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(54) Title: SUPPORTED METAL CATALYST, PREPARATION AND APPLICATIONS FOR DIRECTLY MAKING HYDROGEN PEROXIDE

(54) Titre: CATALYSEUR METALLIQUE SUPPORTE, SA PREPARATION ET SES APPLICATIONS DANS LA FABRICATION DIRECTE DU PEROXYDE D'HYDROGENE

(57) Abstract: The invention concerns a supported metal catalyst based on at least one metal selected in the group M consisting of palladium, platinum, ruthenium, rhodium, iridium, holmium, osmium and gold, used for directly making hydrogen peroxide from hydrogen and oxygen. The invention also concerns a method for making said catalyst comprising successively an impregnating step with a solution based on one or several salt(s) of at least one metal of group M on a support, and a reduction step characterised in that at the end of the reduction step, the catalyst is treated with an aqueous acid solution comprising bromine and bromide ions. The catalyst is characterised by metal or crystallised metal aggregates with size ranging between 0.1 and 20 microns and preferably between 0.1 and 10 microns. The supported bimetal catalyst is preferred, for example Pd-Pt, Au-Pt, Pd-Ho and Pd-Au.

(57) Abrégé: La présente invention concerne un catalyseur métallique supporté à base d'au moins un métal choisi dans le groupe M formé de palladium, platine, ruthénium, rhodium, d'iridium, d'holmium, d'osmium et d'or, utilisé dans la fabrication directe du peroxyde d'hydrogène à partir d'hydrogène et d'oxygène. Le procédé de préparation du catalyseur comprenant successivement une étape d'imprégnation d'une solution à base d'un ou plusieurs sel(s) d'au moins un métal du groupe M sur un support, et une étape de réduction caractérisée en ce qu'à l'issue de l'étape de réduction, le catalyseur est soumis à un traitement avec une solution aqueuse acide comprenant du brome et des ions bromure. Le catalyseur est caractérisé par des amas de métal ou métaux cristallisés de taille comprise entre 0,1 et 20 microns et de préférence comprise entre 0,1 et 10 microns. Le catalyseur bimétallique supporté est préféré, par exemple Pd-Pt, Au-Pt, Pd-Ho et Pd-Au.

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SUPPORTED METAL CATALYST, ITS PREPARATION AND ITS APPLICATIONS IN THE DIRECT MANUFACTURE OF HYDROGEN PEROXIDE

The present invention relates to a supported metal catalyst suitable for the direct manufacture of hydrogen peroxide from hydrogen and oxygen. The subject of the invention is also the process for manufacturing the said catalyst and the process for manufacturing hydrogen peroxide using said catalyst.

The low productivity of the process for catalytic manufacturing of hydrogen peroxide directly from hydrogen and oxygen is an impediment to its development. There have been many attempts to improve this productivity. Mention may be made, for example, of US 3 336 112, US 3 361 533, US 4 007 526, US 4 009 252, US 4 279 883 and US 4 335 092. These studies are mainly based on a general concept, namely the stabilization of hydrogen peroxide using a sequestrate or a decomposition inhibitor.

Other ways of improving the hydrogen peroxide productivity of the direct process have also been explored. Thus, patent US 4 379 778 discloses a process for the direct manufacturing of hydrogen peroxide from hydrogen and oxygen in an aqueous medium containing decomposition inhibitors in the presence of a palladium-carbon catalyst pretreated with an aldehyde

or ketone and preferably also pretreated with a dilute hydrochloric acid solution.

The use of a bromide in the aqueous reaction mixture of the direct hydrogen peroxide manufacturing process is described in the patent US 4 772 458.

Finally, patents US 5 128 114 and US 5 352 645 describe a method of preparing catalysts based on palladium or platinum-palladium supported on non-agglomerated uniform porous silica microspheres which are attrition-resistant thanks to the use of ammonia citrate or of urea as additive and are suitable for the direct manufacture of hydrogen peroxide.

Example 12 of patent US 5 128 114 describes the preparation in two steps of a supported catalyst containing about 0.05% by weight of platinum and 1% by weight of palladium on porous silica microspheres. The support is firstly prepared by spray drying a mixture of Ludox AS 40 silica and urea, which is then calcined at 650°C in nitrogen. This support is then added to a solution of Pt and Pd, prepared beforehand by dissolving H_2PtCl_6 and $PdCl_2$ in water, heated to a temperature of between 60 and 70°C and acidified by concentrated HCl until a pH of about 1.2 is obtained. The resulting mixture is stirred, then spray dried and finally the powder obtained is reduced in a stream of hydrogen at 300°C.

The preparation of the supported catalyst according to Example 15 of patent US 5 352 645 is similar to that described in Example 12 of patent

US 5 128 114 with, however, one difference. This is because the resulting mixture, instead of being spray dried, is vacuum dried at 100°C overnight and then the dried solid is reduced in a stream of hydrogen at 100°C. Metal crystallites of the order of 30 to 50 Å were thus obtained.

The filing company has developed a supported catalyst based on at least one metal selected from the group M formed from palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold and, in particular, a supported bimetallic catalyst. In general the supported bimetallic catalyst consists of a majority metal from the group M and a minority metal from the group M. The majority metal represents about 0.1 to 10% by weight of the catalyst and preferably between 0.5 and 1% by weight. The minority metal represents about 0.001 to 0.1% by weight of the catalyst and preferably between 0.01 and 0.05%.

Palladium and gold are advantageously selected as the majority metal.

Platinum and holmium are advantageously selected as the minority metal.

The supported bimetallic catalyst particularly preferred consists of palladium as the majority metal and platinum as the minority metal.

A supported multi-metal catalyst according to the invention may consist of a majority metal from the group M and of several minority metals from the group M. The preferred supported multi-metal

catalyst comprises palladium as the majority metal and platinum and at least one metal from the group M as minority metals.

The majority metal content in the supported multi-metal catalyst is virtually identical to that of the bimetallic catalyst and each minority metal may be present in the catalyst in an amount representing about 0.001 to 0.1% by weight of the catalyst and preferably between about 0.01 and 0.05%.

The present invention furthermore provides a supported single-metal catalyst with, preferably, platinum or gold as the metallic constituent of the group M. The content of metallic constituent is in general between 0.1 and 10% by weight of the catalyst and preferably between 0.5 and 1% by weight.

Preferably, the supported metal catalyst according to the invention is characterized by clusters of crystallized metal or metals having a size of between 0.1 and 20 μm and preferably between 1 and 10 μm.

Silica, alumina, carbon and aluminosilicates may be suitable as support. However, it is preferred to use silica, and advantageously silica particles having a mean size of between 1 and 50 μm. It is also preferred to use silica having a BET specific surface area greater than 200 m^2/g and usually between 300 and 600 m^2/g. Aldrich's microporous silica referenced 28,851-9 has proved to be particularly useful.

The amount of iron (Fe) in the chosen support is preferably less than 0.001% by weight.

According to one aspect, the invention provides a process for preparing a supported catalyst based on at least one metal from the group M defined above. This process, comprising, in succession, a step of impregnating a solution based on one or more salts of at least one metal, selected from the group M on a support and a reduction step, is characterized in that, after the reduction step, the catalyst is subjected to a treatment with an aqueous acid solution (A) containing bromine and bromide ions.

According to the present invention, the concentration of bromide ions in the aqueous solution (A) may be between 20 and 200 mg/l and preferably between 20 and 100 mg/l. The concentration of bromine (Br_2) may be between 2 and 20 mg/l and preferably between 2 and 10 mg/l.

The pH of the aqueous solution (A) is preferably between 1 and 3.

The aqueous solution (A) may be prepared, for example, by dissolving an alkali or alkaline-earth metal bromide in water, then by adding bromine in bromine water form advantageously with a concentration close to 1% by weight and, finally, the pH may be adjusted using an acid. When the catalyst to be prepared comprises Pd, the solution (A) is made acid by sulfuric acid or phosphoric acid. Orthophosphoric acid (H_3PO_4) is however preferred.

The solution (A) particularly preferred contains about 100 mg/l of NaBr, 10 mg/l of Br_2 and 10 g/l of orthophosphoric acid.

In general, the process is carried out with a small amount of supported catalyst of between 5 and 50 g per liter of solution (A). An amount of catalyst close to 10 g per liter of solution (A) is preferred.

The treatment temperature is in general between 10 and 80°C and preferably between 40 and 60°C.

The treatment time may vary between wide limits. This time may be between 1 and 12 hours and preferably between 4 and 8 hours.

After the treatment, the catalytic solid is separated from the aqueous solution (A) by any known means and then dried at a temperature of between 100 and 140°C and preferably close to 120°C. Usually, the drying is carried out at atmospheric pressure, for example by means of a fan oven.

Impregnation of the support may be carried out by any known means. Advantageously, the impregnation step consists in bringing the chosen support into contact with the most concentrated possible aqueous solution of the salt or salts of at least one metal from the group M so as to form a slurry. This contacting step may be carried out by adding the concentrated aqueous solution of metal salt(s), at room temperature, to a mixer containing the support. The mixing time depends in general on the amount of support employed, but for productivity reasons it is preferred,

after the metal solution has been added, to mix for about 0.5 to 3 hours.

After mixing and before the reduction step, the resulting slurry is preferably filtered, then drained and finally dried. To ensure maximum draining, it is recommended to carefully compress the filtered slurry. After draining, the impregnated support is dried preferably at a temperature of between 20 and 50°C. Advantageously, the drying is carried out under conditions conducive to slow crystallization and preferably in the absence of agitation. The drying time depends in general on the temperature and the pressure. It is usually between 1 and 7 days. As an indication in a vacuum oven heated to 40°C, 48 hours are enough to dry the impregnated and drained solid. The drying may also be carried out at room temperature for a week.

One particular method of preparing the supported catalyst based on at least one metal from the group M comprises, in succession, the following steps:

(a) bringing a support, selected from the group formed by silica, alumina, carbon and aluminosilicates, into contact with a concentrated aqueous solution of one or more salts of at least one metal from the group M so as to form a slurry;

(b) filtering, draining and then drying the slurry under conditions conducive to slow crystallization;

(c) reducing the solid dried in step (b);

(d) treating the solid reduced in step (c) with an aqueous acid solution (A) containing bromine and bromide ions; and

(e) filtering the solid treated in step (d) and drying it at a temperature of between 100 and 140°C.

The preferred operating conditions for each step of the preparation are the same as those described above. With regard to the reduction step, the experimental conditions already used in the prior art, for example US 5 128 114 and US 5 352 645, may be applied.

Any known means for helping the metal salts to dissolve, so as to obtain a concentrated aqueous solution for the impregnation step (a), may be used. The use of a few drops of acid, slight heating and ultrasonic stirring may especially be mentioned.

It is preferred to grind the dried solid from step (b) before subjecting it to the reduction step. In practice, the oven used for the reduction is firstly purged with nitrogen for a sufficient time, generally 15 and 60 minutes, then flushed with hydrogen before being heated to a temperature of between 250 and 350°C. The solid reduction time at the chosen temperature may be between 1 and 3 hours. After reduction, the oven is returned to room temperature and then purged with nitrogen.

According to another aspect, the invention provides a supported catalyst based on at least one metal from the group M defined above, the content of a selected metal being between 0.1 and 10% by weight of the catalyst, the catalyst support being other than aluminia, characterized by clusters of crystallized metal or metals having a size of between 0.1 and 20 μm.

According to a further aspect, the invention provides a process for direct manufacture of hydrogen peroxide from

hydrogen and oxygen. This process is characterized in that the catalyst described and prepared above is used.

The catalyst may be used in a process for the direct manufacture of hydrogen peroxide both in a tube reactor and in a stirred reactor. It is most particularly suitable for the process in which hydrogen and oxygen are injected into the aqueous reaction mixture in the stirred reactor and oxygen is introduced into the continuous gas phase in the stirred reactor.

Advantageously, the catalyst may be used in a direct hydrogen peroxide manufacturing process in which the hydrogen and oxygen are injected into the lower part of the aqueous reaction mixture and oxygen is introduced into the continuous gas phase in the stirred reactor in an amount such that the composition of this continuous gas phase is outside the flamability range.

The catalyst has proved to be very beneficial when the stirred reactor is provided with several turbines arranged along a single vertical axis. When the hydrogen and oxygen are injected in the form of small bubbles into the lower part of the aqueous reaction mixture in proportions such that the ratio of the hydrogen molar flow rate to the oxygen molar flow rate is greater than 0.0416, a higher hydrogen peroxide productivity than that in the prior art is obtained.

The catalyst has proved to be particularly beneficial in a continuous direct hydrogen peroxide manufacturing process with recycling of the reactants, such as hydrogen.

EXPERIMENTAL PART

Preparation of the catalysts

Example 1

The following were added at room temperature into 50 cm^3 of demineralized water:

- 0.33 g of $PdCl_2$ (Aldrich reference: 20,588-5);
- 0.021 g of H_2PtCl_6 (Aldrich reference: 25,402-9);

and a few drops of 30% by weight of HCl in order to aid dissolution;

- 20 g of microporous silica Aldrich (reference 28,851-9) having the following characteristics:

mean particle size:	25 µm
BET surface area:	500 m^2/g
pore volume:	0.75 cm^3/g
mean pore diameter:	60 Å

were placed in a glass beaker, stirred using a bar magnet. 50 cm^3 of the metal salt solution prepared above were then rapidly added.

After stirring for 1 hour 30 minutes at 25°C, a thick stock was obtained, which was filtered over a No. 3 glass frit and vacuum drained for 2 hours 30 minutes. The filter cake was placed in a crystallizer over a glass cloth and dried for 48 hours at 40°C in a vacuum oven. Next, the dried solid was reduced in a stream of 60 Nl/h of H_2 at 300°C for

1 hour 30 minutes and then cooled to room temperature over 6 hours.

The reduced solid was then treated at 40°C for 5 hours with 2000 cm^3 of a solution containing 100 mg/l of NaBr, 10 mg/l of Br_2 and 10 g/l of H_3PO_4.

Next, the resulting mixture was filtered and the catalyst dried for 24 hours in a fan oven at 120°C.

After analysis the catalyst contained 0.7% Pd and 0.03% platinum by weight.

Example 2

The procedure was as in Example 1, with the sole difference that the reduced solid was used directly as a catalyst without treatment with the aqueous brominated solution.

Example 3

After the silica was impregnated in Example 1, instead of filtering the stock and draining the filtered slurry, the stock was dried in a laboratory rotary evaporator (Heidolph with a 500 cm^3 fluted round-bottomed glass flask). The flask was rotated in an oil bath at 120°C in a vacuum of 40 mmHg. After evaporation, the solid was reduced and then treated as described in Example 1.

Example 4

The procedure was as described in Example 3 except that the solid after reduction was not treated with the aqueous brominated solution.

Example 5

The procedure was as described in Example 3 except that after impregnation the stock was left in the ambient air for 1 week instead of being dried in the rotary evaporator.

Example 6

The procedure was as described in Example 1 except that the Pd was replaced with Au.

Example 7

The procedure was as described in Example 1 except that the Pt was replaced with Ho.

Example 8

The procedure was as described in Example 1 except that the Pt was replaced with Au.

Preparation of the hydrogen peroxide solution

General operating method

A chosen amount of aqueous reaction mixture and catalyst was introduced into a cylindrical reactor, having a total capacity of 1500 cm^3, fitted with two or

three flanged turbines 45 mm in diameter, with 4 vertical baffles and with a bundle of cooling tubes.

The aqueous reaction mixture was prepared by adding 12 g of H_3PO_4, 58 mg of NaBr and 5 mg of Br_2 in 1000 cm^3 of demineralized water.

The reactor was pressurized by injecting oxygen into the continuous gas phase with a chosen flow rate. The pressure was kept constant by means of a pressure regulator. The liquid medium was raised to the chosen temperature by the circulation of thermostated water through the bundle of cooling tubes.

The stirring was set at 1900 rpm and oxygen and hydrogen were injected into the liquid phase at the center of the bottom turbine with chosen flow rates.

The flow rate and the hydrogen content of the gas mixture leaving the pressure regulator were measured. After the anticipated reaction time had elapsed, the feed of hydrogen and oxygen into the aqueous reaction mixture was cut and the injection of oxygen into the continuous gas phase was continued until the hydrogen in the latter disappeared. The oxygen fed was then cut and the reactor decompressed.

The aqueous hydrogen peroxide solution was weighed and separated from the catalyst by filtration over a Millipore® filter.

This solution was then assayed by iodometry in order to determine the H_2O_2 concentration. The H_2O_2 selectivity is defined as the percentage ratio of the

number of moles of H_2O_2 formed to the number of moles of H_2 consumed.

The degree of conversion is defined as being the percentage ratio of the volume of H_2 consumed to the volume of H_2 injected.

The catalyst results for each trial are summarized in Table I.

Table I

Trial No.	Catalyst example	REACTION MIXTURE		REACTION CONDITIONS							RESULTS		
		CATALYST Weight (g)	WORKING SOLUTION Weight (g)	P (bar)	Reaction Temp. (°C)	H_2 injected into the liquid phase (Nl/h)	O_2 injected into the liquid phase (Nl/h)	O_2 injected into the gas phase (Nl/h)	Number of turbines	Time (h)	H_2O_2 (%)	H_2O_2 selectivity	H_2 Conversion (%)
1	1	6	700	50	20	80	188	1760	2	3	17.5	97	42.0
2	1	6	700	50	20	80	188	1760	2	3	17.4	96	42.0
3	2	6	700	50	20	80	188	1760	2	3	16.2	85	45.0
4	3	6	700	50	20	80	160	1760	2	3	16.3	84	45.8
5	4	6	700	50	20	80	160	1760	2	3	15.4	82	44.0
6	1	6	700	50	41.2	120	240	2640	2	1	12.2	90	60.2
7	5	6	700	50	41.5	120	240	2640	3	1	12.4	86	64.3
8	1	8.5	1000	50	39.8	120	240	2640	3	1	10.6	90	72.5
9	6	8.5	1000	50	40.5	120	240	2640	3	1	6.4	54	71.6
10	7	8.5	1000	50	39.5	120	240	2640	3	1	7.8	76	61.6
11	8	8.5	1000	50	40	120	240	2640	3	1	7.9	73	65.6

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CLAIMS

1. A process for preparing a supported catalyst based on at least one metal from the group M formed by palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold; comprising, in succession, a step of impregnating a solution based on one or more salt(s) of at least one metal from the group M on a support, and a reduction step, characterized in that, after the reduction step, the catalyst is subjected to a treatment with an aqueous acid solution (A) containing bromine and bromide ions.

2. The process as claimed in claim 1, characterized in that the concentration of bromide ions in the aqueous solution (A) is between 20 and 200 mg/l.

3. The process as claimed in claim 1 characterized in that the concentration of bromide ions in the aqueous solution (A) is between 20 and 100 mg/l.

4. The process as claimed in any one of claims 1 to 3, characterized in that the bromine concentration is between 2 and 20 mg/l.

5. The process as claimed in any one of claims 1 to 3, characterized in that the bromine concentration is between 2 and 10 mg/l.

6. The process as claimed in any one of claims 1 to 5, characterized in that the pH of the aqueous solution (A) is between 1 and 3.

7. The process as claimed in any one of claims 1 to 6, characterized in that the treatment temperature is between 10 and 80°C.

8. The process as claimed in any one of claims 1 to 6, characterized in that the treatment temperature is between 40 and 60°C.

9. The process as claimed in any one of claims 1 to 8, characterized in that after the treatment the catalytic solid is separated from the solution A and then dried at a temperature of between 100 and 140°C.

10. The process as claimed in any one of claims 1 to 9, characterized in that, after impregnation and before the reduction step, the resulting slurry is filtered, then drained and finally dried.

11. The process as claimed in claim 10, characterized in that the drying is carried out under conditions conducive to slow crystallization.

12. The process as claimed in any one of claims 1 to 11, characterized in that palladium and gold are selected.

13. The process as claimed in any one of claims 1 to 11, characterized in that the catalyst is a supported bimetallic catalyst in which the minority metal represents between 0.001 to 0.1% by weight of the catalyst.

14. The process as claimed in claim 13, characterized in that the minority metal is platinum.

15. The process as claimed in any one of claims 1 to 14, characterized in that the support is a silica having a BET specific surface area of greater than 200 m^2/g.

16. A supported catalyst based on at least one metal selected from the group M formed by palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold, the content of a selected metal being between 0.1 and 10% by weight of the catalyst, the catalyst support being other than alumina, characterized by clusters of crystallized metal or metals having a size of between 0.1 and 20 μm.

17. The catalyst as claimed in claim 16, characterized by clusters of crystallised metal or metals having a size of between 0.1 and 10 μm.

18. The catalyst as claimed in claim 16 or 17, characterized in that palladium and gold are selected.

19. The catalyst as claimed in any one of claims 16 to 18, characterized in that the catalyst is a supported bimetallic catalyst in which the minority metal represents between 0.001 to 0.1% by weight of the catalyst.

20. The catalyst as claimed in claim 19, characterized in that the minority metal is platinum.

21. The catalyst as claimed in any one of claims 16 to 20, characterized in that the support is a silica having a BET specific surface area of greater than 200 m^2/g.

22. A process for the direct manufacture of hydrogen peroxide from hydrogen and oxygen, characterized in that a catalyst prepared by the process claimed in any one of claims 1 to 15 or a catalyst as claimed in any one of claims 16 to 21 is used.