Title: HYDROGENATION CATALYST

Abstract: Catalyst comprising palladium and at least one promoter selected from the group consisting of rare earth metals, hafnium and tungsten, its preparation and use as a selective hydrogenation catalyst for unsaturated hydrocarbons, particularly acetylene.
HYDROGENATION CATALYST

The present invention relates to palladium catalysts comprising at least one promoter selected from the group consisting of rare earth metals, hafnium and tungsten, a method for their production and their use in a hydrogenation process.

In refineries and petrochemical facilities large amounts of hydrocarbons are produced and stored which comprise significant amounts of unsaturated hydrocarbons causing problems during the further processing steps and its storage. Such unsaturated compounds are for instance acetylene, propine, propadiene, butadienes, vinylacetylene, butines, phenylacetylene and styrene.

Acetylene is known to reduce the catalyst activity in polymerisation processes and the quality of the polymers is deteriorated. Thus, in the synthesis of polyethylene from ethylene the concentration of acetylene should be minimized.

The undesired, unsaturated compounds are removed mainly by selective hydrogenation wherein these compounds are hydrogenated, preferably to a content of less than a few ppm. It is important for the efficiency of the selective acetylene hydrogenation that the selective hydrogenation of ethylene to ethane and the oligomerization to higher hydrocarbons and the production of coke are avoided.

In the art, it was known to use supported Pd-catalysts based on aluminium oxides and silicium oxides for selective hydrogenation processes.

To improve the selectivity of the catalyst in hydrogenation processes FR 2 603 578 discloses a Pd-Al₂O₃ catalyst with gold as promoting metal. US 2,802,889 discloses a method for the selective hydrogenation of acetylene.
with Pd-catalysts comprising copper, silver, and gold wherein the content of the elements of the eighth subgroup in the metallic phases is 1 to 40%. DE 197 57 990 discloses supported Pd catalysts comprising Ni, Co, or Ag and Na, K, or Ca, and a layer of precipitated organic silanes.

US 4,484,015 discloses a Pd−Ag−αAl₂O₃ catalyst wherein Ag is homogeneously distributed over the total catalyst and 90% of the Pd is distributed in the outer shell region with a penetration depth of 300 µm. DE 198 40 373 discloses catalysts comprising at least one metal of the eighth subgroup with an eggshell distribution and at least one metal of the first subgroup with a homogeneous distribution over the entire catalyst.

KR 2000-0059743 discloses the promotion of Pd with titania oxide, whereby the selectivity of the Pd shall be increased by the SMSI effect. US 7,453,017 discloses a method wherein the SMSI effect is induced at already 300°C. US 6,255,548 discloses supported Pd catalysts promoted with Ge, Sn, Pb, Re, Ga, In, Au, Ag, and Ti.

According to the state of the art catalysts exhibit an unsatisfactory durability and selectivity, in particular when employed in a hydrogenation process, in particular in selective hydrogenation processes for hydrogenating acetylene, propine, propadiene, butadienes, vinylacetylene, butines, phenylacetylene and styrene in gaseous phase.

Therefore, the technical problem underlying the present invention is to overcome the above-identified disadvantages, in particular to provide a catalyst to be suitable for the selective hydrogenation of unsaturated hydrocarbons in a hydrocarbon feed, particularly in a gaseous hydrocarbon feed, comprising unsaturated hydrocarbons, in particular acetylene, propine, propadiene, butadienes, vinylacetylene, butines, phenylacetylene and sty-
rene, which shows a high, in particular improved, durability, selectivity, activity or a combination of two or three thereof, a method for producing said catalyst and its use for the hydrogenation of a hydrocarbon feed.

Furthermore, the technical problem underlying the present invention is to provide a process for the hydrogenation of a hydrocarbon feed, in particular for the selective hydrogenation of unsaturated hydrocarbons in a hydrocarbon feed, particularly in a gaseous hydrocarbon feed, comprising unsaturated hydrocarbons, in particular acetylene, propine, propadiene, butadienes, vinylacetylene, butines, phenylacetylene and styrene, which overcomes the above identified disadvantages and in particular which is characterized by a high, in particular improved activity, durability, selectivity or a combination of two or three thereof.

The technical problem of the present invention is solved according to the teaching of the independent claims.

In particular, the present invention solves its technical problem by the provision of a Pd-catalyst, comprising palladium and at least one promoter selected from the group consisting of rare earth metals, hafnium and tungsten.

In the context of the present invention the term "rare earth metals" means a group of seventeen chemical elements in the periodic table, namely scandium, yttrium and the fifteen lanthanoids. Scandium and Yttrium are considered to be rare earth metals since they tend to occur in the same ore deposits as the lanthanoids and exhibit similar chemical properties. Therefore, in the context of the present invention rare earth metals are scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dys-
prosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu).

In the context of the present invention the term "promoter" means one, more or all of the above-identified elements, that means the rare earth metals, hafnium and tungsten.

In the context of the present invention a "liquid medium" is preferably a solution. In the context of the present invention a "liquid medium" may also be a suspension. In a preferred embodiment of the present invention the solution or suspension is an aqueous solution or suspension.

In the context of the present invention the expression "and/or" used in between two elements is meant to designate that both elements linked by said term are referred to in a cumulative or alternative manner. Thus, the expression "A and/or B" encompasses the meanings "A or B" and "A and B", that means "any one of A, B or both".

"% by weight" values given in the present teaching refer, if not otherwise stated, to the weight of the total dry catalyst. In the context of the present invention, the components of the catalyst are to be selected in an overall amount to add up to 100 % by weight, most preferably not to exceed 100 % by weight.

In the context of the present invention, the term "outer shell region" also called "egg shell region" is the peripheral, preferably outer peripheral, region of the catalyst between the surface of the catalyst and its centre having a maximum depth calculated along an axis in the diffusion direction of impregnating metal ions towards the catalyst interior, in particular along an axis drawn perpendicularly to the tangent of a given point of the surface of the catalyst towards the interior of the catalyst, of 400 µm, 350 µm, 300 µm, 250 µm, preferably 220 µm, preferably 200 µm and most preferably 150 µm and
wherein said outer shell region is characterised by the presence of preferably at least 90% of the total amount of palladium. Thus, the depth of the outer shell region is the cross-sectional depth of the outer shell region and therefore equals the distance between the geometrical surface of the catalyst and the circumference of the catalyst centre.

In the content of the present invention the "outer shell region" is therefore defined by the presence of preferably at least 90% of the total amount of palladium (calculated on the basis of the total catalyst weight) within a maximal depth of 400 µm from the surface of the catalyst. Thus, the peripheral or outer shell region of the catalyst is the region, wherein preferably at least 90% of the total amount of palladium contained in the total catalyst is present and which extends from the surface of the catalyst to not more than 400 µm, 350 µm, 300 µm, 250 µm, preferably 220 µm, preferably 200 µm and most preferably 150 µm beneath the geometrical surface of the catalyst.

In the context of the present invention, the centre of the catalyst is the remainder of the catalyst, i.e. the interior region of the catalyst.

In a preferred embodiment of the present invention the diameter of the centre of the catalyst is at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 times greater than the depth of the outer shell region.

In a preferred embodiment of the present invention the radius of the centre of the catalyst is at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 times greater than the depth of the outer shell region.

In the context of the present invention, the term "support" is understood as being a pure carrier containing no catalytically active metal or as a carrier which comprises at least one catalytically active metal,
preferably the at least one metal selected from the group consisting of palladium, platinum and the promoters. Said catalytically active metal being preferably already present in the catalyst support is distributed homogeneously or inhomogeneously over the entire catalyst support.

Thus, the method of the present invention uses, for instance in step (i), as a support either a carrier containing no catalytically active metal or in another embodiment a carrier which already contains at least one catalytically active metal, preferably at least one metal selected from the group consisting of palladium, platinum and the promoters, and which is therefore in a subsequent process step further impregnated with at least one further metal, in particular at least one metal selected from the group consisting of palladium, platinum and the promoters.

In the context of the present invention, the term "inhomogeneous" means that a metal is unevenly distributed in the entire catalyst. The inhomogeneous distribution of the metal is preferably obtained by impregnation of the support with the catalytically active metal.

Other methods to obtain an inhomogeneous distribution may be used and are known in the art. Accordingly, by an appropriate choice of the support material, the metals and/or metal precursors used and the process conditions, in particular the pH and the temperature, an inhomogeneous distribution may also be achieved, even if the liquid medium is homogeneously distributed in the entire catalyst. Thus, in one embodiment an inhomogeneous distribution of a metal may also be achieved by a homogeneous distribution of the liquid media used in the present invention. Further methods, such as precipitation methods, may be used to achieve the desired inhomogeneous distribution.
In another preferred embodiment a homogeneous distribution of the metal may be achieved by impregnation, precipitation or other methods by applying appropriate process conditions.

In the context of the present invention, the term "homogeneous" means that a metal is evenly distributed in the entire catalyst. The homogenous distribution of the metal is preferably obtained by mixing, extrusion, co-extrusion and co-granulation with a support precursor as to obtain a support provided in the method steps (a) and (1).

In the context of the present invention the term "homogeneous distribution of the liquid medium" means that all accessible surface areas and volumetric regions of at least one, preferably all, species, for instance micropores and macropores, of the pore system are filled, moistened or covered homogeneously.

In the context of the present invention the term "selective hydrogenation of a hydrocarbon feed" is meant to designate a process according to which a hydrocarbon feed containing two groups of unsaturated hydrocarbons is subjected to a hydrogenation, wherein a first group of specific unsaturated hydrocarbons, in particular highly unsaturated hydrocarbons such as alkynes and di- or oligounsaturated hydrocarbons such as alkadienes, alkatrienes or alkapolyenes, in particular acetylene, butadiene, propine and propadiene, is hydrogenated and wherein a second group of other less unsaturated hydrocarbons, in particular monounsaturated hydrocarbons, namely alkenes such as ethylene, remains substantially in the unsaturated form. Thus, a selective hydrogenation according to the present invention is preferably a hydrogenation wherein a first group of specific unsaturated hydrocarbons, in particular comprising acetylene, is hydrogenated, preferably to ethylene, and a second group of
other specific unsaturated hydrocarbons, in particular comprising ethylene, is not hydrogenated and remains monounsaturated.

In the context of the present invention the term "hydrocarbons" refers both to hydrocarbons consisting solely of C- and H-atoms and to hydrocarbons additionally comprising at least one functional group and/or at least one heteroatom, for instance nitroaromatics.

In a particularly preferred embodiment the term "hydrocarbons" therefore refers to hydrocarbons consisting solely of C- and H-atoms.

In a furthermore preferred embodiment the term "hydrocarbons" refers to hydrocarbons additionally comprising at least one functional group and/or at least one heteroatom, for instance nitroaromatics.

Thus, the present invention foresees a Pd-catalyst, wherein palladium and the at least one promoter selected from the group consisting of the rare earth metals, hafnium and tungsten are distributed independently from each other homogeneously or inhomogeneously over the entire catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is in the form of a catalyst mesh or catalyst gauze. In a preferred embodiment the Pd-catalyst being in the form of a catalyst mesh or catalyst gauze comprises palladium, optionally platinum, and the at least one promoter selected from the group consisting of rare earth metals, Hf and W.

In a preferred embodiment of the present invention the Pd-catalyst comprises a support. Therefore, it is foreseen that the Pd-catalyst is preferably a supported Pd catalyst. The preferred supported Pd-catalyst comprises palladium, at least one promoter selected from the group consisting of rare earth metals, hafnium and tungsten, and a support.
In a preferred embodiment the metals selected from the group consisting of Pd, Pt and promoters are distributed independently from each other homogeneously or inhomogeneously over the entire catalyst.

In a preferred embodiment of the present invention the Pd catalyst comprises a monolithic or honeycomb body.

In a preferred embodiment of the present invention the monolithic or honeycomb-based catalyst comprises a monolithic or honeycomb body which can be an inert ceramic or metallic carrier, in particular traversed by parallel floating channels.

In a preferred embodiment of the present invention the metals selected from the group consisting of Pd, Pt and promoters are applied, preferably by impregnating, to the monolithic or honeycomb body.

In a preferred embodiment of the present invention the monolithic or honeycomb-based Pd-catalyst comprises a support, which support is present in form of a layer with a minimum thickness of 200 µm, preferably 150 µm and particularly 100 µm on parts of, preferably on the entire, monolithic or honeycomb body and wherein in said support layer Pd and the metals selected from the group consisting of Pt and the promoters are distributed independently from each other homogeneously or inhomogeneously over the entire support.

In a preferred embodiment of the present invention the outer shell region of the monolithic or honeycomb-based Pd catalyst has a maximum depth of 100 µm, preferably 50 µm, preferably 30 µm and in particular 20 µm, wherein 90% of the total amount of the at least one metal selected from the group consisting of Pd, Pt and promoters is distributed in the outer shell region.

Thus, the invention foresees in a preferred embodiment of the present invention that palladium and the at least one promoter selected from the group consisting of
the rare earth metals, Hf and W are distributed independently from each other homogeneously or inhomogeneously over the entire supported catalyst.

In a preferred embodiment of the present invention palladium, and the at least one promoter selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, hafnium and tungsten are distributed independently from each other homogeneously or inhomogeneously over the entire supported catalyst.

In a preferred embodiment of the present invention the at least one promoter is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, hafnium and tungsten, more preferably from the group consisting of the rare earth metals.

In a preferred embodiment of the present invention the at least one promoter is selected from the group consisting of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

In a preferred embodiment of the present invention the rare earth metals are selected from the group consisting of Er, Eu, Ho, Sc, Sm, Y and Yb.

In a preferred embodiment of the present invention the rare earth metals are selected from the group consisting of Eu and Y.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Eu-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Er-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Y-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Pt-Eu-catalyst.
In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Pt-Yb-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Pt-Sxn-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Pt-W-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Pt-Ho-catalyst.

In a preferred embodiment of the present invention the Pd-catalyst is a Pd-Pt-Hf-catalyst.

Promethium (Pm) is excluded from the group of rare earth metals.

In a preferred embodiment of the present invention cerium (Ce) is excluded from the rare earth metals.

In a preferred embodiment of the present invention lanthanum (La) is excluded from the rare earth metals.

In a preferred embodiment of the present invention praseodymium (Pr) is excluded from the rare earth metals.

In a preferred embodiment the Pd-catalyst according to the present invention is free of rare earth oxides.

In a preferred embodiment of the present invention the Pd-catalyst is free of gold.

In a preferred embodiment of the invention the palladium is distributed homogeneously over the entire catalyst.

In a preferred embodiment of the present invention the Pd-catalyst comprises an outer shell region having a maximum penetration depth of 400 µm and a centre, wherein at least 90% of the total amount of palladium is distributed in the outer shell region.

In a preferred embodiment of the present invention the at least one promoter is distributed homogeneously over the entire catalyst.
In a preferred embodiment of the present invention the Pd-catalyst comprises an outer shell region having a maximum penetration depth of 400 µm and a centre, wherein at least 90% of the total amount of the at least one promoter is distributed in the outer shell region.

In a preferred embodiment of the present invention the Pd-catalyst further comprises platinum, preferably being distributed homogeneously over the entire catalyst.

In a preferred embodiment of the present invention the Pd-catalyst, which comprises an outer shell region having a maximum depth of 400 µm and a centre, further comprises platinum wherein at least 90% of the total amount of platinum is distributed in the outer shell region.

In a preferred embodiment of the present invention all metals selected from the group selected of palladium, platinum, the rare earth metals, hafnium and tungsten are distributed inhomogeneously in the supported Pd-catalyst, preferably 90% of the total amount of the said metals is distributed in the outer shell region.

In a preferred embodiment of the present invention the weight ratio of palladium to the at least one promoter is from 10 to 0.1 (10:1 to 1:10).

In a preferred embodiment of the present invention the weight ratio of palladium to platinum is from 10 to 0.1 (10:1 to 1:10).

In a preferred embodiment a supported Pd-catalyst is provided comprising palladium and at least one metal selected from the group consisting of platinum and the promoters and a support, which catalyst comprises an outer shell region having a maximum depth of 400 µm, 350 µm, 300 µm, 250 µm, 220 µm, 200 µm or 150 µm and a centre, wherein at least 90% of the total amount of palladium and at least 90% of the total amount of the at least one metal selected from the group consisting of platinum
and the promoters are distributed in the outer shell region.

In a preferred embodiment, the present invention provides a catalyst, wherein the concentration maximum of the at least one metal selected from the group consisting of palladium, platinum and the at least one promoter is located in the outer shell region, namely in a subregion thereof within a depth from 50 to 200 μm, preferably 50 to 150 μm, preferably 70 to 130 μm, preferably 90 to 110 μm, calculated from the surface of the catalyst towards its centre. Thus, the invention foresees in a preferred embodiment that within the outer shell region as defined above, that means within the peripheral region of the catalyst, wherein preferably at least 90% of the total amount of palladium, platinum and the at least one promoter are located and which is defined by a maximal depth of 400 pm beneath the geometrical surface, that means counted from the surface of the catalyst, a subregion is present, in which a concentration maximum of the palladium, platinum and the at least one promoter are located and which is defined by a maximal depth from 50 pm counted from the surface of the catalyst to 200 pm counted from the surface of the catalyst. Thus, the maximum of the palladium, platinum and the at least one promoter concentration is preferably contained in a layer in a specified region of the outer shell region.

In a preferred embodiment a catalyst of the present invention is a catalyst comprising palladium and at least one metal selected from the group consisting of platinum and the promoters, that means is a two- or multi-metal catalyst and a support, which catalyst comprises an outer shell region having a maximum depth of 400 pm, 350 μm, 300 μm, 250 pm, 220 pm, 200 pm or 150 pm and a centre, wherein at least 90% of the total amount of palladium and 90% of the total amount of the at least one metal
selected from the group consisting of platinum and the promoters (calculated on the weight of total catalyst) are distributed in the outer shell region. In a particularly preferred embodiment a catalyst according to the above is provided, wherein the concentration maximum of palladium and the at least one metal selected from the group consisting of platinum and the promoters are located in the outer shell region in a subregion thereof which is located in a layer in a depth from 50 to 200 µm of the catalyst. The catalyst prepared by the present invention surprisingly shows a very high catalyst lifetime, e.g. durability, a high activity and a particular high selectivity for the unsaturated hydrocarbons to be removed.

In a preferred embodiment of the present invention at least 90 %, preferably at least 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 % and most preferably 100 % of the total amount of the at least one, preferably at least two metals selected from the group consisting of palladium, platinum and the promoters (calculated on the basis of the total catalyst) is distributed in the outer shell region.

In a preferred embodiment of the present invention at least 90 %, preferably at least 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 % and in particular 100 % of the total amount of the palladium (calculated on the basis of the total catalyst) is distributed in the outer shell region.

In a preferred embodiment of the present invention at least 90 %, preferably at least 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 % and in particular 100 % of the total amount of the platinum (calculated on the basis of the total catalyst) is distributed in the outer shell region.
In a preferred embodiment of the present invention at least 90 %, preferably at least 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 % and in particular 100 % of the total amount of the at least one promoter (calculated on the basis of the total catalyst) is distributed in the outer shell region.

In a preferred embodiment of the present invention at least 90 %, preferably at least 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 % and in particular 100 % of the total amount of the palladium and the at least one promoter (calculated on the basis of the total catalyst) is distributed in the outer shell region.

In a preferred embodiment of the present invention at least 90 %, preferably at least 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 % and in particular 100 % of the total amount of the palladium, the platinum and the at least one promoter (calculated on the basis of the total catalyst) is distributed in the outer shell region.

In a further preferred embodiment of the present invention, the palladium, optionally the platinum, and the promoters are the only metals, in particular the only catalytically active metals in the entire catalyst.

In a preferred embodiment of the present invention the palladium concentration is from 0.01 to 5.0 % by weight, preferably 0.1 to 4.0 % by weight, preferably 0.2 to 3.0 % by weight and in particular 0.2 to 1.6 % by weight (based on the total weight of the catalyst).

In a preferred embodiment of the present invention the concentration of the at least one promoter is from 0.01 to 5.0 % by weight, preferably 0.1 to 3.0 % by weight, preferably 0.2 to 2.0 % by weight and in particular 0.2 to 0.8 % by weight (based on the total weight of the catalyst).

In a preferred embodiment of the present invention the platinum concentration is from 0.01 to 5.0 % by
weight, preferably 0.1 to 3.0 % by weight, preferably 0.2 to 2.0 % by weight and in particular 0.2 to 0.8 % by weight (based on the total weight of the catalyst).

In a preferred embodiment of the present invention the support is selected from the group consisting of C, TiO₂, Al₂O₃, ZrO₂ and SiO₂. As catalyst support, also modifications of C, TiO₂, Al₂O₃, ZrO₂ and SiO₂ can be used. Preferably, combinations of the catalyst supports selected from the group consisting of C, TiO₂, Al₂O₃, ZrO₂ and SiO₂ can be used.

In a preferred embodiment of the present invention the catalyst support is Al₂O₃ or a modification thereof. In a preferred embodiment of the present invention the catalyst may be in the form of hollow-cylinders, tablets, spheres or extrudates.

In a preferred embodiment of the present invention the catalyst has a diameter of 1.5 to 8.0 mm, preferably 3.2 to 5.8 mm, preferably 3.3 to 5.7 mm, preferably 3.4 to 5.5 mm.

In a preferred embodiment of the present invention the centre of the catalyst has a diameter of 1.0 to 7.7 mm, preferably 2.2 to 7.2 mm, preferably 3.0 to 4.35 mm, preferably 3.7 to 4.3 mm, preferably 3.9 to 4.1 mm, in particular 4.0 mm.

In a preferred embodiment of the present invention the ratio of the radius of the centre to the distance between the geometrical surface of the catalyst and the circumference of the catalyst centre is from 15 to 2, preferably 12 to 4, preferably 10 to 6, particularly 9 to 7 and most preferably 8.

In a preferred embodiment of the present invention the, preferably spherical, supported Pd-catalyst has a diameter of 1.5 to 3.0 mm, which catalyst comprises an outer shell region having a maximum depth of 250 µm, 220 µm, 200 µm or 150 µm and a centre, wherein at least 90 %
of the total amount of the at least one metal selected from the group consisting of Pd, Pt, rare earth metals, Hf and W (calculated on the weight of the total catalyst) are distributed in the outer shell region. The centre of said preferred catalyst has a diameter of 1.0 to 2.7 mm and the ratio of the radius of the centre to the distance between the geometrical surface of the catalyst and the circumference of the catalyst centre is from 2 to 15.

In a preferred embodiment of the present invention the supported Pd-catalyst has a diameter of 3.0 to 8.0 mm. The centre of said preferred catalyst has a diameter of 2.2 to 7.7 mm and the ratio of the radius of the centre to the distance between the geometrical surface of the catalyst and the circumference of the catalyst centre is from 2 to 15.

The problem of the present invention is also solved by a method for preparing a Pd-catalyst comprising combining Pd with at least one promoter selected from the group consisting of rare earth metals, Hf and W, so as to obtain a Pd-catalyst.

The problem of the present invention is also solved by a method for preparing a supported Pd-catalyst comprising combining Pd and at least one promoter selected from the group consisting of rare earth metals, Hf and W, with a support, so as to obtain the supported Pd-catalyst.

The problem of the present invention is also solved by a method for preparing a supported Pd-catalyst comprising combining at least one promoter selected from the group consisting of rare earth metals, Hf and W, with a support comprising Pd, so as to obtain the supported Pd-catalyst.

The problem of the present invention is also solved by a method for preparing a supported Pd-catalyst comprising combining Pd with a support comprising at least
one promoter selected from the group consisting of rare earth metals, Hf and W, so as to obtain the supported Pd-catalyst.

In a preferred embodiment of the present invention the method for producing the supported Pd-catalyst comprises the following steps:
(a) providing a support comprising Pd,
(b) impregnating the support of step (a) with a liquid medium comprising at least one metal selected from the group consisting of rare earth metals, Hf and W,
(c) drying the impregnated support of step (b) and
(d) treating the dried, impregnated support obtained in step (c) so as to obtain a supported Pd-catalyst.

In a preferred embodiment of the present invention the method for producing the supported Pd-catalyst comprises the following steps:

(i) providing a support,
(ii) impregnating the support of step (i) with a liquid medium comprising Pd,
(iii) drying the Pd impregnated support of step (ii),
(iv) impregnating the dried, Pd impregnated support of step (iii) with a liquid medium comprising at least one metal selected from the group consisting of rare earth metals, Hf and W,
(v) drying the impregnated support of step (iv) and
(vi) treating the dried, impregnated support obtained in step (v) so as to obtain a supported Pd-catalyst.

In a preferred embodiment the present invention foresees a method for producing a monolithic or honeycomb-based Pd catalyst comprising applying Pd, optionally Pt, and a metal selected from the group consisting of promoters to the monolithic or honeycomb body.

In a preferred embodiment of the present invention the method for producing the monolithic or honeycomb-based Pd catalyst comprises the following steps:
providing a monolithic or honeycomb body,
coating the monolithic or honeycomb body provided in step (s) with a catalyst support,
impregnating the coated monolithic or honeycomb body obtained in step (t) with a liquid medium comprising palladium,
drying the impregnated, coated monolithic or honeycomb body obtained in step (u),
impregnating the dried monolithic or honeycomb body obtained in step (w) with a liquid medium comprising a metal selected from the group consisting of rare earth metals, hafnium and tungsten,
drying the impregnated monolithic or honeycomb body obtained in step (x) and
treating the impregnated and dried monolithic or honeycomb body obtained in step (y) so as to obtain the monolithic or honeycomb-based Pd-catalyst.

In a preferred embodiment of the present invention the liquid medium of step (b), (ii), (iv), (u) and/or (x) further comprises Pt.

In a preferred embodiment of the present invention the liquid medium of step (b), (x) and/or (iv) comprises 1, 2, 3, 4, 5 and 6 metals selected from the group consisting of Pt, rare earth metals, Hf and W.

In a preferred embodiment of the present invention the dried, impregnated support obtained in step (c), (y) and/or (v) is further impregnated in a step (c'), (y') and (v') carried out with a further liquid medium comprising at least one other metal selected from the group consisting of Pt, rare earth metals, Hf and W.

In a preferred embodiment of the present invention the impregnation and drying steps are repeated, until the desired contents of the different metals are present in the supported Pd-catalyst.
In a preferred embodiment of the present invention the impregnation steps (ii) and (iv) are carried out simultaneously, thus rendering the intermediate drying step (iii) unnecessary.

In a preferred embodiment of the present invention the impregnation steps (u) and (x) are carried out simultaneously, thus rendering the intermediate drying step (w) unnecessary.

In a preferred embodiment of the present invention the impregnation step (iv) and the subsequent drying step (v) are carried out before the impregnation step (ii).

In a preferred embodiment of the present invention the impregnation step (x) and the subsequent drying step (y) are carried out before the impregnation step (u).

In a preferred embodiment of the present invention the metals in the liquid medium of step (b), (u), (x), (ii) and/or (iv) are present in form of their salts, preferably in form of their nitrates.

In a preferred embodiment of the present invention the impregnation in step (b), (u), (x), (ii) and/or (iv) is carried out by spraying the liquid medium onto the support. By spraying the liquid mediums onto the catalyst support a particular homogeneous distribution is obtained.

In a preferred embodiment of the present invention the spraying of the liquid medium onto the catalyst is carried out with a nozzle capable of finely dispersing liquids such as solutions or suspensions.

In a preferred embodiment of the present invention the liquid medium is homogeneously distributed in the pores of the catalyst support.

In a preferred embodiment of the present invention the drying temperature in step (c), (w), (y), (iii) and/or (v) is from 80 to 350 °C, preferably 90 to 300 °C,
preferably 100 to 250 °C, preferably 110 to 200 °C and in particular 120 to 150 °C.

In a preferred embodiment of the present invention the drying of the impregnated precursor in step (c), (y), (iii) and/or (v) is carried out to a dry residue of 99 %, preferably 99.5 %, preferably 99.9 % and in particular 100 %.

In a preferred embodiment the drying step is performed by microwave treatment.

In a preferred embodiment of the present invention the drying can be carried out under static or dynamic conditions, for instance in a fixed bed, or in a moving bed.

In a preferred embodiment of the present invention the catalyst according to the present invention is inerted, preferably at a temperature from 300 to 350°C, preferably 350°C, preferably after the drying and preferably before the treating, preferably the calcining.

In a preferred embodiment of the present invention the inerting is carried out at the same temperature as the drying.

In a preferred embodiment of the present invention the dried impregnated precursor obtained in step (c), (y) and/or (v) is in a further step (c''), (y'') and/or (v'') flushed with hydrogen, preferably before the treating, in particular the calcining, in step (d), (z) and/or (vi).

In a preferred embodiment of the present invention the flushing with hydrogen carried out in step (c''), (y'') and/or (v'') is performed for 2 to 20 minutes, preferably 2 to 5 min.

In a preferred embodiment the present invention comprises both the inerting and the flushing step.

A preferred embodiment foresees that subsequently to the drying step (c), (y) and/or (v) the dried, impregnated catalyst is inerted, subsequently flushed with hy-
drogen and then treated, preferably calcined, in step (d), (z) and/or (vi).

In a preferred embodiment of the present invention the treating, especially the calcining, in step (d), (z) and/or (vi) is carried out at a temperature from 350 to 700 °C, preferably 500 to 700 °C and in particular 600 to 700 °C.

In a preferred embodiment of the present invention the process foresees to subject the catalyst to a nitrogen stream while the temperature is increased to the temperature of treating, preferably calcining.

In a preferred embodiment of the present invention the treatment, preferably calcining, is carried out in a fixed bed or in a moving bed reactor.

In a preferred embodiment of the present invention the treating in step (d), (z) and/or (vi) is carried out with a nitrogen-containing gas, preferably air or nitrogen.

In a preferred embodiment of the present invention the selectivity and/or durability of the catalysts is further increased by adding before and/or during the treating in step (d), (z) and/or (vi) to the nitrogen-containing gas, preferably to the nitrogen, used therefore a gas which is preferably selected from the group consisting of hydrogen, air, oxygen, water vapour and NOₓ, with a content from 0 to 500 ppmv (parts per million per volume), preferably 10 to 400 ppmv, preferably 20 to 300 ppmv, preferably 30 to 200 ppmv and in particular 50 to 100 ppmv.

In a preferred embodiment of the present invention the Pd-catalyst is reduced after the treating in step (d), (z) and/or (vi) in a step (e), (ζ) and/or (vii), to be preferably suitable for the hydrogenation of a hydrocarbon feed, preferably at a temperature of 50 °C to 650
°C, preferably 150 to 500 °C and in particular 400 °C for four hours in a hydrogen stream.

In a preferred embodiment of the present invention Pd-catalyst is dried, preferably at a temperature of 120 °C, before said Pd-catalyst is reduced.

In a preferred embodiment of the present invention during and/or after the reduction of the Pd-catalyst the presence of oxygen, oxygen containing gases and/or gases causing oxidation of rare earth metals is prevented, due to the fact that reduced rare earth metals, preferably with the oxidation state of zero, can be oxidized easily to their oxides.

In a preferred embodiment of the present invention the dried and impregnated support is treated, preferably is calcined, in step (d), (z) and/or (vi) for 1 to 20 hours, preferably 2 to 18 hours, preferably 3 to 15 hours, preferably 4 to 10 hours and in particular 4 to 8 hours.

In a preferred embodiment of the present invention the dried and impregnated support is treated, preferably is calcined, in step (d), (z) and/or (vi) at a GHSV (gas hourly space velocity) from 10 to 5000 v/vh, preferably 1000 to 4500 v/vh and in particular 3000 to 4000 v/vh.

In a preferred embodiment of the present invention the catalyst is cooled after the treating, preferably calcining, in step (d), (z) and/or (vi) in a nitrogen containing gas, for instance under nitrogen protective atmosphere, preferably to a temperature below 50 °C.

The supported Pd-catalysts can be used preferably for the hydrogenation, preferably for the selective hydrogenation, preferably for the selective hydrogenation of the hydrocarbon feed, preferably comprising a first and a second group of unsaturated hydrocarbons, wherein preferably the first group is hydrogenated thereby, with a particular long catalyst lifetime allowing signifi-
cantly increased cycle times. Based on the particular high durability of said catalyst hydrogenation processes can be repeated more often, before the said catalyst has to be regenerated. Advantageously, the catalyst according to the present invention reduces the formation of green oil.

The technical problem of the present invention is also solved by a method for the hydrogenation of a hydrocarbon feed, preferably in gaseous phase, in particular a method for the selective hydrogenation of a hydrocarbon feed containing unsaturated hydrocarbons, in particular a first group of undesired, that means highly unsaturated hydrocarbons, in particular aromatics, alkynes and/or di-, tri- or polyunsaturated hydrocarbons, particularly alkadienes, alkatrienes or alkapolymenes, such as acetylene, propine, propadiene, butadienes, vinylacetylene, butines, phenylacetylene and/or styrene and a second group of desired, that means less unsaturated hydrocarbons, in particular monounsaturated hydrocarbons, namely alkenes, particularly ethylene, wherein the hydrocarbon feed is contacted under suitable hydrogenating conditions with the catalyst according to the present invention so as to remove the undesired first group of unsaturated hydrocarbons, in particular to hydrogenate them, preferably to a desired less unsaturated hydrocarbon, thereby leaving the second group of unsaturated hydrocarbons in their monounsaturated form. Thus, the present invention provides a process for the selective hydrogenation of highly unsaturated hydrocarbons in the presence of less unsaturated hydrocarbons characterized by the use of a catalyst according to the present invention.

The catalyst according to the present invention can be used in a hydrogenation process, in particular a selective hydrogenation of a hydrogen feed comprising unsaturated hydrocarbons, with a particular long catalyst
lifetime allowing significantly increased cycle times. Based on the particular high durability of said catalyst hydrogenation processes can be repeated more often, preferably in case of a batch-wise operation, before the said catalyst has to be regenerated or in a continuous fixed bed the lifetime and/or conversion is increased. Advantageously, the catalyst according to the present invention reduces the formation of higher hydrocarbons.

Thus, in a preferred embodiment of the present invention the hydrogenation is carried out in the gas phase.

In a further preferred embodiment, the present hydrogenation process is carried out according to the conditions of a front-end or tail-end hydrogenation process, preferably for the hydrogenation of CI to C3 hydrocarbons.

In a preferred embodiment of the present invention the hydrocarbon feed comprises in its first group of unsaturated hydrocarbons acetylene, in particular in the presence of less unsaturated hydrocarbons. In a preferred embodiment, the present process foresees to preferably reduce acetylene to ethylene, in particular in the presence of less unsaturated hydrocarbons, preferably ethylene.

In a preferred embodiment acetylene is hydrogenated selectively.

In a preferred embodiment of the present invention the hydrocarbon feed is contacted in the hydrogenation process with the catalyst according to the present invention at a temperature from 10 to 250 °C, preferably 30 to 200 °C, preferably 40 to 180 °C and in particular 40 to 100 °C.

In a preferred embodiment of the present invention the hydrocarbon feed is contacted in the hydrogenation process with the catalyst at a pressure from 0.5 to 90
bars, preferably 0.5 to 60 bars, preferably 5 to 20 bars, preferably 0.5 to 2 bars and in particular 10 to 20 bars.

In a preferred embodiment of the present invention the hydrocarbon feed is conducted in the hydrogenation process with the catalyst at a GHSV (gas hourly space velocity) from 1000 to 15000 v/vh, from 5000 to 12000 v/vh, preferably from 3000 to 7000 v/vh and in particular 5000 to 7000 v/vh.

In a preferred embodiment of the present invention the hydrocarbon feed is contacted in the hydrogenation process with a catalyst without the use of carbon monoxide as moderator. Furthermore, the hydrogenation can be carried out without carbon monoxide, namely in a monocarboxide-free process.

In a preferred embodiment of the present invention the molar ratio of hydrogen to the acetylene is from 0.8 to 1.8, preferably 1.0 to 1.5 and in particular 1.0 to 1.3, particularly 1.2.

In a preferred embodiment of the present invention the molar ratio of the hydrogen to the acetylene is from 1.8 to 100, preferably 1.8 to 70, preferably 1.8 to 30 and in particular 1.8 to 10.

In a preferred embodiment of the present invention poisoning metals, such as mercury and arsenic, are removed prior to the hydrogenation process, preferably using a guard bed.

In a preferred embodiment for the process of hydrogenation the hydrocarbon feed is contacted with hydrogen to obtain the hydrogenated products.

Further preferred embodiments are the subject matter of the subclams.

Further advantages of the present invention are illustrated by way of the following examples:

Example 1:

Production of the catalysts...
An oxidic support, preferably a $\text{AI}_2\text{O}_3$ modification, for instance $\alpha$-$\text{Al}_2\text{O}_3$ or $\gamma$-$\text{Al}_2\text{O}_3$, was impregnated with an aqueous $\text{Pd(NO}_3)_2$ solution, optionally with the Pt solution, and subsequently with a solution comprising at least one promoter. The volume of impregnation solutions corresponded to the pore volume of the support. Between the impregnation steps the support or the impregnated support was dried at about 120°C and finally calcined at 400°C for four hours in air. The order of the impregnation steps can be changed and the impregnation solutions can be combined with each other.

The following compositions were used for the impregnation solutions:

Table 1

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<tr>
<th>Element</th>
<th>Composition</th>
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<tr>
<td>Er</td>
<td>Erbium (III) nitrate, 99.9% (REO*)</td>
<td>$\text{Er(NO}_3)_3 \cdot \text{X} % \text{O}$</td>
</tr>
<tr>
<td>Eu</td>
<td>Europium (III) nitrate, 99.9% (REO)</td>
<td>$\text{Eu(NO}_3)_3 - 5\text{H}_2\text{O}$</td>
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<tr>
<td>Hf</td>
<td>Hafnium dinitrate oxide, 99.9% (metals basis excluding Zr), Zr &lt;0.1%, 10% w/v aqueous solution</td>
<td>$\text{HfO(NO}_3)_2$</td>
</tr>
<tr>
<td>Ho</td>
<td>Holmium (III) nitrate, 99.9% (REO)</td>
<td>$\text{Ho(NO}_3)_3 \cdot 5\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Pd</td>
<td>Tetraamminepalladium (II) nitrate solution, 99.9% (metals basis), Pd 5.0% max (cont. Pd)</td>
<td>($\text{NH}_3)_4\text{Pd(NO}_3)_2$</td>
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<tr>
<td>Pt</td>
<td>Tetraammineplatinum (II) nitrate, Premion®, 99.99% (metals basis), Pt 50% min</td>
<td>$\text{Pt(NH}_3)_4(\text{NO}_3)_2$</td>
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<tr>
<td>Sc</td>
<td>Scandium (III) nitrate, 99.9% (REO)</td>
<td>$\text{Sc(NO}_3)_3 \cdot \text{X} % \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
Samarium (III) nitrate, \( \text{Sm(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \)
99.9% (REO)

Ammonium tungsten oxide, \( \text{NH}_4\text{WO}_4 \cdot 5\text{H}_2\text{O} \)
99.999% (metals basis)

Yttrium (III) nitrate, \( \text{Y(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \)
99.9% (REO)

Ytterbium (III) nitrate, \( \text{Yb(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} \)
99.9% (REO)

* REO = rare earth oxides

Example 2:

Catalytic Properties of the Catalysts

Prior to testing, the catalysts were dried at 120 °C and reduced for 4 hours at 400 °C in a hydrogen stream. The catalytic performances of the catalysts were characterized by the following test:

- GHSV: 7,000 v/vh
- Feed composition (Vol-%): 1.0 \( \text{C}_2\text{H}_2 \) 1.0 \( \text{H}_2 \) 30 \( \text{C}_2\text{H}_4 \) 1.0 \( \text{C}_3\text{H}_8 \) rest: Ar
- Pressure: 1 bar
- Temperature: 40 °C

Results of the Catalytic Tests:

From table 2 below it is evident that the catalysts according to the present invention provide in particular for a high degree of conversion of the acetylene.

The acetylene conversion, selectivity to ethylene and selectivity to ethane in table 2 are defined as follows.

The acetylene conversion is defined as:

\[
X_{Ac} = \frac{n_{Ac}^0 - n_{Ac}^\infty}{n_{Ac}^0} \cdot 100\%
\]

The selectivity towards ethylene is defined as:
The selectivity towards ethane is defined as:

\[
S_{Ea} = \frac{\left( n - \dot{n}_{Ac} \right) - 2 \left( \frac{1}{4} - \dot{n}_{Ca} \right)}{\left( \dot{n}_{Ac} - \dot{n}_{Ac} \right)} \cdot 100\%
\]

\[
S_{Ey} = \frac{\left( n - \dot{n}_{Ac} \right) - \left( \dot{n}_{Ey} - \dot{n}_{Ey} \right)}{\left( \dot{n}_{Ac} - \dot{n}_{Ac} \right)} \cdot 100\%
\]

\( n = \text{mole flow} \)

\( n^0 = \text{mole flow at the inlet} \)

\( Ac = \text{acetylene} \)

\( Ey = \text{ethylene} \)

\( Ea = \text{ethane} \)
<table>
<thead>
<tr>
<th>Catalyst composition + (numbers indicate % by weight)</th>
<th>Conversion of acetylene, %</th>
<th>Selectivity to ethene, %</th>
<th>Selectivity to ethane, %</th>
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<tr>
<td>Pd-Ag control catalyst</td>
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<tr>
<td>Ag0.8Pd0.8*</td>
<td>30</td>
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<td>Pd-Pt control catalyst</td>
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<td>Pd0.2Pt1*</td>
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<td>Pt1Pd0.2*</td>
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<td>Pd-Eu catalyst</td>
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<td>Eu0.2Pd1</td>
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<tr>
<td>Eu0.4Pd0.8</td>
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<td>Pdl1.6Eu0.2</td>
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<tr>
<td>Y0.2Pd0.8</td>
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<td>Pd-Er catalyst</td>
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<tr>
<td>Pdl1.6Er0.2</td>
<td>57</td>
<td>65</td>
<td>35</td>
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<tr>
<td>Pd-Pt-Eu catalyst</td>
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<tr>
<td>Pd0.8Pt0.2Eu0.2</td>
<td>58</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>Pt0.8Pd0.8Eu0.2</td>
<td>60</td>
<td>75</td>
<td>25</td>
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<tr>
<td>Catalyst Type</td>
<td>X0</td>
<td>Pd-Pt-Hf catalyst</td>
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<tr>
<td>Yb0.2Pd0.8Pt0.8</td>
<td>64</td>
<td>63</td>
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<tr>
<td>Pd0.8Pd0.2Yb0.2</td>
<td>73</td>
<td>68</td>
<td>81</td>
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<tr>
<td>Pd0.8Pd0.2Pt0.2</td>
<td>32</td>
<td>19</td>
<td>24</td>
</tr>
</tbody>
</table>

according to the state of the art
1. A Pd-catalyst, comprising palladium and at least one promoter selected from the group consisting of rare earth metals, Hf and W.

2. The Pd-catalyst according to claim 1, which comprises a support.

3. The Pd-catalyst according to claim 1 or 2, which comprises a monolithic or honeycomb body.

4. The Pd-catalyst according to any one of the preceding claims, wherein the at least one promoter is selected from the group consisting of Sc, Y, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Hf.

5. The Pd-catalyst according to any one of the preceding claims, wherein the palladium is distributed homogeneously over the entire catalyst.

6. The Pd-catalyst according to any one of claims 1 to 4, which comprises an outer shell region having a maximum depth of 400 µm and a centre, wherein at least 90 % of the total amount of the palladium is distributed in the outer shell region.

7. The Pd-catalyst according to any one of the preceding claims, wherein the at least one promoter is distributed homogeneously over the entire catalyst.

8. The Pd-catalyst according to any one of claims 1 to 6, which comprises an outer shell region having a maximum depth of 400 pm and a centre, wherein at least 90 % of the total amount of the at least one promoter is distributed in the outer shell region.

9. The Pd-catalyst according to any one of the preceding claims, which further comprises platinum.

10. The Pd-catalyst according to any one of the preceding claims, which comprises an outer shell region having a maximum depth of 400 µm and a centre, further comprises
platinum, wherein at least 90% of the total amount of the platinum is distributed in the outer shell region.

11. The Pd-catalyst according to any of the preceding claims, wherein the weight ratio of the palladium to the at least one promoter is from 10:1 to 1:10.

12. The Pd-catalyst according to any one of claims 9 to 11, wherein the weight ratio of the palladium to the platinum is from 10 to 0.1 (10:1 to 1:10).

13. The Pd-catalyst according to any of the preceding claims, wherein the support is Al₂O₃ or a modification thereof.

14. A method for preparing a Pd-catalyst comprising combining Pd with at least one promoter selected from the group consisting of rare earth metals, Hf and W, so as to obtain the Pd-catalyst.

15. A method for the hydrogenation, preferably for the selective hydrogenation, of a hydrocarbon feed, preferably comprising a first and a second group of unsaturated hydrocarbons, wherein the hydrocarbon feed is contacted under suitable hydrogenation conditions with the catalyst according to any one of the claims 1 to 13 and the unsaturated hydrocarbons in the hydrocarbon feed, preferably in the first group, are hydrogenated.

16. The method for the hydrogenation according to claim 15, wherein the hydrocarbon feed comprises in its first group of unsaturated hydrocarbons acetylene.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C10G45/40 B01J23/44 B01J23/63 B01J23/652 C07C5/05 C07C7/167

**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C10G B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

- EPO-Internal
- WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category*</th>
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<td>EP 0 884 102 AI (INST FRANCAIS DU PETROLE [FR]) 16 December 1998 (1998-12-16) examples 2, 5, 6-10 claims 1-15</td>
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<td>X</td>
<td>WD 2008/041756 AI (NI PPON CATALYTIC CHEM IND [JP]; KUMA RYOJI [JP]) 10 April 2008 (2008-04-10) table 1 page 12</td>
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* Further documents are listed in the continuation of Box C. See patent family annex.

**T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

**Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

**A** document member of the same patent family

**Date of the actual completion of the international search**

12 April 2011

**Date of mailing of the international search report**

20/04/2011

**Name and mailing address of the ISA/**

European Patent Office P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

**Authorized officer**

Bernet, Olivier

Form PCT/ISA/210 (second sheet) (April 2005)

Page 1 of 2
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