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(54) Title: PROCESS FOR MANUFACTURING A POWDER OF ALUMINA PARTICLE COATED BY ZIRCONIUM OXIDE

(57) Abstract: The present invention relates to a process for manufacturing a powder, comprising the following steps: • a) preparing a solution containing a solvent and zirconium oxalate, • b) adjusting the pH of the solution to a value above 5 and below 8, • c) introducing into the said solution a boehmite particle powder in an amount such that the ratio of the number of moles of zirconium element provided by the zirconium oxalate divided by the number of moles of aluminium element provided by the boehmite particles is between 0.27 and 0.41, the boehmite particle powder having: • - a specific surface area of greater than 220 m^2/g and less than 390 m^2/g, and • - a pore volume of greater than 0.6 cm^3/g and less than 1.1 cm^3/g, and • - strong acidity, measured after calcination at 800°C for 2 hours, greater than 7 pmol/g and less than 12 pmol/g, • d) after the end of step c) and at least up to the end of step e), adjusting the pH to a value above 1 and below 4; • e) mixing with stirring at a temperature between 30°C and 90°C; • f) rinsing with an acidic solution having a pH above 1 and below 4, and filtering so as to recover boehmite particles covered with a zirconium coating; • g) optionally, but preferentially, rinsing with a water preferably having an electrical resistivity of greater than or equal to 2 MQ/cm, and filtering so as to recover boehmite particles covered with a zirconium coating, • h) optionally drying, • i) optionally performing calcination at a temperature between 400°C and 1200°C, • j) optionally deaggregating. It is also directed to boehmite particle coated with a zirconium compound (setp f) of the preparation process) and alumina part coated with zirconium oxide.

PROCESS FOR MANUFACTURING A POWDER OF ALUMINA PARTICLE COATED BY ZIRCONIUM OXIDE

Technical field

The invention relates to a process for manufacturing a powder of boehmite particles at least partially coated with a zirconium coating, to a process for manufacturing a powder of alumina particles at least partially coated with a layer of zirconium, to the powders thus manufactured, and to the use of these powders in the field of catalysis.

Technological background

Catalysis concerns numerous reactions in varied technical fields, in particular for environmental applications, petrochemistry or fine chemistry. It consists in modifying the rate of a chemical reaction by placing the reagents of this reaction in contact with a catalyst, for example platinum, which does not appear in the reaction balance. Generally, the catalyst is deposited beforehand on a support, for example in the form of a powder or a body consisting of such a powder. The powder may also itself occasionally serve as catalyst.

Powders which have:

- high specific surface area thermal stability,
- high hydrothermal resistance, and
- high strong acidity,

are generally sought to improve catalysis reactions, in particular when vapour-reforming reactions are involved.

Alumina particle powders have limited hydrothermal resistance. This is why zirconia-coated alumina particle powders were developed. The application of an undoped zirconia coating however reduces the strong acidity.

There is thus a need for a novel powder which has a good compromise between specific surface area thermal stability, hydrothermal resistance and strong acidity.

One aim of the invention is to at least partially satisfy this need.

Summary of the invention

This aim is achieved by means of a process for manufacturing a powder, comprising the following successive steps:

a) preparing a solution containing a solvent and zirconium oxalate,
b) adjusting the pH of the solution to a value above 5 and below 8,

c) introducing into the said solution a boehmite particle powder in an amount such that the ratio of the number of moles of zirconium element provided by the zirconium oxalate divided by the number of moles of aluminium element provided by the boehmite particles is between 0.27 and 0.41, the boehmite particle powder having:
   - a specific surface area of greater than 220 m^2/g and less than 390 m^2/g, and
   - a pore volume of greater than 0.6 cm^3/g and less than 1.1 cm^3/g, and
   - strong acidity, measured after calcination at 800°C for 2 hours, greater than 7 µmol/g and less than 12 µmol/g,

d) after the end of step c) and at least up to the end of step e), adjusting the pH to a value above 1 and below 4;

e) mixing with stirring at a temperature between 30°C and 90°C;

f) rinsing with an acidic solution having a pH above 1 and below 4, and filtering so as to recover boehmite particles covered with a zirconium coating;

g) optionally, but preferentially, rinsing with a water preferably having an electrical resistivity of greater than or equal to 2 MΩ/cm, and filtering so as to recover boehmite particles covered with a zirconium coating,

h) optionally drying,

i) optionally performing calcination at a temperature between 400°C and 1200°C,

j) optionally deaggregating.

The inventors have found that the powder obtained after step f) makes it possible to manufacture, after the calcination step, a powder which has a particularly high specific surface area thermal stability, hydrothermal resistance and strong acidity.

Preferably, a process according to the invention comprises yet another, and preferably several, of the following optional characteristics:

- The zirconium oxalate concentration in the solution obtained after step a) is greater than 1.5 mol/l and less than 2.1 mol/l. Advantageously, the homogeneity of the dispersion of boehmite particles in the solution containing a solvent and zirconium oxalate is thereby improved.
- In step c), the boehmite particle powder is introduced in the form of an aqueous suspension of boehmite particles.
- In step c), the amount of boehmite particle powder introduced is such that the ratio of the number of moles of Zr element provided by the zirconium oxalate divided by the number of moles of Al element provided by the boehmite particles is greater than 0.29, preferably greater than 0.34 and/or less than 0.365.

- In step c), the boehmite particle powder has:
  - a specific surface area of greater than 240 m^2/g and less than 350 m^2/g, preferably less than 300 m^2/g, and/or
  - a pore volume of less than 0.9 cm^3/g, and/or
  - strong acidity, measured after calcination at 800°C for 2 hours, of greater than 8 µmol/g, and/or
  - a chemical composition, after calcination at 800°C, such that, in mass percentages:
    - N < 0.2%, and/or
    - C < 0.3%, and/or
    - Cl < 300 ppm, and/or
    - S < 1000 ppm, and/or
    - CaO < 900 ppm, and/or
    - Na_2O < 400 ppm, and/or
    - SiO_2 < 500 ppm.
- In step d), the pH is adjusted to a value above 2, preferably above 3, and/or below 3.5.
- In step e), the mixing is performed at a temperature below 80°C.
- The process comprising a step i) of calcination, preferably at a temperature of between 600°C and 1100°C.

The invention also relates to a powder of coated boehmite particles, each coated boehmite particle comprising a boehmite grain or an aggregate of boehmite grains, and a zirconium coating, the said coating extending on average over more than 90% of the surface of the said coated boehmite particle, the zirconium being bridged via a $C_2O_4^{2-}$ group.

Preferably, the powder of coated boehmite particles according to the invention comprises more than 95%, preferably more than 98%, more than 99% and preferably substantially 100%, by number, of coated boehmite particles each consisting of a single grain of boehmite and a zirconium coating.

Preferably, more than 90% by number of the boehmite grains have an ovoid shape, the largest ellipse that may be inscribed in the contour of a grain of ovoid shape, on a photograph of the said grain, having a large axis with a length of greater than 10 nm and less than 20 nm, the largest dimension perpendicular to the said large axis being greater than 4 nm and less than 10 nm, or have the form of a fibre, the length of a boehmite grain in fibre form, on a photograph of the said boehmite grain, being greater than 60 nm and less than 100 nm and the largest dimension of this grain perpendicular to the said length being between 2 and 5 nm.

Such a powder may especially be obtained or be liable to have been obtained at the end of a step f) of a process according to the invention.

The invention also relates to a powder of coated alumina particles, each coated alumina particle comprising an alumina grain or an aggregate of alumina grains, and a layer of zirconium, the said layer covering on average more than 60% of the surface of the said coated alumina particle,

the mass content of zirconium, expressed in the form of zirconia, on the basis of the mass of the powder, being between 14% and 20%, and

the strong acidity, measured after calcination at 800°C for 2 hours, being greater than 9 μmol/g.

Preferably, the zirconium of the zirconium layer is in the form of zirconia.

Preferably, the zirconia layer is obtained by calcination, at a temperature of greater than 400°C, preferably greater than 600°C, preferably greater than 800°C and less than 1200°C, of a zirconium coating. Such a powder may thus be obtained or may be liable to have been obtained at the end of a step i) of a process according to the invention.

Preferably, the powder of coated alumina particles according to the invention comprises more than 50%, preferably more than 70%, more than 80%, more than 90%, more than 95%, by number, of coated alumina particles according to the invention each consisting of a single grain of alumina and a zirconium layer, preferably in the form of zirconia.

A powder of coated alumina particles according to the invention may in particular also comprise one or more of the following optional characteristics:

- The mass content of zirconium, expressed in the form of zirconia, on the basis of the mass of the powder, is greater than 15%, preferably greater than 16%, preferably greater than 17% and/or less than 19%, preferably less than 18%.
- The zirconia of the layer is amorphous for more than 95% of its mass, or is crystalline, for more than 50% of its mass, in a quadratic and/or cubic crystallographic form, and/or is at least partially stabilized, the stabilizer content being between 1 mol% and 10 mol% on the basis of the molar sum of the contents of stabilizer and of zirconia.
- The content of stabilized alumina in the periphery of the grain or of the aggregate of grains is greater than that in the central region of the said grain or of the said aggregate of grains.
- The zirconium of the layer is not in a metallic form.

A powder of coated alumina particles according to the invention may especially have:

- a specific surface area of less than 300 m^2/g and greater than 100 m^2/g, and/or
- a pore volume of greater than 0.3 cm^3/g, and less than 1 cm^3/g, and/or
- a median pore diameter of greater than 3 nm and less than 15 nm.

Preferably, it has

- a specific surface area of less than 250 m^2/g and greater than 120 m^2/g, and/or
- a pore volume of greater than 0.45 cm^3/g and less than 0.65 cm^3/g, and/or
- a median pore diameter of greater than 6 nm and less than 13 nm.

The invention relates to the use of a powder of coated boehmite particles according to the invention as a catalyst or a catalyst support in a catalytic reaction.

Finally, the invention relates to the use of a powder of coated alumina particles according to the invention as a catalyst or a catalyst support in a catalytic reaction, preferably chosen from the group formed by:

- hydrocarbon conversion reactions including selective oxidation reactions, hydrogenation reactions, dehydrogenation reactions, hydrogenolysis reactions, isomerization reactions, dehydrocyclization reactions and reforming reactions;
- selective hydrogenation reactions, and in particular selective hydrogenation reactions of molecules containing at least one carbonyl function CO, and selective hydrogenation reactions of molecules containing at least two double bonds;
- methane formation reactions (methanation reactions);
- Fischer-Tropsch synthesis reactions (including methanol synthesis reactions), i.e. the formation of oxygenated hydrocarbons from carbon monoxide (CO), hydrogen (H_2) and/or organic molecules (for example biomass),

preferably in the group formed by reforming reactions, preferably vapour-reforming reactions.

A powder of coated alumina particles or of coated boehmite particles preferably comprises more than 10, more than 1000, more than 1 000 000 coated alumina particles or coated boehmite particles, respectively.

Definitions

The percentiles or “centiles” 10 (D_{10}), 50 (D_{50}) and 90 (D_{90}) are the particle sizes of a powder corresponding to the volume percentages, 10%, 50% and 90%, respectively, on the cumulative particle size distribution curve of the particle sizes of the powder, the particle sizes being classified in increasing order. For example, 90% by volume of the particles of the powder have a size less than D_{90} and 10% by volume of the particles have a size greater than or equal to D_{10}. The percentiles may be determined by means of a particle size distribution established by means of a laser granulometer. The laser granulometer used herein is a Partica LA-950 machine from the company Horiba.

D_{50} corresponds to the "median size" of a set of particles, i.e. the size dividing the particles of this set into first and second populations that are equal by volume, these first and second populations comprising only particles having a size greater than or equal to, or less than, respectively, the median size.

The specific surface area of a powder is calculated via the BET (Brunauer-Emmett-Teller) method as described in the *Journal of the American Chemical Society 60* (1938), pages 309 to 316.

The term "covered" or "coated" particle means a particle consisting of a single grain or an aggregate of several grains and a coating or a layer at least partially covering and preferably totally covering the said grain or the said aggregate.

An "aggregate" is an assembly of grains bound together, for example via charge effects or by polarity.

The term "coating" or "layer" means a deposit of solid material extending over the surface of a particle. The coating or layer may penetrate into any pores at the surface of the particle. A coating or layer is, however, delimited by an interface with the particle marking a break in the chemical composition.

The terms "coating" and "layer" are synonymous. For the sake of clarity, the term "coating" has been used when the particle concerned is made of boehmite and the term "layer" has been used when the particle concerned is made of alumina.

A grain (for example an alumina or boehmite grain), a particle, a coating (for example a zirconium coating) or a layer (for example a zirconium or zirconia layer) is considered as being made of a constituent when this constituent is that whose content is the highest (main constituent). For example, alumina constitutes the main constituent of an alumina grain.

A powder of given particles, for example a powder of coated boehmite or alumina particles, is a powder comprising more than 90% by mass of such particles.

The pore volume is the volume occupied by all of the open pores of a material, per unit volume of this material.

The "degree of coverage" of a particle powder means the ratio between the total surface area of coating on the said particles and the total surface area of the said particles, as an arithmetic mean on all of the said particles.

The means are arithmetic means.

A “zirconium salt” is a compound of the form $Zr(OH)_x(N')_y,z.(H_2O)$, N’ being an anion or a mixture of anions, indices x, y and z being zero or positive numbers, x+y>0, or is a compound

of the form $ZrO(N''^{n-})_{y'},z'.(H_2O)$, N'' being an anion or a mixture of anions, indices y' and z' being zero or positive numbers, and n.y'=2. Anions N' and N'' can be either mineral (e.g. Cl^-) and organic (e.g. acetate anion CH_3-COO^-), and either monoatomic (e.g. F^-) and polyatomic (e.g. SO_4^{2-}). Typical zirconium salts are zirconium oxychloride $ZrOCl_2,8(H_2O)$, zirconium chloride $ZrCl_4$, zirconium sulphate $Zr(SO_4)_2$, zirconium basic carbonate which formula is $Zr(OH)_{x''}(CO_3)_{y''},z''.(H_2O)$, with y'' being between 0.2 and 2, x'' being such that x''+2y''=4, and z'' being zero or a positive number, zirconium tartrate, zirconium acetate, zirconium formiate, and zirconium proprionate.

The oxide contents refer to the overall contents for each of the corresponding chemical elements, expressed in the form of the most stable oxide, according to the usual convention in the industry.

Unless otherwise mentioned, all the percentages are mass percentages on the basis of the oxides.

The terms "containing a", "comprising a" and "including a" mean "containing at least one", unless otherwise indicated.

Detailed description

Process according to the invention

In step a), a solvent, preferably water, is mixed with zirconium oxalate so as to obtain a solution.

The zirconium oxalate is dissolved in the solvent and the solution then comprises a solvent, oxalate ions $(C_2O_4)^{2-}$ and a compound comprising a zirconium ion. A person skilled in the art knows how to adapt the conditions, especially the pH and/or the temperature of the solution, in order to obtain dissolution of the zirconium oxalate in the solvent.

Chemical Encyclopedia, volume III, fifth book, paragraph 48, Frémy Edmond, Dunod, 1882-1905 describes conditions for preparing the solution obtained in step a).

Preferably, the concentration of zirconium oxalate in the solution is greater than 1.5 mol/l, preferably greater than 1.6 mol/l, preferably greater than 1.7 mol/l, preferably greater than 1.8 mol/l and less than 2.1 mol/l, preferably less than 2 mol/l, preferably less than 1.9 mol/l.

Zirconium oxalate can be obtained by dissolution of a zirconium salt, in a nitric acid and oxalic acid solution, in a solvent, preferably water, in amounts such that:

- the ratio of the number of moles of oxalic acid to the number of moles of zirconium salt is greater than or equal to 1 and less than or equal to 3, preferably less than or equal to 2, a ratio of 1.5 being preferred;

- the ratio of the number of moles of nitric acid to the number of moles of zirconium salt is greater than or equal to 1 and less than or equal to 3, preferably less than or equal to 2, a ratio of 1.5 being preferred.

The obtained mixture is then stirred until a clear, homogeneous solution is obtained, eventually being heated at 80°C. Among possible zirconium salts, salts of monocarboxylic acids or dicarboxylic acids which general formulas are $Zr(RCOO)_4$, $ZrO(RCOO)_2$, $Zr[R(COO_2)]_2$ and $ZrO[R(COO_2)]$, R being hydrogen or any hydrogeno-carbonated chain such as CH_3, C_2H_5, C_3H_7 or C_4H_9, can be cited. Preferably, zirconium formiate, zirconium acetate, zirconium proprionate or zirconium tartrate are used. Double salts which are soluble in any acidic media can also be used, such as ammonium zirconium carbonate ($Zr(OH)_2(CO_3)_2(NH_4)_2$).

Another way to prepare zirconium oxalate consists in dissolving a zirconium hydroxide $Zr(OH)_4$ precipitate in a mixture of nitric acid, or hydrochloric acid, and oxalic acid in quantities such that:

- the ratio of the number of moles of oxalic acid to the number of moles of zirconium hydroxide is greater than or equal to 1 and less than or equal to 3, preferably less than or equal to 2, a ratio of 1.5 being preferred;

- the ratio of the number of moles of nitric acid, or of hydrochloric acid, to the number of moles of zirconium hydroxide is greater than or equal to 1 and less than or equal to 3, preferably less than or equal to 2, a ratio of 1.5 being preferred.

The mixture is then stirred until a clear, homogeneous solution is obtained. The zirconium hydroxide precipitate can be obtained by neutralizing any acidic solution comprising zirconium ion with a base. Preferred bases for preparing zirconium hydroxide precipitate are ammonia, soda, potash and amines. Preferred acidic solutions for preparing zirconium hydroxide precipitate are zirconyl nitrate, zirconium oxychloride and zirconium acetate.

Zirconium oxalate is preferably obtained by mixing oxalic acid and zirconium oxynitrate or zirconium oxychloride, in a solvent, preferably in water, in amounts such that the ratio of the number of moles of oxalic acid to the number of moles of zirconium oxynitrate or of zirconium oxychloride is greater than or equal to 1 and less than or equal to 3, preferably less than or

equal to 2. A ratio equal to about 1.5 is preferred. The mixture is then stirred until a clear, homogeneous solution is obtained.

In another preferred embodiment, zirconium oxalate is obtained by mixing zirconium basic carbonate, a nitric acid and oxalic acid solution, in a solvent, preferably in water, in amounts such that:

- the ratio of the number of moles of oxalic acid to the number of moles of zirconium basic carbonate is greater than or equal to 1 and less than or equal to 3, preferably less than or equal to 2, a ratio of about 1.5 being preferred;

- the ratio of the number of moles of nitric acid to the number of moles of zirconium basic carbonate is greater than or equal to 1 and less than or equal to 3, preferably less than or equal to 2, a ratio of about 1.5 being preferred.

Then the mixture is stirred until a clear, homogeneous solution is obtained.
All the known processes for manufacturing zirconium oxalate may be used.

In step b), the pH of the solution is adjusted to a value preferably above 6 and preferably below 7.5. Preferably, the pH value is adjusted to a value substantially equal to 7.
To this end, aqueous ammonia (for example 1M) may, for example, be added.

In step c), the powder of boehmite particles is preferably a powder having

- a specific surface area preferably greater than 240 m^2/g and/or, preferably, less than 350 m^2/g, preferably less than 300 m^2/g, preferably less than 280 m^2/g, and/or
- a pore volume less than 0.9 cm^3/g, and/or
- strong acidity, measured after calcination at 800°C for 2 hours, preferably greater than 8 µmol/g, and/or
- a chemical composition, after calcination at 800°C, preferably such that, as mass percentages:
  - N < 0.2%, preferably N < 0.15%, and/or
  - C < 0.3%, preferably C < 0.25%, and/or
  - Cl < 300 ppm, preferably Cl < 200 ppm, and/or
  - S < 1000 ppm, preferably S < 700 ppm, preferably S < 500 ppm, preferably S < 100 ppm, preferably S < 50 ppm, preferably S < 10 ppm, and/or
  - CaO < 900 ppm, preferably CaO < 500 ppm, preferably CaO < 100 ppm, preferably CaO < 50 ppm, and/or

- Na_2O < 400 ppm, preferably Na_2O < 100 ppm, preferably Na_2O < 40 ppm, and/or
- SiO_2 < 500 ppm, preferably SiO_2 < 250 ppm.

Preferably, the boehmite particle powder has a median size of greater than 1 μm and less than 40 μm.

Preferably, the boehmite particles of the powder contain more than 90%, more than 95%, preferably more than 99% or even substantially 100% of boehmite.

The amount of boehmite particle powder introduced is preferably such that the ratio of the number of moles of Zr element provided by the zirconium oxalate divided by the number of moles of Al element provided by the boehmite particles is greater than 0.29, preferably greater than 0.34 and/or preferably less than 0.365.

Preferably, the boehmite particle powder is introduced, into the solution obtained at the end of step b), preferably at room temperature, preferably with stirring and quite slowly so as to obtain a homogeneous mixture.

In step d), the pH is adjusted to a value preferably above 2, preferably above 3 and/or preferably below 3.5. In one embodiment, the pH is adjusted to a value of between 2 and 4, and preferably between 3 and 3.5.

To this end, nitric acid (for example 1M) may, for example, be added.

In step e), mixing is performed, preferably for a time of greater than 10 minutes, preferably greater than 20 minutes. A mixing time of 30 minutes is suitable for use.

The temperature is adjusted to a value of greater than 30°C and less than 90°C, preferably less than 80°C. A temperature equal to 50°C is suitable for use.

In step f), all the known filtration techniques may be performed, and in particular filtration through a Buchner funnel. Preferably, the filtration is performed after rinsing with an acidic solution with a pH above 2, preferably above 3, and/or preferably below 3.5. In one embodiment, the filtration is performed after rinsing with an acidic solution with a pH of between 2 and 4, and preferably between 3 and 3.5.

In step g), which is optional, the solution filtered in step f) is rinsed with water preferably having an electrical resistivity of greater than or equal to 2 MΩ/cm, preferably with deionized water. The solution is then filtered again, preferably through a Buchner funnel with deionized water. The coated boehmite particles according to the invention may be in the form of a paste.

Coated boehmite particle powder

A coated boehmite particle of a powder according to the invention consists of a boehmite grain covered with a zirconium coating or an aggregate of boehmite grains covered with such a coating.

The boehmite grain(s) preferably comprise more than 90%, more than 95%, preferably more than 99%, preferably substantially 100% of boehmite (AlO(OH)), as a mass percentage.

The mass of the zirconium coating preferably represents more than 64%, more than 65%, more than 68% and/or less than 73%, less than 69% of the mass of the boehmite grain or of the aggregate of boehmite grains.

On average, the coating preferably covers more than 92%, more than 95% or substantially 100% of the surface of the boehmite grain or of the aggregate of boehmite grains.

Preferably, the zirconium content in a coated boehmite particle is greater than 32.6%, preferably greater than 33%, preferably greater than 34% and/or less than 37%, preferably less than 35%, as a mass percentage on the basis of the mass of the coated boehmite particle.

The zirconium of the coating is bridged to the boehmite grain(s) via $C_2O_4^{2-}$ groups. The Zr, C and O atoms together preferably represent more than 90%, more than 95%, preferably substantially 100% of the mass of the coating, Zr being bridged via $C_2O_4^{2-}$groups.

Preferably, the zirconium coating is in the form of a monolayer of Zr^{4+} ions bridged with $C_2O_4^{2-}$ groups.

Preferably, the powder of coated boehmite particles according to the invention comprises more than 50%, preferably more than 70%, more than 80%, more than 90%, more than 95%, by number, of coated boehmite particles consisting of a single boehmite grain covered with a zirconium coating.

A coated boehmite particle may have an ovoid shape, the largest ellipse that may be inscribed in the contour of such a particle preferably having a large axis with a length of greater than 10 nm, greater than 12 nm, greater than 13 nm and less than 20 nm, or even less than 19 nm. Preferably, the largest dimension perpendicular to the said large axis is greater than 4 nm, greater than 5 nm, greater than 6 nm and less than 10 nm.

A coated boehmite particle may also have the form of a fibre and the length of the said particle in fibre form is greater than 60 nm, or even greater than 70 nm and less than 100 nm, or even less than 90 nm, or even less than 80 nm. Preferably, the largest dimension of this particle perpendicular to the said length is between 2 and 5 nm.

The specific surface area of a powder of coated boehmite particles is preferably less than 390 m^2/g, less than 350 m^2/g, less than 300 m^2/g, less than 250 m^2/g, and/or greater than 100 m^2/g, greater than 120 m^2/g.

The pore volume of a powder of coated boehmite particles is preferably greater than 0.3 cm^3/g, preferably greater than 0.45 cm^3/g, and/or less than 1 cm^3/g, preferably less than 0.65 cm^3/g.

The median pore diameter is preferably greater than 3 nm, preferably greater than 6 nm and/or less than 15 nm, preferably less than 13 nm.

Preferably,

- the median size D_{50} of the powder of coated boehmite particles, determined by laser granulometry, is preferably between 6 and 20 µm, and/or
- the size D_{90} of the powder of coated boehmite particles, determined by laser granulometry, is preferably between 12 and 40 µm, and/or
- the size D_{10} of the powder of coated boehmite particles, determined by laser granulometry, is preferably between 3 and 10 µm.

In step h), the drying is preferably performed at a temperature of between 80°C and 200°C, preferably for a time of between 5 hours and 24 hours. Drying at 110°C for 12 hours is suitable for use. Any known technique for drying powders may be performed.

In step i), the calcination is preferably performed at a temperature of between 600°C and 1100°C. The calcination may or may not be performed at the same site as the preceding steps. In particular, it may be performed *in situ*, i.e. after the powder has been installed for use. For example, the boehmite particles coated with a zirconium coating may be installed in the form of a washcoat, and then calcined during a first temperature rise. They then become transformed only into a powder of coated alumina particles according to the invention.

Coated alumina particle powder

A coated alumina particle of a powder according to the invention consists of a single grain of alumina covered with a layer of zirconium or an aggregate of alumina grains covered with such a layer.

The alumina is preferably obtained by calcination of boehmite, in particular during a step i) of a process according to the invention.

In one embodiment, the oxides represent more than 98%, more than 99%, or even substantially 100% of the mass of the alumina grain(s).

The alumina grain(s) preferably comprise more than 90%, more than 95%, preferably substantially 100% of alumina, as a mass percentage.

The alumina may be in a crystallographic form corresponding to a transition alumina, preferably delta alumina and/or theta alumina and/or gamma alumina, preferably delta alumina and/or theta alumina.

In one embodiment, the oxides represent more than 95%, more than 98%, more than 99%, or even substantially 100% of the mass of the zirconia layer.

On average, the layer preferably covers more than 60%, more than 70%, more than 80%, more than 85%, more than 90%, or even more than 92%, more than 95% or substantially 100% of the surface of the alumina grain or of the aggregate of alumina grains. The hydrothermal resistance is thereby improved.

Preferably, the zirconium is in the form of zirconia.

The layer preferably comprises more than 90%, more than 95%, preferably substantially 100% of zirconia, as a mass percentage on the basis of the mass of the layer.

The zirconia content in a coated alumina particle according to the invention is greater than 14%, preferably greater than 15%, preferably greater than 16%, preferably greater than 17% and/or less than 20%, preferably less than 19%, preferably less than 18%, as a mass percentage on the basis of the oxides.

The zirconia may be amorphous or crystalline, and optionally doped.

In one embodiment, the zirconia of the layer is amorphous for more than 95% of its mass.

In one embodiment, the zirconia of the layer is crystalline, for more than 50%, preferably for more than 60%, preferably for more than 70%, preferably for more than 80%, or even for more than 90%, or even for more than 95%, or even for more than 99%, or even for substantially 100% of its mass in a quadratic and/or cubic crystallographic form, the remainder being amorphous or monoclinic, preferably amorphous.

A coated alumina particle may have an ovoid shape, the largest ellipse that may be inscribed in the contour of such a particle preferably having a large axis with a length of greater than 8 nm, greater than 10 nm, greater than 12 nm and less than 20 nm, or even less than 19 nm, or even less than 17 nm. Preferably, the largest dimension perpendicular to the said large axis is greater than 3 nm, greater than 4 nm, greater than 5 nm and less than 10 nm, less than 9 nm.

A coated alumina particle may also have the form of a fibre and the length of the said particle in fibre form is greater than 50 nm, or even greater than 60 nm and less than 100 nm, or even

less than 90 nm, or even less than 85 nm. Preferably, the largest dimension of this particle perpendicular to the said length is between 2 nm and 5 nm.

The zirconia of the layer may be doped with a known zirconia stabilizer such as yttrium, magnesium, cerium, scandium or tungsten, preferably yttrium. Preferably, the stabilizer content is between 1 mol% and 10 mol%, preferably between 2 mol% and 9 mol% on the basis of the molar sum of the contents of stabilizer and of zirconia.

In one embodiment, the zirconia layer consists of only one layer of zirconia molecules.

Moreover, the inventors have found that, in the powders specifically manufactured according to a process according to the invention, part of the zirconia of the layer may migrate to stabilize the surface alumina of the alumina grain.

Preferably,

- the median size D_{50} of the powder of coated alumina particles, determined by laser granulometry, is between 5 µm and 20 µm, and/or
- the size D_{90} of the powder of coated alumina particles, determined by laser granulometry, is between 10 µm and 40 µm, and/or
- the size D_{10} of the powder of coated alumina particles, determined by laser granulometry, is between 2 µm and 10 µm.

Preferably, the strong acidity, measured after calcination at 800°C for 2 hours, is greater than 10 µmol/g. The strong acidity, measured after calcination at 800°C for 2 hours, is preferably less than 50 µmol/g, preferably less than 40 µmol/g, preferably less than 30 µmol/g, or even less than 20 µmol/g, or even less than 15 µmol/g, or even less than 12 µmol/g.

In one embodiment, the oxides represent more than 98%, more than 99%, or even substantially 100% of the powder of coated alumina particles according to the invention.

The chemical composition of the powder of coated alumina particles, after calcination at 800°C, is preferably such that, as mass percentages:

- N < 0.2%, preferably N < 0.15%, and/or
- C < 0.3%, preferably C < 0.2%, preferably C < 0.15%, and/or
- Cl < 300 ppm, preferably Cl < 200 ppm, and/or
- S < 1000 ppm, preferably S < 700 ppm, preferably S < 500 ppm, preferably S < 100 ppm, preferably S < 50 ppm, preferably S < 10 ppm, and/or
- CaO < 900 ppm, preferably CaO < 500 ppm, preferably CaO < 100 ppm, preferably CaO < 50 ppm, and/or

- Na_2O < 400 ppm, preferably Na_2O < 100 ppm, preferably Na_2O < 40 ppm, and/or
- SiO_2 < 500 ppm, preferably SiO_2 < 250 ppm.

Preferably, the zirconia content in a powder of coated alumina particles according to the invention is greater than 14%, preferably greater than 15%, preferably greater than 16%, preferably greater than 17% and/or less than 20%, preferably less than 19%, preferably less than 18%, as mass percentages on the basis of the oxides of the powder.

The specific surface area of a powder of coated alumina particles according to the invention is preferably less than 300 m^2/g, less than 250 m^2/g, and/or greater than 100 m^2/g, greater than 120 m^2/g.

The pore volume of a powder of coated alumina particles according to the invention is preferably greater than 0.3 cm^3/g, preferably greater than 0.45 cm^3/g, and/or less than 1 cm^3/g, preferably less than 0.65 cm^3/g.

The median pore diameter is preferably greater than 3 nm, preferably greater than 6 nm and/or less than 15 nm, preferably less than 13 nm.

During the implementation of a process according to the invention, the shape and size of the coated alumina particles according to the invention are substantially identical to those of the boehmite particles from which they are derived.

In step j), a deaggregation may optionally be performed after step h) or step i), in order to break down any aggregates in the final powder.

Use

A powder of coated boehmite particles or a powder of coated alumina particles according to the invention may be used as catalyst or as catalyst support. It may also be placed in the form of a body which may be used as catalyst or as catalyst support.

The catalyst deposited on the surface of the support may be a metal, preferably chosen from the group of metals from columns 8, 9 and 10 of the Periodic Table of the Elements.

The catalyst may also be an oxide, preferably chosen from lanthanum oxide and/or transition metal oxides, for instance V_2O_5 or Cr_2O_3, and/or oxides of elements from columns 14 and 15, preferably tin (Sn), lead (Pb) and/or bismuth (Bi) oxides.

The catalyst may also be a carbide, preferably chosen from transition metal carbides, for instance molybdenum carbide and/or tungsten carbide.

The catalyst may also be a sulfide, preferably chosen from transition metal sulfides, preferably molybdenum sulfides and tungsten sulfides, optionally doped with cobalt or nickel (for example CoMoS).

Methods for growing catalyst crystallites on the support are known. Preferably, the support is impregnated with an aqueous or non-aqueous solution containing a catalyst precursor. The impregnated support then undergoes a maturation step to enable the impregnation solution to penetrate by capillary action into the pores of the support. The duration of this step is generally greater than 5 hours. The impregnated support is then dried by any drying means known to those skilled in the art, for instance by baking, optionally under vacuum. The drying temperature is generally less than 500°C, or even less than 250°C, in particular when the powder is a boehmite powder according to the invention, the drying time being adjusted such that the impregnated support has, at the end of this step, a residual moisture content of less than 1% by mass.

When the impregnated support is a powder of coated alumina particles according to the invention, the said impregnated and dried support then undergoes a calcination step, generally at a temperature of greater than 800°C and less than 1000°C, and generally for a stage time of greater than 1 hour. The calcination step makes it possible to remove any binders contained in the support and originating from the impregnation solution.

The drying step and the calcination step may be performed as a single operation.

The dried and optionally calcined impregnated support then undergoes an activation operation, known to those skilled in the art. This step proceeds under a controlled atmosphere, adjusted to the selected catalyst (for example under a sulfurizing mixture for a sulfide-based catalyst). After activation, the support may be termed a "catalytic system". Optionally, this activation step may be performed directly in the catalysis reactor.

An additional optional step of passivation, known to those skilled in the art, may be performed after activation, especially to facilitate the transportation of the catalytic system. Generally, this step is performed under a flush of gas in an oxidizing medium, at temperatures below 100°C. A reactivation step must then be performed in the reactor.

Preferably, the catalyst represents less than 15%, less than 10%, less than 7%, less than 5% of the mass of the catalytic system.

Examples

The examples that follow are given for illustrative purposes and are non-limiting.

The **pore volume** is conventionally measured by adsorption and desorption of nitrogen at -196°C, on a Nova 2000 model machine sold by the company Quantachrome. The samples are desorbed beforehand under vacuum at 250°C for 2 hours.

The **hydrothermal resistance** is measured by evaluation of the stability of the specific surface area and of the pore volume.

A sample of 30 g of powder to be tested, dried beforehand at 110°C for 12 hours, is placed in a U-shaped quartz reactor. The sample is brought to a temperature of 800°C, at an increase rate equal to 2°C/minute. Starting from 150°C, steam is injected into the reactor, via a stream of helium, so as to maintain a content of steam in contact with the powder of 10% by volume. The powder is maintained at 800°C for 16 hours. The temperature is then returned to room temperature at a rate equal to 5°C/minute, the introduction of steam being stopped at a temperature of 200°C.

The change in the specific surface area, as a percentage, is equal to 100×(1-[[(specific surface area before heat treatment) - (specific surface area after heat treatment)]/(specific surface area before heat treatment)]). A change of close to 100 shows high stability of the specific surface area.

The change in the pore volume, as a percentage, is equal to 100×(1×[[(pore volume before heat treatment) - (pore volume after heat treatment)]/(pore volume before heat treatment)]). A change of close to 100 shows high stability of the pore volume.

The **strong acidity** of a particle powder calcined beforehand at 800°C is determined by adsorption and desorption of NH_3, measured as a function of the temperature, on an Atochem 2920 machine sold by the company Micromeritics. NH_3 is adsorbed onto the acid sites and the desorption of NH_3 as the temperature increases is recorded. This desorption is linked to the number of acid sites present. The desorption of NH_3 at temperatures below 500°C gives the weak acidity of the powder. The desorption of NH_3 at temperatures above 500°C gives the strong acidity of the powder.

The **degree of coverage** is evaluated by comparison of the adsorption-desorption of SO_2 of the test sample and of a reference powder of particles consisting of the material of the grains of the test sample, the particle size distributions of the sample and of the said reference powder being substantially identical.

For example, a comparison of the amounts of SO_2 measured after desorption on an alumina powder at least partially coated with zirconia and on a reference alumina powder makes it possible to determine the degree of coverage of the said coated alumina powder.

A boehmite powder Versal calcined at a temperature equal to 800°C may be used as reference powder to evaluate the degree of coverage of a powder of alumina particles coated with a zirconium coating.

The measurements are performed on powders calcined beforehand for 2 hours, at a temperature equal to 800°C for Examples 1, 4, 6, 10 and 11, equal to 900°C for Examples 2, 7 and 9, and equal to 1000°C for Examples 3 and 8.

0.2 to 0.5 g of a sample of test powder is placed in a mass spectrometer. The sample is then brought to 800°C and maintained for 1 hour at this temperature. The temperature of the sample is then reduced to 150°C and the said sample is exposed to a flush of helium containing 1031 ppm of SO_2, at a flow rate equal to 50 ml/minute, for 30 minutes. The sample is then cooled to room temperature and exposed to a flush of nitrogen, at a flow rate equal to 50 ml/minute, for 1 hour. The amount of SO_2 desorbed is then measured by temperature-programmed spectroscopy (thermal programmed desorption, TPD), with a temperature increase rate of 5°C/minute up to 1050°C, under a stream of nitrogen equal to 50 ml/minute. The amount of SO_2 desorbed is calculated by the area of the peaks of the TPD curve. SO_2 is desorbed with alumina at a temperature below 700°C, and with zirconia at a temperature above 700°C. The degree of coverage Dc of a coated particle powder is evaluated by the following ratio:

Dc = 100×[1 - [(amount of SO_2 desorbed below 700°C on the sample)/(amount of SO_2 desorbed below 700°C on the reference powder)]].

The **thermal stability of the specific surface area** is determined via the following method: a sample of the test powder is brought to and maintained at 800°C, 900°C or 1000°C, respectively, for 2 hours, and then returned to room temperature. Measurement of the specific surface area is then performed. For each of the calcination temperatures, the thermal stability of the specific surface area is evaluated via the following ratio:

100×(1 - [(specific surface area before calcination - specific surface area after calcination)/(specific surface area before calcination)]).

The thermal stability of the test powder at a given temperature is compared with the measurement of the specific surface area of a boehmite powder Versal which has undergone a heat treatment at an identical temperature.

The **particle form** may be determined using a bright-field transmission electron microscope.

The starting materials used for the examples are the following:

- a boehmite powder Versal sold by the company Sasol, which has a specific surface area equal to 286 m^2/g and a pore volume equal to 0.72 cm^3/g;
- a boehmite powder Catapal B sold by the company Sasol, which has a specific surface area equal to 210 m^2/g and a pore volume equal to 0.34 cm^3/g;
- a zirconium oxynitrate of purity equal to 99%, sold by the company Sigma-Aldrich;
- a zirconium basic carbonate, sold by the company Saint-Gobain Zirpro.

Examples 1*, 2* and 3*, which are outside the invention, are powders of theta and delta alumina particles, obtained after calcination at a temperature T equal to 800°C, 900°C and 1000°C, respectively, for 2 hours of a boehmite powder Versal.

Example 4*, which is outside the invention, is a zirconium hydrate powder sold by the company Saint-Gobain Zirpro, calcined at 800°C for 2 hours.

Example 5, according to the invention, was manufactured according to the process below according to the invention:

In step a), a mixture of zirconium basic carbonate, nitric acid and oxalic acid in water is prepared. The ratio of the number of moles of oxalic acid/number of moles of zirconium basic carbonate is equal to 1.5 and the ratio of the number of moles of nitric acid/number of moles of zirconium basic carbonate is equal to 1.5. The said mixture is then stirred until a clear, homogeneous solution is obtained.

In step b), the pH of the solution is adjusted to a value equal to 7 by adding 1M aqueous ammonia.

In step c), an aqueous suspension containing 77 g of a boehmite powder Versal is introduced into the mixture obtained at the end of step b), so as to obtain a homogeneous mixture. The ratio of the number of moles of zirconium element provided by the zirconium oxalate divided by the number of moles of aluminium element provided by the boehmite particles is equal to 0.31.

In step d), the pH of the suspension is adjusted to a value equal to 3, by adding 1N nitric acid and/or 1N ammonia.

In step e), the mixture is stirred for 30 minutes, at a temperature equal to 50°C, with a pH maintained at a value of 3.

In step f), the mixture obtained is filtered through a Buchner funnel with an acidic solution at a pH equal to 3 (solution of water + nitric acid) and then rinsed with deionized water and filtered in step g) through a Buchner funnel with deionized water.

The mixture obtained is then dried in a step h) at 110°C for 12 hours. The powder obtained is a powder of boehmite particles covered with a zirconium coating, the mass of the zirconium coating representing 68% of the mass of the coated boehmite particles.

Examples 6 to 8 according to the invention are theta and delta alumina powders, obtained after calcination (step i)) at a temperature T equal to 800°C, 900°C and 1000°C, respectively, for 2 hours of the powder according to Example 5, the temperature increase and decrease rates being equal to 100°C/hour. The zirconium layer consists for more than 99% of zirconia.

Example 9*, which is outside the invention, is a theta and delta alumina powder manufactured as in Example 6, but in step b) the boehmite powder used was a boehmite powder Catapal B.

Example 10*, which is outside the invention, is a theta and delta alumina powder manufactured as in Example 6, but, in step a), a mixture of zirconium oxynitrate and of citric acid in water was prepared, the ratio of the number of moles of citric acid/number of moles of zirconium oxynitrate being equal to 2. The obtained solution contained zirconium citrate, and not zirconium oxalate.

Example 11*, out of the invention, is a powder of particles of alumina coated with a zirconium layer, manufactured as according to the following process, known of the prior art:

a zirconium oxynitrate concentrated solution is diluted with de-ionized water in order to obtain 600 ml of a solution of zirconium oxynitrate having a zirconia concentration of 80 g/l.

The pH of this solution being 2, a 28% NH_4OH solution is immediately added in order to adjust the pH to a value of 10 and such that formation of a precipitate is observed.

Said precipitate is filtered and washed with 6 liters of de-ionized water. The obtained cake is resuspended in de-ionized water at a pH of 7.5, and the suspension is acidified by adding a 68% nitric acid solution such that the zirconia concentration of the solution is 10 % as a percentage by weight.

After stirring for 12 hours, a clear solution is obtained. The mean particle size measured with the quasi-elastic light dispersion method is equal to 4 nm.

Aminocaproic (98%, Aldrich 6-aminocaprioic acid) is added to the solution while stirred, in order to increase and stabilize the pH to 4.5.

100 g of a powder of gamma transition alumina particles calcined at a temperature of 500°C, and having a specific surface of 320 m^2/g, a porous volume of 0.82 cm^3/g and a fire loss of 5.1 % is added to 430g of the solution.

The obtained suspension is stirred for 30 minutes, then dried at a temperature of 110°C in an atomizer with a suspension yield of 1 l/h. The obtained powder is then calcined at 700°C for 4 hours.

Table 1 below gives the results obtained on the powders:

An example is considered as satisfactory if

- the thermal stability of the textural properties is close to that of alumina, at identical calcination temperatures, and
- the hydrothermal resistance is close to that of zirconia, at identical calcination temperatures, and
- the strong acidity, measured after calcination at 800°C for 2 hours, is greater than 9 µmol/g.

Examples	1*	2*	3*	4*	5	6	7	8	9*	10*	11*
Calcination temperature T (°C)	800	900	1000	800	-	800	900	1000	800	800	700
% of coated particles in the powder (by mass)	-	-	-	-	> 90%	> 90%	> 90%	> 90%	> 90%	n.d.	n.d.
Degree of coverage (%)	0	0	0	-	> 90%	65	62	90	n.d.	n.d.	n.d.
Zirconia layer: crystallographic form of the zirconia	-	-	-	-	-	Amor-phous	Amor-phous	80% crystalline	Amor-phous	Amor-phous	tetragonal
Strong acidity (µmol/g)	10	13	n.d.	n.d.	n.d.	10	12	11	n.d.	n.d.	6.1
ZrO_2 (%)	-	-	-	-	16.1	16.1	16.1	16.1	6.6	11	17
N (%)	0.13	0.13	0.13	n.d.	0.13	0.17	n.d.	n.d.	0.11	0.15	0.18
C (ppm)	2500	2500	2500	135	2800	2200	n.d.	n.d.	1100	3500	2700
Cl (ppm)	100	100	100	n.d.	100	n.d.	n.d.	n.d.	28	30	45
CaO ppm	25	25	25	n.d.	25	<200	<200	<200	<200	170	180
Na_2O ppm	25	25	25	n.d.	25	<200	<200	<200	<500	50	75
SiO_2 ppm	200	200	200	n.d.	200	<200	<200	<200	<500	260	630
Specific surface area (m^2/g)	200	166	118	4	268	211	179	111	190	209	204
Pore volume (cm^3/g)	0.81	0.8	0.54	n.d.	0.72	0.62	0.63	0.49	0.39	0.7	0.66
Size D_{10} (nm)	7	n.d.	n.d.	11	6	n.d.	n.d.	n.d.	17.5	6.5	6.2
Size D_{50} (nm)	11	n.d.	n.d.	20	10	n.d.	n.d.	n.d.	45.5	12.5	12.1
Size D_{90} (nm)	18	n.d.	n.d.	32	15	n.d.	n.d.	n.d.	77.4	20.9	22
Thermal stability of the specific surface area (%)	74.3	58.6	42.5	1.3	-	84.4	71.6	44.4	71.1	74.6	n.d.
Hydrothermal resistance stability of the specific surface area (%)	78	n.d.	n.d.	n.d.	-	75	n.d.	n.d.	n.d.	n.d.	n.d.
Hydrothermal resistance stability of the pore volume (%)	77.5	n.d.	n.d.	n.d.	-	100	n.d.	n.d.	n.d.	n.d.	n.d.

*: example outside the invention

n.d.: not determined

Table 1

Example 9* illustrates the fact that the use, in step c), of a boehmite powder not having the required characteristics does not make it possible to obtain an alumina powder according to the invention, the measured percentage of zirconia not making it possible to cover more than 60% of the surface of the theta and delta alumina particles.

Similarly, Example 10* illustrates the fact that it is necessary to use zirconium oxalate in step a).

Examples 6, 7 and 8 according to the invention illustrate the impact of the calcination temperature T applied during step i) on the characteristics of the powders, and also the possibility of using a mixture of zirconium basic carbonate, nitric acid and oxalic acid as zirconium oxalate precursors.

The powder according to Example 6 has an amount of SO_2 desorbed before 700°C equal to 520 µmol/g. The boehmite powder Versal, calcined at 800°C for 2 hours, has an amount of SO_2 desorbed before 700°C equal to 1510 µmol/g. The degree of coverage Dc of the powder according to Example 6 is: Dc = 1-[(520) / (1510)] = 0.65.

The powders of Examples 3*, 4* and 11*, which are outside the invention, and 8, according to the invention, were used in the manufacture of catalytic systems using nickel as catalyst and having a mass content of nickel of about 10%.

The preparation was performed by impregnation, without excess of solution, of the powder of each example with a solution of nickel nitrate ($Ni(NO_3)_2.6H_2O$ (from Panreac). This method, which is simple to perform, is well known to those skilled in the art. After impregnation of the powder, it is left to undergo maturation for 8 hours at room temperature, in order to allow the solution to penetrate by capillary action into the pores. The various impregnated powders are dried in an oven at 210°C for a stage time of 12 hours. The various dried impregnated powders are calcined in air for 2 hours (temperature increase and decrease ramps of 10°C/minute) at a temperature of 900°C.

Catalytic tests were performed on a methane vapour-reforming reaction ($CH_4 + H_2O \leftrightarrow CO + 3H_2$), in an open fixed-bed Pyrex reactor, operating at low conversion and at atmospheric pressure. The tests were performed according to the following procedure: 75 mg of the catalytic system (in the present case the powder of Examples 3*, 4*, 11* and 8, coated with nickel) are placed in the reactor. The bed of powders is reduced at 900°C for 90 minutes under H_2 with a flow rate equal to 100 Nml/minute (temperature increase ramp equal to 10°C/minute). The temperature is then set at 800°C and the reaction mixture of methane-steam in a stream of nitrogen is introduced into the reactor over 10 hours. The methane flow rate is 12 000 ml/hour and per gram of catalyst, the H_2O/CH_4 mole ratio set at 3 and the N_2/CH_4 mole ratio set at 1.5. The degree of conversion of the methane, as a percentage, defined as the ratio of the amount of methane that has reacted and of the amount of methane introduced into the reactor, is measured continuously after the introduction of the reaction medium.

Table 3 below gives the results obtained:

Powder used as catalyst support	Degree of conversion of methane (%) measured after						
	60 min	120 min	180 min	240 min	300 min	450 min	600 min
Example 3*	-	-	95	96	96	97	97
Example 4*	35	35	35	42	47	50	55
Example 8	97	97	98	98	98	99	99
Example 11*	95	91	94	95	98	96	94

*Comparative example outside the invention

Table 3

The methane vapour-reforming reaction is stabilized at and above 180 minutes with the powder according to Example 3*, which is outside the invention. Before, it is not possible to determine a degree of conversion of methane. This phenomenon is well known in certain catalysis reactions, for which a stabilization time is necessary. When this stabilization is reached, after 180 minutes, the degree of conversion of the methane is between 95% and 97%.

The methane vapour-reforming reaction is stabilized more quickly with the powder according to Example 4*, which is outside the invention. This stabilization time is less than 30 minutes. When this stabilization is reached, the degree of conversion of methane changes between 35% and 55%, after 600 minutes.

The stabilization time of the vapour-reforming reaction of methane obtained with the powder according to Example 8 is also less than 30 minutes: the stabilization time is less than 5 minutes. When this stabilization is reached, the degree of conversion of methane changes between 97% and 99%, after 600 minutes.

The stabilization time of the vapour-reforming reaction of methane obtained with the powder according to Example 11* is about 20 minutes. When this stabilization is reached, the degree of conversion of methane changes between 91% and 98%, after 600 minutes.

These results show that a higher degree of conversion of methane is reached more quickly with a catalytic system obtained from a powder according to the invention, thus enabling more rapid production than with the powders according to Examples 3*, 4* and 11*, which are outside the invention.

More generally, a particle powder composed for more than 90% by number of coated alumina particles, each coated alumina particle comprising an alumina grain or an aggregate of

alumina grains, and a layer of zirconium, which doesn't have the said layer covering on average more than 60% of the surface of the said coated alumina particle and the mass content of zirconium, expressed in the form of zirconia, on the basis of the mass of the powder, being between 14% and 20%, and the strong acidity, measured after calcination at 800°C for 2 hours, being greater than 9 μmol/g, will not provide a higher degree of conversion of methane reached more quickly.

As is now clearly apparent, the powder according to the invention makes it possible to improve the catalytic performance.

Needless to say, the present invention is not limited to the embodiments described, which are given as non-limiting illustrations.

CLAIMS

1. Process for manufacturing a powder, comprising the following steps:
   a) preparing a solution containing a solvent and zirconium oxalate,
   b) adjusting the pH of the solution to a value above 5 and below 8,
   c) introducing into the said solution a boehmite particle powder in an amount such that the ratio of the number of moles of zirconium element provided by the zirconium oxalate divided by the number of moles of aluminium element provided by the boehmite particles is between 0.27 and 0.41, the boehmite particle powder having:
      - a specific surface area of greater than 220 m^2/g and less than 390 m^2/g, and
      - a pore volume of greater than 0.6 cm^3/g and less than 1.1 cm^3/g, and
      - strong acidity, measured after calcination at 800°C for 2 hours, greater than 7 µmol/g and less than 12 µmol/g,
   d) after the end of step c) and at least up to the end of step e), adjusting the pH to a value above 1 and below 4;
   e) mixing with stirring at a temperature between 30°C and 90°C;
   f) rinsing with an acidic solution having a pH above 1 and below 4, and filtering so as to recover boehmite particles covered with a zirconium coating;
   g) optionally, but preferentially, rinsing with a water preferably having an electrical resistivity of greater than or equal to 2 MΩ/cm, and filtering so as to recover boehmite particles covered with a zirconium coating,
   h) optionally drying,
   i) optionally performing calcination at a temperature between 400°C and 1200°C,
   j) optionally deaggregating.

2. Process according to the preceding claim, in which the concentration of zirconium oxalate in the solution obtained after step a) is greater than 1.5 mol/l and less than 2.1 mol/l.

3. Process according to any one of the preceding claims, in which, in step a), zirconium oxalate is obtained:

   - by dissolution of a zirconium salt in a nitric acid and oxalic acid solution, in a solvent, in amounts such that:

- the ratio of the number of moles of oxalic acid to the number of zirconium salt is greater than or equal to 1 and less than or equal to 3,
- the ratio of the number of moles of nitric acid to the number of moles of zirconium salt is greater than or equal to 1 and less than or equal to 3,

the mixture being then stirred until a clear and homogeneous solution is obtained,

or

- by dissolution of a zirconium hydroxyde $Zr(OH)_4$ precipitate in a mixture of nitric acid, or of hydrochloric acid, and of oxalic acid in amounts such that:
  - the ratio of the number of moles of oxalic acid to the number of zirconium hydroxide is greater than or equal to 1 and less than or equal to 3,
  - the ratio of the number of moles of nitric acid, or of hydrochloric acid, to the number of moles of zirconium hydroxyde is greater than or equal to 1 and less than or equal to 3,

  the mixture being then stirred until a clear and homogeneous solution is obtained,

or

- by mixing oxalic acid and zirconium oxynitrate or zirconium oxychloride, in a solvent, in amounts such that the ratio of the number of moles of oxalic acid to the number of moles of zirconium oxynitrate or of zirconium oxychloride is greater than or equal to 1 and less than or equal to 3, the mixture being then stirred until a clear and homogeneous solution is obtained.

4. Process according to the preceding claim, in which, in step a), the zirconium oxalate is obtained:

- by mixing zirconium oxynitrate and oxalic acid, in a solvent, in an amount such that the ratio of the number of moles of oxalic acid to the number of moles of zirconium oxynitrate is greater than or equal to 1 and less than or equal to 3, the mixture then being stirred until a clear, homogeneous solution is obtained,

or

- by mixing zirconium basic carbonate with a nitric acid and oxalic acid solution, in a solvent, in amounts such that:
  - the ratio of the number of moles of oxalic acid to the number of moles of zirconium basic carbonate is greater than or equal to 1 and less than or equal to 3;
  - the ratio of the number of moles of nitric acid to the number of moles of zirconium basic carbonate is greater than or equal to 1 and less than or equal to 3, the mixture then being stirred until a clear, homogeneous solution is obtained.

5. Process according to any one of the preceding claims, in which, in step c), the boehmite particle powder is introduced in the form of an aqueous suspension of boehmite particles.

6. Process according to any one of the preceding claims, in which, in step c), the amount of boehmite particle powder introduced is such that the ratio of the number of moles of Zr element provided by the zirconium oxalate divided by the number of moles of Al element provided by the boehmite particles is greater than 0.29 and/or less than 0.365.

7. Process according to the preceding claim, in which, in step c), the amount of boehmite particle powder introduced is such that the ratio of the number of moles of Zr element provided by the zirconium oxalate divided by the number of moles of Al element provided by the boehmite particles is greater than 0.34.

8. Process according to any one of the preceding claims, in which, in step c), the aqueous suspension of boehmite particles is obtained from a boehmite powder having
   - a specific surface area of greater than 240 m^2/g and less than 350 m^2/g, preferably less than 300 m^2/g, and/or
   - a pore volume of less than 0.9 cm^3/g, and/or
   - strong acidity, measured after calcination at 800°C for 2 hours, of greater than 8 µmol/g, and/or
   - a chemical composition, after calcination at 800°C, such that, in mass percentages:
     - N < 0.2%, and/or
     - C < 0.3%, and/or
     - Cl < 300 ppm, and/or
     - S < 1000 ppm, and/or
     - CaO < 900 ppm, and/or

- Na_2O < 400 ppm, and/or
- SiO_2 < 500 ppm.

9. Process according to any one of the preceding claims, in which, in step d), the pH is adjusted to a value above 2 and below 3.5.

10. Process according to any one of the preceding claims, in which, in step d), the pH is adjusted to a value above 3.

11. Process according to any one of the preceding claims, in which, in step e), the mixing is performed at a temperature below 80°C.

12. Process according to any one of the preceding claims, comprising a step i) of calcination.

13. Process according to the preceding claim, the calcination being performed at a temperature of between 600°C and 1100°C.

14. Particle powder composed for more than 90% by number of coated boehmite particles, each coated boehmite particle comprising a boehmite grain or an aggregate of boehmite grains, and a zirconium coating, the said coating extending on average over more than 90% of the surface of the said coated boehmite particle, the zirconium being bridged via a $C_2O_4^{2-}$ group.

15. Powder according to the preceding claim, in which more than 90% by number of the boehmite grains have an ovoid shape, the largest ellipse that may be inscribed in the contour of the said boehmite grain, on a photograph of the said grain, having a large axis with a length of greater than 10 nm and less than 20 nm, the largest dimension perpendicular to the said large axis being greater than 4 nm and less than 10 nm, or have the form of a fibre, the length of the said boehmite grain, on a photograph of the said grain, being greater than 60 nm and less than 100 nm and the largest dimension of the said grain perpendicular to the said length being between 2 and 5 nm.

16. Powder according to either of the two immediately preceding claims, which is obtained or which may be obtained at the end of a step f) of a process according to any one of Claims 1 to 12.

17. Particle powder composed for more than 90% by number of coated alumina particles, each coated alumina particle comprising an alumina grain or an aggregate of alumina

grains, and a layer of zirconium, the said layer covering on average more than 60% of the surface of the said coated alumina particle,
the mass content of zirconium, expressed in the form of zirconia, on the basis of the mass of the powder, being between 14% and 20%, and

the strong acidity, measured after calcination at 800°C for 2 hours, being greater than 9 μmol/g.

18. Powder according to the preceding claim, which is obtained or which may be obtained at the end of a step i) of a process according to any one of Claims 1 to 13.

19. Powder according to either of the two immediately preceding claims, in which the mass content of zirconium expressed in the form of zirconia, on the basis of the mass of the powder, is greater than 16% and/or less than 19%.

20. Powder according to any one of the three immediately preceding claims, in which the zirconium of the layer is not in a metallic form.

21. Powder according to any one of the four immediately preceding claims, in which the zirconium is in the form of zirconia.

22. Powder according to any one of the five immediately preceding claims, in which the zirconia of the coating is amorphous for more than 95% of its mass.

23. Powder according to any one of Claims 17 to 21, in which the zirconia of the coating is crystalline, for more than 50% of its mass, in a quadratic and/or cubic crystallographic form, and/or is at least partially stabilized, the stabilizer content being between 1 mol% and 10 mol% on the basis of the molar sum of the contents of stabilizer and of zirconia.

24. Powder according to any one of the seven immediately preceding claims, in which the content of stabilized alumina in the periphery of the grain or of the aggregate of grains is greater than that in the central region of the said grain or of the said aggregate of grains.

25. Powder according to any one of the eight immediately preceding claims, having:
- a specific surface area of less than 300 m^2/g and greater than 100 m^2/g, and/or
- a pore volume of greater than 0.3 cm^3/g, and less than 1 cm^3/g, and/or
- a median pore diameter of greater than 3 nm and less than 15 nm.

26. Powder according to the preceding claim, having:

- a specific surface area of less than 250 m^2/g and greater than 120 m^2/g, and/or
- a pore volume of greater than 0.45 cm^3/g and less than 0.65 cm^3/g, and/or
- a median pore diameter of greater than 6 nm and less than 13 nm.

27. Use of a powder according to any one of Claims 14 to 26, as a catalyst or a catalyst support.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/056296

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J21/04 B01J21/06 B01J37/02 B01J37/06 B01J37/08
B01J35/02 B01J35/06 B01J35/10 C10G45/34 C07C1/04
C01B3/26 B01J35/00 C01B3/40 C07C5/22

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 C10G C07C 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	CN 101 491 775 A (CHINA PETROCHEMICAL CORP [CN] CHINA PETROLEUM & CHEMICAL; SINOPEC FUSH) 29 July 2009 (2009-07-29) the whole document abstract examples 5,6 claim _ -----	1-27
X	FR 2 427 844 A1 (RAFFINAGE CIE FRANCAISE [FR] RAFFINAGE CIE FRANCAISE) 4 January 1980 (1980-01-04) the whole document page 1, lines 1-4 page 2, line 14 - page 4, line 31 example 1 claims 1-3,6,8-13 ----- -/--	1-27

[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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 November 2013	12/11/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/056296

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2012/047864 A1 (PACIFIC IND DEV CORP [US]; WU WEI [US]; LI YUNKUI [US]; LACHAPELLE JEF) 12 April 2012 (2012-04-12) the whole document paragraphs [0004], [0006], [0013], [0015], [0016], [0018] - [0020], [0022] - [0025] examples 1,2 claims	1-27
A	"Nabaltec introduces new mineral flame retardants", PLASTICS ADDITIVES AND COMPOUNDING, ELSEVIER SCIENCE, OXOFRD, GB, vol. 8, no. 6, 1 November 2006 (2006-11-01), page 25, XP028056938, ISSN: 1464-391X, DOI: 10.1016/S1464-391X(06)70663-8 [retrieved on 2006-11-01] the whole document boehmite and aluminum hydroxide are synonyms	1
A	US 3 642 933 A (HECKELSBERG LOUIS F) 15 February 1972 (1972-02-15) the whole document column 1, lines 14-17,62-72 column 2, lines 15-23,37-69 example 1	1-27

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Information on patent family members

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