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(54) Title: PROCESS FOR THE PREPARATION OF AN AQUEOUS COLLOIDAL PRECIOUS METAL SUSPENSION

(57) **Abrégé/Abstract:**

The invention is directed to a process for the preparation of an aqueous colloidal precious metal suspension, which process comprises reducing a precious metal salt in aqueous solution using a functionalised, water soluble quaternary ammonium salt in the absence of organic solvents, to form elementary nanoparticles.



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Title: Process for the preparation of an aqueous colloidal precious metal suspension

The invention is directed to a process for the preparation of an aqueous colloidal precious metal suspension, as well as to the preparation of a supported precious metal catalyst, using the said suspension.

5 Metal colloids, more in particular precious metal colloids, are used as starting materials for the preparation of supported (precious) metal catalysts. Precious metal colloids are usually prepared by reducing a precious metal ion in an organic solvent, mostly at elevated temperature.

10 The most often used method is reduction using an alcohol. This can either be a low boiling alcohol, such as the C₁ to C₄ alcohols, more in particular methanol, or high boiling solvents containing a hydroxyl group, such as ethylene glycol, or diethylene glycol mono-n-butyl ether. When low boiling alcohols are used, a separate stabilizer is added. The metal salt (ion) is mixed with the stabilizer in an alcoholic solution and refluxed for several hours. The high boiling materials require very high temperatures and often a protective
15 atmosphere (nitrogen) and/or a high pH.

There are some methods which do not require the use of organic solvents or additives, such as the use of citrate as reductant and stabilizer. The lower limit of the particle size is, however, about 5 nm. It is difficult, or even impossible to produce nanoparticles of lower particle size.

20 The use of borate as reducing agent has the disadvantage of high pH and a very cumbersome feed method, if one needs a narrow particle size distribution. This method is already difficult at laboratory scale, but impossible to operate at industrial scale. The same applies to the use of 3-acetic acid thiophene as reducing and stabilizing agent.

Accordingly it is an object of the present invention to provide a process that has one or more of the following advantages over the prior art:

- absence of organic solvent;
- mild conditions of pH and temperature
- 5 - short reaction times
- no specific requirements as to protective atmosphere
- no special mixing and stirring conditions
- broad range of particle sizes that can be produced; even below 5 nm
- use of environmentally safe reactants.

10

An important use of the colloidal nanoparticles resides in the preparation of supported precious metal catalysts. Traditional methods for the preparation thereof generally yield catalysts that have small metal crystallites, but show a rather broad size distribution. It would be useful to
15 have a process wherein the crystallite size distribution of the nanoparticles is rather narrow, thereby enabling the production of catalysts having a narrow crystallite size distribution.

The present invention encompasses in a first embodiment a process for the preparation of an aqueous colloidal precious metal suspension, which
20 process comprises reducing a precious metal salt in aqueous solution using a functionalised, water soluble quaternary ammonium salt in the absence of organic solvents, to form elementary nanoparticles.

An essential element of the process of the present invention resides in the use of the specific quaternary ammonium salt, namely a functionalised
25 quaternary ammonium salt. In this respect the functionalisation comprises the presence of at least one reducing group, such as $-\text{CH}_2\text{OH}$ or cyclohexenyl, preferably in combination with at least one bulky group selected from the group of C_6^+ -alkyl, cycloalkyl, aralkyl, alkaryl or aryl groups. In addition the quaternary ammonium salt can be chiral, such as a quaternised cinchonine or
30 cinchonidine.

Preferred quaternary ammonium salts to be used in the process of the present invention are of the formula I:



wherein R, R', and R'' are independently of each other C₁-alkyl and higher and X is Cl, Br, H₂PO₄, NO₃, SO₄, etc. Preferably, R and R' are C₁-alkyl, and R'' is C₆- and higher, more preferred C₁₆-alkyl.

The particle size of the elementary nanoparticles that are obtained by the process of the present invention is between 1 and 50, preferably between 1 and 10 nm.

The precious metal is selected from the group of platinum, palladium, iridium, rhodium, ruthenium, rhenium, silver, gold and combinations thereof, preferably palladium. Preferably a palladium salt is used, more specifically Na₂PdCl₄.

The process of the invention is very simple, as it suffices to combine the precious metal salt and the quaternary ammonium compound in an aqueous system, for example by mixing aqueous solutions of respectively the quaternary ammonium compound and the precious metal salt at a suitable temperature. Suitable temperatures are mainly determined by the reaction rate and the requirement that the compounds remain dissolved in a liquid system. Suitable temperatures for the solutions and the reaction mixture are between room temperature (20°C) and near boiling point (95°C).

According to a second embodiment the colloidal suspension may be used as catalytic material or for the preparation thereof.

According to a third embodiment of the invention, the colloidal suspension is used to produce supported precious metal catalysts. This process comprises preparing an aqueous colloidal precious metal suspension in accordance with the above process according to the invention, followed by contacting the suspension with a support material and recovering the precious metal catalyst or catalyst precursor by filtration and washing, optionally after addition of an aqueous alkaline solution (NaOH and the like) or ethanol.

The support is selected from the group of oxidic supports, such as silica, alumina, zirconia, titanium oxide and zinc-oxide, silicates, aluminates and active carbon. The amount of precious metal, calculated on the weight of the final catalyst is between 0.01 and 10 wt.%, preferably between 0.05 and 5
5 wt.% of the catalyst. The support may be in powder form, in the form of shaped particles, such as extrudates, or in the form of a structured material, such as a monolith.

The colloidal suspension produced in accordance with the process of the first embodiment of the invention as well as the heterogeneous catalyst
10 produced in accordance with the process of this third embodiment of the invention may be used generally for all reactions for which precious metal catalysts are suitable. Examples are the usual hydrogenation reactions, such as hydrogenation itself, hydro-isomerisation, hydro-desulfurisation and hydro-dewaxing. The catalyst may also have been used in dehydrogenation reactions,
15 such as catalytic reforming.

More in particular the catalyst is suitable for the production of 3-hexenol, which process comprises reducing 3-hexyn-1-ol in the presence of a catalyst as produced in accordance with the process above.

This process may conveniently be carried out in slurry phase or in a
20 fixed bed in an organic solvent and the presence of hydrogen, either in a three phase system or in a two phase system, where the hydrogen is dissolved in the organic solvent. Preferred conditions for a slurry phase reaction are the use of an alkanol, such as hydrous ethanol as solvent, in the presence of 1 to 20 bar of gaseous hydrogen at a temperature between room temperature and about
25 75°C.

Examples

Example 1

5 Preparation of a colloidal suspension of palladium.

A solution of 15 g hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogen phosphate in 1 L water is heated to 60°C. A solution of 0.75 g Pd (as Na₂PdCl₄) in 10 mL water is added in 3 minutes under vigorous stirring. The mixture is
10 heated to 85°C and stirred at this temperature for 2 hours. The heating is stopped and the colloidal suspension, thus obtained, is stirred for an additional hour, during which it cools down to 40°C.

Example 2

15

Preparation of supported palladium catalyst.

A slurry of 75 g carbon powder in 750 mL water is vigorously stirred for an hour at room temperature. The colloidal suspension obtained according to
20 Example 1, containing 0.75 g Pd in 1 L water is added in 40 minutes. The mixture is stirred for an additional 45 minutes. The pH of the mixture is adjusted from 2.4 to 9.3 by addition of a 10% NaOH solution in 28 minutes. The mixture is stirred an additional 30 minutes, while the pH is kept between 9.0 and 9.3 by addition of 10% NaOH. The solid supported catalyst is filtered
25 off and washed with water until the filtrate is chlorine-free according to a precipitation test with AgNO₃.

Example 3

Hydrogenation of 3-hexyn-1-ol using a supported palladium catalyst.

- 5 A 250 mL stainless steel autoclave is charged with 500 mg of the catalyst produced according to Example 2 (1%Pd/C (dry weight)), 100 mL 96% ethanol, and 10 mL 3-hexyn-1-ol. The autoclave is closed and the mixture is heated to 30°C with stirring. The stirring is stopped, and the air is replaced by flushing hydrogen over the mixture. After flushing the autoclave is pressurised with 3
- 10 bars of hydrogen. The stirring is resumed (1500 rpm) and the hydrogen consumption is recorded. After 2.0 L hydrogen is consumed the stirring is stopped, the hydrogen is vented off, and the autoclave is opened. Conversion and selectivity are determined by GC measurement of the crude reaction mixture. Conversion: 97%. Selectivity: >99% 3-hexenol of which 95% is the cis-
- 15 isomer.

Claims

1. Process for the preparation of an aqueous colloidal precious metal suspension, which process comprises reducing a precious metal salt in aqueous solution using a functionalised, water soluble quaternary ammonium salt in the absence of organic solvents, to form elementary nanoparticles.
- 5 2. Process according to claim 1, wherein the functionalised, water soluble quaternary ammonium salt has a hydroxyl functionality.
3. Process according to claim 1 or 2, wherein the functionalised, water soluble quaternary ammonium salt has the formula:
RR'R''-N⁺-CH₂CH₂OH X⁻, wherein R, R' and R'' are independently of each other
10 C₁-alkyl and higher and X is Cl, Br, H₂PO₄, NO₃, or SO₄.
4. Process according to claim 1-3, wherein the precious metal is selected from the group of platinum, palladium, iridium, rhodium, ruthenium, rhenium, silver, gold and combinations thereof, preferably palladium.
5. Process according to claim 4, wherein a palladium salt is used,
15 preferably Na₂PdCl₄.
6. Process according to claim 1-5, wherein the particle size of the elementary nanoparticles is between 1 and 50, preferably between 1 and 10 nm
7. Process according to claim 1-6, wherein the quaternary ammonium
20 salt is a quaternary ammonium phosphate.
8. Process for the production of a supported precious metal catalyst, which process comprises preparing an aqueous colloidal precious metal suspension in accordance with the process of any one of the claims 1-7, followed by contacting the suspension with a support material and recovering
25 the precious metal catalyst.

9. Process according to claim 8, wherein the support is selected from the group of oxidic supports, such as silica, alumina, zirconia, titanium oxide and zinc-oxide, silicates, aluminates and active carbon.
10. Process according to claim 1-9, wherein the amount of precious
5 metal is between 0.01 and 10 wt.%, preferably between 0.5 and 5 wt.% of the catalyst.
11. Process for the production of 3-hexenol, which process comprises reducing 3-hexyn-1-ol in the presence of a catalyst produced in accordance with the process of claims 8-10.
- 10 12. Process for the production of 3-hexenol, which process comprises reducing 3-hexyn-1-ol in the presence of a colloidal suspension produced in accordance with the process of claims 1-7.