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CATALYST AND PROCESS FOR THE DIRECT SYNTHESIS OF HYDROGEN PEROXIDE.

The present invention relates to a bimetallic catalyst and a process for the direct synthesis of hydrogen peroxide from hydrogen and oxygen which uses said catalyst.

Hydrogen peroxide is a commercially important compound which is widely used as bleach in the textile and paper industry, as a biocide in the environmental field and in oxidation processes in the chemical industry.

Examples of these processes are those using titanium silicalite as catalysts, such as the epoxidation of olefins (EP-100,119), the ammoximation of carbonyl compounds (U.S. 4,794,198), the oxidation of ammonia to hydroxylamine (U.S. 5,320,819) and the hydroxylation of aromatic hydrocarbons (U.S. 4,369,783).

The industrial production of aqueous solutions of H_2O_2 by means of a complex two-step process, is known. In this process a solution of an anthraquinone, such as butylanthraquinone or ethylanthraquinone, in an organic medium im-

miscible with water is first hydrogenated and then oxidized with air to produce H_2O_2 which is subsequently extracted in aqueous phase.

This procedure is expensive owing to the high investment costs necessary for the complex production unit involved and the necessity of separating and disposing of the by-products generated during the oxidation phase and purifying and reintegrating the anthraquinone solution before being re-used.

Processes for the direct synthesis of hydrogen peroxide from H_2 and O_2 have been proposed in the art for overcoming these disadvantages. These processes generally use a catalytic system consisting of a noble metal, particularly metals of the platinum group or their mixtures, in the form of salts or as supported metals.

For example, U.S. patents 4,772,458 and 4,832,938 describe a process for the synthesis of aqueous solutions of H_2O_2 using a catalyst based on palladium and/or platinum supported on carbon, in the presence of hydrogen ions and bromide ions. Quantities of acids ranging from 2.5 to 10 g/liter are generally required for obtaining high concentrations of H_2O_2 .

The use of high quantities of acids creates serious problems linked to the dissolution of the active phase (metal) of the catalyst in the reaction medium, with the

consequent instability of both the catalyst and hydrogen peroxide solution produced.

In addition, under these conditions, the solutions of H_2O_2 produced are difficult to use owing to the high acid content. These processes also operate under critical conditions as concentrations of H_2 higher than 5% (17% or over) are used with respect to the reaction mixture and consequently fall within the explosivity limit of H_2/O_2 mixtures.

Patent application EP-492.064 describes a process for the synthesis of hydrogen peroxide from hydrogen and oxygen which uses a catalyst based on palladium supported on a halogenated resin, in particular a brominated styrene/divinylbenzene resin.

The reaction is carried out in water, in the presence of an acid selected from sulfuric, phosphoric or nitric acid. Operating according to this process however concentrations of H_2O_2 of about 0.58% are obtained.

Patent application EP-504,741 describes a process for the synthesis of H_2O_2 from hydrogen and oxygen which uses a catalyst based on palladium or platinum supported on an acid or superacid carrier selected from oxides of molybdenum, zirconium or tungsten.

Operating according to this process, hydrogen peroxide is obtained in concentrations of not more than 1%.

Patent U.S. 5,320,921 describes a process for the synthesis of H_2O_2 from hydrogen and oxygen which uses a catalyst based on palladium or platinum supported on a heteropolyacid made insoluble in water. The reaction is carried out in water in the presence of bromide ions (0.5 mmoles/liter of sodium bromide). Concentrations of H_2O_2 equal to about 1.1% are obtained.

These processes of the known art are consequently characterized by a low productivity and selectivity of the reaction and by the production of H_2O_2 solutions which are too dilute for an economic industrial exploitation.

Italian patent application MI 98-A-01843, filed by the Applicant, relates to a process for the direct synthesis of hydrogen peroxide using a catalyst based on palladium and/or platinum co-impregnated on a sulfonated activated carbon.

It has now been found that by carrying out the reaction between hydrogen and oxygen in the presence of a bimetallic catalyst prepared by dispersing in sequence and alternating the precursors of the single metal components of the catalyst on a carrier, it is possible to overcome the drawbacks of the known art described above. This preparation method also allows the activity and selectivity of the catalyst, the concentration of hydrogen peroxide or consumption of hydrogen, to be modulated in relation to the

process requirements and availability of raw materials, for example low cost hydrogen.

In particular, the use of these catalysts gives the following advantages:

(i) the possibility of using extremely low quantities of halides ($< 10^{-4}$ moles/l) and free acids ($H^+ < 10^{-2}$ moles/l) in the reaction medium. This has beneficial effects on the stability of the catalytic system and H_2O_2 solutions obtained, thus allowing the possibility of directly using the above solutions in oxidation processes. The presence of only traces of halides and acidity is not a disadvantage for direct use in the above reactions as the possible introduction of salts or acidity in downstream processes is minimized.

(ii) the production of hydrogen peroxide solutions in adequate concentrations for direct use and economically valid in oxidation processes, generally ranging from 2% to 10% by weight.

(iii) the possibility of carrying out the reaction under high safety conditions. In fact, below 4% by volume of hydrogen means operating well outside the explosivity range of inert H_2-O_2 mixtures.

In accordance with this, the present invention relates to a bimetallic catalyst obtained by dispersing in sequence and alternating the precursors of the single metal components

of the catalyst on a carrier, and a process for the synthesis of hydrogen peroxide by the direct reaction of hydrogen with oxygen, in a solvent medium containing a halogenated promoter and an acid promoter, in the presence of said catalyst.

In particular, the catalyst used for the purposes of the present invention is obtained by:

- (a) preparation of the solutions or suspensions of precursors of the single metal components of the catalytic system;
- (b) dispersion of the solutions or suspensions obtained in (a) in sequence on a carrier;
- (c) treatment of the catalyst with a reducing agent of the metal and drying at 120-140°C between one dispersion and another.

In the preparation of said catalyst, steps (b) and (c) can be repeated once or several times.

The metal components of the catalyst are selected from those of the platinum group. Palladium and platinum are preferably used.

In these catalysts the palladium is normally present in a quantity ranging from 0.01 to 5% by weight and the platinum in a quantity ranging from 0.01 to 1% by weight, with an atomic ratio between platinum and palladium ranging from 0.1/99.9 to 50/50.

The palladium is preferably present in a quantity ranging from 0.4 to 2% by weight and the platinum in a quantity ranging from 0.05 to 0.5% by weight, with an atomic ratio between platinum and palladium ranging from 1/99 to 30/70.

The dispersion of the active components on the carrier can be effected by means of precipitation, impregnation or adsorption starting from solutions of their salts or soluble complexes selected from acetates, halides and nitrates.

The reduction of the catalyst components to the metal state can be carried out by means of thermal and/or chemical treatment with reducing substances such as hydrogen, sodium formate, sodium citrate, using preparative methods well known in the art.

The inert carrier can consist of activated carbon, silica, alumina, silica-alumina, zeolites and other materials well known in the art. Activated carbon is preferred for the preparation of the catalysts useful for the invention.

Activated carbons which can be used for the purposes of the invention are those with a low ash content and a surface area of at least 100 m²/g, in particular those having a surface area greater than 300 m²/g.

Sulfonated activated carbons described in Italian patent application MI 98-A-01843 can also be used for the pur-

pose.

The carriers can be in powder, grain or pellet form, etc.

Before supporting the precursors of the single metals, the activated carbon can be subjected to treatment such as washing with distilled water or treatment with acids, bases or diluted oxidizing agents, for example acetic acid, hydrochloric acid, sodium carbonate and hydrogen peroxide.

In particular, it has been observed that the catalyst obtained by dispersing first the palladium and then the platinum on the carrier, is more active, whereas that obtained by dispersing first the platinum and then the palladium in sequence, is more selective.

The catalyst of the present invention is particularly advantageous in a process for the direct synthesis of hydrogen peroxide from hydrogen and oxygen in a solvent in the presence of a halogenated promoter and an acid promoter.

The catalyst is used in catalytic quantities generally ranging from 10^{-6} to 10^{-2} moles of total metal contained in the catalyst per liter of reaction medium.

Advantageous results are obtained using quantities of catalyst ranging from 10^{-4} to 10^{-3} moles of total metal contained in the catalyst per liter of reaction medium.

The reaction solvent can consist of water, a C_1 - C_3 al-

cohol or their mixtures.

Among C_1 - C_3 alcohols, methanol is preferred for the purposes of the invention. Among the mixtures, a mixture of methanol and water with a weight ratio ranging from 50/50 to 99.9/0.1, preferably from 90/10 to 99/1, is preferred.

The acid promoter can be any substance capable of generating H^+ hydrogen ions in the liquid reaction medium and is generally selected from inorganic acids such as sulfuric, phosphoric, nitric acids or from organic acids such as sulfonic acids. Sulfuric acid and phosphoric acid are preferred. The concentration of the acid generally ranges from 20 to 1000 mg per kg of solution and preferably from 50 to 500 mg per kg of solution.

The halogenated promoter can be any substance capable of generating halogen ions in the liquid reaction medium. Substances capable of generating bromide ions are preferred. These substances are generally selected from hydrobromic acid and its salts soluble in the reaction medium, for example sodium bromide, potassium bromide, sodium or ammonium bromate. Hydrobromic acid, sodium bromide and potassium bromide are particularly preferred.

The concentration of halogenated promoter generally ranges from 0.1 to 50 mg per kg of solution and preferably from 1 to 10 mg per kg of solution.

The production of hydrogen peroxide is carried out by

reacting the oxygen and hydrogen in the reaction medium in the presence of the catalyst and promoters and in the presence of or without an inert gas selected from nitrogen, helium, argon. The gas is preferably nitrogen.

The molar ratio H_2/O_2 in the feeding ranges from 1/2 to 1/100, preferably from 1/3 to 1/15 and the concentration of hydrogen in the gaseous phase in contact with the liquid reaction medium is conveniently maintained at a value lower than 4.5% molar, outside the explosivity limits of the H_2/O_2 /inert gas mixture.

According to an embodiment of the process of the present invention, the reaction can be carried out using air instead of pure oxygen.

The reaction is typically carried out at temperatures ranging from -5° to $90^\circ C$, preferably from 2 to $50^\circ C$ and at a total pressure higher than atmospheric pressure, preferably ranging from 50 to 300 atmospheres.

The process according to the present invention can be carried out batchwise, or, preferably, in continuous using a reactor suitable for the purpose and selected from those described in the art.

Operating under the above conditions, it is possible to produce hydrogen peroxide in safety conditions with a reaction productivity normally ranging from 30 to 200 g of H_2O_2 (expressed as 100% H_2O_2) per liter of reaction medium

per hour and with a molar selectivity towards the formation of H_2O_2 , referring to the hydrogen used up, ranging from 60% to 90%. The hydrogen peroxide solutions thus obtained can be used directly in oxidation processes which comprise the use of H_2O_2 without costly intermediate processing, such as acid and solvent removal operations.

The process of the present invention enables the reagents to be transformed into H_2O_2 with high conversions and selectivities, obtaining H_2O_2 solutions without acidity or containing only traces of acidity and/or salts.

The following examples, whose sole purpose is to describe the present invention in greater detail, should in no way be considered as limiting its scope.

EXAMPLE 1

Preparation of the catalyst

a) 8 g of activated maritime pine charcoal in powder form (Ceca 2S/E) are charged into a 0.5 liter glass flask, containing 90 ml of demineralized water and 0.28 g of Na_2CO_3 . The suspension is maintained at room temperature (20-25°C), under stirring, for 10 minutes.

0.101 g of a solution of H_2PtCl_6 (8% by weight of Pt) diluted in 10 ml of water are subsequently added dropwise.

The suspension is kept at room temperature for 10 minutes and is then heated in a water bath for 10 minutes to 90°C. A solution containing 0.76 g of sodium formiate in 10

ml of water is then added and the stirring is continued at 90°C for 2 hours.

After cooling to room temperature, the suspension is filtered and the recovered charcoal is washed with distilled water until the chlorides have been eliminated and dried in an oven at 120°C for 2 hours.

b) the carbon thus obtained is re-suspended in a solution containing 0.4 g of Na_2CO_3 in 90 ml of water and then treated following the procedure described in a), but using a solution of 0.8 g of Na_2PdCl_4 at 10% of Pd, instead of the solution of H_2PtCl_6 .

After drying at 120°C, a catalyst containing 1% of Pd and 0.1% of Pt on activated carbon is obtained.

EXAMPLE 2

The same procedure is adopted as described in example 1, but inverting the sequence of Pt-Pd deposit.

In step a) the solution Na_2PdCl_4 is used, and in step b) the solution of H_2PtCl_6 , maintaining the same quantities. A catalyst containing 0.1% of Pt and 1% of Pd on activated carbon, is obtained.

EXAMPLE 3 (comparative)

Preparation of a co-impregnated catalyst

8 g of activated maritime pine charcoal in powder form (Ceca 2S/E) are charged into a 0.5 liter glass flask, containing 90 ml of demineralized water and 0.28 g of Na_2CO_3 .

The suspension is maintained at room temperature (20-25°C), under stirring, for 10 minutes.

0.101 g of a solution of H_2PtCl_6 (8% by weight of Pt) and 0.80 g of Na_2PdCl_4 (10% Pd) diluted in 10 ml of water, are subsequently added dropwise, under stirring.

The suspension is kept at room temperature for 10 minutes and is then heated in a water bath for 10 minutes to 90°C. A solution containing 760 mg of sodium formate in 10 ml of water is then added and the stirring is continued at 90°C for 2 hours.

After cooling to room temperature, the suspension is filtered and the recovered charcoal is washed with distilled water until the chlorides have been eliminated and dried in an oven at 120°C for 2 hours.

The end catalyst contains 1% of Pd and 0.1% of Pt, the active phase was obtained by co-impregnation of Pd and Pt.

EXAMPLE 4 (comparative)

The same procedure is adopted as described in example 3, but using only the Pd salt in the preparation.

A catalyst is obtained, containing 1% of Pd on activated carbon.

EXAMPLE 5 (comparative)

The same procedure is adopted as described in example 3, but using only the Pt salt in the preparation.

A catalyst is obtained, containing 0.1% of Pt on acti-

vated carbon.

EXAMPLE 6

Synthesis of H_2O_2

A micropilot plant is used, consisting of a Hastelloy C autoclave equipped with a thermostat-regulation system, magnetic drag stirring, a regulation and control system of the pressure during the reaction, a filter for continuously removing the liquid phase containing the reaction products, a feeding system of the solvent mixture in which the reaction takes place and a series of instruments for the regulation and control of the gaseous feeds. The reaction trend is followed by continuously analyzing the hydrogen and oxygen in the feeding and at the outlet of the reactor.

The selectivity with respect to the converted hydrogen is calculated on the basis of the concentration of H_2O_2 in the reaction effluent and on the basis of analysis of the H_2 leaving the reactor. The concentration of H_2O_2 which is formed is determined by titration with potassium permanganate.

0.6 g of catalyst prepared as described in example 1 and 200 g of methanol:water solution (95/5 by weight) containing 6 ppm of HBr and 300 ppm of H_2SO_4 are charged into the reactor.

The autoclave is pressurized, without stirring, at 100 bars with a gaseous mixture consisting of 3.6% of H_2 , 10%

of O₂ and 86.4% of N₂. The stirring is then started up to 800 revs/minute, the pressure is maintained with a continuous stream, 700 normal liters (Nl), of the same gaseous mixture, and 300 g/hour of a methanol:water solution having the composition defined above, is fed at the same time. The temperature inside the reactor is kept at 6°C. The results are indicated in Table 1.

Table 1

Hrs of reaction	H ₂ O ₂ wt %	Molar selectivity H ₂ O ₂ %
5	4.7	83
10	4.6	84
20	4.6	84
50	4.5	86

EXAMPLE 7

Example 6 is repeated using the catalyst prepared in example 2.

The results obtained are indicated in Table 2.

Table 2

Hrs of reaction	H ₂ O ₂ wt %	Molar selectivity H ₂ O ₂ %
5	6.5	70
10	6.6	71
20	6.4	71
50	6.6	72

EXAMPLE 8

Example 6 is repeated using a catalyst prepared as in example 2, but using a sulfonated carbon as carrier, prepared as described in example 1 of Italian patent MI 98-A-01843.

The results are indicated in Table 3.

Table 3

Hrs of reaction	H ₂ O ₂ wt %	Molar selectivity H ₂ O ₂ %
5	6.2	73
10	6.4	74
20	6.5	73
30	6.3	75
50	6.6	76
100	6.5	75

EXAMPLE 9 (comparative)

Example 6 is repeated using the catalyst prepared in example 3. The results obtained are indicated in Table 4.

Table 4

Hrs of reaction	H ₂ O ₂ wt %	Molar selectivity H ₂ O ₂ %
5	4.8	75
10	4.9	76
20	4.7	77
50	4.6	77

EXAMPLE 10 (comparative)

Example 6 is repeated using the catalyst prepared in example 4.

The results obtained are indicated in Table 5.

Table 5

Hrs of reaction	H ₂ O ₂ wt %	Molar selectivity H ₂ O ₂ %
5	0.9	35
10	0.8	37

EXAMPLE 11 (comparative)

Example 6 is repeated using the catalyst prepared in example 5.

The results obtained are indicated in Table 6.

Table 6

Hrs of reaction	H ₂ O ₂ wt %	Molar selectivity H ₂ O ₂ %
5	1.7	22
10	1.5	25

CLAIMS

1. A process for the synthesis of hydrogen peroxide by means of the direct reaction of hydrogen with oxygen, in a solvent medium containing a halogenated promoter and an acid promoter, in the presence of a bimetallic catalyst obtained by dispersing in sequence and alternating the single metal components of the catalyst on a carrier.
2. The process according to claim 1, wherein the metal components of the catalyst are selected from those of the platinum group.
3. The process according to claim 2, wherein the metals are palladium and platinum.
4. The process according to claim 3, wherein the catalyst contains a quantity of palladium ranging from 0.01 to 5% by weight and a quantity of platinum ranging from 0.01 to 1% by weight, with an atomic ratio platinum/palladium ranging from 0.1/99.9 to 50/50.
5. The process according to claim 4, wherein the catalyst contains a quantity of palladium ranging from 0.4 to 2% by weight and a quantity of platinum ranging from 0.05 to 0.5% by weight, with an atomic ratio platinum/palladium ranging from 1/99 to 30/70.
6. The process according to any one of the preceding claims, wherein the carrier is selected from activated carbon, activated carbon



functionalized with sulfonic groups, silica, alumina, silica-alumina and zeolites.

7. The process according to claim 6, wherein the carrier is an activated carbon with a low ash content and a surface area of at least 100 m²/g.
8. The process according to claim 7, wherein the activated carbon has a surface area higher than 300 m²/g.
9. The process according to any one of the preceding claims, wherein the bimetallic catalyst is obtained by:
 - (a) preparation of the solutions or suspensions of the precursors of the single metal components of the catalytic system;
 - (b) dispersion of the solutions or suspensions obtained in (a) in sequence on a carrier;
 - (c) treatment of the catalyst with a reducing agent of the metal and drying at 120-140°C between one dispersion and another.
10. The process according to claim 9, wherein steps (b) and (c) can be repeated once or several times.
11. The process according to claim 9 or 10, wherein the precursors of the metals are their salts or soluble complexes selected from acetates, halides and nitrates.
12. The process according to claim 9, 10 or 11, wherein the dispersion of the precursors of the single metal components of the catalytic system on the carrier is carried out



by means of precipitation, impregnation or adsorption.

13. The process according to any one of claims 9 to 12, wherein the reduction of the metals is carried out by means of thermal and/or chemical treatment with reducing substances such as hydrogen, sodium formiate or sodium citrate.
14. The process according to any one of the preceding claims, wherein the reaction medium is selected from water, a C₁-C₃ alcohol or a mixture of these.
15. The process according to claim 14, wherein the alcohol is methanol.
16. The process according to claim 14 or 15, wherein the reaction medium is a mixture of alcohol:water with a weight ratio between the two ranging from 50:50 to 99.9:0.1.
17. The process according to claim 16, wherein the weight ratio alcohol:water ranges from 90:10 to 99:1.
18. The process according to any one of the preceding claims, wherein the halogenated promoter is selected from substances capable of generating halogen ions in the liquid reaction medium.
19. The process according to claim 18, wherein the halogenated promoter is selected from substances capable of generating bromide ions such as hydrobromic acid and its salts soluble in the reaction medium such as alkaline bromides, sodium bromate or ammonium bromide.
20. The process according to claim 19, wherein the com-



pound is hydrobromic acid, sodium bromide or potassium bromide.

21. The process according to any one of the preceding claims, wherein the concentration of halogenated promoter ranges from 0.1 to 50 mg per kg of solution.
22. The process according to claim 21, wherein the concentration of halogenated promoter ranges from 1 to 10 mg per kg of solution.
23. The process according to any one of the preceding claims, wherein the acid promoter is selected from substances capable of generating H^+ hydrogen ions in the reaction medium.
24. The process according to claim 23, wherein the acid promoter is selected from inorganic acids such as sulfuric, phosphoric, nitric acid or from organic acids such as sulfonic acids.
25. The process according to claim 24, wherein the acid promoter is sulfuric acid or phosphoric acid.
26. The process according to any one of the preceding claims, wherein the concentration of the acid promoter ranges from 20 to 1000 mg per kg of solution.
27. The process according to claim 26, wherein the concentration of the acid promoter ranges from 50 to 500 mg per kg of solution.
28. The process according to any one of the preceding claims, wherein the catalyst is used in quantities ranging from 10^{-6} to 10^{-2} moles



of total metal contained in the catalyst per liter of reaction medium.

29. The process according to claim 28, wherein the catalyst is used in quantities ranging from 10^{-4} to 10^{-3} moles of total metal contained in the catalyst per liter of reaction medium.
30. The process according to any one of the preceding claims, wherein the reaction is carried out at a temperature ranging from -5 to 90°C.
31. The process according to claim 30, wherein the temperature ranges from 2 to 50°C.
32. The process according to any one of the preceding claims, wherein the reaction is carried out at a total pressure higher than atmospheric pressure.
33. The process according to claim 32, wherein the total pressure ranges from 50 to 300 atmospheres.
34. The process according to any one of the preceding claims, wherein the molar ratio hydrogen:oxygen in the feeding ranges from 1:2 to 1:100.
35. The process according to claim 34, wherein the molar ratio hydrogen:oxygen in the feeding ranges from 1:3 to 1:15.
36. The process according to any one of the preceding claims, wherein the reaction is carried out in the presence of an inert gas selected from nitrogen, helium, argon.



37. The process according to claim 36, wherein the inert gas is nitrogen.
38. The process according to any one of the preceding claims, wherein the concentration of hydrogen in the gaseous phase in contact with the liquid reaction medium is maintained at a value lower than 4.5% molar.
39. The process according to any one of the preceding claims, wherein the reaction is carried out using air as oxygen source.
40. The process according to any one of the preceding claims, wherein the reaction is carried out batchwise or in continuous.
41. The process according to any one of the preceding claims, wherein the solution of hydrogen peroxide is used directly in an oxidation process of a substrate selected from olefins, aromatic hydrocarbons, ammonia and carbonyl compounds using titanium silicalite as catalyst.
42. A bimetallic catalyst useful for the production of hydrogen peroxide obtained by dispersing in sequence and alternating the precursors of the single metal components of the catalyst by :
- (a) preparation of the solutions or suspensions of the precursors of the single metal components of the catalytic system;
 - (b) dispersion of the solutions or suspensions obtained in (a) in sequence on a carrier;
 - (c) treatment of the catalyst with a reducing agent of



the metal and drying at 120-140°C between one dispersion and another.

43. The catalyst according to claim 42, wherein steps (b) and (c) can be repeated once or several times.
44. The catalyst according to claim 42 or 43, wherein the metal components of the catalyst are selected from those of the platinum group.
45. The catalyst according to claim 44, wherein the metals are palladium and platinum.

