hydroisomerization stage c) is between 0.01 and 10% by weight relative to the total mass of said catalyst.

4 Process according to Claim 1, in which said catalyst that is used in the hydroisomerization stage c) comprises at least one metal of group VIB in combination with at least one non-noble metal of group VIII, whereby the metal content of group VIB encompasses, in oxide equivalent, between 5 and 40% by weight relative to the total mass of said catalyst, and the non-noble metal content of group VIII encompasses, in oxide equivalent, between 0.5 and 10% by weight relative to the total mass of said catalyst.

5 Process according to one of Claims 1 to 4, in which the initial dealuminified Y zeolite has, before being modified, an initial overall atomic ratio of silicon to aluminum of between 2.7 and 10.0

6 Process according to one of Claims 1 to 5, in which the initial dealuminified Y zeolite, before being modified, has a fraction by weight of initial extra-network aluminum atoms that is greater than 30% by weight relative to the total mass of aluminum that is present in the zeolite.

7 Process according to one of Claims 1 to 6, in which the alkaline bases that are used in the basic aqueous solution of stage a') are selected from among the alkaline carbonates and the alkaline hydroxides, and the non-alkaline bases are selected from among the quaternary ammonium compounds, taken by themselves or in a mixture

8 Process according to Claim 7, in which the aqueous solution is a sodium carbonate or sodium hydroxide solution

9 Process according to one of Claims 1 to 8, in which in the case where the basic treatment stage a') consists of the mixing of said initial dealuminified Y zeolite with a basic aqueous solution of compounds that are selected from among the alkaline bases, the process for modification of said zeolite comprises a stage b') of at least one partial or total exchange of said alkaline cations that belong to the groups IA and IIA of the periodic table, introduced during stage a), by NH_4^+ cations.

10 Process according to one of Claims 1 to 8, in which in the case where the basic treatment stage a') consists in mixing said initial dealuminified Y zeolite with a basic aqueous solution of compounds that are selected from among the non-alkaline bases that are selected from among the quaternary ammonium compounds, taken by themselves or in a mixture, the process for modification of said initial dealuminified Y zeolite does not comprise stage b') of at least one intermediate partial or total exchange.

11 Process according to one of Claims 1 to 10, in which the feedstocks that are obtained from renewable sources are selected from among the oils and fats of plant or animal origin, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters and said vegetable oils being able to be raw or refined, totally or partially, and obtained from the following plants: canola, sunflower, soybean, palm, palm-kernel, olive, coconut, jatropha, and the animal fats being selected from among lard or fats composed of waste from the food industry or obtained from catering industries.