(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 October 2013 (31.10.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/160163 A1

(51) International Patent Classification:
B01J 23/44 (2006.01) *B01J 37/02* (2006.01)
B01J 23/50 (2006.01) *B01J 37/03* (2006.01)
B01J 23/52 (2006.01) *B01J 37/18* (2006.01)
B01J 23/38 (2006.01) *C01B 15/023* (2006.01)
B01J 35/00 (2006.01) *C01B 15/01* (2006.01)

(21) International Application Number:
PCT/EP2013/057962

(22) International Filing Date:
17 April 2013 (17.04.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12165962.7 27 April 2012 (27.04.2012) EP

(71) Applicant: **SOLVAY SA** [BE/BE]; Rue de Ransbeek, 310, B-1120 Bruxelles (BE).

(72) Inventors: **GANHY, Jean-Pierre**; Rue des Bégonias, 81, B-1170 Brussels (BE). **LEMAIRE, Arnaud**; 1, avenue des Combattants, B-5000 Namur (BE). **DOURNEL, Pierre**; rue Joseph Coosemans 13, B-1030 Brussels (BE).

(74) Agents: **VANDE GUCHT, Anne** et al.; Rue de Ransbeek, 310, B-1120 Bruxelles (BE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2013/160163 A1

(54) Title: HYDROGENATION CATALYSTS, METHOD FOR MAKING SAME AND USE THEREOF FOR PREPARING HYDROGEN PEROXIDE

(57) Abstract: The present invention describes a hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), on an aluminium oxide (Al_2O_3), or on an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst and an amount of silver 0.1 to 0.5 % by weight with respect to the weight of the catalyst, and wherein preferably the catalyst further comprises gold in an amount of up to 0.1 % by weight with respect to the weight of the catalyst. The preferred support in an embodiment of the invention is a delta-aluminium oxide (delta-Al_2O_3) support. The catalyst may be used in manifold hydrogenation types, and preferably the catalyst is proposed to be used in the manufacture of hydrogen peroxide by the auto-oxidation process.

Hydrogenation catalysts, method for making same and use thereof for preparing hydrogen peroxide

This application claims priority to European application No. EP 12165962.7 filed on 27 Apr 2012, the whole content of this application being incorporated herein by reference for all purposes.

The present invention relates to hydrogenation catalysts based on palladium which is deposited on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support and which also contains a small amount of an additive metal compound, to their process of manufacture and to their use in hydrogenation reactions and in particular in preparing hydrogen peroxide.

Next to catalytically active noble metals like platinum or rhodium, a frequently used catalytic metal for hydrogenations is palladium (Pd), optionally in combination with other catalytic metals. The catalytically active noble metals can be non-supported or supported on inorganic materials such as silica (SiO_2) or alumina (Al_2O_3).

Processes that utilize such catalytically active metals dispersed on refractory supports are common in the chemical process industry. A major group of processes included in this category are catalytic hydrogenations. Several important catalytic hydrogenations include, for example, the conversion of benzene to cyclohexane, the hydrogenation of edible oils to yield margerine-type products and the conversion of unsaturated oxygen-containing compounds, aldehydes and ketones, to alcohols.

Catalytic hydrogenations are also used in processes for the production of hydrogen peroxide. The synthesis of hydrogen peroxide with the involvement of hydrogenation catalysts comprising e.g. palladium non-supported or supported (e.g. supported on silica or alumina) is a reaction which has been known for a long time.

For example, on the one hand, catalysts based on palladium (Pd) are also used in the direct production of hydrogen peroxide, e.g. as described in the US 6,346,228 related to a hydrophobic multicomponent catalyst comprising a hydrophobic polymer membrane deposited on a Pd containing acidic catalyst, or as described in US 6,432,376 and in US 6,448,199 for a membrane process for

the production of hydrogen peroxide by direct oxidation of hydrogen by oxygen using a hydrophobic composite Pd-membrane catalysts that may comprise silver in addition to palladium.

The Patent Application EP 1 038 833 A1 discloses precious metal-based hydrogenation catalysts for direct synthesis of hydrogen peroxide from hydrogen and oxygen in the presence of a supported catalyst having, as active components, palladium or at least two metals selected from platinum group metals and the first subgroup metals. The catalysts preferably contain active components of palladium >80, and/or gold 0.05-5, and/or platinum 0.05-15, and/or Ag 0-5 weight % and are supported on Al_2O_3, TiO_2, ZrO_2, SiO_2, and zeolites, optionally in the presence of an inorganic binder (especially water glass). The catalysts are manufactured by spray or flame pyrolysis.

The Patent Application EP 1 308 416 A1 employs a catalyst in the direct synthesis which comprises noble metal and wherein the catalysts preferably are bonded to supports. The catalytically active component of the catalyst comprises one or more noble metals in the pure form or in the form of alloys. Preferred noble metals are the platinum metals, in particular palladium and platinum, and gold. Elements from the series consisting of Rh, Ru, Ir, Cu and Ag can additionally be present. Particularly preferred catalysts according to EP 1308416 A1 comprise as the catalytically active metal at least 80 wt. % palladium and 0-20 wt. % platinum, and 0-20 wt. % gold and/or 0-5 wt. % silver in alloyed or non-alloyed form. In a particularly preferred embodiment, a catalyst fixed bed in which the catalytically active particles have been produced by a spray or flame pyrolysis process according to EP 1 038 833 A1 is used.

In the International Patent Application WO 98/16463 A1 a process is disclosed for manufacture of hydrogen peroxide solutions with a H_2O_2 content of equal or greater than 2.5 wt. % by continuous reaction of hydrogen and oxygen in an aqueous or alcoholic reaction medium on a Pd-containing catalyst. The catalyst is e.g. a Pd-Ag catalyst for direct production of H_2O_2 with a molar ratio of Pd to Ag in the range of 100:1 to 1:10.

On the other hand, for example, catalysts like palladium non-supported or e.g. supported on SiO_2 or Al_2O_3 may be used in the process for the production of hydrogen peroxide by the autoxidation process (AO process). An integral part of this process involves the catalytic hydrogenation of various substituted anthraquinones to the corresponding anthrahydroquinones. A catalyst commonly employed in this hydrogenation process is palladium either supported or as

palladium black. One supported catalyst currently in use is produced by solution precipitation and deposition of palladium on the chosen support. Commonly used support materials are silica, alumina or aluminosilicate. In the following some examples for catalysts described in the state of the art for the production of hydrogen peroxide by the AO process shall be given.

The Patent Application EP 1 195 197 A1 discloses a catalyst carrier comprising a fiber paper impregnated with a slurry comprising silica sol, micro fibers and a filler. Particularly disclosed amongst other things are a method for preparing the catalyst carrier ; a catalyst comprising the catalyst carrier on which at least one catalytically active material is deposited ; and a process for producing hydrogen peroxide according to anthraquinone process, which involves alternate oxidizing and hydrogenating the anthraquinones or derivatives in a working solution of organic solvents, where the working solution and gaseous hydrogen are brought to flow through a bed of at least one structured catalyst.

The International Patent Application WO 97/43042 discloses catalyst compositions comprising a nanoparticulate catalytically active metal on a refractory support and a process for preparing the said compositions by the physical vapor deposition of the active metal by sputtering onto a refractory support which has been cooled such that the deposited metal atoms have limited mobility. Also, a process for the reduction of anthraquinones to anthrahydroquinones in the preparation of hydrogen peroxide by hydrogenation is disclosed, wherein the above catalyst is used as the hydrogenation catalyst to prepare hydrogen peroxide. The catalytically active metal, or combination of active metals, is selected from the group consisting of platinum, palladium, rhodium, iridium, ruthenium, silver, gold, copper, mercury and rhenium. Especially, the catalytically active metal is palladium, including combinations therewith. The refractory support is e.g. selected from the group consisting of alumina, (various forms), silica, titania, carbon (various forms), zirconia and magnesia. Especially, the refractory support is alumina, preferably gamma-alumina.

The International Patent Application WO 98/015350 A2 concerns hydrogenation catalysts with a palladium, platinum or rhodium base comprising at least one other metal M, deposited on silicon and zirconium oxide supports. The WO 98/015350 A2 also concerns the method for making these catalysts by successive impregnation of the support using palladium, platinum or rhodium

and another metal M. These catalysts may be used in hydrogenation reactions and particularly for preparing hydrogen peroxide. For example, such a catalyst can have a metal composition of 0.5-2.5 wt. % Pd and 0.5-2.5 wt. % Ag.

In the International Patent Application WO 2010/077262 A1 a catalyst comprising palladium and silver supported on an inorganic carrier is disclosed in the context of a process for regenerating a used catalyst comprising two or more noble metals supported on a carrier. Described noble metals include palladium, gold, silver, platinum, iridium, ruthenium, rhodium, osmium, rhenium, and mixtures thereof, and particularly the noble metals are Pd, Pt, Au, Ag, and mixtures thereof. Typically, the amount of noble metal present in the catalyst is in the range of from 0.005 to 20 weight percent (wt. %), e.g. in the range of from 0.01 to 5 wt. %. Catalysts comprising 0.001 to 2 wt. % palladium are disclosed. The catalyst comprises as a transition metal a group 3-12 element. The first row of them is from Sc to Zn. Particular transition metals are Pd, Pt, Au, Ag, Ni, Cu, Zn, Mn, Fe, Co, Pb, Ru, Rh, Re, Os, and especially the transition metals are Pt, Au, Ag, Cu, Ru, Rh, Re, and mixtures thereof. As preferred transition metals Ag, Au, and mixtures thereof are proposed. Typically, the amount of the transition metal present in the catalyst is in the range of from 0.01 to 20 wt. %, preferably 0.1 to 5 wt. %.

As stated already above, it is known to use aluminium oxide (Al_2O_3) supported palladium catalyst in the synthesis of hydrogen peroxide. Commonly, such alumina support is a gamma-aluminium oxide (gamma-alumina, gamma-Al_2O_3). The standard synthesis of hydrogen peroxide is an auto-oxidation (AO) process is a cyclic process for the production of hydrogen peroxide based on three basic steps : catalytic hydrogenation of active anthraquinone species solvated in organic media, oxidation and then separation (liquid-liquid extraction) of hydrogen peroxide from organic phase. Typically, ethyl or amyl anthraquinone are used. For the sake of clarity, anthraquinone in the following text states for alkyl anthraquinone derivative. Industrial synthesis of hydrogen peroxide is predominantly achieved by using the Riedel-Pfleiderer process (originally disclosed in US patents 2,158,525 and 2,215,883). This well-known large scale cyclic production process of hydrogen peroxide makes use of the autoxidation of a 2-alkylanthrahydroquinone compound to the corresponding 2-alkylanthraquinone which results in the formation of hydrogen peroxide.

Such AO-processes based on the original Riedel-Pfleiderer concept are designed for the industrial large-scale and even up to mega-scale production of

hydrogen peroxide, and have been widely described in the art and are well-known as large-to-mega scale manufacturing processes. Thus, conventional hydrogen peroxide production processes are normally carried out in large- to mega-scale hydrogen peroxide production plants with production capacities of about 40,000 to 330,000 (metric) tons per annum of hydrogen peroxide (100 %) per year. Thus, currently there are plants in industrial operation with a production capacity of e.g. 40 to 50 ktpa (kilo tons per annum) at the low end, with a capacity of up to 160 ktpa, and the world largest mega-plants provide a capacity of 230 ktpa (Antwerp) and 330 ktpa (Thailand). In these processes, normally the production capacity in case of fixed beds is limited to 50 ktpa and usually plants with production capacities above 50 ktpa are operated with fluid-bed reactors.

Today, there is also an interest in smaller size AO-processes (mini-AO processes) with production capacities for example in the range of 3 to 10 kt/a (calculated as 100 % hydrogen peroxide) production unit, which may be installed on customer site and provides a simple low-productivity and user-friendly plant. Although, hydrogenation catalysts know from the classical large-to-mega scale AO-processes can be used also in such smaller size AO-processes (mini-AO processes), there is a need to adapt and optimize the hydrogenation catalyst for the purpose of such a smaller size AO-processes (mini-AO processes) for the synthesis of hydrogen peroxide (H_2O_2). On the other hand, such optimized catalysts could also provide advantages in a classical large-to-mega scale AO-process. As an example, but without limitation, such desired advantages can pertain to high and stable catalytic activity, the selectivity of the catalyst in terms of in terms of anthraquinone derivative degradation, meaning less over-hydrogenation, i.e. limited formation of tetrahydro species and derivatives of the anthraquinone, and to the long-term stability of the catalyst, i.e. the thermodynamic stability or reduced leaching of the catalytic metal (palladium).

The object of the present invention is to provide other hydrogenation catalysts which exhibit a high and stable catalytic activity.

Another object of the present invention is to provide hydrogenation catalysts which exhibit a high catalytic selectivity. Thus, the catalysts according to the invention, when they are used for the synthesis of hydrogen peroxide by the AO process (auto-oxidation process), limit the formation of decomposition products.

Yet another object of the present invention is to provide hydrogenation catalysts which are suitable for being used in the synthesis of hydrogen peroxide by smaller size AO-processes (mini-AO processes).

To this end, the invention relates to hydrogenation catalysts based on palladium which is deposited on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support and which also contains a small amount of silver as an additive metal compound.

The invention also relates to the process for the manufacture of these catalysts and to the use of these catalysts in hydrogenation reactions and in particular in preparing hydrogen peroxide, e.g. in preparing hydrogen peroxide by the AO process (auto-oxidation process) and preferably in the synthesis of hydrogen peroxide by smaller size AO-processes (mini-AO processes).

Brief Description of the Figures :

Fig. 1 : Batch test of the Pd/SiO_2 ; e.g. hydrogen uptake Nl H2*kg-1 ws versus time (min.).

Fig. 2 : Batch test of the $AgPd/SiO_2$ via impregnation ; e.g. hydrogen uptake Nl H2*kg-1 ws ; (ws = working solution) versus time (min.)

Fig. 3 : ATQ formation (g/kg ws) versus produced hydrogen peroxide (g/kg ws)

Fig. 4 : AA formation (g/kg ws) versus produced hydrogen peroxide (g/kg ws)

Fig. 5 : AO formation (g/kg ws) versus produced hydrogen peroxide (g/kg ws)

The meanings of the abbreviations used in the Figures are the following : "ws" means "working solution" ; "ATQ" means "amyl tetrahydro anthraquinone" ;"AA" means "amyl anthrone" or shortly "anthrone" ;"AO" means "amyl oxanthrone" or shortly "oxanthrone" ; "Nl herein means "normal liter".

In a first embodiment of the invention, the catalysts comprise, on the one hand, a defined amount of palladium and, on the other hand, a defined amount of silver on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support. Beneficial results have been obtained by combining palladium and silver on such supports. The catalysts of the first embodiment of the invention is therefore a hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst and an amount of silver 0.1 to 0.5 % by weight with respect to the weight of the catalyst.

In a preferred embodiment of the invention, the catalysts additionally comprise a very small amount of gold. The catalysts of this preferred embodiment of the invention is therefore a hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst and an amount of silver 0.1 to 0.5 % by weight with respect to the weight of the catalyst, and wherein the catalyst further comprises gold in an amount of up to 0.1 % by weight with respect to the weight of the catalyst.

These catalysts, preferably those containing additionally a very small amount of gold, are particularly suitable for being used in the synthesis of hydrogen peroxide by the AO process (auto-oxidation process), and preferably for being used in the synthesis of hydrogen peroxide by smaller size AO-processes (mini-AO processes).

The amount of palladium in the catalysts is advantageously in the range of 1.5 to 2.5 % by weight with respect to the total weight of the catalyst, that is to say of the combined metal compounds and support materials. In particular embodiments of the invention the catalysts comprises an amount of palladium from 1.8 to 2.2 % by weight with respect to the total weight of the catalyst, and in a preferred embodiment of the invention the catalysts comprises an amount of palladium from 1.9 to 2.1 % by weight with respect to the total weight of the catalyst. As an example, but without limitation, the catalytic metal palladium can be present in the catalyst in an amount of about 1.5 % by weight, about 1.6 % by weight, about 1.7 % by weight, about 1.8 % by weight, about 1.9 % by weight, about 2.0 % by weight, about 2.1 % by weight, about 2.2 % by weight, about 2.3 % by weight, about 2.4 % by weight, or about 2.5 % by weight ; each amount in % by weight being recited here before with respect to the total weight of the catalyst.

In a very preferred embodiment of the invention the catalyst comprises palladium in an amount from 1.9 to 2.1 % by weight, and most preferred in amount of about 2.0 % by weight, with respect to the weight of the catalyst. As an example, but without limitation, the catalytic metal palladium can be present in these preferred catalysts in an amount of about 1.95 % by weight, about 2.0 % by weight, about 2.05 % by weight, or about 2.1 % by weight ; each amount in % by weight being recited here before with respect to the total weight of the catalyst.

The meaning of the term "about" is that the amount of palladium in the fresh catalyst may somewhat vary around the given values by e.g. up to +/- 0.1 % by weight, preferably up to +/- 0.05 % by weight with respect to the total weight of the catalyst. Thus, for example, a catalyst with an amount of 2 % (2.0 %) by weight may slightly vary in the exact amount of palladium such as 2 % (2.0 %) +/- 0.1 % by weight, preferably such as 2 % (2.0 %) +/- 0.05 % by weight, each with respect to the total weight of the catalyst.

The catalyst of the invention contains as additional catalytic metal silver in a defined amount. The amount of silver in the catalysts is advantageously in the range of 0.1 to 0.5 % by weight with respect to the total weight of the catalyst, that is to say of the combined metal compounds and support materials. In particular embodiments of the invention the catalysts comprises an amount of silver from 0.2 to 0.4 % by weight with respect to the total weight of the catalyst, and in a preferred embodiment of the invention the catalysts comprises an amount of silver from 0.25 to 0.35 % by weight with respect to the total weight of the catalyst. As an example, but without limitation, the additional catalytic metal silver can be present in the catalyst in an amount of about 0.2 % by weight, about 0.25 % by weight, about 0.26 % by weight, about 0.27 % by weight, about 0.28 % by weight, about 0.29 % by weight, about 0.30 % by weight, about 0.31 % by weight, about 0.32 % by weight, about 0.33 % by weight, about 0.34 % by weight, or about 0.35 % by weight ; each amount in % by weight being recited here before with respect to the total weight of the catalyst.

In a very preferred embodiment of the invention the catalyst comprises silver in an amount from 0.28 to 0.32 % by weight, more preferred in amount of 0.29 to 0.31 % and most preferred in amount of about 0.3 % by weight, with respect to the weight of the catalyst. As an example, but without limitation, the additional catalytic metal silver can be present in these preferred catalysts in an amount of about 0.28 % by weight, about 0.29 % by weight, about 0.30 % by weight, about 0.31 % by weight, or about 0.32 % by weight ; each amount in % by weight being recited here before with respect to the total weight of the catalyst.

The meaning of the term "about" is that the amount of silver in the fresh catalyst may somewhat vary around the given values by e.g. up to +/- 0.02 % by weight, preferably up to +/- 0.01 % by weight with respect to the total weight of the catalyst. Thus, for example, a catalyst with an amount of 0.3 % (0.30 %) by weight may slightly vary in the exact amount of silver such as 0.3 % (0.30 %)

+/- 0.02 % by weight, preferably such as 0.3 % (0.30 %) +/- 0.01 % by weight, each with respect to the total weight of the catalyst.

The very preferred catalysts of the invention contain as a further catalytic metal gold in a defined small amount. The amount of gold in the catalysts is advantageously in the range of 0.01 to 0.1 % by weight with respect to the total weight of the catalyst, that is to say, of the combined metal compounds and support materials. In particular embodiments of the invention the catalysts comprises an amount of gold from 0.04 to 0.06 % by weight with respect to the total weight of the catalyst, and in a preferred embodiment of the invention the catalysts comprises an amount of gold from 0.045 to 0.055 % by weight with respect to the total weight of the catalyst. As an example, but without limitation, the additional catalytic metal gold can be present in the catalyst in an amount of about 0.01 % by weight, about 0.02 % by weight, about 0.03 % by weight, about 0.04 % by weight, about 0.05 % by weight, about 0.06 % by weight, about 0.07 % by weight, about 0.08 % by weight, about 0.09 % by weight, or about 0.1 % by weight ; each amount in % by weight being recited here before with respect to the total weight of the catalyst.

In a very preferred embodiment of the invention the catalyst comprises gold in an amount from 0.045 to 0.055 % by weight, more preferred in amount of 0.048 to 0.052 % and most preferred in amount of about 0.05 % by weight, with respect to the weight of the catalyst. As an example, but without limitation, the additional catalytic metal gold can be present in these preferred catalysts in an amount of about 0.045 % by weight, about 0.046 % by weight, about 0.047 % by weight, about 0.048 % by weight, about 0.049 % by weight, about 0.050 % by weight, about 0.051 % by weight, or about 0.052 % by weight ; each amount in % by weight being recited here before with respect to the total weight of the catalyst.

The meaning of the term “about” is that the amount of gold in the fresh catalyst may somewhat vary around the given values by e.g. up to +/- 0.002 % by weight, preferably up to +/- 0.001 % by weight with respect to the total weight of the catalyst. Thus, for example, a catalyst with an amount of 0.05 % (0.050 %) by weight may slightly vary in the exact amount of gold such as 0.05 % (0.050 %) +/- 0.002 % by weight, preferably such as 0.05 % (0.050 %) +/- 0.001 % by weight, each with respect to the total weight of the catalyst.

Typically, the hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst ; silver from 0.1 to 0.5 % by weight with respect to the weight of the catalyst ; and preferably further an optional small amount of gold of up to 0.1 % by weight, more preferably an amount of gold of 0.01 to 0.1 % by weight with respect to the weight of the catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support from 97.0 to 98,4 % by weight with respect to the weight of the catalyst if no gold is present, or preferably from 96.9 to 98,39 % by weight with respect to the weight of the catalyst if gold is present. Particularly, if gold is present, the hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst ; silver from 0.1 to 0.5 % by weight with respect to the weight of the catalyst ; and gold in an amount of 0.01 to 0.1 % by weight with respect to the weight of the catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support from 96.9 to 98.39 % by weight with respect to the weight of the catalyst. The given amounts of the metals palladium, silver and gold in % by weight may take the ranges or individual amounts as stated above for each of the metals.

Therefore, typical hydrogenation catalyst compositions based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : from 15 to 25 g of palladium per kg of catalyst ; from 1 to 5 g of silver per kg of catalyst ; and preferably further an optional small amount of gold of up to 1 g of per kg of catalyst, more preferably an amount of gold of 0.1 to 1 g of per kg of catalyst ; and in case of no presence of the optional gold from 984 to 970 g of the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst, and in case gold is present from 983.39 to 969.0 g of the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst. Particularly, if gold is present, typical hydrogenation catalyst compositions based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist

of : from 15 to 25 g of palladium per kg of catalyst ; from 1 to 5 g of silver per kg of catalyst ; and gold in an amount of 0.1 to 1 g of per kg of catalyst ; and from 983.9 to 969.0 g of the silicon oxide (SiO2), an aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst.

Preferred typical hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : palladium from 1.8 to 2.2 % by weight with respect to the weight of the catalyst ; silver from 0.2 to 0.4 % by weight with respect to the weight of the catalyst ; and preferably further an optional small amount of gold of 0.04 to 0.06 % by weight with respect to the weight of the catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support from 98.0 to 97.4 % by weight with respect to the weight of the catalyst if no gold is present, and preferably from 97.96 to 97.34 % by weight with respect to the weight of the catalyst if gold is present. The given amounts of the metals palladium, silver and gold in % by weight may take the ranges or individual amounts as stated above for each of the metals. Therefore, typical hydrogenation catalyst compositions based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : from 18 to 22 g of palladium per kg of catalyst ; from 2 to 4 g of silver per kg of catalyst ; and gold in an amount of 0.4 to 0.6 g of gold per kg of catalyst ; and from 980.0 to 974.0 g of the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst if no gold is present, and preferably from 979.6 to 973.4 g of the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst if gold is present.

In particular, the preferred typical hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : palladium from 1.9 to 2.1 % by weight with respect to the weight of the catalyst ; silver from 0.25 to 0.35 % by weight with respect to the weight of the catalyst ; and preferably further an optional small amount of gold of 0.045 to 0.055 % by weight with respect to the weight of the catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support from 97.85 to 97.55 % by weight with respect to the weight of the catalyst if no gold is present, and preferably the silicon

oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support from 97.805 to 97.495 % by weight with respect to the weight of the catalyst if gold is present. The given amounts of the metals palladium, silver and gold in % by weight may take the ranges or individual amounts as stated above for each of the metals. Therefore, typical hydrogenation catalyst compositions based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : from 19 to 21 g of palladium per kg of catalyst ; from 2.5 to 3.5 g of silver per kg of catalyst ; and gold in an amount of 0.45 to 0.55 g of per kg of catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support from 978.5 to 975.5 g by weight with respect to the weight of the catalyst if no gold is present, and preferably from 978.05 to 974.95 g of the silicon oxide (SiO_2),an aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst if gold is present.

A most preferred hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprises, and preferably essentially consists of : palladium of about 2 % (2.0 %) by weight with respect to the weight of the catalyst ; silver of about 0.3 % by weight with respect to the weight of the catalyst ; gold of about 0.05 % by weight with respect to the weight of the catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support of about 97.7 % by weight with respect to the weight of the catalyst if no gold is present, and preferably the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support of about 97.65 % by weight with respect to the weight of the catalyst if gold is present. The meaning of the term “about” is that the amount of palladium, silver and gold in the fresh catalyst may somewhat vary around the given values as indicated above for each of the metals. Consequently, the most preferred hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprises, and preferably essentially consists of : palladium in an amount of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight, with respect to the weight of the catalyst ; silver in an amount of 0.3 % (0.30 %) +/- 0.02 % by weight, preferably in an amount of 0.3 % (0.30 %) +/- 0.01 % by weight, with respect to the weight of the catalyst ; gold in an amount of 0.05 % (0.050 %) +/- 0.002 % by weight,

preferably such as 0.05 % (0.050 %) +/- 0.001 % by weight, with respect to the weight of the catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support in an amount to add up to 100 % by weight for the total catalyst ; for example, in case of Pd varying by +/- 0.1 % (preferably by +/- 0.05 %) and Ag by +/- 0.02 % (preferably by +/- 0.01 %), then if no gold is present the support is accounting for 97.7 % (97.70 %) +/- 0.12 % (preferably +/- 0.06 %) by weight with respect to the weight of the catalyst, and if preferably gold is present and varying by +/- 0.002 % (preferably by +/- 0.001 %) then the support is preferably accounting for 97.65 % (97.650 %) +/- 0.122 % (preferably +/- 0.061 %) by weight with respect to the weight of the catalyst.

Therefore, expressed in g per kg catalyst, the most preferred hydrogenation catalyst compositions based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprise, and preferably essentially consist of : about 20 g of palladium per kg of catalyst ; about 3.0 g of silver per kg of catalyst ; and gold in an amount of about 0.5 g of per kg of catalyst ; and about 977.0 g of the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst if no gold is present, and preferably about 976.5 g of the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support per kg of catalyst if gold is present. The meaning of the term “about” is that the g amount of palladium, silver and gold in the fresh catalyst may somewhat vary around the given g values, analogously as indicated above for each of the metals for the % by weight values. Thus, such a most preferred hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention comprises, and preferably essentially consists of : 20 g (20.0 g) +/- 0.1 g palladium per kg of catalyst, preferably 20 g (20.0 g) +/- 0.05 g of palladium per kg of catalyst ; 3 g (3.0 g) +/- 0.02 g of silver per kg of catalyst, preferably 3 g (3.0 g) +/- 0.01 g of silver per kg of catalyst ; 0.05 g (0.050 g) +/- 0.002 g of gold per kg of catalyst, preferably 0.05 g (0.050 g) +/- 0.001 g of gold per kg of catalyst ; and the silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support in an amount to add up to 1 kg for the total catalyst ; for example, in case of Pd varying by +/- 0.1 g (preferably by +/- 0.05 g) and Ag by +/- 0.02 g (preferably by +/- 0.01 g), then if no gold is present the support is accounting for 977.0 g (977.00 g) +/- 0.12 g (preferably +/- 0.06 g) per kg of catalyst, and if

preferably gold is present and varying by +/- 0.002 g (preferably by +/- 0.001 g) then the support is preferably accounting for 976.5 % (976.50 %) +/- 0.122 g (preferably +/- 0.061 g) per kg of catalyst.

In the catalysts according to the invention as described above, the palladium, silver and/or gold can be in the elemental state or in the form of a compound, such as a salt or an oxide. The catalysts preferably comprise palladium, silver and gold in the elemental state.

The support of the catalysts according to the invention is a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate. In a variant the hydrogenation catalyst support in the present invention is silicon oxide (SiO_2). In another variant the hydrogenation catalyst support in the present invention is silicon oxide (SiO_2) comprising aluminium oxide (Al_2O_3, extra-framework aluminium) and/or intra-framework aluminium. Typically in the art gamma-aluminium oxide (gamma-Al_2O_3) or delta-alumina (delta-Al_2O_3) or a mixture of both gamma and delta alumina are used as a catalyst support. Thus, the aluminium oxide (Al_2O_3) comprised in the silicon oxide (SiO_2) may be such gamma-aluminium oxide (gamma-Al_2O_3), delta alumina (delta-Al_2O_3) or a mixture of both delta and gamma alumina. In still another variant the hydrogenation catalyst support in the present invention is aluminium oxide (Al_2O_3). As mentioned in the art typically gamma-aluminium oxide (gamma-Al_2O_3) or delta-alumina (delta-Al_2O_3) or a mixture of both gamma and delta alumina are used as a catalyst support. Thus, the aluminium oxide (Al_2O_3) support may be a gamma-aluminium oxide (gamma-Al_2O_3) or delta-alumina (delta-Al_2O_3) or a mixture of both gamma and delta alumina.

The catalyst support in the present invention, e.g. the silicon oxide (SiO_2), the silicon oxide (SiO_2) comprising aluminium oxide (Al_2O_3, extra-framework aluminium) and/or intra-framework aluminium, or the aluminium oxide, can be in a crystalline, partially crystalline, amorphous or partially amorphous form. The catalyst support is advantageously amorphous. If the catalyst support is a composition of silicon oxide (SiO_2) and aluminium oxide (Al_2O_3), then preferably it exhibits a homogeneous distribution between the silicon oxide (SiO_2) and the aluminium oxide (Al_2O_3), resulting into an aluminosilicate support. The skilled person knows how to provide the required support materials as this is well established in the art.

The term "homogeneous distribution between the silicon oxide (SiO_2) and aluminium oxide (Al_2O_3)" is understood to mean a distribution such that the

aluminium is atomically dispersed into the whole silica framework (intra-framework aluminium species) in such extent that first ; the Nuclear Magnetic Resonance of the aluminium, spinning at the magical angle (^{27}Al MAS-NMR), provides one major signal located between 45 to 70 ppm, attributed to tetrahedral intra-framework aluminium species. Preferably, a single signal located between 45 to 70 ppm should be obtained. Secondly, the experimental Si/Al ratio, measured by X-ray photoelectron spectroscopy (XPS), does not differ by more than 20 % from the theoretical Si/Al ratio drawn up by calculation on the basis of the chemical composition of the support. The supports in which the difference between the experimental Si/Al ratio, measured by XPS, and the theoretical Si/Al ratio does not exceed 10 % are very particularly preferred.

The size of the catalyst support is not critical to the practice of the invention but may be important in the subsequent use of the catalyst. In gas phase reactions and in fixed bed reactors, a suitable support size would generally be about 2-3 mm in diameter as spherical or cylindrical shapes. For slurry liquid phase reactions, a suitable support size would generally have a mean particle diameter of about 40 to about 250 microns depending on substrate density. Preferably, the standard particle size distribution for the slurry type catalyst is adjusted such that 99 % of the particles are ranging from 63 μm to 250μm.

The above mentioned metallic composition ranges for the catalysts of the present invention, e.g. any possible option and preferred variant regarding ranges or amounts of the catalytic metals palladium, silver and gold, individually, are very suitable for embodiments as slurry catalysts.

The hydrogenation catalysts according to the present invention provide several advantages.

In a first aspect an advantageous high selectivity catalyst of combined catalytic metals Pd+Ag, and preferably Pd+Ag+Au, on SiO_2 is provided which is particularly suitable for the production of hydrogen peroxide by the AO-processes. The catalyst may be well employed in large-to-mega scale AO-processes, but preferably is suitable for small-to-medium scale, in particular for mini-AO scale processes. Typically, a small-to-medium scale AO-process (mini-AO process) is run with a capacity of up to 20 ktpa, preferably with a capacity of up to 10 ktpa, (as 100 %) hydrogen peroxide production, and most preferably 2 to 10 ktpa (as 100 %) hydrogen peroxide production. Laboratory trials have been carries out. Preferred operating conditions of the hydrogenator (lowest degradation) have been identified in the case of fixed bed operation and

slurry hydrogenators which both may be industrially operated with the catalyst according to the invention.

Compared to the standard AO-process catalyst (Pd on alumina (Al_2O_3) or silica (SiO_2) modified alumina), the new catalyst (Pd and Ag alloy on SiO_2) – with an example for a best composition : 2 % Pd + 0.3 % Ag on SiO_2, allows achieving much higher selectivity in terms of anthraquinone derivative degradation (typically, ethyl or amyl anthraquinone are used ; for the sake of clarity, anthraquinone in the following text states for alkyl anthraquinone derivative), e.g. that is to say, lower anthrone and tetrahydroanthraquinone levels. This implies lower need for regeneration of the working solution and lower anthraquinone consumption and is directly beneficial for the economy of the process.

Long term stability of the Pd and Ag alloy on SiO_2 catalyst is favorable. It can be increased by adding gold as the third metal, with an example for a best composition : 2 % Pd + 0.3 % Ag +0.05 % Au on SiO_2. Catalyst activity for anthraquinone hydrogenation is somewhat decreased for such a gold comprising catalyst, but its selectivity remains high. Such a catalyst of e.g. 2 % Pd + 0.3 % Ag + 0.05 % Au on SiO_2 is stable on longer term.

As described before, the hydrogenation catalyst based on palladium according to the present invention comprise the catalytic metal or combination of catalytic metals as defined above on a silicon oxide (SiO_2) support. According to the invention the catalyst based on palladium may be also on an aluminium oxide (Al_2O_3) support or on a silicon oxide (SiO_2) support which may additionally comprise aluminium oxide (Al_2O_3) and/or intra-framework aluminium. Thus, in a preferred embodiment of the invention, the support is silicon oxide (SiO_2) comprising aluminium oxide (Al_2O_3), e.g. such as a gamma-aluminium oxide (gamma-Al_2O_3), preferably a delta-aluminium oxide (delta-Al_2O_3) or a mixture of both gamma- and delta-aluminium oxide, and/or intra-framework aluminium species in an amount ranging from 1 to 99 % Al_2O_3 by weight, and preferably in an amount ranging from 15 to 25 % Al_2O_3 by weight.

The before explained advantages of the hydrogenation catalysts may be further enhanced when using a theta-aluminium oxide (theta-Al_2O_3), delta-aluminium oxide (delta-Al_2O_3), a gamma-aluminium oxide (gamma-Al_2O_3), a mixture of both delta and gamma phases, a mixture of both theta and delta phases and an alpha-aluminium oxide (alpha-Al_2O_3) as a component of the

catalyst support. Therefore, in a second embodiment the invention relates to hydrogenation catalysts that comprise delta-aluminium oxide (delta-Al_2O_3), a theta-aluminium oxide (theta-Al_2O_3), a gamma-aluminium oxide (gamma-Al_2O_3), a mixture of both delta and gamma phases, a mixture of both theta and delta phases or an alpha-aluminium oxide (alpha-Al_2O_3) as a component of the catalyst support. The theta-aluminium oxide (theta-Al_2O_3), the gamma-aluminium oxide (gamma-Al_2O_3), the mixture of both delta and gamma phases or the mixture of both theta and delta phases can be added as a component to a, e.g. conventional, silicon oxide (SiO_2) support in an amount ranging from 1 to 99 % Al_2O_3 by weight, and preferably 15 to 25 % Al_2O_3 by weight. In a particular embodiment the invention relates to hydrogenation catalysts that comprise delta-aluminium oxide (delta-Al_2O_3) as a component of the catalyst support, wherein for example delta phases can be added as a component to a, e.g. conventional, silicon oxide (SiO_2) support in an amount ranging from 1 to 99 % Al_2O_3 by weight, and preferably 15 to 25 % Al_2O_3 by weight.

In another variant of this embodiment of the invention the hydrogenation catalyst based on palladium on an aluminosilicate support resulting from the homogeneous distribution between the silicon oxide (SiO_2) and the aluminium oxide (Al_2O_3).

In a preferred variant of this embodiment of the invention the hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support is a catalyst, wherein the support is aluminium oxide (Al_2O_3), most preferably a delta-aluminium oxide (delta-Al_2O_3).

Particularly, the hydrogenation catalyst according to the invention is a catalyst based on palladium and silver, and optionally gold, deposited on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support. In case of the present invention, the hydrogenation catalyst is preferably an eggshell dispersion of Pd on the catalyst support, that is to say that Pd is dispersed in the outer layer of the support particle, with no internal diffusion.

The hydrogenation catalysts according to the present invention comprising silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate as support provide several advantages. For example in one aspect of the invention an advantageous high selectivity catalyst comprising or having silicon oxide SiO_2 (a beneficial support regarding selectivity) is provided. Silicon

oxide SiO_2 is observed to provide the most selective catalysts. Thus, compared to the standard AO-process catalyst Pd on alumina (Al_2O_3, typically gamma-Al_2O_3) or silica (SiO_2) modified alumina, the new catalyst comprising Pd supported on SiO_2 as described above or supported on delta-Al_2O_3 in the alternative embodiment of the invention allows achieving much higher selectivity in terms of anthraquinone derivative degradation. Furthermore, for example, hydrogenation catalysts of the present invention, wherein the Pd is deposited on a support comprising delta-Al_2O_3 has several further advantages : low Pd leaching, which is significantly improved even over Pd catalysts supported only on SiO_2 ; and a higher activity.

A particular advantage of hydrogenation catalysts according to the present invention which comprise alumina in the support (with Pd) is its ability to further reduce ATEQ (amyl tetrahydro epoxy anthraquinone) to ATHQ (amyl tetrahydro hydroxyl anthraquinone), which could be considered as a part of a reversion process. This is an additional benefit of the invention when using Pd as catalyst supported (in addition) on Al_2O_3 compared to Pd on only SiO_2. Therefore, the presence of Al_2O_3 as support allows for auxiliary solid state reversion, because Al_2O_3 is typically used as solid state reversion agent in the AO-process for the manufacture of H_2O_2.

The binary and ternary catalysts according to the invention are generally prepared depositing the catalytic metals, e.g. in the context of this invention the palladium (Pd), the silver (Ag) and the optional gold (Au) by simultaneous or subsequent impregnation and/or precipitation of different metals, for example, first depositing the Pd, then Ag and thereafter optionally Au.

The invention also is directed to a process for the manufacture of hydrogenation catalysts according to the invention, as described above, based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support, wherein the catalyst comprises palladium and silver, and wherein the catalyst preferably further comprises gold, the process comprising simultaneously or successively impregnating and/or precipitating the required amount by weight with respect to the total weight of the catalyst of palladium, silver, and preferably further gold, on the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or on an aluminosilicate support. Thus, a catalyst is prepared which comprises an amount of palladium in % by weight with respect to the weight of the catalyst and an amount of silver in % by weight with respect to the weight of the catalyst, and wherein the catalyst preferably optionally further

comprises an amount of gold in % by weight with respect to the weight of the catalyst on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support.

The hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support according to the present invention can be prepared by the usual techniques, such as, for example by co-impregnation of the metals on the support, by co-precipitation of the metals on the support or by simultaneous or successive depositions of the metals on the support, for example, by impregnation and/or precipitation. The catalysts according to the invention are advantageously prepared by successive depositions of the metals palladium, silver and optionally gold in any order on a silicon oxide (SiO_2), on an aluminium oxide (Al_2O_3) or on an aluminosilicate support by impregnation and/or precipitation.

Preferably, the support is first impregnated with the palladium, then silver and subsequently with the optional metal gold. The support can be impregnated using organic or inorganic solutions comprising respectively an organic or an inorganic precursor of the metal constituents of the catalyst. The impregnation solutions are preferably aqueous inorganic solutions of metallic salts. The salts used to this end are in particular chlorides, nitrates, acetates or ammoniacal complexes.

The silver is preferably deposited by impregnation of a Pd/SiO_2, a $Pd/SiO_2/Al_2O_3$ or a Pd/Al_2O_3 with a solution comprising the silver constituent under a reducing atmosphere, such as, for example, a hydrogen atmosphere. The deposition of the silver by reduction with hydrogen or by any other form of reduction also results in the further reduction of the palladium. The catalysts can subsequently be filtered off, washed and dried. Thus, the $Pd.Ag/SiO_2$, the $Pd.Ag/SiO_2/Al_2O_3$ or the $Pd.Ag/Al_2O_3$ catalysts can be prepared by suspending a Pd/SiO_2, a $Pd/SiO_2/Al_2O_3$ or a Pd/Al_2O_3 catalyst in an $AgNO_3$ solution and by reducing the metals by sparging with hydrogen.

The silver is more preferably deposited by the precipitation of a silver salt in a suspension of an alkali impregnated Pd/SiO_2, a $Pd/SiO_2/Al_2O_3$ or a Pd/Al_2O_3 catalyst. The catalysts can subsequently be filtered off, washed, dried and reduced. Thus, the $Pd.Ag/SiO_2$, the $Pd.Ag/SiO_2/Al_2O_3$ or the $Pd.Ag/Al_2O_3$ catalysts can be prepared by suspending a Pd/SiO_2, a $Pd/SiO_2/Al_2O_3$ or a Pd/Al_2O_3 catalyst in an NaOH solution, by successively precipitating the $AgNO_3$ solution on the catalysts, and by calcinating it in a H_2 atmosphere.

The respective catalysts with gold as further catalytic component can be prepared in the following way. The gold is preferably deposited by impregnation of a Pd.Ag/SiO_2, a Pd.Ag/SiO_2/Al_2O_3 or a Pd.Ag/Al_2O_3 with a solution comprising the gold constituent under a reducing atmosphere, such as, for example, a hydrogen atmosphere. The catalysts can subsequently be filtered off, washed and dried. Thus, the Pd.Ag/SiO_2, the Pd.Ag/SiO_2/Al_2O_3 or the Pd.Ag/Al_2O_3 catalysts can be prepared by suspending a Pd.Ag/SiO_2, a Pd.Ag/SiO_2/Al_2O_3 or a Pd.Ag/Al_2O_3 catalyst in a $HAuCl_4$ solution and by reducing the metals by sparging with hydrogen.

The gold is more preferably deposited by the precipitation of an aurous salt in a suspension of an alkali impregnated Pd.Ag/SiO_2, a Pd.Ag/SiO_2/Al_2O_3 or a Pd.Ag/Al_2O_3 catalyst. The catalysts can subsequently be filtered off, washed, dried and reduced. Thus, the Pd.Ag.Au/SiO_2, the Pd.Ag.Au/SiO_2/Al_2O_3 or the Pd.Ag.Au/Al_2O_3 catalysts can be prepared by suspending a Pd.Ag/SiO_2, a Pd.Ag/SiO_2/Al_2O_3 or a Pd.Ag/Al_2O_3 catalyst in an NaOH solution, by successively precipitating the $HAuCl_4$ solution on the catalysts, and by calcinating it in a H_2 atmosphere.

Thus, the present invention also relates to a process for the manufacture of hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3), or an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst and an amount of silver 0.1 to 0.5 % by weight with respect to the weight of the catalyst, and wherein the catalyst preferably further comprises gold in an amount of up to 0.1 % by weight with respect to the weight of the catalyst, the process comprising successively impregnating the palladium, silver, and preferably further gold, on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3), or an aluminosilicate support. The preferred embodiments of hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support can be prepared in the same manner by simply applying in the process for the manufacture of hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support the respective amounts of palladium, silver and optionally for preferred hydrogenation catalysts gold selected from the ranges or values described above in the context of the hydrogenation catalyst compositions. Thus, as an example, but without limiting, the invention relates to a process for the manufacture of hydrogenation catalysts based on palladium on a

silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.9 to 2.1 % by weight with respect to the weight of the catalyst and an amount of silver 0.25 to 0.35 % by weight with respect to the weight of the catalyst, and wherein the catalyst preferably further comprises gold in an amount of 0.045 to 0.055 % by weight with respect to the weight of the catalyst, the process comprising successively impregnating the palladium, silver, and preferably further gold, on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support. As a further example, again without limiting, the invention relates to a process for the manufacture of hydrogenation catalysts based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support, wherein the catalyst comprises an amount of palladium of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight, and an amount of silver of 0.3 % (0.30 %) +/- 0.02 % by weight, preferably in an amount of 0.3 % (0.30 %) +/- 0.01 % by weight with respect to the weight of the catalyst, and wherein the catalyst preferably further comprises gold in an amount of 0.05 % (0.050 %) +/- 0.002 % by weight, preferably such as 0.05 % (0.050 %) +/- 0.001 % by weight, with respect to the weight of the catalyst, the process comprising successively impregnating the palladium, silver, and preferably further gold, on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support. As described above, the support material can be a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or an aluminosilicate. According to the variants described above the support is silicon oxide (SiO_2), is a silicon oxide (SiO_2) comprising only or a certain amount of intra-framework aluminium (aluminosilicate), is a silicon oxide (SiO_2) comprising extra-framework aluminium oxide (Al_2O_3), e.g. as typically in the art a gamma-aluminium oxide (gamma-Al_2O_3) ; or the support is aluminium oxide (Al_2O_3), e.g. as typically in the art a gamma-aluminium oxide (gamma-Al_2O_3) ; or the support is in a preferred embodiment a delta-aluminium oxide (delta-Al_2O_3) ; or the support is a mixture of said support materials.

The catalysts according to the present invention are suitable for all types of hydrogenation catalysis. The invention consequently also relates to their use in hydrogenation reactions. Mention may be made, as examples of hydrogenation reactions, of the hydrogenation of alkynes to alkenes, the hydrogenation of CO to methanol and the reduction of unsaturated aldehydes to unsaturated alcohols. The catalysts according to the invention are used with very good results in

processes for the manufacture of hydrogen peroxide. Consequently, the invention also relates to a process for the manufacture of hydrogen peroxide in the presence of catalyst according of the present invention. In principle, the catalyst of the present invention is suitable for any process of manufacturing hydrogen peroxide involving a catalytic hydrogenation.

In a particularly aspect the invention pertains to the use of a hydrogenation catalyst according to the invention, as described above, based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support, wherein the catalyst comprises palladium in any of the above indicated ranges or amounts and silver in any of the above indicated ranges or amounts, and wherein the catalyst preferably further comprises gold in any of the above indicated ranges or amounts, in a process for the manufacture of hydrogen peroxide. Preferably the hydrogenation catalyst according to the invention is used in a process for the manufacture of hydrogen peroxide by the autoxidation process (AO-process), more preferably in a small-to-medium scale AO-process (mini-AO process) which is run with a capacity of up to 20 ktpa, preferably with a capacity of up to 10 ktpa, (as 100 %) hydrogen peroxide production. In most preferred variants of this aspect of the invention the hydrogenation catalyst according to the invention is used in such of said processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process) which are run without a reversion unit for regenerating the working solution. This latter aspect of working without a reversion unit is described in more detail below in the context of the process for the manufacture of hydrogen peroxide comprising carrying out a hydrogenation reaction using a catalyst of the present invention. For more details about capacity or capacity ranges reference is made to the below described process for the manufacture of hydrogen peroxide using a hydrogenation catalyst of the present invention. These details about capacity or capacity ranges given for the process for the manufacture of hydrogen peroxide equally apply to the present variant of the invention of the use of a hydrogenation catalyst as described above. Furthermore, for any possible option and preferred variant regarding ranges or amounts of the catalytic metals palladium, silver and gold, as well as for the details about the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or aluminosilicate support and any composition, range or amount thereof, reference is made to the above described hydrogenation catalyst of the present invention. These details given above for the hydrogenation catalyst of

the present invention equally apply to the present aspect of the invention of using said hydrogenation catalyst of the invention.

Thus, the hydrogenation catalyst of the invention is particularly suitable for the manufacture of hydrogen peroxide by the AO-process wherein said process is a small to medium scale AO-process with a production capacity of hydrogen peroxide of up to 20 kilo tons per year (ktpa). Preferably said process is operated with a production capacity of hydrogen peroxide of up to 15 kilo tons per year (ktpa), and more preferably with a production capacity of hydrogen peroxide of up to 10 kilo tons per year (ktpa). The dimension ktpa (kilo tons per annum) relates to metric tons. Further, said small- to medium-scale hydrogen peroxide production process scale is referred herein as "mini-AO-process" when mentioned in the context of any aspect of the invention.

The process for the manufacture of hydrogen peroxide by an anthraquinone autoxidation process using the catalysts of the present invention may be a large-to-mega scale AO- processes, but preferably is a process for the manufacture of hydrogen peroxide by an anthraquinone autoxidation in small-to-medium scale, in particular a mini-AO scale processes. Typically, a mini-AO process is run with a capacity of 2 to 10 ktpa (as 100 %) hydrogen peroxide production. Laboratory trials have been carried out showing that the hydrogenation can be performed as fixed bed operation or in slurry hydrogenators, and that the process may be industrially operated with the hydrogenation catalyst according to the invention as well.

In a preferred aspect the invention also relates to a process for the manufacture of hydrogen peroxide using an anthraquinone autoxidation process (AO process) comprising carrying out a reaction using a catalyst based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support according to the invention, wherein the process is a small-to-medium scale AO-process (mini-AO process), preferably a mini-AO process which is run with a production capacity of, for example, 2 to 10 ktpa (as 100 %) hydrogen peroxide. In this AO-process, in particular in the mini-AO process, when catalysts in accordance with the present invention are used in the synthesis of hydrogen peroxide, a reduced rate of formation of the decomposition products of amylanthraquinone (AQ) and of amyltetrahydroanthraquinone (ATQ) is observed. In these AO-processes according to the invention the catalysts according to the invention as described above may be used in the general and in the preferred embodiments and the

respective compositions and/or respective supports. Particularly preferred are ternary catalysts with palladium, silver and gold as catalytic metals as described above in the respective compositions and on the respective, in particular preferred supports. In these AO-processes according to the invention the catalysts according to the invention as described above may be used on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support, preferably on a silicon oxide (SiO_2) support comprising aluminium oxide (Al_2O_3), and more preferably on a delta-aluminium oxide (delta-Al_2O_3).

More generally, in this aspect the invention pertains to a process for the manufacture of hydrogen peroxide comprising carrying out a hydrogenation reaction using a catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to any of the above described embodiments of the invention, wherein the catalyst comprises palladium in any of the above indicated ranges or amounts and silver in any of the above indicated ranges or amounts, and wherein the catalyst preferably further comprises gold in any of the above indicated ranges or amounts. Preferably, in this aspect of the invention relates to a process for the manufacture of hydrogen peroxide by the autoxidation process (AO-process), and in particular the invention relates to a small-to-medium scale AO-process (mini-AO process) which is run with a capacity of up to 20 ktpa, more preferably with a capacity of up to 10 ktpa, (as 100 %) hydrogen peroxide production. In most preferred variants of this aspect of the invention of processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process) said processes are run without a reversion unit for regenerating the working solution. This latter aspect of working without a reversion unit is described in more detail below.

In the embodiments of the invention relating to a small-to-medium scale AO-process (mini-AO process), as indicated herebefore, such processes are run with a capacity of up to 20 ktpa, more preferably with a capacity of up to 10 ktpa, (as 100 %) hydrogen peroxide production. Variants of this small-to-medium scale AO-process (mini-AO process) for the manufacture of hydrogen peroxide according to the invention are characterized in that the hydrogenation reaction using a catalyst based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or on an aluminosilicate support according to any of the above described embodiments of the hydrogenation catalyst according to the invention, are run as a small-to-medium scale AO-process (mini-AO process)

with a capacity in the range of 2 to 15 ktpa, preferably in the range of 2 to 10 ktpa, (as 100 %) hydrogen peroxide production. This small-to-medium scale AO-process (mini-AO process) with said capacity, in the more preferred variants, is also run without a reversion unit for regenerating the working solution.

In such mini-AO-process according to the invention may be designed in a flexible manner for a variety of any other ranges within said capacity scope, e.g. to provide a capacity which best fits to the local needs where the process is operated. Thus, as an example and without limitation, possible capacity ranges are from 2-5 ktpa, 2-6 ktpa, 2-7 ktpa, 2-8 ktpa, 2-9 ktpa, 2-10 ktpa, 2-11 ktpa, 2-12 ktpa, 2-13 ktpa, 2-14 ktpa, 2-15 ktpa ; 3-5 ktpa, 3-6 ktpa, 3-7 ktpa, 3-8 ktpa, 3-9 ktpa, 3-10 ktpa, 3-11 ktpa, 3-12 ktpa, 3-13 ktpa, 3-14 ktpa, 3-15 ktpa ; 4-5 ktpa, 4-6 ktpa, 4-7 ktpa, 4-8 ktpa, 4-9 ktpa, 4-10 ktpa, 4-11 ktpa, 4-12 ktpa, 4-13 ktpa, 4-14 ktpa, 4-15 ktpa ; 5-6 ktpa, 5-7 ktpa, 5-8 ktpa, 5-9 ktpa, 5-10 ktpa, 5-11 ktpa, 5-12 ktpa, 5-13 ktpa, 5-14 ktpa, 5-15 ktpa ; 6-7 ktpa, 6-8 ktpa, 6-9 ktpa, 6-10 ktpa, 6-11 ktpa, 6-12 ktpa, 6-13 ktpa, 6-14 ktpa, 6-15 ktpa ; 7-8 ktpa, 7-9 ktpa, 7-10 ktpa, 7-11 ktpa, 7-12 ktpa, 7-13 ktpa, 7-14 ktpa, 7-15 ktpa ; 8-9 ktpa, 8-10 ktpa, 8-11 ktpa, 8-12 ktpa, 8-13 ktpa, 8-14 ktpa, 8-15 ktpa ; 9-10 ktpa, 9-11 ktpa, 9-12 ktpa, 9-13 ktpa, 9-14 ktpa, 9-15 ktpa ; 10-11 ktpa, 10-12 ktpa, 10-13 ktpa, 10-14 ktpa, 10-15 ktpa ; 11-12 ktpa, 11-13 ktpa, 11-14 ktpa, 11-15 ktpa ; 12-13 ktpa, 12-14 ktpa, 12-15 ktpa ; 13-14 ktpa, 13-15 ktpa ; 14-15 ktpa.

In a preferred process for the manufacture of hydrogen peroxide by the AO-process according to the invention the process has a production capacity of hydrogen peroxide of 2,000 to 10,000 metric tons per year. Typically, the size of a plant for the manufacture of hydrogen peroxide depends on the production capacity. For example, within the preferred design range between 2 and 10 ktpa, a plant of 3 ktpa capacity will be much smaller than a 10 ktpa plant. Therefore, in a more preferred embodiment of the invention, e.g. for economic reasons, the design of the mini-AO-process pertains to manufacture of hydrogen peroxide by the AO-process or to mini-AO-plants with narrower capacity ranges, as for instance, 2-3 ktpa, 3-5 ktpa, 5-7.5 ktpa or 7.5-10 ktpa. Similarly, also for higher capacities the more narrow capacity ranges are preferred, as for instance, 10-12.5 ktpa, 12.5-15 ktpa.

The hydrogenation catalyst used in the processes according to the invention may comprise palladium in any of the above indicated ranges or

amounts and silver in any of the above indicated ranges or amounts, and the catalyst preferably may further comprise gold in any of the above indicated ranges or amounts. Thus, in an embodiment the invention also pertains to a process for the manufacture of hydrogen peroxide using an anthraquinone auto-oxidation process comprising carrying out a reaction using a catalyst based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst and an amount of silver 0.1 to 0.5 % by weight with respect to the weight of the catalyst, and wherein the catalyst preferably further comprises gold in an amount of up to 0.1 % by weight with respect to the weight of the catalyst. For any other possible option and preferred variant regarding ranges or amounts of the catalytic metals palladium, silver and gold, as well as for the details about the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or aluminosilicate support and any composition, range or amount thereof, reference is made to the above described hydrogenation catalyst of the present invention. These details given above for the hydrogenation catalyst of the present invention equally apply to the present aspect of the invention of the manufacture of hydrogen peroxide using said hydrogenation catalyst of the invention.

As mentioned above, the hydrogenation catalyst of the present invention is suitable for the use in processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process) which are run without a reversion unit for regenerating the working solution. Therefore, the hydrogenation catalyst of the present invention is beneficially used in a small to medium scale, also remotely controllable, process for the production of hydrogen peroxide, which process is feasible to be performed at a customer site, especially a remote (customer) site and thus is suitable for an end user friendly plant, which may also be remotely controlled from a different and even distant site, e.g. from a distant large-scale hydrogen peroxide production site, and which process stably runs for longer periods, e.g. for periods of at least several months, and at minimum for at least 3 months, in continuous operation with a minimum need of local (e.g. on customer site) technical and/or physical intervention, in particular with regard to the reversion of the working solution and/or the regeneration of the hydrogenation catalyst. The intermittent and/or periodical reversion of the working solution and/or the regeneration of the hydrogenation catalyst may be performed in various manners. For instance, normally the working solution

and/or the catalyst are removed together at the same time from the mini-AO reactor system or they are removed separately at different times, as appropriate according to the process parameters and the process efficiency related to either the working solution or the hydrogenation catalyst.

In this case of running the manufacture of hydrogen peroxide by the autoxidation process (AO-process) without a reversion unit, the working solution is regenerated in separate equipment for the reversion of the working compounds contained in the working solution. This reversion of the working solution may be performed, for instance, at a different site in the equipment of another hydrogen peroxide production plant, e.g. in the respective regeneration equipment of a similar or preferably a larger scale hydrogen peroxide production plant. Alternatively, the working solution may be regenerated in separate mobile regeneration equipment for the reversion of the working compounds contained in the working solution, e.g. in a mobile regeneration unit that is used on demand or as appropriate in a number of different locations where a small to medium hydrogen peroxide manufacturing process according to the AO-process is performed. Another option is to intermittently or periodically perform the regeneration of the working solution under particular conditions in the main equipment of the small to medium hydrogen peroxide manufacturing process according to the AO-process itself.

Similarly, as described above for the reversion of the working solution, the hydrogenation catalyst of the present invention may be regenerated at a different site in the equipment of another similar scale or preferably a larger scale hydrogen peroxide production plant. Or, the hydrogenation catalyst may be regenerated in separate mobile regeneration equipment, e.g. in a mobile catalyst regeneration unit that is used on demand or as appropriate in a number of different locations where a small to medium hydrogen peroxide manufacturing process according to the AO-process is performed. Another option is to intermittently or periodically perform the regeneration of hydrogenation catalyst under particular conditions in the main equipment of the small to medium hydrogen peroxide manufacturing process according to the AO-process itself.

According to this embodiment of the invention, wherein the AO-process, preferably the mini-AO-process, for the manufacture of hydrogen peroxide is performed such that the working solution and/or the hydrogenation catalyst are only periodically replaced for regeneration or reactivation, the process may be operated for periods of several months without replacement of the working

solution for regeneration (reversion) or reactivation of the hydrogenation catalyst. The periodical replacement of the working solution and the catalyst are each independent from each other, but may be reasonably also be replaced at the same time or at different times or after the same or different periods of operation. Thus, the reversion and/or the regeneration of the catalyst is only intermittently performed after a continuous operation period of the process for at least 3 months, e.g. the working solution and/or the hydrogenation catalyst is normally replaced only after periods of at least 3 months operation of the process. Depending on the type of working solution and/or catalyst, and the particular design and capacity of the AO-process, in particular of the mini-AO-process, the process may be such robust that it may be operated even for periods of individually at least 4, 5, 6, 7, 8, 9, 10, 11 or 12 months without replacement of the working solution for regeneration (reversion) and/or replacement or reactivation of the catalyst.

Therefore, in preferred embodiments, the invention in this aspect also relates to a process for the manufacture of hydrogen peroxide using a hydrogenation catalyst according to the invention in any of the above described ranges and amounts, characterized in that the processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process), preferably the small-to-medium scale AO-process (mini-AO process), is run without a reversion unit for regenerating the working solution, and characterized in that the working solution and/or the catalyst are replaced and/or treated for regeneration or reactivation only intermittently with a low frequency, preferably characterized in that the working solution and/or the catalyst are replaced and/or treated for regeneration or reactivation only periodically after periods of at least 3 months, preferably at least 6 month, more preferably at least 9 months, and most preferred at least 12 months.

Usually, in practice the continuous working period may be individually from 3-4 months, 3-5 months, 3-6 months, 3-7 months, 3-8 months, 3-9 months, 3-10 months, 3-11 months, 3-12 months ; 4-5 months, 4-6 months, 4-7 months, 4-8 months, 4-9 months, 4-10 months, 4-11 months, 4-12 months ; 5-6 months, 5-7 months, 5-8 months, 5-9 months, 5-10 months, 5-11 months, 5-12 months ; 6-7 months, 6-8 months, 6-9 months, 6-10 months, 6-11 months, 6-12 months ; 7-8 months, 7-9 months, 7-10 months, 7-11 months, 7-12 months ; 8-9 months, 8-10 months, 8-11 months, 8-12 months ; 9-10 months, 9-11 months, 9-12 months ; 10-11 months, 10-12 months or 11-12 months.

In carrying out the process of the invention, using a hydrogenation catalyst as defined in the present invention, a working solution containing an anthraquinone working compound is dissolved in a suitable organic solvent. Working compounds that can be used in the process of the invention are those anthraquinones, in particular alkylanthraquinones, and mixtures thereof conventionally used for the manufacture of hydrogen peroxide by the AO-process.

Suitable anthraquinones are 2-alkylanthraquinones and include for example 2-ethylanthraquinone, 2-isopropylanthraquinone, 2-n-butylanthraquinone, 2-sec butylanthraquinone, 2-tert-butylanthraquinone, 2-amylanthraquinone, 2-sec amylanthraquinone, 2-tert-amylanthraquinone or mixtures thereof. Although the hydrogen peroxide AO-process is normally possible also with 2-alkyl-5,6,7,8-tetrahydroanthraquinones and their mixtures, the concentrations of these tetrahydroanthraquinones are minimized in the process according to the present invention.

The organic solvents that can be used in the process of the invention, using a hydrogenation catalyst as defined in the present invention, are those solvents and mixtures thereof conventionally used in the manufacture of hydrogen peroxide by the AO-process. In particular, solvent mixtures of two or more solvents are used which are equally suitable for the different dissolution properties of quinones. Thus, usually mixtures of nonpolar aromatic solvents (quinone solvents) and polar solvents (hydroquinone solvents) are used in the manufacture of hydrogen peroxide by the AO-process.

Examples of suitable aromatic solvents include alkyl-substituted aromatics, particularly C 8 and C 12 alkyl benzenes or mixtures thereof. Examples of suitable polar solvents include higher alcohols (e. g. diisobutylcarbinol or 2-octanol), alkylated and arylated urea, phosphoric acid esters (e. g. trioctyl phosphate), 2-pyrrolidone, 2-methylcyclohexyl acetate or mixtures thereof. Examples of suitable solvent mixtures include mixtures of C 10 alkyl aromatics with diisobutylcarbinol or with 2-methylcyclohexyl acetate. Generally the working solution contains from 2 to 40 % by wt of the anthraquinone or the mixture thereof.

As a matter of example, but without limitation a preferred working solution used in the process for the manufacture of hydrogen peroxide by the AO-process according to the invention may be a AQ/SX/S-150 composition, wherein AQ means a 2-alkylanthraquinone or a mixture thereof. A suitable

2-alkylanthraquinone may be a 2-amylanthraquinone or a mixture thereof, for instance, a mixture of tertiary amyl substituted anthraquinone and the secondary amyl substituted anthraquinone), SX means sextate or 2-methylcyclohexyl acetate (CAS no. 5726-19-2) which is a commercially available industrial solvent ; and S-150 means a commercially available aromatic hydrocarbon solvent of type 150 from the Solvesso® series. S-150 (Solvesso®-150 ; CAS no. 64742-94-5) is known as an aromatic solvent of high aromatics which offer high solvency and controlled evaporation characteristics that make them excellent for use in many industrial applications and in particular as process fluids. The Solvesso® aromatic hydrocarbons are available in three boiling ranges with varying volatility, e.g. with a distillation range of 165-181°C, of 182-207°C or 232-295°C. They may be obtained also naphthalene reduced or as ultra-low naphthalene grades. Solvesso® 150 (S-150) is characterized as follows : distillation range of 182-207°C ; flash point of 64°C ; aromatic content of greater than 99 % by wt ; aniline point of 15°C ; density of 0.900 at 15°C ; and an evaporation rate (nButAc=100) of 5.3.

The process for the manufacture of hydrogen peroxide according to the invention, using a hydrogenation catalyst as defined in the present invention, which is performed without any simultaneous regeneration (reversion) of the working solution, may optionally comprise an acidity control of the working solution. Thus, the process may involve facilities or means suited to measure the acidity of the working solution and further facilities or means suited for adapting and/or maintaining the acidity within predetermined ranges for running a continuous AO-process, in particular a continuous mini-AO-process, without any simultaneous regeneration (reversion) of the working solution. Thus, instead of involving a reversion unit, optionally the AO-process, in particular the mini-AO-process, may foresee e.g. an alumina bed or other means for acidity control of the working solution. The acidity control may also be performed, as an example but without limitation, by e.g. inorganic oxides or e.g. carbonates.

The hydrogenation using a catalyst as defined according the present invention may be performed in a conventional manner as in the manufacture of hydrogen peroxide by the Riedel-Pfleiderer AO-process and its variants. Thus, the hydrogenation may be operated with a fixed-bed catalyst made of a bimetallic Pd/Ag, or a trimetallic Pd/Ag/Au catalyst, as defined according the present invention. Alternatively, the hydrogenation may also be operated with a slurry catalyst made of a bimetallic Pd/Ag, or a trimetallic Pd/Ag/Au catalyst, as

defined according the present invention. The fixed-bed catalyst usually consists of a packing of solid hydrogenation catalyst particles. It is generally desirable that the average diameter of these particles should be in the range of from about 0.2 to 10 mm. In a preferred embodiment of the process according to the invention the catalyst granules in the fixed bed have an average particle diameter of from 1 to 5 mm. The bimetallic Pd/Ag, or the trimetallic Pd/Ag/Au catalyst, as defined according the present invention display high initial selectivity and long-term stability. Productivities may be improved and/or costs (carrier/manufacture) may decreased by using lower particle sizes (e.g.1-2 mm).

The hydrogenation using a catalyst as defined according the present invention in the anthraquinone cyclic process can be performed continuously and conventional hydrogenation reactors can be used, such as e. g. stirred-tank reactors, tubular-flow reactors, fixed-bed reactors, loop reactors or air-lift pump reactors. Optionally, the reactors can be equipped with distribution devices, such as e. g. static mixers or injection nozzles, to distribute the hydrogen in the working solution. Hydrogenation is typically performed at a temperature in the range from 20 to 100°C, particularly preferably 45 to 75°C. The pressure is preferably in the range from 0.1 MPa to 1 MPa (absolute), particularly preferably 0.2 MPa to 0.5 MPa (absolute). The hydrogenation is typically performed in such a way that the hydrogen introduced into the hydrogenation reactor is in practical terms entirely consumed in the hydrogenation stage. The amount of hydrogen is preferably chosen so that between 30 and 80 % of the total amount of reactant is converted from the quinone form into the hydroquinone form. Although in some of the AO-processes in the state of the art a mixture of alkyl anthraquinones and alkyl tetrahydroanthraquinones is used as the reactant, the present invention does not use such mixtures but only alkyl anthraquinones, and the amount of hydrogen is preferably chosen so that in the hydrogenation stage the alkyl anthraquinones are only converted into the hydroquinone form and no alkyl tetrahydroanthraquinones are formed.

The hydrogenating gas in the process can be hydrogen or the hydrogen may be diluted in an inert gas. The term inert gas is intended to denote a gas which does not react with the working solution including the alkylanthraquinone, nor with the hydrogenation catalyst or the alkylhydroanthraquinone produced. Examples of these inert gases are in particular rare gases, carbon dioxide, fluorinated gases such as HFA and nitrogen. Nitrogen has given good results. The proportion of inert gas in the hydrogen containing gas mixture can vary in

the range of from about 0.5 to 99 % and preferably, in the range of from about 10 to 40 %.

In particular in the case of the mini-AO-process, for example but without limitation, some further process condition shall be mentioned. In this regard, the invention also pertains to a process for the manufacture of hydrogen peroxide using a hydrogenation catalyst according to the invention in any of the above described ranges and amounts, characterized by at least one of the following hydrogenation process conditions or any combination thereof : a) a pressure of the hydrogenator degasser in the range of about 0.5 barg to about 5 barg ; b) a temperature of the hydrogenator outlet in the range of about 40 to about 65°C ; c) a differential pressure in the hydrogenation filtration in the range of about 0 to about 1 barg) ; d) a differential pressure in the hydrogenation column in the range of about 0 to about 2 barg.

Should the disclosure of any of the patents, patent applications, and publications that are incorporated herein by reference be in conflict with the present description to the extent that it might render a term unclear, the present description shall take precedence over them.

The examples which follow are intended to illustrate the present invention without, however, limiting the scope thereof.

EXAMPLE 1

Synthesis of a Palladium Catalyst

100.0 g of SiO_2, SiO_2/Al_2O_3 or Al_2O_3 supports are suspended in 350 ml of demineralized water warmed and kept at 70°C. 20.0 g of sodium carbonate (Na_2CO_3) are dissolved in the mixture. 105.0 ml of an aqueous solution of chloropalladic acid (H_2PdCl_4, 2 % Pd by weight) is added dropwise over a period of 1 hour. The solids are filtered and washed with demineralized water till the total removal of alkaline excess. 2 g of formic acid are added to the suspension of catalysts for the palladium reduction. The solids are again filtered and washed with demineralized water (3 times with 200 ml H_2O). The catalyst is finally dried at 110°C.

The characteristics of the support obtained and of the catalyst formed are as follows :

The catalyst comprises an amount of palladium of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight with respect to the weight of the support. The Pd loading on supports has been determined by the ICP-OES method. Preferably, the Pd is dispersed on the outer

surface of the support (eggshell type), with a Pd thickness inferior to 50 μm, and preferably inferior to 10 μm. The Pd profile in the support is characterized by Energy Dispersive X-ray coupled with a Scanning Electronic Microscope (SEM-EDX). Preferably, the catalyst particle size is ranging from 60 μm to 200 μm large. The catalyst granulometry is determined by laser granulometry. Accessible surface areas (BET method), porous volume and pore size distribution (BJH method) are respectively and preferably ranging from 100 to 500 m^2/g, 0.1 to 0.6 cm^3/g and 2 to 20 nm. Textural properties are determined by N_2 adsorption-desorption method.

EXAMPLE 2

Synthesis of Catalysts According to the Invention (impregnation)

100.0 g of chlorine-free Pd/SiO_2, $Pd/SiO_2/Al_2O_3$ or Pd/Al_2O_3 reduced catalyst are suspended in 350 ml of demineralized water. The suspension is then poured into a sealed glass reactor which is then degassed with N_2. After 10 minutes, 30.0 mg of silver nitrate ($AgNO_3$) are added to the suspension and the system is purged with H_2. The mixture is then maintained under a flowing reducing H_2 atmosphere for further 30 minutes. The solids are subsequently filtered off, and washed with demineralized water (5 times with 50 ml H_2O). The $Pd.Ag/SiO_2$, the $Pd.Ag /SiO_2/Al_2O_3$ or the $Pd.Ag/Al_2O_3$ solids are then dried overnight at 110°C, then calcined at 500°C for 4 h under N_2.

The characteristics of the support obtained and of the catalyst formed are as follows :

The catalyst comprises an amount of palladium of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight, and an amount of silver of 0.3 % (0.30 %) +/- 0.02 % by weight, preferably in an amount of 0.3 % (0.30 %) +/- 0.01 % by weight with respect to the weight of the catalyst. The Pd and Ag loading on supports have been determined by the ICP-OES method. Preferably, the Pd and Ag are dispersed on the outer surface of the support (eggshell type), with a Pd.Ag thickness inferior to 50 μm, and preferably inferior to 10 μm. The Pd.Ag profile in the support is characterized by Energy Dispersive X-ray coupled with a Scanning Electronic Microscope (SEM-EDX). Preferably, the catalyst particle size is ranging from 60 μm to 200 μm large. The catalyst granulometry is determined by laser granulometry. Accessible surface areas (BET method), porous volume and pore size distribution (BJH method) are respectively and preferably ranging from 100

to 500 m^2/g, 0.1 to 0.6 cm^3/g and 2 to 20 nm. Textural properties are determined by N_2 adsorption-desorption method.

EXAMPLE 3

Synthesis of Catalysts According to the Invention (precipitation)

100.0 g of chlorine-free Pd/SiO_2, $Pd/SiO_2/Al_2O_3$ or Pd/Al_2O_3 catalyst are suspended in 350 ml of demineralized water. The pH is adjusted to 10 with NaOH. 30.0 mg of silver nitrate are then added to the alkaline suspension, and the mixture is stirred for 1 hour. The suspension is filtrated and the obtained solids are washed with demineralized water till the total removal of the alkaline excess. The $Pd.Ag/SiO_2$, the $Pd.Ag /SiO_2/Al_2O_3$ or the $Pd.Ag/Al_2O_3$ solids are dried overnight at 110°C, then calcined at 500°C for 4 h under O_2 and finally reduced under a mixture of H_2 (10 %) and N_2 for 1 h at 110°C.

The characteristics of the support obtained and of the catalyst formed are as follows :

The catalyst comprises an amount of palladium of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight, and an amount of silver of 0.3 % (0.30 %) +/- 0.02 % by weight, preferably in an amount of 0.3 % (0.30 %) +/- 0.01 % by weight with respect to the weight of the catalyst. The Pd and Ag loading on supports have been determined by the ICP-OES method. Preferably, the Pd and Ag are dispersed on the outer surface of the support (eggshell type), with a Pd.Ag thickness inferior to 50 µm, and preferably inferior to 10 µm. The Pd.Ag profile in the support is characterized by Energy Dispersive X-ray coupled with a Scanning Electronic Microscope (SEM-EDX). Preferably, the catalyst particle size is ranging from 60 µm to 200 µm large. The catalyst granulometry is determined by laser granulometry. Accessible surface areas (BET method), porous volume and pore size distribution (BJH method) are respectively and preferably ranging from 100 to 500 m^2/g, 0.1 to 0.6 cm^3/g and 2 to 20 nm. Textural properties are determined by N_2 adsorption-desorption method.

EXAMPLE 4

Synthesis of Catalysts According to the Invention (impregnation)100.0 g of $Pd.Ag/SiO_2$, $Pd.Ag/SiO_2/Al_2O_3$ or $Pd.Ag/Al_2O_3$ reduced catalyst are suspended in 350 ml of demineralized water. The suspension is then poured into a sealed glass reactor which is then degassed with N_2. After 10 minutes, 2 ml of hydrogen tetrachloroaurate ($HAuCl_4$) solution (2.49 % Au by weight) are added to the suspension and the system is purged with H_2. The mixture is then

maintained under a flowing reducing H_2 atmosphere for further 30 minutes. The solids are subsequently filtered off, and washed with demineralized water (5 times with 50 ml H_2O). The Pd.Ag.Au/SiO_2, the Pd.Ag.Au /SiO_2/Al_2O_3 or the Pd.Ag.Au/Al_2O_3 solids are then dried overnight at 110°C, then calcined at 500°C for 4 h under N_2.

The characteristics of the support obtained and of the catalyst formed are as follows :

The catalyst comprises an amount of palladium of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight, and an amount of silver of 0.3 % (0.30 %) +/- 0.02 % by weight, preferably in an amount of 0.3 % (0.30 %) +/- 0.01 % by weight with respect to the weight of the catalyst, and wherein the catalyst comprises gold in an amount of 0.05 % (0.050 %) +/- 0.002 % by weight, preferably such as 0.05 % (0.050 %) +/- 0.001 % by weight, with respect to the weight of the catalyst. The Pd, Ag and Au loading on supports have been determined by the ICP-OES method. Preferably, the Pd, Ag and Au are dispersed on the outer surface of the support (eggshell type), with a Pd.Ag.Au thickness inferior to 50 µm, and preferably inferior to 10 µm. The Pd.Ag.Au profile in the support is characterized by Energy Dispersive X-ray coupled with a Scanning Electronic Microscope (SEM-EDX). Preferably, the catalyst particle size is ranging from 60 µm to 200 µm large. The catalyst granulometry is determined by laser granulometry. Accessible surface areas (BET method), porous volume and pore size distribution (BJH method) are respectively and preferably ranging from 100 to 500 m^2/g, 0.1 to 0.6 cm^3/g and 2 to 20 nm. Textural properties are determined by N_2 adsorption-desorption method.

EXAMPLE 5

Synthesis of Catalysts According to the Invention (precipitation)

100.0 g of chlorine-free Pd/SiO_2, Pd/SiO_2/Al_2O_3 or Pd/Al_2O_3 catalyst are suspended in 350 ml of demineralized water. The pH is adjusted to 10 with NaOH. 2 ml of hydrogen tetrachloroaurate ($HAuCl_4$) solution (2.49 % Au by weight) are added to the alkaline suspension, and the mixture is stirred for 1 hour. The suspension is filtrated and the obtained solids are washed with demineralized water till the total removal of the alkaline excess. The Pd.Ag.Au/SiO_2, the Pd.Ag.Au/SiO_2/Al_2O_3 or the Pd.Ag.Au/Al_2O_3 solids are dried overnight at 110°C, then calcined at 500°C for 4 h under O_2 and finally reduced under a mixture of H_2 (10 %) and N_2 for 1 h at 110°C.

The characteristics of the support obtained and of the catalyst formed are as follows :

The catalyst comprises an amount of palladium of 2 % (2.0 %) +/- 0.1 % by weight, preferably in an amount of 2 % (2.0 %) +/- 0.05 % by weight, and an amount of silver of 0.3 % (0.30 %) +/- 0.02 % by weight, preferably in an amount of 0.3 % (0.30 %) +/- 0.01 % by weight with respect to the weight of the catalyst, and wherein the catalyst comprises gold in an amount of 0.05 % (0.050 %) +/- 0.002 % by weight, preferably such as 0.05 % (0.050%) +/- 0.001% by weight, with respect to the weight of the catalyst. The Pd, Ag and Au loading on supports have been determined by the ICP-OES method. Preferably, the Pd, Ag and Au are dispersed on the outer surface of the support (eggshell type), with a Pd.Ag.Au thickness inferior to 50 μm, and preferably inferior to 10 μm. The Pd.Ag.Au profile in the support is characterized by Energy Dispersive X-ray coupled with a Scanning Electronic Microscope (SEM-EDX). Preferably, the catalyst particle size is ranging from 60 μm to 200 μm large. The catalyst granulometry is determined by laser granulometry. Accessible surface areas (BET method), porous volume and pore size distribution (BJH method) are respectively and preferably ranging from 100 to 500 m^2/g, 0.1 to 0.6 cm^3/g and 2 to 20 nm. Textural properties are determined by N_2 adsorption-desorption method.

EXAMPLES 6-8

Evaluation of Acivity and Selectivity of Catalysts of the Invention

The catalysts of Examples 1, 2 and 3 were evaluated from the viewpoint of their activity and of their selectivity in the hydrogenation of amylanthraquinone (AQ) in solution in a Sextate-Solvesso 150 or Diisobutlcarbinol-Xylene mixtures. The initial rate of consumption of hydrogen was measured and the significance of the processes for the conversion of amylanthraquinone to amyltetrahydro-anthraquinone (ATQ), amyloxanthrone (AO) and amylanthrone (AA) are expressed as a function of the amount of hydrogen peroxide produced over time.

Procedure for the hydrogenation of amylamthraquinone in a batch reactor : the working solution (333.0 g), composed of 70 g/kg of amylanthraquinone dissolved in the Diisobutlcarbinol-Xylene mixture (20/80 ratio by weight), which is saturated with water, was hydrogenated at 55°C under a constant pressure of 1.1 bar absolute. The catalyst (6 g/kg working solution) was kept in suspension using a stirrer of turbine type rotating at 1300 rpm.

The results obtained are combined in Table I below :

	k1 (s^{-1})	k2 (s^{-1})	k1/k2
Pd 2%/SiO_2 (Fig.1)	$4.33.10^{-4}$	$1.78.10^{-6}$	243
Pd 2%-Ag 0.3%/SiO_2 impregnation (Fig.2)	$3.25.10^{-4}$	$1.58.10^{-8}$	20630

Where k1 is the kinetic constant of the first AQ to AQH hydrogenation reaction, whereas k2 is the kinetic constant related to the AQH to ATQH over-hydrogenation reaction. These k1 and k2 kinetics are respectively recovered from the first and the second rate of the test-batch hydrogenation curve. High k1/k2 ratio can be understood as selective process toward the hydrogenation of AQ to AQH. It can be deduced from the above results that the selectivity of hydrogenation of the starting quinone is clearly improved by the addition of silver onto the Pd catalyst. The Ag.Pd mixture reduces k1 but especially k2.

Procedure for evaluating the catalysts in a continuous hydrogenation reactor : the plant was composed of a CSTR-hydrogenator, an oxidizer and an extraction column placed in series, the oxidized working solution being recycled to the hydrogenator after extraction of the hydrogen peroxide produced by oxidation with oxygen of the hydroanthraquinone manufactured in the hydrogenator. The working solution was composed of 70 g/kg of amylanthraquinone in the Sextate (20 weight %)-Solvesso 150 (80 weight %) mixture. The total working solution volume was 1260 ml and its flow rate was 15 ml/min. The temperature in the hydrogenator was 60-65°C the hydrogen pressure was 1.5 bar absolute and the concentration of the catalyst was 75g/L. The mean residence time of the working solution in the hydrogenator was 17 min. The oxidizer operated at 45°C. The composition of the working solution was established by HPLC chromatography and its change was monitored over time and as a function of the amount of hydrogen peroxide produced. The selectivity of the catalysts was established on the basis of the amounts of AQ converted to ATQ, AO and AA produced from ATQ, with respect to a unit amount of hydrogen peroxide produced, and at a constant activity (40 g/kg WS of AQH).

The results obtained are combined in Table II below. The rates are expressed therein as g of product considered per kg of solution and per g of H_2O_2 produced.

	Pd 2 %/SiO_2	Pd 2 %-Ag 0.3 %/SiO_2 precipitation	Pd 2 %-Ag 0.3 %/SiO_2 impregnation
ATQ rate (Fig.3)	13.0 10^{-2}	0.3 10^{-2}	1.4 10^{-2}
AA rate (Fig.4)	0.9 10^{-2}	Negligible	Negligible
AO rate (Fig.5)	8.6 10^{-2}	1.1 10^{-2}	4.4 10^{-2}

It can be deduced from the above results and more particularly from the rate of formation of ATQ, AA and AO, the main degraded compounds, that the selectivity of hydrogenation of the starting quinone is significantly improved by the impregnation and preferably by the precipitation of a desired amount of silver on the Pd-based catalyst.

The graphs in FIG. 1 to 5 further represent the findings of the experiments in the context of the present invention (catalyst, silica support, hydrogen peroxide manufacture).

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

CLAIMS

1. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support, wherein the catalyst comprises an amount of palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst and an amount of silver 0.1 to 0.5 % by weight with respect to the weight of the catalyst, and wherein preferably the catalyst further comprises gold in an amount of up to 0.1 % by weight with respect to the weight of the catalyst.

2. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to claim 1, wherein the catalyst comprises an amount of palladium from 1.8 to 2.2 % by weight, preferably from 1.8 to 2.2 % by weight, more preferably from 1.9 to 2.1 % by weight, and most preferably of about 2 % by weight, with respect to the weight of the catalyst.

3. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 2, wherein the catalyst comprises an amount of silver from 0.1 to 0.5 % by weight, preferably from 0.2 to 0.4 % by weight, more preferably from 0.25 to 0.35 % by weight, and most preferably of about 0.3 % by weight, with respect to the weight of the catalyst.

4. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 3, wherein the catalyst comprises an amount of gold from 0.01 to 0.1 % by weight, preferably from 0.04 to 0.06 % by weight, more preferably 0.045 to 0.055 % by weight, and most preferably of about 0.05 % by weight, with respect to the weight of the catalyst.

5. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or on an aluminosilicate support according to claim 1 comprising :

palladium from 1.5 to 2.5 % by weight with respect to the weight of the catalyst, silver from 0.1 to 0.5 % by weight with respect to the weight of the catalyst, and wherein preferably the catalyst further comprises gold in an amount of up to 0.1 % by weight, and the silicon oxide (SiO_2) and/or aluminium oxide (Al_2O_3) support from 96.9 to 98,4 % by weight with respect to the weight of the catalyst.

6. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to claim 1 comprising :

from 15 to 25 g of palladium per kg of catalyst,

from 1 to 5 g of silver per kg of catalyst,

and preferably of up to 1 g of gold per kg of catalyst,

from 984 to 969 g of the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or aluminosilicate support per kg of catalyst.

7. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 6, wherein the support is silicon oxide (SiO_2).

8. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 7, wherein the support is silicon oxide (SiO_2) comprising intraframework aluminium or aluminium oxide (Al_2O_3), preferably wherein the support is silicon oxide (SiO_2) comprising a delta-aluminium oxide (delta-Al_2O_3).

9. Hydrogenation catalyst based on palladium on a silicon oxide (SiO_2) and/or aluminium oxide (Al_2O_3) support according to anyone of claim 1 to 6, wherein the support is aluminium oxide (Al_2O_3), preferably a delta-aluminium oxide (delta-Al_2O_3).

10. Process for the manufacture of a hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 9, wherein the catalyst comprises palladium and silver, and wherein the catalyst preferably further comprises gold, the process comprising simultaneously or successively impregnating and/or precipitating the required amount by weight with respect to the total weight of the catalyst of palladium, silver, and preferably further gold, on the silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or on an aluminosilicate support.

11. Use of a hydrogenation catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 9, wherein the catalyst comprises palladium and silver, and wherein the catalyst preferably further comprises gold, in a process for the manufacture of hydrogen peroxide, preferably in a process for the manufacture of hydrogen peroxide by the autoxidation process (AO-process), more preferably in a small-to-medium scale AO-process (mini-AO process) which is run with a capacity of up to 20 ktpa, preferably with a capacity of up to 10 ktpa, (as 100 %) hydrogen peroxide production, and most preferably in such of said processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process) which are run without a reversion unit for regenerating the working solution.

12. Process for the manufacture of hydrogen peroxide comprising carrying out a hydrogenation reaction using a catalyst based on palladium on a silicon oxide (SiO_2), an aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 9, wherein the catalyst comprises palladium and silver, and wherein the catalyst preferably further comprises gold, preferably a process for the manufacture of hydrogen peroxide by the autoxidation process (AO-process), more preferably in a small-to-medium scale AO-process (mini-AO process) which is run with a capacity of up to 20 ktpa, preferably with a capacity of up to 10 ktpa, (as 100 %) hydrogen peroxide production, and most preferably in such of said processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process) which are run without a reversion unit for regenerating the working solution.

13. Process for the manufacture of hydrogen peroxide according to claim 12, characterized in that the hydrogenation reaction using a catalyst based on palladium on a silicon oxide (SiO_2), aluminium oxide (Al_2O_3) or on an aluminosilicate support according to anyone of claim 1 to 9 is a small-to-medium scale AO-process (mini-AO process) which is run with a capacity in the range of 2 to 15 ktpa, preferably in the range of 2 to 10 ktpa, (as 100 %) hydrogen peroxide production, and more preferably a small-to-medium scale AO-process (mini-AO process) with said capacity which is run without a reversion unit for regenerating the working solution.

14. Process for the manufacture of hydrogen peroxide according to anyone of claim 12 to 13, characterized in that the processes for the manufacture of hydrogen peroxide by the autoxidation process (AO-process), preferably the small-to-medium scale AO-process (mini-AO process), is run without a reversion unit for regenerating the working solution, and characterized in that the working solution and/or the catalyst are replaced and/or treated for regeneration or reactivation only intermittently with a low frequency, preferably characterized in that the working solution and/or the catalyst are replaced and/or treated for regeneration or reactivation only periodically after periods of at least 3 months, preferably at least 6 month, more preferably at least 9 months, and most preferred at least 12 months.

15. Process for the manufacture of hydrogen peroxide according to anyone of claim 12 to 14, characterized by at least one of the following hydrogenation process conditions or any combination thereof :

a) a pressure of the hydrogenator degasser in the range of about 0.5 barg to about 5 barg ;

b) a temperature of the hydrogenator outlet in the range of about 40 to about 65°C ;

c) a differential pressure in the hydrogenation filtration in the range of about 0 to about 1 barg) ;

d) a differential pressure in the hydrogenation column in the range of about 0 to about 2 barg.

Figure 1 : Batch test of the Pd/SiO2

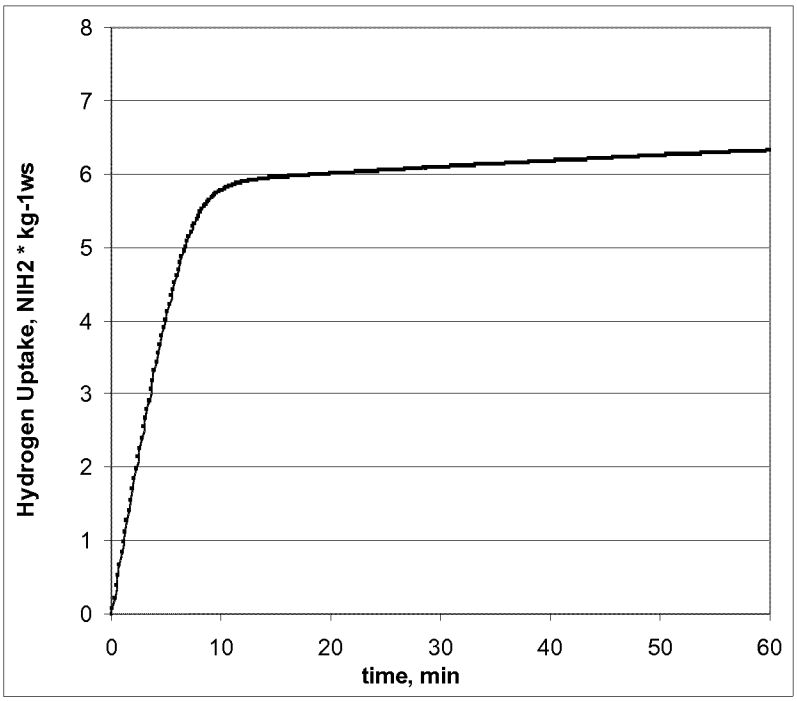


Figure 2 : Batch test of the AgPd/SiO2 via impregnation

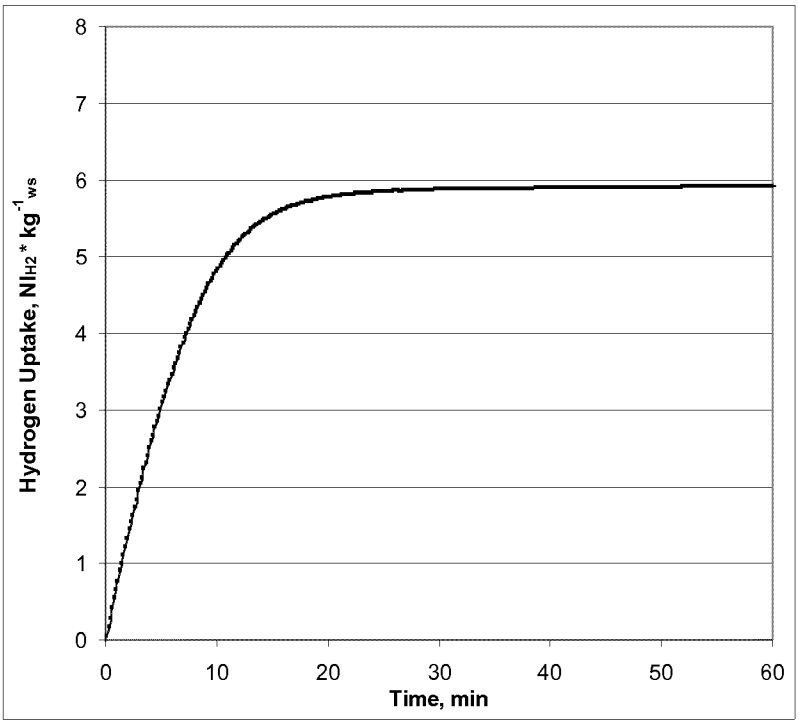


Figure 3 : ATQ formation

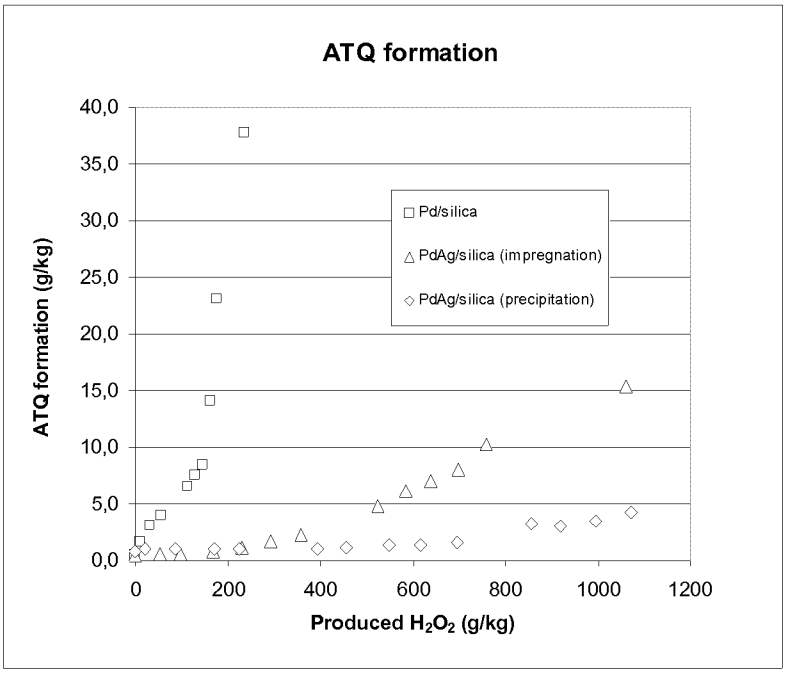


Figure 4 : AA formation

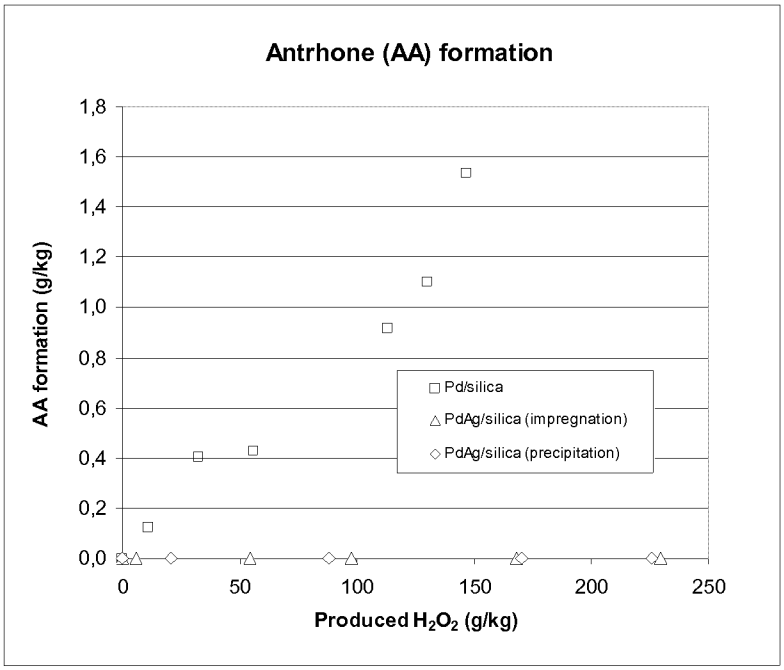
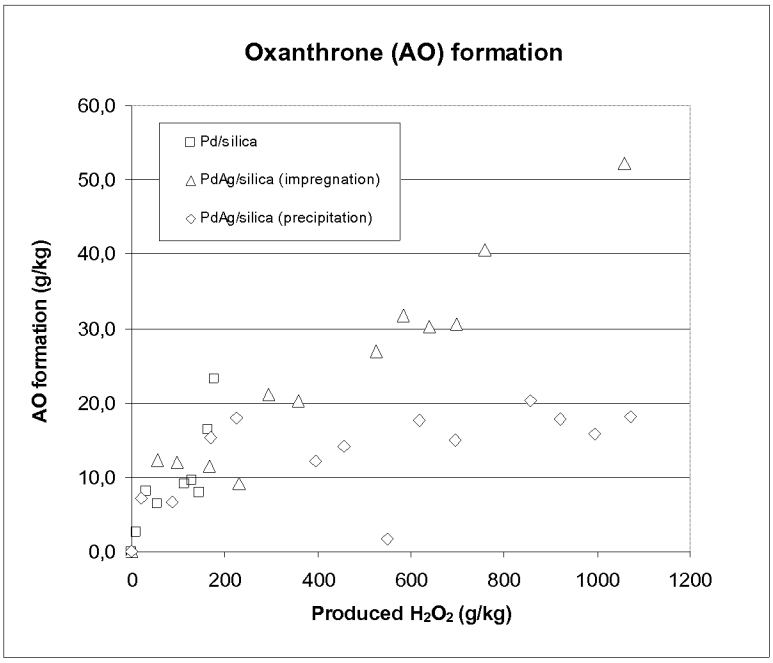


Figure 5 : AO formation



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057962

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/44 B01J23/50 B01J23/52 B01J23/38 B01J35/00
B01J37/02 B01J37/03 B01J37/18 C01B15/023 C01B15/01
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)
B01J C01B

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/15350 A2 (SOLVAY INTEROX [BE]; MATHIEU VERONIQUE [BE]; PENNETREAU PASCAL [BE]) 16 April 1998 (1998-04-16) cited in the application abstract page 1, line 24 - page 2, line 5 page 2, line 27 - page 3, line 5 page 3, line 19 - line 33 page 4, line 6 - page 5, line 19 examples 7,13 figures	1-15
X	EP 1 308 416 A1 (DEGUSSA [DE] EVONIK DEGUSSA GMBH [DE]) 7 May 2003 (2003-05-07) cited in the application abstract paragraphs [0018] - [0022] examples	1-12

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 May 2013	05/06/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Omegna, Anna

2

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

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 038 833 A1 (DEGUSSA [DE]) 27 September 2000 (2000-09-27) cited in the application abstract paragraphs [0015], [0017], [0018] examples table 1 claims 1-5	1-12
X	WO 2010/077262 A2 (LYONDELL CHEMICAL TECH LP [US]; EQUISTAR CHEM LP [US]) 8 July 2010 (2010-07-08) cited in the application abstract page 3, line 10 - page 4, line 14	1-10
X	JP S49 5120 B1 (MITSUBISHI GAS CHEM CO INC) 5 February 1974 (1974-02-05) abstract table 1	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/057962

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9815350 A2	16-04-1998	AU 4446997 A	05-05-1998
		BR 9712193 A	31-08-1999
		EP 0930938 A2	28-07-1999
		US 6306359 B1	23-10-2001
		WO 9815350 A2	16-04-1998
EP 1308416 A1	07-05-2003	AT 531670 T	15-11-2011
		DE 10153546 A1	22-05-2003
		EP 1308416 A1	07-05-2003
		ES 2376420 T3	13-03-2012
		US 2003083510 A1	01-05-2003
		US 2004223904 A1	11-11-2004
EP 1038833 A1	27-09-2000	AT 240262 T	15-05-2003
		DE 19912733 A1	21-09-2000
		EP 1038833 A1	27-09-2000
		US 6387346 B1	14-05-2002
WO 2010077262 A2	08-07-2010	CN 102307658 A	04-01-2012
		EP 2365875 A2	21-09-2011
		KR 20110105779 A	27-09-2011
		US 2010152022 A1	17-06-2010
		WO 2010077262 A2	08-07-2010
JP S495120 B1	05-02-1974	NONE	