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Description

Technical field

5 The present invention relates to the preparation of alumina gels exhibiting high dispersibility.

Prior art

10 Several operating protocols known in the prior art lead to dispersible alumina gels. Several patents describe in particular a preparation method referred to as "sol-gel".

US Patent 4 676 928 describes a method for producing a water  
15 dispersible alumina comprising a step of forming an aqueous alumina slurry, an acidification step for producing an acidified slurry having a pH comprised between 5 and 9, an ageing step at an elevated temperature above 70°C for a sufficient period of time to convert the alumina to a colloidal gel, followed by a  
20 step of drying said colloidal gel obtained.

US Patent 5 178 849 also describes a method for producing an alpha alumina comprising a step of dispersing an aluminium hydrate having a dispersibility below 70%, a step of acidifying  
25 the slurry obtained to a pH below 3.5 to at least partially dissolve the aluminium hydrate, a step of hydrothermally treating the acidified slurry obtained at a temperature comprised between 150 and 200°C, at a pressure comprised between 5 and 20 atm for a duration comprised between 0.15 and 4 hours  
30 to obtain a colloidal boehmite having a dispersibility greater than 90%.

The preparation of alumina gel by precipitation is also well known in the prior art.

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In particular, US Patent 7 790 652 describes the preparation by precipitation of an alumina support material having a very specific pore distribution, capable of being used as a catalyst

support in a process of hydroconversion of heavy hydrocarbon feedstock.

5 The alumina support material is prepared according to a method comprising a first step of forming an alumina slurry by mixing, in a controlled fashion, a first alkaline aqueous solution and a first acidic aqueous solution, at least one of said acidic and basic solutions, or both, comprising an aluminium compound. The acidic and basic solutions are mixed in proportions such that  
10 the pH of the resulting slurry is comprised between 8 and 11. The acidic and basic solutions are also mixed in quantities making it possible to obtain a slurry containing the desired quantity of alumina, in particular, the first step makes it possible to obtain 25 to 35% by weight of alumina relative to  
15 the total quantity of alumina formed at the end of the two precipitation steps. The first step takes place at a temperature comprised between 20 and 40°C. When the desired quantity of alumina is formed, the temperature of the suspension is increased to a temperature between 45 and 70°C, then the heated  
20 suspension is subjected to a second precipitation step by contacting said suspension with a second alkaline aqueous solution and a second acidic aqueous solution, at least one of the two solutions, or both, comprising an aluminium compound. Similarly, the pH is adjusted to between 8 and 10.5 by the  
25 proportions of the acidic and basic solutions added and the remaining quantity of alumina to be formed in the second step is contributed by the quantities of the second acidic and basic solutions added. The second step takes place at a temperature comprised between 20 and 40°C. The alumina gel thus formed  
30 comprises at least 95% boehmite. The dispersibility of the alumina gel thus obtained is not mentioned. The alumina gel is then filtered, washed and optionally dried by methods known to the person skilled in the art, without a preliminary maturing step, to produce an alumina powder which is then formed by  
35 methods known to the person skilled in the art, then calcined to produce the final alumina support.

The first precipitation step of the preparation method of US

Patent 7 790 652 is limited to a low production of alumina, comprised between 25 and 35% by weight, as a higher alumina production at the end of the first step does not permit optimal filtration of the gel obtained. Furthermore, increasing the production of alumina in the first step of US Patent 7 790 652 would not permit forming of the gel thus obtained.

The present invention proposes to overcome the drawbacks of the preparation method according to US Patent 7 790 652.

The applicant has thus discovered a novel method for preparing an alumina gel by precipitation according to Claim 1.

Furthermore, the novel preparation method according to the invention is characterised by the presence of a final heat treatment step and in particular a final maturing step making it possible to obtain an alumina gel having improved filterability, providing higher productivity of the method according to the invention, and making it easier to scale up the method to the industrial level. Said method according to the invention also makes it possible to obtain an alumina gel having a better dispersibility index compared with alumina gels of the prior art, thereby facilitating the forming thereof by the techniques known to the person skilled in the art.

An object of the present invention is to provide a novel method for preparing said alumina gel by precipitation, in an aqueous reaction medium, of at least one basic precursor and at least one acidic precursor, at least one of the basic or acidic precursors, or both, comprising aluminium, in relative proportions and in very specific quantities and making it possible to obtain an alumina gel having an elevated dispersibility index, and in particular a dispersibility index greater than 70%, preferably comprised between 70 and 100%, preferably comprised between 80 and 100%, more preferably comprised between 85 and 100%, and even more preferably between 90 and 100%.

Summary and interest of the invention

The subject of the present invention is the preparation of an alumina gel having an elevated dispersibility index, and in particular a dispersibility index greater than 70%, a crystallite size comprised between 1 and 35 nm, and a sulphur content comprised between 0.001% and 2% by weight, and a sodium content comprised between 0.001% and 2% by weight, the weight percentages being expressed in relation to the total mass of alumina gel.

One advantage of the invention is that it provides a novel alumina gel having a very high dispersibility compared with alumina gels of the prior art.

An alumina gel characterised by an elevated dispersibility index will be more readily formed by all of the forming techniques known to the person skilled in the art, such as for example by mixing-extrusion, pelletizing or the oil drop technique, than a gel having a low dispersibility index.

In particular, the subject of the present invention is a method for preparing an alumina gel having a dispersibility index greater than 70%, the dispersibility index being defined as the percentage by weight of peptised alumina gel that can be dispersed by centrifugation in a polypropylene tube at 3600G for 10 minutes, the dispersibility being measured by dispersing 10% of boehmite or alumina gel in a suspension of water also containing 10% nitric acid relative to the mass of boehmite, the suspension then being centrifuged at 3600G rpm for 10 minutes, the collected sediments being dried at 100°C overnight then weighed, obtaining the dispersibility index, denoted DI, by the following calculation:  $DI(\%) = 100\% - \text{mass of dried sediments}(\%)$ , a crystallite size comprised between 1 and 35 nm, and a sulphur content comprised between 0.001% and 2% by weight, and a sodium content comprised between 0.001% and 2% by weight, the weight percentages being expressed in relation to the total mass of alumina gel, said method comprising at least the following

steps:

a) at least one first step of precipitating alumina, in an aqueous reaction medium, of at least one basic precursor selected from sodium aluminate, potassium aluminate, ammonia, sodium hydroxide and potassium hydroxide and of at least one acidic precursor selected from aluminium sulphate, aluminium chloride, aluminium nitrate, sulphuric acid, hydrochloric acid, and nitric acid, in which at least one of the basic or acidic precursors includes aluminium, the relative feed rate of the acidic and basic precursors is chosen so as to obtain a pH of the reaction medium comprised between 8.5 and 10.5 and the feed rate of the acidic and basic precursor(s) containing aluminium is adjusted so as to obtain a progression rate of said first step comprised between 45 and 90%, the progression rate being defined as the proportion of alumina formed in  $\text{Al}_2\text{O}_3$  equivalent during said first precipitation step relative to the total quantity of alumina formed at the end of the precipitation step(s), said first precipitation step taking place at a temperature comprised between 10 and 50°C, and for a duration comprised between 2 minutes and 30 minutes, a step of heating the suspension obtained at the end of precipitation step a) is implemented between the two precipitation steps a) and a'), said heating step taking place at a temperature comprised between 20 and 90°C and for a duration comprised between 7 and 45 minutes,

a') a second step a') of precipitating the suspension obtained at the end of the heating step, carried out by adding to said suspension at least one basic precursor selected from sodium aluminate, potassium aluminate, ammonia, sodium hydroxide and potassium hydroxide and at least one acidic precursor selected from aluminium sulphate, aluminium chloride, aluminium nitrate, sulphuric acid, hydrochloric acid, and nitric acid, in which at least one of the basic or acidic precursors includes aluminium, the relative feed rate of the acidic and basic precursors is chosen so as to obtain a pH of the reaction medium comprised between 8.5 and 10.5 and the feed rate of the acidic and basic precursor(s) containing aluminium is adjusted so as to obtain a

progression rate of the second step comprised between 10 and 55%, said progression rate of the second step being defined as the proportion of alumina formed in  $\text{Al}_2\text{O}_3$  equivalent during said second precipitation step a') relative to the total quantity of alumina formed at the end of step a'), said second step a') taking place at a temperature comprised between 40 and 90°C, and for a duration comprised between 2 minutes and 50 minutes, and a second step of heating the suspension obtained at the end of said second precipitation step a'), at a temperature comprised between 50 and 95°C,

b) a step of heat treating the suspension obtained at the end of step a'), at a temperature comprised between 50 and 200°C for a duration comprised between 30 minutes and 5 hours,

c) a step of filtering the suspension obtained at the end of heat treatment step b), followed by at least one step of washing the gel obtained.

The method according to the invention characterised by the combination of alumina precipitation steps allowing the production of an elevated quantity of alumina and a final step of heat treating the suspension obtained makes it possible to obtain an alumina gel having improved filterability, thus providing higher productivity of the method according to the invention, and making it easier to scale up the method to the industrial level.

Another advantage of the invention is that it provides a novel method of preparation by precipitation of an alumina gel having an elevated dispersibility index compared with gels of the prior art.

#### Description of the invention

The subject of the present invention is the preparation of an alumina gel having a dispersibility index greater than 70%, a crystallite size comprised between 1 and 35 nm, and a sulphur



content measured by X-ray fluorescence comprised between 0.001% and 2% by weight, and a sodium content measured by ICP or inductively coupled plasma spectrometry comprised between 0.001% and 2% by weight, the weight percentages being expressed in relation to the total mass of alumina gel.

Throughout the remainder of the text, the dispersibility index is defined as the percentage by weight of peptised alumina gel that can be dispersed by centrifugation in a polypropylene tube at 3600G for 10 minutes.

The dispersibility is measured by dispersing 10% of boehmite or alumina gel in a suspension of water also containing 10% nitric acid relative to the mass of boehmite. The suspension is then centrifuged at 3600G rpm for 10 minutes. The collected sediments are dried at 100°C overnight then weighed.

The dispersibility index, denoted DI, is obtained by the following calculation:  $DI(\%) = 100\% - \text{mass of dried sediments}(\%)$ .

Preferably, the alumina gel prepared according to the invention has a dispersibility index comprised between 70 and 100%, preferably between 80 and 100%, more preferably between 85 and 100%, and even more preferably between 90 and 100%.

Preferably, the alumina gel prepared according to the invention has a crystallite size comprised between 2 and 35 nm.

In particular, the alumina gel or boehmite in powder form prepared according to the invention is composed of crystallites of which the size, obtained by the Scherrer formula in X-ray diffraction in the crystallographic directions (020) and (120), is respectively comprised between 2 and 20 nm and between 2 and 35 nm.

Preferably, the alumina gel prepared according to the invention has a crystallite size in the crystallographic direction (020) comprised between 2 and 15 nm and a crystallite size in the

crystallographic direction (120) comprised between 2 and 35 nm.

X-ray diffraction was carried out on the alumina gels or boehmites using the conventional powder method using a  
5 diffractometer.

The Scherrer formula is a formula used in X-ray diffraction on powders or polycrystalline samples which relates the mid-height width of the diffraction peaks to the size of the crystallites.  
10 It is described in detail in the reference: Appl. Cryst. (1978). 11, 102-113 Scherrer after sixty years: A survey and some new results in the determination of crystallite size, J. I. Langford and A. J. C. Wilson.

15 According to the invention, the alumina gel prepared according to the invention has an impurities content, and in particular a sulphur content, measured by X-ray fluorescence comprised between 0.001% and 2% by weight, and a sodium content measured by ICP or inductively coupled plasma spectrometry comprised  
20 between 0.001 and 2% by weight, the weight percentages being expressed in relation to the total mass of alumina gel.

Preferably, the alumina gel prepared according to the invention includes a sulphur content comprised between 0.001% and 1% by  
25 weight, preferably between 0.001 and 0.40% by weight, more preferably between 0.003 and 0.33% by weight, and even more preferably between 0.005 and 0.25% by weight.

Preferably, the alumina gel prepared according to the invention includes a sodium content comprised between 0.001% and 1% by  
30 weight, preferably between 0.001 and 0.15% by weight, more preferably between 0.0015 and 0.10% by weight, and even more preferably between 0.002 and 0.040% by weight.

### 35 Preparation method

According to the invention, said preparation method comprises at least a first step a) of precipitating alumina, in an aqueous

reaction medium, of at least one basic precursor selected from sodium aluminate, potassium aluminate, ammonia, sodium hydroxide and potassium hydroxide and of at least one acidic precursor selected from aluminium sulphate, aluminium chloride, aluminium nitrate, sulphuric acid, hydrochloric acid, and nitric acid, in which at least one of the basic or acidic precursors includes aluminium, the relative feed rate of the acidic and basic precursors is chosen so as to obtain a pH of the reaction medium comprised between 8.5 and 10.5 and the feed rate of the acidic and basic precursor(s) containing aluminium is adjusted so as to obtain a progression rate of the first step comprised between 45 and 90%, the progression rate being defined as the proportion of alumina formed in  $\text{Al}_2\text{O}_3$  equivalent during said precipitation step a) relative to the total quantity of alumina formed at the end of the precipitation steps and more generally at the end of the preparation method according to the invention, said step a) taking place at a temperature comprised between 10 and  $50^\circ\text{C}$ , and for a duration comprised between 2 minutes and 30 minutes.

In a general manner, the "progression rate" of the  $n^{\text{th}}$  precipitation step is understood to mean the percentage of alumina formed in  $\text{Al}_2\text{O}_3$  equivalent at said  $n^{\text{th}}$  step relative to the total quantity of alumina formed at the end of all the precipitation steps and more generally at the end of the steps of preparing the alumina gel.

#### **Precipitation step a)**

Mixing of at least one basic precursor and at least one acidic precursor in the aqueous reaction medium requires either that at least the basic precursor or the acidic precursor includes aluminium, or that both the basic and acidic precursors include aluminium.

Basic precursors that include aluminium are sodium aluminate and potassium aluminate. The preferred basic precursor is sodium aluminate.

Acidic precursors that include aluminium are aluminium sulphate, aluminium chloride and aluminium nitrate. The preferred acidic precursor is aluminium sulphate.

- 5 Preferably, the basic and acidic precursor(s) are added at said first precipitation step a) in aqueous solutions.

Preferably, the aqueous reaction medium is water.

- 10 Preferably, said step a) takes place while stirring.

Preferably, said step a) is performed in the absence of organic additive.

- 15 The acidic and basic precursors, whether or not they contain aluminium, are mixed, preferably in solution, in the aqueous reaction medium, in proportions such that the pH of the resulting suspension is comprised between 8.5 and 10.5.

- 20 According to the invention, it is the relative feed rate of the acidic and basic precursors, whether or not they contain aluminium, that is chosen so as to obtain a pH of the reaction medium comprised between 8.5 and 10.5.

- 25 In the preferred case where the basic and acidic precursors are respectively sodium aluminate and aluminium sulphate, the mass ratio of said basic precursor to said acidic precursor is advantageously comprised between 1.6 and 2.05.

- 30 For the other basic and acidic precursors, whether or not they contain aluminium, the base/acid mass ratios are established by a curve of neutralisation of the base by the acid. Such a curve is readily obtained by the person skilled in the art.

- 35 Preferably, said precipitation step a) is performed at a pH comprised between 8.5 and 10 and more preferably between 8.7 and 9.9.

The acidic and basic precursors are also mixed in quantities making it possible to obtain a suspension containing the desired quantity of alumina, depending on the final alumina concentration to be achieved. In particular, said step a) makes it possible to obtain 45 to 90% by weight of alumina in  $\text{Al}_2\text{O}_3$  equivalent relative to the total quantity of alumina formed at the end of the precipitation step(s). According to the invention, it is the feed rate of the acidic and basic precursor(s) containing aluminium that is adjusted so as to obtain a progression rate of the first step comprised between 45 and 90%.

For preference, the progression rate of said precipitation step a) is comprised between 50 and 85%. The progression rate is defined as the proportion of alumina formed in  $\text{Al}_2\text{O}_3$  equivalent during said precipitation step a) relative to the total quantity of alumina formed at the end of the two precipitation steps of the preparation method according to the invention.

Thus, depending on the target alumina concentration at the end of the precipitation step(s), preferably comprised between 20 and 100 g/l, the quantities of aluminium to be contributed by the acidic and/or basic precursors are calculated and the feed rate of the precursors is adjusted depending on the aluminium concentration of said added precursors, on the quantity of water added to the reaction medium, and on the required progression rate for the precipitation step(s).

The feed rate of the acidic and/or basic precursor(s) containing aluminium depends on the size of the reaction vessel used and thus on the quantity of water added to the reaction medium.

For preference, said precipitation step a) is performed at a temperature comprised between 10 and 45°C, preferably between 15 and 45°C, more preferably between 20 and 45°C, and even more preferably between 20 and 40°C.

It is important that said precipitation step a) takes place at

low temperature. In the case where said preparation method according to the invention comprises two precipitation steps, precipitation step a) is advantageously performed at a temperature below the temperature of the second precipitation step.

For preference, said precipitation step a) is performed for a duration comprised between 5 and 20 minutes, and preferably between 5 and 15 minutes.

According to the invention, a step of heating the suspension obtained at the end of precipitation step a) is implemented between the two precipitation steps a) and a'), said heating step taking place at a temperature comprised between 20 and 90°C, preferably between 30 and 80°C, more preferably between 30 and 70°C, and even more preferably between 40 and 65°C and for a duration comprised between 7 and 45 minutes and preferably between 7 and 35 minutes.

Said heating step is advantageously implemented according to all heating methods known to the person skilled in the art.

According to the invention, said preparation method comprises a second precipitation step a') after the first precipitation step.

Said second precipitation step makes it possible to increase the proportion of alumina produced.

Said second precipitation step a') is implemented between said first precipitation step a) and the heat treatment step b).

According to the invention, said preparation method comprises a second step of precipitating the suspension obtained at the end of the heating step, said second step being carried out by adding to said suspension at least one basic precursor selected from sodium aluminate, potassium aluminate, ammonia, sodium hydroxide and potassium hydroxide and at least one acidic precursor

selected from aluminium sulphate, aluminium chloride, aluminium nitrate, sulphuric acid, hydrochloric acid, and nitric acid, in which at least one of the basic or acidic precursors includes aluminium, the relative feed rate of the acidic and basic precursors is chosen so as to obtain a pH of the reaction medium comprised between 8.5 and 10.5 and the feed rate of the acidic and basic precursor(s) containing aluminium is adjusted so as to obtain a progression rate of the second step comprised between 10 and 55%, said progression rate being defined as the proportion of alumina formed in Al<sub>2</sub>O<sub>3</sub> equivalent during said second precipitation step relative to the total quantity of alumina formed at the end of the two precipitation steps and preferably at the end of step a') of the method according to the invention, said step taking place at a temperature comprised between 40 and 90°C, and for a duration comprised between 2 minutes and 50 minutes.

As in the first precipitation step a), the addition of at least one basic precursor and at least one acidic precursor to the heated suspension requires either that at least the basic precursor or the acidic precursor includes aluminium, or that both the basic and acidic precursors include aluminium.

Basic precursors that include aluminium are sodium aluminate and potassium aluminate. The preferred basic precursor is sodium aluminate.

Acidic precursors that include aluminium are aluminium sulphate, aluminium chloride and aluminium nitrate. The preferred acidic precursor is aluminium sulphate.

Preferably, said second precipitation step takes place while stirring.

Preferably, said second step is performed in the absence of organic additive.

The acidic and basic precursors, whether or not they contain

aluminium, are mixed, preferably in solution, in the aqueous reaction medium, in proportions such that the pH of the resulting suspension is comprised between 8.5 and 10.5.

- 5 As in precipitation step a), it is the relative feed rate of the acidic and basic precursors, whether or not they contain aluminium, that is chosen so as to obtain a pH of the reaction medium comprised between 8.5 and 10.5.
- 10 In the preferred case where the basic and acidic precursors are respectively sodium aluminate and aluminium sulphate, the mass ratio of said basic precursor to said acidic precursor is advantageously comprised between 1.6 and 2.05.
- 15 For the other basic and acidic precursors, whether or not they contain aluminium, the base/acid mass ratios are established by a curve of neutralisation of the base by the acid. Such a curve is readily obtained by the person skilled in the art.
- 20 For preference, said second precipitation step is performed at a pH comprised between 8.5 and 10 and preferably between 8.7 and 9.9.

The acidic and basic precursors are also mixed in quantities making it possible to obtain a suspension containing the desired quantity of alumina, depending on the final alumina concentration to be achieved. In particular, said second precipitation step makes it possible to obtain 10 to 55% by weight of alumina in  $\text{Al}_2\text{O}_3$  equivalent relative to the total quantity of alumina formed at the end of the two precipitation steps and preferably at the end of step a').

As in precipitation step a), it is the feed rate of the acidic and basic precursor(s) containing aluminium that is adjusted so as to obtain a progression rate of the second step comprised between 10 and 55%, the progression rate being defined as the proportion of alumina formed during said second precipitation step relative to the total quantity of alumina formed at the end



of the two precipitation steps of the method according to the invention and preferably at the end of step a').

For preference, the progression rate of said second precipitation step a) is comprised between 15 and 55%.

Thus, depending on the target alumina concentration at the end of the precipitation step(s), preferably comprised between 20 and 100 g/l, the quantities of aluminium to be contributed by the acidic and/or basic precursors are calculated and the feed rate of the precursors is adjusted depending on the aluminium concentration of said added precursors, on the quantity of water added to the reaction medium, and on the required progression rate for each of the precipitation steps.

As in precipitation step a), the feed rate of the acidic and/or basic precursor(s) containing aluminium depends of the size of the reaction vessel used and thus on the quantity of water added to the reaction medium.

By way of example, if a 3-litre reaction vessel is used and it is proposed to obtain 1 litre of alumina suspension with a final  $\text{Al}_2\text{O}_3$  concentration of 50 g/l, the target progression rate is 50% in  $\text{Al}_2\text{O}_3$  equivalent for the first precipitation step. Thus, 50% of the total alumina must be added during precipitation step a). The alumina precursors are sodium aluminate at a concentration of 155 g/l of  $\text{Al}_2\text{O}_3$  and aluminium sulphate at a concentration of 102 g/l of  $\text{Al}_2\text{O}_3$ . The pH of precipitation of the first step is fixed at 9.5 and the second at 9. The quantity of water added to the reaction vessel is 622 ml.

For the first precipitation step a) taking place at 30°C for 8 minutes, the feed rate of aluminium sulphate must be 10.5 ml/min and the feed rate of sodium aluminate is 13.2 ml/min. The mass ratio of sodium aluminate to aluminium sulphate is therefore 1.91.

For the second precipitation step, taking place at 70°C for 30

minutes, the feed rate of aluminium sulphate must be 2.9 ml/min and the feed rate of sodium aluminate is 3.5 ml/min. The mass ratio of sodium aluminate to aluminium sulphate is therefore 1.84.

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For preference, the second precipitation step is performed at a temperature comprised between 40 and 80°C, preferably between 45 and 70°C, and even more preferably between 50 and 70°C.

10 For preference, the second precipitation step is performed for a duration comprised between 5 and 45 minutes, and preferably between 7 and 40 minutes.

The second precipitation step generally makes it possible to  
15 obtain an alumina suspension having an Al<sub>2</sub>O<sub>3</sub> concentration comprised between 20 and 100 g/l, for preference between 20 and 80 g/l, and preferably between 20 and 50 g/l.

According to the invention, said preparation method also  
20 comprises a second step of heating the suspension obtained at the end of said second precipitation step at a temperature comprised between 50 and 95°C and preferably between 60 and 90°C.

25 For preference, said second heating step is implemented for a duration comprised between 7 and 45 minutes.

Said second heating step is advantageously implemented according to all heating methods known to the person skilled in the art.

30

Said second heating step makes it possible to increase the temperature of the reaction medium before subjecting the suspension obtained to heat treatment step b).

35 **Heat treatment step b)**

According to the invention, said preparation method comprises a step b) of heat treating the suspension obtained at the end of

precipitation step a'), said heat treatment step taking place at a temperature comprised between 50 and 200°C for a duration comprised between 30 minutes and 5 hours, in order to obtain the alumina gel.

5

For preference, said heat treatment step b) is a maturation step.

For preference, said heat treatment step b) is performed at a temperature comprised between 65 and 150°C, preferably between 65 and 130°C, more preferably between 70 and 110°C, and even more preferably between 70 and 95°C.

For preference, said heat treatment step b) is performed for a duration comprised between 40 minutes and 5 hours, preferably between 40 minutes and 3 hours, and more preferably between 45 minutes and 2 hours.

#### **Filtration step c)**

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In accordance with the invention, the method of preparing alumina gel according to the invention also comprises a step c) of filtering the suspension obtained at the end of heat treatment step b), followed by at least one step of washing the gel obtained. Said filtration step is advantageously implemented according to the methods known to the person skilled in the art.

The filterability of the suspension obtained at the end of precipitation step a) or of the two precipitation steps is improved by the presence of said final heat treatment step b) of the suspension obtained, said heat treatment step being conducive to the productivity of the method according to the invention, and to the scaling up of the method to the industrial level.

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Said filtration step is advantageously followed by at least one step of washing with water and preferably by one to three washing steps, with a quantity of water equal to the quantity of

precipitate filtered.

The preparation method according to the present invention therefore makes it possible to obtain an alumina gel having a dispersibility index greater than 70% and a crystallite size comprised between 2 and 35 nm.

The present invention also relates to the alumina gel capable of being obtained by the preparation method according to the invention.

The invention is illustrated by the following examples which are in no way limitative thereof.

**Examples:**

Example 1: (comparative)

A commercial powder of an alumina gel Pural SB3 is prepared via a sol-gel route by hydrolysis-polycondensation of an aluminium alcoxide.

The characteristics of the Pural SB3 boehmite gel are summarised in Table 1.

Table 1: Characteristics of Pural SB3.

	Commercial alumina gel
Dispersibility index	98
Size (020) (nm)	3.1
Size (120) (nm)	4.7
Sodium Na (ppm)	< detection limit
Sulphur S (ppm)	< detection limit

The sulphur content is measured by the X-ray fluorescence method, and the sodium content is measured by ICP or inductively coupled plasma spectrometry are below the detection limit of these measuring methods.

Example 2 (comparative):

5 An alumina gel is synthesised by a preparation method not according to the invention in that the precipitation step is performed at high temperature, that is at a temperature of 60°C. Stirring at 350 rpm is maintained throughout the synthesis.

10 The synthesis takes place in a 5-litre reaction vessel in 2 steps, a precipitation step and a step of maturation of the suspension obtained.

The target final alumina concentration is 50 g/l.

15 A step of precipitating aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium aluminate  $\text{NaAlOO}$  is performed at 60°C and pH=10.2 for a duration of 20 minutes. The concentrations of the aluminium precursors used are as follows:  $\text{Al}_2(\text{SO}_4)$  at 102 g/l in  $\text{Al}_2\text{O}_3$  and  $\text{NaAlOO}$  at 155 g/l in  $\text{Al}_2\text{O}_3$ .

20 A solution of aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  is added continuously for 30 minutes at a rate of 25.9 ml/min to a solution of sodium aluminate  $\text{NaAlOO}$  in a base/acid mass ratio = 2.0 so as to adjust the pH to a value of 10.2. The entirety of the precursors is placed in contact at a temperature of 60°C.

A suspension containing an alumina precipitate is obtained.

30 The target final alumina concentration being 50 g/l, the feed rates of the precursors aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium aluminate  $\text{NaAlOO}$  containing aluminium introduced in the first precipitation step are respectively 25.9 ml/min and 34.1 ml/min.

35 These feed rates of acidic and basic precursors containing aluminium make it possible to obtain a progression rate of 100% at the end of the first precipitation step.

The suspension obtained is then subjected to a temperature

increase from 60 to 90°C.

The suspension then undergoes a maturation step in which it is maintained at 90°C for 60 minutes.

5

The suspension obtained is then filtered by passing water through a sintered disc Buchner funnel and the alumina gel obtained is washed 3 times with 3.5 litres of distilled water at 70°C. The filtering and washing time is 3h.

10

The characteristics of the alumina gel thus obtained are summarised in Table 2.

15 Table 2: Characteristics of the alumina gel obtained according to Example 2.

	Example 2
Dispersibility index Ta (10% (%))	0
Size (020) (nm)	2.9
Size (120) (nm)	3.4
Sodium Na (%)	0.0068
Sulphur S (%)	0.042
Filtration time	3 h

20 Example 2 not according to the invention indicates the importance of working at low temperature during the precipitation step and in particular during the first precipitation step. Thus, a precipitation step performed at a temperature of 70°C, outside the ranges claimed, does not make it possible to obtain a dispersible gel. On the contrary, the dispersion of 10% of alumina gel thus obtained in a water suspension also containing 10% nitric acid relative to the mass of alumina gel, followed by centrifugation of the suspension at 25 3600G for 10 minutes, yields 100% sediments.

Example 3 (comparative):

30

An alumina gel is synthesised by a preparation method not according to the invention in that the method of preparing the gel in Example 3 does not include a heat treatment step and in that the first precipitation step a) does not produce a quantity  
5 of alumina greater than 40% relative to the total quantity of alumina formed at the end of the second precipitation step. Example 3 is carried out according to the preparation method described in US Patent 7 790 562.

10 The synthesis is performed in a 7-litre reaction vessel with a final suspension of 5 litres in two precipitation steps. The quantity of water added to the reaction vessel is 3868 ml.

The target final alumina concentration is 30 g/l.

15

A first step of co-precipitating aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium aluminate  $\text{NaAlOO}$  is performed at  $30^\circ\text{C}$  and  $\text{pH}=9.3$  for a duration of 8 minutes. The concentrations of the aluminium precursors used are as follows:  $\text{Al}_2(\text{SO}_4)$  at 102 g/l in  $\text{Al}_2\text{O}_3$  and  
20  $\text{NaAlOO}$  at 155 g/l in  $\text{Al}_2\text{O}_3$ . Stirring at 350 rpm is maintained throughout the synthesis.

A solution of aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  is added continuously for 8 minutes at a rate of 19.6 ml/min to a solution of sodium aluminate  $\text{NaAlOO}$  in a base/acid mass ratio = 1.80 so as to adjust  
25 the pH to a value of 9.3. The temperature of the reaction medium is maintained at  $30^\circ\text{C}$ .

A suspension containing an alumina precipitate is obtained.

30

The target final alumina concentration being 30 g/l, the feed rates of the precursors aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium aluminate  $\text{NaAlOO}$  containing aluminium introduced in the first precipitation step are respectively 19.6 ml/min and 23.3 ml/min.

35

These feed rates of acidic and basic precursors containing aluminium make it possible to obtain a progression rate of 30% at the end of the first precipitation step.

The suspension obtained is then subjected to a temperature increase from 30 to 57°C.

5 A second step of co-precipitation of the suspension obtained is then performed by adding aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  at a concentration of 102 g/l in  $\text{Al}_2\text{O}_3$  and sodium aluminate  $\text{NaAlOO}$  at a concentration of 155 g/l in  $\text{Al}_2\text{O}_3$ . A solution of aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  is therefore added continuously to the heated  
10 suspension obtained at the end of the first precipitation step for 30 minutes at a rate of 12.8 ml/min to a solution of sodium aluminate  $\text{NaAlOO}$  in a base/acid mass ratio = 1.68 so as to adjust the pH to a value of 8.7. The temperature of the reaction medium in the second step is maintained at 57°C.

15

A suspension containing an alumina precipitate is obtained.

The target final alumina concentration being 30 g/l, the feed rates of the precursors aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium  
20 aluminate  $\text{NaAlOO}$  containing aluminium introduced in the second precipitation step are respectively 12.8 ml/min and 14.1 ml/min.

These feed rates of acidic and basic precursors containing aluminium make it possible to obtain a progression rate of 70%  
25 at the end of the second precipitation step.

The suspension thus obtained is not subjected to a maturation step.

30 The suspension obtained is then filtered by passing water through a sintered disc Buchner funnel and the alumina gel obtained is washed 3 times with 5 litres of distilled water at 70°C. The filtering and washing time is 4h.

35 The characteristics of the alumina gel thus obtained are summarised in Table 3.

Table 3: Characteristics of the alumina gel obtained according



to Example 3.

	Example 3
Dispersibility index Ta = 10% (%)	60
Size (020) (nm)	2.9
Size (120) (nm)	4.1
Sodium Na (ppm)	0.011
Sulphur S (ppm)	0.057
Filtration time	4 h

Example 4 (according to the invention):

5

An alumina gel is synthesised by a preparation method according to the invention in a 7-litre reaction vessel with a final suspension of 5 litres in 3 steps, two precipitation steps followed by a maturation step.

10

The target final alumina concentration is 45 g/l. The quantity of water added to the reaction vessel is 3267 ml. Stirring at 350 rpm is maintained throughout the synthesis.

15

A first step of co-precipitation in water of aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium aluminate  $\text{NaAlOO}$  is performed at 30°C and pH=9.5 for a duration of 8 minutes. The concentrations of the aluminium precursors used are as follows:  $\text{Al}_2(\text{SO}_4)$  at 102 g/l in  $\text{Al}_2\text{O}_3$  and  $\text{NaAlOO}$  at 155 g/l in  $\text{Al}_2\text{O}_3$ .

20

A solution of aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  is added continuously for 8 minutes at a rate of 69.6 ml/min to a solution of sodium aluminate  $\text{NaAlOO}$  at a rate of 84.5 ml/min in a base/acid mass ratio = 1.84 so as to adjust the pH to a value of 9.5. The temperature of the reaction medium is maintained at 30°C.

25

A suspension containing an alumina precipitate is obtained.

30

The target final alumina concentration being 45 g/l, the feed rates of the precursors aluminium sulphate  $\text{Al}_2(\text{SO}_4)$  and sodium

aluminate NaAlOO containing aluminium introduced in the first precipitation step are respectively 69.6 ml/min and 84.5 ml/min.

5 These feed rates of acidic and basic precursors containing aluminium make it possible to obtain a progression rate of 72% at the end of the first precipitation step.

The suspension obtained is then subjected to a temperature increase from 30 to 68°C.

10

A second step of co-precipitation of the suspension obtained is then performed by adding aluminium sulphate  $Al_2(SO_4)$  at a concentration of 102 g/l in  $Al_2O_3$  and sodium aluminate NaAlOO at a concentration of 155 g/l in  $Al_2O_3$ . A solution of aluminium sulphate  $Al_2(SO_4)$  is therefore added continuously to the heated suspension obtained at the end of the first precipitation step for 30 minutes at a rate of 7.2 ml/min to a solution of sodium aluminate NaAlOO in a base/acid mass ratio = 1.86 so as to adjust the pH to a value of 9. The temperature of the reaction medium  
15  
20 in the second step is maintained at 68°C.

A suspension containing an alumina precipitate is obtained.

25 The target final alumina concentration being 45 g/l, the feed rates of the precursors aluminium sulphate  $Al_2(SO_4)$  and sodium aluminate NaAlOO containing aluminium introduced in the second precipitation step are respectively 7.2 ml/min and 8.8 ml/min.

30 These feed rates of acidic and basic precursors containing aluminium make it possible to obtain a progression rate of 28% at the end of the second precipitation step.

The suspension obtained is then subjected to a temperature increase from 68 to 90°C.

35

The suspension then undergoes a heat treatment step in which it is maintained at 90°C for 60 minutes.

The suspension obtained is then filtered by passing water through a sintered disc Buchner funnel and the alumina gel obtained is washed 3 times with 5 litres of distilled water. The filtering and washing time is 3h.

5

The characteristics of the alumina gel thus obtained are summarised in Table 4.

Table 4: Characteristics of the alumina gel obtained according to Example 4.

10

	Example 4
Dispersibility index Ta = 10% (%)	100
Size (020) (nm)	2.8
Size (120) (nm)	3.5
Sodium Na (%)	0.074
Sulphur S (%)	0.0364
Filtration time	3 h

A gel having a dispersibility index of 100% is thus obtained. Furthermore, the gel obtained by the method according to the invention characterised by the presence of a final heat treatment step makes it possible to obtain an alumina gel with good filterability, that is a filtration time compatible with scaling up of the method to the industrial level, thereby facilitating improved productivity of said method.

15

20

It will also be noted that the alumina gel obtained by the preparation method according to the invention is readily formable.

25

The preparation method according to the invention making it possible to obtain a 100% dispersible gel is also less expensive than the conventional alumina preparation methods of the prior art such as for example the sol-gel type methods of preparing Pural SB3 in Example 1.

30

Example 5 (comparative):

Example 5 not according to the invention is carried out in the same manner and under the same operating conditions as Example 5 3 with the difference that the suspension obtained at the end of the second precipitation step does not undergo a maturation step.

The suspension obtained at the end of the second precipitation step is filtered by passing water through a sintered disc Buchner funnel and the alumina gel obtained is washed 3 times with 3.5 litres of distilled water.

The filtering and washing time is 24h.

The characteristics of the alumina gel thus obtained are summarised in Table 5.

Table 5: Characteristics of the alumina gel obtained according to Example 5.

	Example 5:
Dispersibility index $T_a = 10\%$ (%)	100
Size (020) (nm)	2.8
Size (120) (nm)	3.5
Sodium Na (%)	0.442
Sulphur S (%)	0.0284
Filtration time	24 h

Patentkrav

1. Fremgangsmåde til fremstilling af en aluminagel med et dispergerbarhedsindeks på mere end 70 %, hvor  
5 dispergerbarhedsindekset er defineret som vægtprocenten af peptiseret aluminagel, som kan dispergeres ved centrifugering i et polypropylenrør ved 3600 G i 10 min, idet dispergerbarheden måles ved at dispergere 10 % bøhmit eller aluminagel i en opslæmning af vand, der også indeholder 10 % salpetersyre i  
10 forhold til vægten af bøhmit, hvorefter opslæmningen centrifugeres ved 3600 G r/min i 10 min, de indvundne sedimenter tørres ved 100 °C natten over og derefter vejes, og dispergerbarhedsindekset, som betegnes ID (indice de dispersibilité), opnås ved følgende beregning:  $ID(\%) = 100\% -$   
15 vægten af tørrede sedimenter (%), en krystallitstørrelse på mellem 1 og 35 nm, samt et svovlindhold på mellem 0,001 og 2 vægt-% og et natriumindhold på mellem 0,001 og 2 vægt-%, idet vægtprocenterne er udtrykt i forhold til den samlede vægt af aluminagel, hvilken fremgangsmåde omfatter mindst følgende trin:  
20 a) mindst ét første trin til udfældning af alumina i vandigt reaktionsmedium ud fra mindst én basisk precursor valgt blandt natriumaluminat, kaliumaluminat, ammoniak, natriumhydroxid og kaliumhydroxid og mindst én sur precursor valgt blandt aluminiumsulfat, aluminiumchlorid, aluminiumnitrat, svovlsyre,  
25 saltsyre og salpetersyre, hvor mindst én af de basiske eller sure precursorer omfatter aluminium, den relative strømningshastighed for de sure og basiske precursorer er valgt med henblik på at opnå en pH for reaktionsmediet på mellem 8,5 og 10,5, og strømningshastigheden for den eller de sure og  
30 basiske precursorer, som indeholder aluminium, justeres med henblik på at opnå en grad af fremadskriden af det første trin på mellem 45 og 90 %, hvilken grad af fremadskriden er defineret som andelen af alumina, der dannes som Al<sub>2</sub>O<sub>3</sub>-ækvivalent under det første trin til udfældning, i forhold til den samlede mængde  
35 alumina, der er dannet ved afslutningen af udfældningstrinet eller -trinene, idet det første trin til udfældning gennemføres ved en temperatur på mellem 10 og 50 °C og i et tidsrum på mellem 2 minutter og 30 minutter, og et trin til opvarmning af den ved

afslutningen af trin a) til udfældning opnåede opslæmning gennemføres mellem de to trin til udfældning a) og a'), hvilket opvarmningstrin gennemføres ved en temperatur på mellem 20 og 90 °C og i et tidsrum på mellem 7 og 45 minutter,

5 a') et andet trin til udfældning a') af den ved afslutningen af opvarmningstrinet opnåede opslæmning, som gennemføres ved tilsætning til opslæmningen af mindst én basisk precursor valgt blandt natriumaluminat, kaliumaluminat, ammoniak, natriumhydroxid og kaliumhydroxid og mindst én sur precursor  
10 valgt blandt aluminiumsulfat, aluminiumchlorid, aluminiumnitrat, svovlsyre, saltsyre og salpetersyre, hvor mindst én af de basiske eller sure precursorer omfatter aluminium, den relative strømningshastighed for de sure og basiske precursorer er valgt med henblik på at opnå en pH for  
15 reaktionsmediet på mellem 8,5 og 10,5, og strømningshastigheden for den eller de sure og basiske precursorer, som indeholder aluminium, justeres med henblik på at opnå en grad af fremadskriden af det andet trin på mellem 10 og 55 %, hvilken grad af fremadskriden af det andet trin er defineret som andelen  
20 af alumina, der dannes som  $\text{Al}_2\text{O}_3$ -ækvivalent under det andet trin til udfældning a'), i forhold til den samlede mængde alumina, der er dannet ved afslutningen af trin a'), idet det andet trin a') gennemføres ved en temperatur på mellem 40 og 90 °C og i et tidsrum på mellem 2 minutter og 50 minutter, og et andet  
25 trin til opvarmning af den ved afslutningen af det andet trin til udfældning a') opnåede opslæmning ved en temperatur på mellem 50 og 95 °C,

b) et trin til termisk behandling af den ved afslutningen af trin a') opnåede opslæmning ved en temperatur på mellem 50 og  
30 200 °C i et tidsrum på mellem 30 minutter og 5 timer,

c) et trin til filtrering af den ved afslutningen af trin b) til termisk behandling opnåede opslæmning, efterfulgt af mindst ét trin til vask af den opnåede gel.

35 2. Fremgangsmåde til fremstilling ifølge krav 1, hvor den basiske precursor er natriumaluminat.

3. Fremgangsmåde til fremstilling ifølge et af kravene 1 eller

2, hvor den sure precursor er aluminiumsulfat.

4. Fremgangsmåde til fremstilling ifølge et af kravene 2 og 3, hvor vægtforholdet mellem den basiske precursor og den sure precursor er på mellem 1,6 og 2,05.

5. Fremgangsmåde til fremstilling ifølge et af kravene 1-4, hvor trinnet a) til udfældning gennemføres ved en temperatur på mellem 20 og 45 °C.

10

6. Fremgangsmåde til fremstilling ifølge et af kravene 1-5, hvor vægtforholdet mellem den basiske precursor og den sure precursor i det andet trin til udfældning a') er på mellem 1,6 og 2,05, idet den basiske precursor og den sure precursor er henholdsvis natriumaluminat og aluminiumsulfat.

15

7. Fremgangsmåde til fremstilling ifølge et af kravene 1-6, hvor det andet trin til udfældning a') gennemføres ved en temperatur på mellem 45 og 70 °C.