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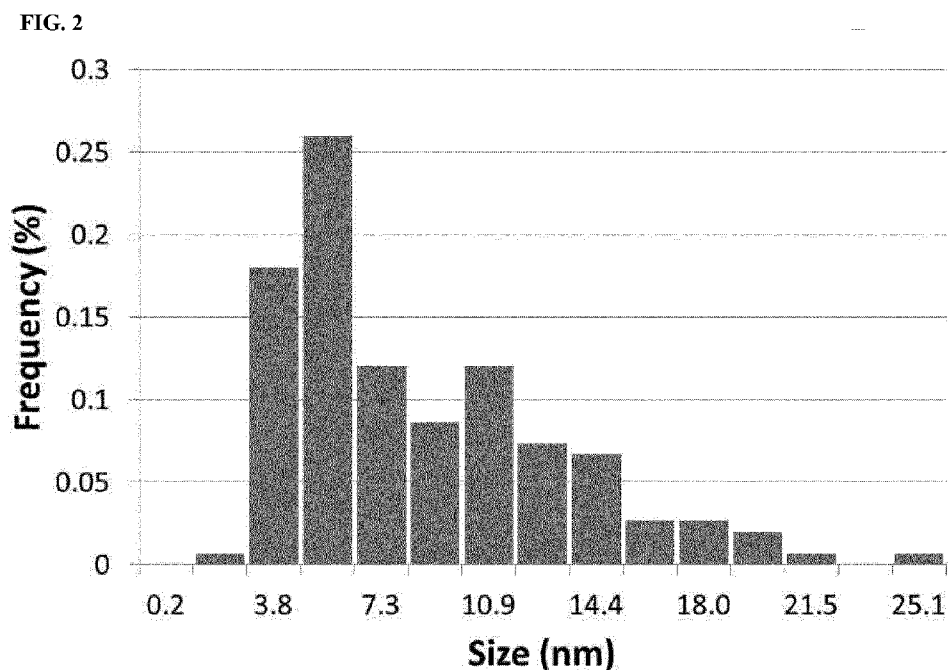
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(54) Title: CATALYST MATERIALS COMPRISING NANOPARTICLES ON A CARRIER AND METHODS FOR THEIR PRODUCTION



(57) Abstract: Subject of the invention is a method for producing a catalyst material, comprising the steps of (a) providing an alloy powder, wherein the alloy consists of 20% to 98% by weight of at least one carrier element selected from Al, Si, Ti, Zr, Y, La, Ce, Pr, Nd and Mg, and 2% to 80% by weight of at least one catalyst metal selected from Pd, Pt, Rh, Co, Ni, Ru, Os, Ir, Fe and Au, and (b) oxidizing the alloy powder in liquid medium, such that an oxide of at least one carrier element is obtained. Subject of the invention is also a catalyst material produced from such carrier elements and catalyst metals, wherein catalyst metal particles are present on the surface of the carrier, wherein the catalyst metal particles have a medium particle size D50 between nm and 50nm.

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**Catalyst materials comprising nanoparticles on a carrier
and methods for their production**

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The invention relates to catalyst materials comprising catalyst metal particles on the surface of a carrier, and methods for their production.

State of the art

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Catalyst materials comprising finely distributed metal particles are used for a broad range of catalytic reactions. Many of these catalyst materials comprise catalytic precious metals, such as platinum or palladium. Typically, the catalytic metals are bound to carrier materials, such as metal oxides. There is a special need for such catalyst materials in
15 exhaust gas purification.

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Such catalyst materials should combine various properties to have adequate catalytic efficiency. Typically, the catalyst metals are provided in fine particulate form in order to increase the surface area and thus catalytic performance. It is desirable to provide such
20 catalyst metals in the form of nanoparticles, especially with diameters below 50 nm. Further, such fine catalyst metal particles have to be combined with appropriate carrier materials. This is important for an efficient and optimal performance of the metal catalysts, especially when precious metals are comprised. It is also desirable that the catalyst metal particles have a highly homogenous structure and size, which can also improve catalytic
25 performance and efficiency. Specifically, it is advantageous that the catalyst metal particles have a narrow particle size distribution and narrow composition range. Besides, it is desirable to provide such catalyst metal particles in a highly pure and crystalline state, which may also increase catalytic performance and efficiency. It is also desirable to provide simple and efficient methods for producing such catalyst materials. Further, there
30 is a strong need for such catalyst materials, which comprise catalytic alloys of two or more different metals.

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Many attempts have been described in the prior art to provide catalytic materials consisting of fine catalytic metal particles on carrier materials.

EP 0 645 464 A2 discloses methods for producing quasi-crystalline aluminum alloy particles comprising precious metals, such as palladium. The production process is carried out in a gas phase plasma reaction. Such plasma reactions are relatively complicated and difficult to control. They require plasma devices and relatively consume high amounts of energy. The particles have sizes up to 200 nm and are thus relatively large. In order to dilute the metal catalysts and thus use them more efficiently, it would be desirable to combine such catalytic metals with an inert carrier. Thus, the methods and materials disclosed in this document could still be improved.

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US 5,090,997 discloses a method for producing powdered aluminum alloys. A melt of aluminum and a further catalytic metal, such as nickel or iron, is atomized, such that a metal powder is obtained. The alloy powder may be treated with alkali, such as sodium hydroxide, to obtain catalysts which are suitable for hydrogenation. The particle size of the aluminum/metal alloys in the range of 50 μm to 400 μm is very large. In the reaction with concentrated sodium hydroxide, formation of metal hydroxides can be expected, which have limited catalytic properties. Thus, the methods and materials disclosed in this document could still be improved.

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US 8,669,202 B2 discloses methods for providing a catalyst material comprising an interior region comprising a mixed metal oxide and an exterior surface comprising a pure metal. The materials are prepared either by a plasma gun method or by a wet chemistry process, in which a precursor composition is precipitated from solution and calcined. The plasma process requires a plasma device and is energy-consuming. The precipitation process is relatively complicated, because it requires various precursor compounds, which can lead to contaminations. The document does not disclose a specific working example or experimental data regarding the product structure or properties. Thus, it remains unclear whether the process is practically applicable and whether the products would have advantageous properties.

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Wong et al. ("The catalytic behavior of precisely synthesized Pt-Pd bimetallic catalysts for use as diesel oxidation catalysts", 2016, Catalysis Today, 267, pages 145 to 156) discloses methods for producing catalytic materials comprising platinum and palladium coated on alumina and silica supports. The method is based on wet precipitation from

precursor materials and calcination. Various catalyst materials are described, which comprise catalytic nanoparticles in the range of 5 to 44 nm diameter. The precipitation process is relatively complicated and can lead to impurities from the precursor compounds. The uniformity of the catalyst materials and catalytic performance could still be improved.

US 2016/0288103 A1 discloses a method for producing amorphous metal alloy powders. The process comprises melting the metal components, cooling to obtain an alloy and pulverizing. It is suggested to carry out a subsequent oxidation in an oxygen atmosphere at a temperature ranging from 300°C to 600°C, such that an amorphous metal alloy powder having catalytic performance would be obtained. However, the particle size of the powders is in the range of 0.1 µm and 10 µm and thus relatively high. Further, the catalytic performance of amorphous metals can be relatively low. Thus, the methods and products could still be improved.

EP 1 712 645 A1 discloses methods for producing oxide-dispersed alloys. In such alloys, a low amount of particles of a first metal is dispersed in a matrix of a second metal. An oxidation step is performed with an intermediate powder in the presence of water as an oxidizing agent. Subsequently, the powder is molded and solidified at high temperature to obtain a uniform alloy, which has a high mechanical strength. For example, an alloy is produced comprising 0.3% zirconia particles dispersed in a Pt matrix. Such alloys are not applicable as catalysts, because the particles in the interior are not accessible to a substrate.

Overall, there is strong need for improved catalyst materials comprising fine catalytic metal particles associated with carrier oxides. Specifically, it would be desirable to provide the catalytic metals in uniform structure and distribution, and preferably in crystalline form.

Moreover, it would be desirable to provide such catalytic metal particles comprising not only a single metal, but alloys of two or more metals bound to such carriers. The prior art in the technical field provides evidence that it is already difficult to provide an appropriate catalyst material which comprises a single metal distributed in fine and homogenous form on a carrier. Therefore, it would be even more ambitious to provide such materials comprising fine and homogenous alloys of catalytic metals.

Problem underlying the invention

5 The problem underlying the invention is to provide methods and catalyst materials, which overcome the above-mentioned drawbacks.

Thus, the problem is to provide simple and efficient methods for producing such catalyst materials comprising fine catalyst metal particles bound to a carrier. The methods should be energy-efficient and should not require complicated devices, such as plasma devices. 10 Preferably, they should not require precursor chemicals, such as salts and additives which are required for wet chemistry and precipitation, which could lead to impurities. The starting materials should be simple and easily accessible.

It is a further problem underlying the invention to provide catalyst metal particles having improved catalytic properties. Therefore, catalyst materials shall be provided in which the catalytic metal has a fine and uniform structure. Especially, the catalytic metal particles shall have a narrow size distribution. Preferably, the catalytic metal should be pure and highly crystalline. 15

It is a specific problem underlying the invention to provide such methods and catalyst materials, which comprise catalytic alloys of two or more metals on a carrier. The alloy particles should be fine, have a uniform structure and a high crystallinity. 20

The catalyst materials shall have advantageous properties in various catalytic reactions, especially oxidation reactions. Especially, they shall be efficient in exhaust gas purification. 25

Disclosure of the invention

Surprisingly, it was found that the problem underlying the invention is overcome by methods and catalyst materials according to the claims. Further embodiments of the invention are outlined throughout the description.

Subject of the invention is a method comprising the steps of

- (a) providing an alloy powder, wherein the alloy consists of
20% to 98% by weight of at least one carrier element selected from Al, Si, Ti, Zr, Y, La, Ce, Pr, Nd and Mg, and
2% to 80% by weight of at least one catalyst metal selected from Pd, Pt, Rh, Co, Ni, Ru, Os, Ir, Fe and Au,
- (b) oxidizing the alloy powder in liquid medium, such that at least one carrier element is oxidized,
- (c) obtaining a catalyst material.

The method is for producing a catalyst material. As used herein, a catalyst material is a composition which is capable of catalyzing a chemical reaction.

In step (a), an alloy in particulate form is provided. The alloy is a precursor material for producing the catalyst material. The alloy consists of metals and/or metalloids as defined above.

The alloy comprises at least one carrier element. Preferably, the alloy comprises one, two or three carrier elements, more preferably one or two carrier elements. As used herein, the term "carrier element" indicates that in the product (the catalyst material) the element functions as a carrier for the at least one catalyst metal. Preferably, in the catalyst material the catalyst metal is present on the surface of the carrier element. In addition, or alternatively, the catalyst metal can be distributed within the carrier element, such that the carrier element forms a matrix. The carrier element may be inert in the catalytic reaction mediated by the at least one catalyst metal. Alternatively, it may participate in the catalyst reaction directly or indirectly, for example by binding or storing compounds, such as the substrate or intermediates.

The alloy comprises at least one catalyst metal. The catalyst metals function as catalysts in the catalytic reaction mediated by the catalyst material. Preferably, the alloy comprises one, two or three catalyst metals, more preferably one or two catalyst metals.

5 The total amount of all carrier elements in the alloy powder is 20% to 98% by weight, preferably 30% to 90% by weight. The total amount of catalyst metal in the alloy powder is 2% to 80% by weight, preferably 10% to 70% by weight. When adjusting the components in such amounts, a catalyst material is obtainable, in which the catalyst metal is supported by the carrier and is accessible for the catalytic substrate.

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For many catalyst applications, it can be advantageous that the amount of precious metals in the catalyst material is relatively low. Thus, especially if precious metals are included, such as Pt or Pd, it is preferred that the total amount of all catalyst metals in the alloy is between 2% to 20% by weight, or even between 2% and 10% by weight, the remainder being carrier elements. From such alloys, catalyst materials are obtainable which comprise relatively low levels of precious metal supported by relatively high amounts of carrier, wherein 100% is the total sum of carrier elements and catalyst metals in the material, excluding oxygen.

20 In subsequent step (b), the alloy powder is subjected to an oxidation in liquid medium, such that at least one carrier element is oxidized. Preferably, it is at least the carrier element which is most abundant (by weight) in the carrier which is oxidized. The oxidation can be carried out at a relatively low temperature, for example below 200°C, in a mild oxidizing agent, such as water. Thus, the conditions of the oxidation step are relatively mild. It was found that such a mild oxidation step can provide novel and advantageous catalyst materials, which comprise fine and uniform catalytic metal particles on the surface of an oxide carrier. Thus, the method is distinct from methods of the art, in which a precursor material is oxidized under harsh conditions, for example by calcining in the presence of oxygen. Step (b) is carried out in a dispersion of the alloy powder in the liquid.

25

30 Preferably, the liquid is water and/or an organic liquid, such as an alcohol, or a mixture thereof. Preferably, the liquid medium is aqueous medium. Preferably, the liquid medium is the oxidizing agent.

The at least one carrier element in the alloy is oxidized at least partially in step (b). Preferably, in oxidation step (b) the oxidized carrier element is obtained at least in part in the form of an oxide and/or hydroxide. Preferably, this oxidized carrier element is completely converted into an oxide in a subsequent calcination step.

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In addition, one or all of the catalyst metals in the alloy may be oxidized at least partially in step (b). In one embodiment, all carrier elements of the alloy are oxidized at least partially, whereas the catalyst metals are not oxidized. In another embodiment, all carrier elements and at least one of the catalyst elements or all catalyst elements are oxidized at least partially. In step (b), mixed oxidation products can be formed. Preferably, the at least on
10 carrier element oxidized in step (b) has a uniform oxidative state. In another embodiment, the carrier element may be obtained in more than one oxidation state.

The oxidation of the carrier elements in step (b) can be incomplete. For example, it is
15 possible that after oxidation step (b), at least 50% by weight, at least 80% by weight, or at least 90% by weight of the carrier elements are oxidized, whereas the remaining part is not oxidized. If desired, the oxidation can be completed in a subsequent step, such as a calcining step or a further oxidation step during or after milling.

20 The alloy provided in step (a) can have any metallurgical structure. However, it is highly preferred that it is or that it comprises an intermetallic compound. Preferably, the alloy in step (a) comprises at least 5%, at least 10% or at least 20% by weight of the intermetallic compound. In one preferred embodiment, it comprises between 50% to 100%, or between 50% to 80% intermetallic compounds, most preferably in brittle form. This is
25 advantageous especially when precious catalyst metals are used, because catalytic materials can be obtained comprising relatively low amounts of catalyst metal and a relatively high amount of carrier elements.

An intermetallic compound is an alloy that forms a solid-state compound having defined
30 stoichiometry and ordered crystal structure. Specifically, the intermetallic is an alloy according to the definition of Schulze, 1967 (Schulze, Metallphysik, Akademie-Verlag, Berlin, 1967), which includes electron (or Hume-Rothery) compounds, size packing phases (such as Laves phases, Frank-Kasper phases and Nowotny phases) and Zintl phases. The intermetallic compounds can be formed from metals and metalloids. Methods

for producing intermetallics or alloys comprising intermetallic phases are known in the art, for example from US 3,147,111, US 3,826,886 or US 7,374,717 B2. Aluminum alloys which comprise precious metals typically form intermetallics.

5 According to the invention, it is preferred that the alloy which is used as a substrate for the oxidizing step (b) comprises a single intermetallic compound. According to the invention, it was found that especially such an alloy can yield a highly uniform catalyst material, which has a low particle size and a narrow compositional distribution. In contrast, it was found that an alloy which comprises two or more different intermetallics can yield less uniform
10 catalyst materials.

In a preferred embodiment, the alloy powder in step (a) has an average particle size of less than 50 μm , more preferably less than 25 μm . Preferably, the average particle size is in the range from 1 μm to 50 μm , more preferably from 5 μm to 25 μm . According to the
15 invention, it was found that such particle sizes are advantageous for an efficient oxidation in step (b). The average particle size can best be determined according to DIN ISO 13320 "Particle size analysis - laser diffraction methods" (latest version at the filing day).

Before step (a), the method of the invention may comprise a preceding step (a0), in which
20 the alloy powder is prepared from an alloy precursor. Preferably, the preceding step comprises:

(a0) providing the at least one carrier element and the at least one catalyst metal, combining and heating the elements to obtain a melt, solidifying the melt to obtain a solid alloy, and optionally pulverizing the solid alloy.

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Solidifying the melt to obtain the solid alloy can be carried out by cooling such that an ingot is obtained, followed by pulverizing to obtain the alloy powder. In another embodiment, the melt can be solidified by atomization, such that an alloy powder is obtained as the product of the atomizing step. In this embodiment, a melt of the alloy
30 components is sprayed by an atomizer to obtain the alloy powder. In a further embodiment, the melt can be solidified by melt spinning, such that ribbons or strips of the alloy are obtained, which are pulverized to obtain the alloy powder. In another embodiment, an ingot is formed into a shape having a high surface/volume ratio, such as a wire or thin plate, followed by chipping.

In general, the melt can be obtained by combining and heating the alloy components. The amounts and ratios of the starting materials are selected such that a desired alloy and catalyst material can be obtained. The alloy can be produced according to known methods and conditions, such that undesired oxidation or side reactions are suppressed. If necessary, this can be achieved by known measures, such as a protective atmosphere, sequential mixing of the constituents, temperature control or the like.

Pulverizing of the alloy ingots, fibers, strips or other precursors is carried out by known means, for example optionally crushing the ingot into rough particles and milling, for example ball milling; or chipping.

The oxidation in step (b) is carried out in the presence of an oxidizing agent. At least one carrier element and optionally also at least one catalyst metal of the alloy powder reacts with the oxidizing agent. The alloy can be oxidized partially or completely.

Preferably, the oxidizing agent is selected from water, alcohols, hydrogen peroxide and oxygen, or mixtures thereof. In such methods, the oxidation can be mediated by more than one of the oxidizing agents. Such oxidizing agents are preferred because they are relatively mild, such that harsh oxidation conditions can be avoided. Further, they do not lead to undesired impurities which could impair catalyst performance.

Preferably, the alcohol is an aliphatic alcohol. More preferably, the aliphatic alcohol comprises from 1 to 5 carbon atoms. Preferably, it is methanol or ethanol. When oxygen is used as the oxidizing agent, it is preferred that the reaction is carried out in aqueous medium. For example, oxygen or air can be bubbled through the water.

In a highly preferred embodiment, the oxidizing agent is water. Preferably, the oxidation in step (b) is carried out in water as the oxidizing agent, which is at the same time the liquid medium. In this reaction, at least the carrier elements in the alloy are oxidized, whereas water is reduced to hydrogen. Preferably, the water is demineralized water. The use of water is highly advantageous, because it is a mild oxidizing agent, which is cheap, freely available, non-toxic, easy to handle and does not yield undesired side products. In the reaction with water, an oxide of the carrier element is formed, whilst water is reduced to

hydrogen. The progression of the reaction can be controlled precisely by monitoring hydrogen formation. If desired, the hydrogen can be stored and/or used in the reaction and/or for other purposes, such that the overall energy balance of the process is favorable.

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It was unexpected that the reaction would yield an advantageous catalyst material under such mild conditions, and especially with water as the oxidizing agent. In the prior art, it was known that reactive metals, such as aluminum, can be oxidized under mild conditions and in the presence of water. However, in the inventive process, an alloy precursor, which
10 comprises such reactive metals, is oxidized under mild conditions in the presence of additional catalyst metals. Surprisingly, a catalyst material is provided which comprises oxides of the carrier elements; and fine, uniform and crystalline catalyst metal particles in metallic or oxide form associated therewith. Thus, the carrier elements form a carrier, on
15 which distinct catalytic particles are distributed on the surface. Thereby, the catalyst metal particles may be obtained in metallic form or oxidized form. Overall, it was unexpected that an effective catalyst material could be obtained with such a single mild oxidation step from a single alloy precursor.

It is advantageous that oxidation step (b) can be carried out at relatively low temperature.
20 This is possible because the alloy powder particles are in intimate contact with the liquid medium. In a preferred embodiment, in step (b) the oxidation is carried out at a temperature at a temperature below 200°C. Preferably, the temperature is at least 0°C, at least 50°C or at least 80°C. Preferably, the temperature is less than 150°C or less than 120°C. Preferably, the temperature is between 0°C and 200°C. More preferably, the
25 temperature is between 0°C and 120°C, especially when the reaction is carried out in water. Even more preferably, the temperature is between 80°C and 120°C, more preferably between 90°C and 110°C, even more preferably about 100°C, especially when carried out in water. In a highly preferred embodiment, in step (b) the oxidation is carried out in boiling water.

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In another embodiment, the oxidation is carried out in an autoclave. In this embodiment, the reaction is carried out at enhanced pressure, for example at a temperature between 120°C and 250°C.

Preferably, the oxidation is carried out under normal pressure. This is advantageous, because the reaction can be controlled easily. When carrying out oxidizing step (b) in boiling water or at temperatures below 120°C, and/or under ambient pressure, the energy consumption is relatively low, and the control of the reaction is relatively simple.

5

In a preferred embodiment, the liquid is the oxidizing agent and no additional oxidizing agent is added and/or present or used in the overall process and/or in step (b). It is preferred that water is the only oxidizing agent. This is highly advantageous, because no other reactants are required which may lead to side products, which may have to be removed or which may have a detrimental effect on the catalytic efficiency of the product. Especially, it is advantageous that no salts or organic reaction products are formed. Therefore, it is preferred that step (b) is carried out in a reaction mixture which consists of the alloy powder and water.

15 In a preferred embodiment, an oxide of at least one of the at least carrier element is added to the alloy powder before step (b). Preferably, the oxide is alumina. Surprisingly, it was found that oxides of the carrier element can support the oxidation. In this embodiment, it is advantageous that the additive is identical to the final product, i.e. the oxide of the carrier element. Therefore, no undesired side products are obtained.

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In another embodiment, oxidation step (b) may be carried out in the presence of additives, which are not oxidizing agents. For example, a salt can be added, such as NaCl. Further, a mixture of water with another oxidizing agent can be used, such as an alcohol, hydrogen peroxide or oxygen, which can modify and/or enhance the oxidation reaction. Preferably, at least 10%, at least 50% or at least 80% of the oxidation (based on transferred O-atoms) uses water as the oxidation agent.

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Preferably, the oxidation is not carried out in an alkaline solution. Preferably, the pH of the liquid medium is less than 10, more preferably less than 8, and preferably in the range of 4 to 10, or between 5 to 9, before the alloy powder is added.

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Preferably, for obtaining the catalyst material in step (c) residual liquid medium is removed after oxidation step (b). Preferably, the product is dried. This can be achieved by heating and/or by other drying means.

In a preferred embodiment, the method comprises in step (c):

- calcining the oxidized product obtained in step (b).

5 During calcining, the oxidized product is subjected to a high temperature for a prolonged time period, typically in the range of hours. Typically, water is removed from the product of step (b) during calcining. Further, the oxidized carrier element of the intermediate product from step (b) is converted into the oxide form. For example, a metal hydroxide carrier from step (b) is converted into the metal oxide in the calcination step.

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In a preferred embodiment, the calcining in step (c) is carried out at a temperature between 400°C and 800°C, more preferably between 500°C and 650°C. Preferably, the calcining is carried out for 20 minutes to 24 hours, more preferably for 30 minutes to 10 hours, or for 30 minutes to 5 hours. Preferably, the calcining is carried out until the at least one oxidized carrier element, typically the most abundant carrier element (by weight), is present in oxide form. Calcining may be carried out in the presence of air and/or oxygen. Temperature and gaseous environment are adjusted and controlled during calcining such that the desired structure of the product is maintained or obtained.

20 In a preferred embodiment, the method comprises a subsequent step of:

- (d) reducing the particle size of the oxidized product obtained in step (b) and/or of the calcined product obtained in step (c).

25 Step (d) can be carried out after step (b) and/or step (c). It can be advantageous to reduce the particle size of the catalyst material in order to enhance the catalytic performance. A further size reduction in step (d) can further improve the catalyst performance. Specifically, the particle size can be reduced with the oxidized product obtained in step (b), or after calcination in step (c), or after both steps. It is also conceivable to reduce the particle size during oxidation step (b).

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The particle size can be reduced by known means, especially by milling, for example by bead milling. In a preferred embodiment, the particle size reduction is carried out during and/or after oxidation in step (b). The oxidation step (b) can be carried out simultaneously with particle size reduction, for example in a bead mill. This can be advantageous,

because the oxidation can proceed and/or can be completed during particle size reduction. For example, when introducing the direct reaction product of step (b) into a mill, particle size reaction concurs with oxidation of residual non-oxidized carrier element. Accordingly, the oxidation reaction can be finalized or accelerated by the milling process.

5 In principle, the oxidation can be terminated when not further hydrogen is formed.

Alternatively, and/or in addition, reduction of the particle size can be carried out after calcining step (c). In another embodiment, the reaction product of the oxidation (b) can be subjected to a particle size reduction step, followed by a calcining step (c), followed by a
10 second particle size reduction step. If desired, the particle size reduction step or calcining step can be repeated, such that the overall method comprises two or more calcining steps (c) and/or two or more particle size reduction steps (d).

In another preferred embodiment, the method does not comprise a calcining step as step
15 (c). This may not be required, because in some conventional catalytic applications the catalyst is applied to a solid substrate and subjected to a firing step. For exhaust gas purification, a washcoat comprising the catalyst material is typically applied to an inert substrate, such as a monolithic support, followed by a firing treatment at high temperature. Such a firing step can also provide the effects of the calcining step described above.

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By the method of the invention, a catalyst material is obtainable, which is described in more detail in the following.

Subject of the invention is also a catalyst material made according to the invention,
25 comprising

a carrier, which comprises at least one carrier element in oxidized form selected from Al, Si, Ti, Zr, Y, La, Ce, Pr, Nd and Mg, and

catalyst metal particles, which comprise at least one catalyst metal selected from Pd, Pt, Rh, Co, Ni, Ru, Os, Ir, Fe and Au, wherein the catalyst metal is present in metallic
30 or oxide form,

wherein catalyst metal particles are present on the surface of the carrier,

wherein the catalyst metal particles have a medium particle size D50 between 1 nm and 50 nm.

In the inventive catalyst material, the catalyst metal particles are present on the surface of the carrier. As used herein, the term "catalyst metal particles" refers to particles comprising the catalyst metals in metallic or oxide form, or both. Surprisingly, it was found that when subjecting the alloy powder of the precursor elements to an oxidation step (b) under mild conditions, especially with water as an oxidizing agent, the carrier elements can be oxidized, whereas catalyst metal particles in metallic or oxide form thereof are formed having a very small particle size in the low nanometer range, which are distributed on the surface of the carrier. This does not preclude that catalyst metal particles are also present within the carrier, i.e. embedded in the carrier particles. However, it was found that the majority of catalyst metal particles can be present on the surface of the carrier. This is advantageous in catalytic reactions, because the catalyst is easily accessible for the catalytic substrate. Moreover, the particle size in the low nanometer range is advantageous in the catalytic process, because the catalyst has a very high surface area, and thus a high catalytic efficiency. In view of the very low size of the catalyst metal particles, and their distribution on the surface of the carrier particles, the overall efficiency of the catalyst material can be very high.

Preferably, the total amount of the carrier elements in the catalyst material is 20% to 98% by weight, more preferably 50% to 90% by weight and/or preferably the total amount of the catalyst metals is 10% to 70% by weight, more preferably 2% to 50% by weight; wherein 100% is the total sum of carrier elements and catalyst metals in the material, excluding oxygen.

For many catalyst applications, it can be advantageous that the amount of precious metals in the catalyst material is relatively low. Thus, especially if precious metals are included, such as Pt or Pd, it is preferred that the total amount of all catalyst metals in the catalytic material is between 2% to 20% by weight, or even between 2% and 10% by weight, wherein 100% is the total sum of carrier elements and catalyst metals in the material, excluding oxygen.

Preferably, at least 50%, more preferably at least 80% or at least 90% of the catalyst metal particles (by number) are present on the surface of the carrier. When the catalyst material has such a structure, a high catalytic performance can be achieved.

The catalyst metal particles may comprise a relatively low amount of the carrier element or an oxide of the carrier element. Preferably, the catalyst metal particles comprise more than 80% by weight, preferably more than 90% by weight or more than 95% by weight of the catalyst metals, wherein 100% is the sum of carrier elements and catalyst metals in the particles, excluding oxygen. More preferably, they comprise more than 98% or more than 99% by weight of the catalyst metals, or substantially consist of the catalyst metals.

Preferably, the carrier consists of the carrier elements, wherein at least one carrier element is in oxidized form, preferably in oxide form. However, the carrier may encapsulate residual amounts of the catalyst metals used in the inventive method. It is preferred that the amount of catalyst metal in the carrier is relatively low such that more than 80%, preferably more than 90% or more than 95% by weight of the total catalyst metal is present in the catalyst metal particles of the catalyst material. Preferably, less than 20%, more preferably less than 10% or less than 5% by weight of the catalyst metals is present in the carrier, wherein 100% is the sum of carrier elements and catalyst metals in the carrier, excluding oxygen.

In the catalyst material, the carrier comprises at least one carrier element in oxidized form, preferably in the form of an oxide. It is preferred that the carrier element which is most abundant is present in oxidized form. This most abundant carrier element (by weight) may form a matrix, in which the other carrier elements are enclosed. It is preferred that this most abundant carrier element is aluminum. Other carrier elements can be present in the carrier in relatively small amounts to modify the properties. This is also referred to as doping of the carrier oxide. For example, it is known in the art that lanthanum can support the desired formation of γ -alumina, whereas Si can be added to adjust the isoelectric point of alumina. In one embodiment, the carrier consists of carrier oxides.

The catalyst metal particles comprise the catalyst metals, which can be present in metallic or oxide form. In one embodiment, the catalyst metals are in metallic form. In another embodiment, the catalyst metals are in oxide form. Depending on the process conditions, some catalyst metals, such as Pt, may be obtained in metallic form, whereas others, such as Pd or Rh, may be obtained in oxide form. Whether the catalyst metal is metallic, or an oxide depends from the conditions of the production method, especially the final step, for example from the atmosphere and temperature in a calcining step (c). Further, it depends

on the oxidation potential of a catalyst metal if it will be obtained in metallic or oxide form in the inventive process. Typically, precious metals will be obtained in the metallic form more easily than other non-precious metals which have a higher tendency towards oxidation. However, for many applications of such catalyst materials, it is not relevant if
5 the catalyst metals are present in metallic or oxide form. The reason is that in many catalyst applications the catalyst metals switch between the metallic and oxide form, depending on the environment and catalytic reaction.

The inventive catalyst materials are applicable in various catalytic applications. The
10 catalyst metal may change its oxidation state during the catalytic application. The catalyst metal particles may comprise some or all catalyst metal in oxide form, which is reduced to the metallic form or vice versa under catalytic conditions.

In a preferred embodiment, the catalyst material consists of the carrier oxides and the
15 catalyst metals (in metallic or oxide form). In a preferred embodiment, the catalyst material consists of more than 98%, preferably more than 99.5% or more than 99.8% by weight of the carrier elements and the catalyst metals, the remainder being inevitable impurities. This means that the catalyst material is highly pure. Such a highly pure catalyst material is obtainable by the inventive method by oxidation with water, which does not yield
20 undesired impurities. However, the catalyst material may comprise inevitable impurities, such as traces of other metals from the educts and production process. If the oxidation is carried out in the presence of additives, the catalyst material may comprise residual additives or impurities resulting from the additives. In such embodiments, it is preferred that such impurities are removed or at least reduced in a subsequent step, especially
25 during calcining step (c) or a final firing step.

In a preferred embodiment, the catalyst metal particles are crystalline. It was not only found that the catalyst metal particles can be very fine and distributed on the surface of the carrier, but also that they can be obtained in crystalline form. This can be
30 advantageous because crystals have a highly ordered structure and can have a high catalytic performance. The crystalline catalyst metal particles comprise no or substantially no non-crystalline fractions. This means that less than 5% by weight, more preferably less than 2% or less than 1% by weight of the catalyst metal particles are non-crystalline, i.e. amorphous.

The catalyst metal particles have a medium particle size D50 in the range of 1 nm to 50 nm. Preferably, all catalyst metal particles, or at least more than 98%, have a particle size in the range of 1 nm to 50 nm. The medium particle size can best be determined by
5 TEM (transmission electron microscopy) analysis, for example as described in ISO/DIS 21363 (latest version at the filing day). More preferably, the medium particle size is between 2 nm and 30 nm, or between 3 and 20 nm. Such particle sizes are very small and highly advantageous for catalysis of chemical reactions, because the surface area of the catalyst is very high.

10

According to the invention, it was found that the catalytic metal particles are not only very small, but also have a uniform size and composition. In a preferred embodiment, the particle size distribution (D90 – D10) / D50 of the catalyst metal particles is below 4, more preferable below 3, even more preferably below 2. Preferably, all catalyst metal particles
15 in a given catalyst materials have diameters in the range of 1 nm to 100 nm, more preferably in the range of 2 nm to 50 nm, most preferably between 3 nm and 40 nm. The narrow particle size distribution and compositional range is indicative of the uniformity of the catalyst metal particles. This is advantageous, because accessibility of the catalyst to the substrate and thus stability and efficiency of the catalytic reaction is generally
20 improved in a homogenous catalyst material.

In a preferred embodiment, the standard deviation (STD) of the particle size of the catalyst metal particles is below 6 nm, preferably below 5 nm or even below 3 nm. Preferably, the ratio of standard deviation to average compositional range of the catalyst metal particles is
25 below 0.3, preferably below 0.2, more preferably below 0.1. Such materials have a highly uniform particle size distribution and compositional range.

In a preferred embodiment, the catalyst metal particles comprise at least two of the catalyst metals. When the two metals are present in metallic form, the at least two catalyst
30 metals preferably form an alloy. According to the invention, it was surprisingly found that the inventive method can provide very small and uniform catalyst materials comprising two or more catalyst metals. The catalyst metals can be provided as alloys in uniform fine nanoparticles. It was unexpected that such finely distributed catalyst metal alloys are formed during oxidation of the carrier elements from a single alloy powder, in which all

precursor elements are combined. Catalyst materials which comprise two or more catalyst metals are highly advantageous in many catalytic reactions, for example in exhaust gas purification from engines.

5 In a preferred embodiment, the carrier comprises aluminium oxide and at least one further carrier element, preferably one or two more carrier elements. In a preferred embodiment, the carrier comprises aluminium oxide and/or silicon oxide, and optionally lanthanum oxide. Preferably, the carrier comprises at least 60%, more preferably at least 80% or at least 90% by weight aluminium. In a preferred embodiment, the ratio of aluminium to the
10 other carrier element(s), especially silicon, in the carrier is between 2:1 and 20:1, preferably between 5:1 and 15:1. It was found that the method is highly efficient and that an advantageous catalyst material can be obtained when aluminum is the main component of the carrier.

15 Preferably, all catalyst metals in the method and catalyst material are selected from Pd, Pt, Rh, Co, Ni, Ru, Os, Ir, Fe and Au. In a preferred embodiment, the at least one catalyst metal is selected from Pd, Pt, Rh, Co, Ni, Ir, Fe and Au. Os and Ru are less preferred, since they tend to form toxic and volatile oxides. More preferably, the catalyst metal particles comprise or consist of platinum group metals, especially Pd, Pt, Rh and Ir, in
20 metallic or oxide form. Preferably, the catalyst metals comprise two or more, preferably two or three, especially two catalyst metals which are platinum group metals. In a preferred embodiment, the catalyst metal particles comprise Pd and/or Pt, in metallic or oxide form. Preferably, the catalyst metal particles comprise Pt and/or Pd in combination with Rh, in metallic or oxide form.

25 In a preferred embodiment, the carrier elements are Al, Si and/or La whereas the catalyst metals are Pd and/or Pt, and optionally at least one further metal selected from Rh and Ir. It was found that the method is applicable for providing highly uniform and fine particles of these catalyst metal bound to carrier oxides. Catalyst metal particles from platinum group
30 metals are advantageous for the purification of exhaust gas from engines.

Exemplified embodiments of the invention and aspects of the invention are shown in the figures.

Figure 1 shows a TEM picture of the product of example 2 (a: high-angle annular dark-field imaging (HAADF); b: Pd and Al, c: O).

Figure 2 shows a histogram of the particle size distribution of the Pd particles of example 3 (150 particles were measured). The D50 value is 7.7 nm.

5 Figure 3 shows a TEM picture of the product of example 4 (top left: high-angle annular dark-field imaging (HAADF), top right: Pt, middle left: Rh, middle right: Al, bottom left: O, bottom right: Si).

Figure 4 shows a TEM picture of the product of example 7 (top left: high-angle annular dark-field imaging (HAADF), top center: Pt; top right: Rh; bottom left: Al; bottom middle: O; 10 bottom right: Si).

Figure 5 shows two XRD graphs of melt-spun ribbons obtained according to examples 8/9 (upper graph: from top side of ribbon; lower graph: from bottom side of ribbon).

Figure 6 shows an XRD graphs of the oxidized product of example 1.

Figure 7 shows an XRD graphs of the calcined product of example 2.

15 Figure 8 shows an XRD graphs of the calcined product of example 4 without Rh reference peaks.

Figure 9 shows an XRD graphs of the calcined product of example 4 with Rh reference peaks.

ExamplesExamples 1 and 2: AlPd

2 kg of an alloy Al – 55 wt% Pd was prepared in an alumina crucible. An Al melt was prepared at 700°C. Ar was blown above the melt to prevent oxidation. Pd was added gradually, to prevent excessive temperature rise due to the external reaction between Al and Pd. Gradually, the T was raised to 850°C, where all material was molten. After solidification, the ingot was crushed and further milled in a planetary mill to <25 µm. To obtain the desired Pd concentration, the product was blended with alumina at a ratio of 1 part alloy / 4.1 parts Al₂O₃. The blend was oxidized in boiling demineralized water during 72 hours. Approximately, the reaction can be described as: $2 \text{ Al} + 3 \text{ H}_2\text{O} \Rightarrow 2 \text{ Al}_2\text{O}_3 + 3 \text{ H}_2$. Most of the Al was oxidized then, but not quantitatively. The resulting dispersion was bead milled during 3 hours in a Dispermat SL-12 bead mill (VMA-GETZMANN, DE) with 3 mm YZT beads. Total milling energy was 8390 Wh/kg. During milling, further oxidation occurred, which was visible because of H₂ formation. Malvern particle size distribution yielded a D50 of 176 nm.

An XRD analysis was carried out with the oxidized product. The result is shown in FIG. 6 and demonstrates that the product is crystalline. The diffractogram indicates the presence of AlO(OH), Pd and Al₂O₃.

Compound Name	Chemical Formula	Crystal System	Space Group
Aluminium Oxide Hydroxide	Al O (OH)	Orthorhombic	Cmcm
Palladium	Pd	Cubic	Fm-3m
Aluminium Oxide	Al ₂ O ₃	Cubic	Fd-3m

The product was dried and calcined for 1 h at 550°C in air. The product obtained was split in 2. Half of the sample was maintained as a final product was (Example 1), the other half was bead milled again under the same conditions as outlined above. No further hydrogen evolution was observed. After drying and subsequent calcination, the sample was maintained as a final product (Example 2).

Both samples were analyzed by TEM. They consisted of PdO particles on alumina. The average size of the PdO particles was 9.8 and 8.3 nm for Example 1 and 2, respectively.

(average of ± 150 particles). FIG. 1 shows the presence of Pd nanoparticles (partly agglomerated) on an Al_2O_3 matrix (Example 2).

An XRD analysis was carried out with the calcined product. The result is shown in FIG. 7 and demonstrates that the product is crystalline. The diffractogram indicates the presence of PdO and Al_2O_3 .

Compound Name	Chemical Formula	Crystal System	Space Group
Palladium Oxide	Pd O	Tetragonal	P42/mmc
Aluminium Oxide	$\text{Al}_2.667 \text{ O}_4$	Cubic	Fd-3m

10 Example 3: AlLaPd

900g Al was melted in a ZrO_2 crucible. Ar was blown above the melt. To this melt, 58 g La was added, and subsequently 1100 g Pd. The Pd was added gradually, because of the strong exothermic reaction. In the beginning, the temperature of the melt was 700°C . When the melt consisted of 25% Pd relative to Al, the T was gradually increased to 950°C . After solidification, the ingot was crushed and milled in a ring mill. The product then was treated in the same way as described above for AlPd: milling in a planetary mill to $<25 \mu\text{m}$, blending with alumina to obtain the right Pd content, oxidation in boiling water, bead milling. The product was dried and calcined 1 h at 550°C in air. After calcination, the product was bead milled again as described above. No further hydrogen evolution was seen. After drying and again calcination, the product was maintained (Example 3). FIG. 2 shows a TEM histogram of the particle size distribution of the Pd particles (150 particles were measured). The D50 value is 7.7 nm.

25

Examples 4 to 9: AlSiPtRhExamples 4 and 5: Route 1 - Milling

2 kg of an alloy of 35.9% Al, 3.0% Si, 45.2% Pt and 15.9% Rh was prepared in a zirconia crucible. First the Al was melted. The Si was added at about 730°C. Then, the Pt and Rh were added gradually in the correct ratio. Because of the increasing liquidus temperature with increasing Pt and Rh content, the temperature was gradually increased to 1260°C. The product was solidified in the crucible. The ingot was crushed, milled in a ring mill and planetary mill to < 25 µm, and blended with alumina at a ratio of 1 part alloy / 4.73 parts alumina. The further process steps were similar to those described above for Examples 1 and 2. The further steps were oxidation in boiling water for 10 days, bead milling, calcination for 1 h at 550°C, and splitting in 2 fractions. The sample of the first fraction was the product of Example 4. The second fraction was bead milled again, dried and calcined for 1 h at 550°C to obtain the product of Example 5.

TEM analysis was carried out with both samples. The average size of the precious metal particles was 8.6 and 8.2 nm, respectively. FIG. 3 shows the product of Example 4. It can be seen clearly that alloyed precious metal particles were obtained, because Pt and Rh are present at the same location.

An XRD analysis was carried out with the calcined product. The result is shown in FIG. 8 and 9 and demonstrates that the product is crystalline. The difference between both diagrams is that the positions of the Rh peaks are indicated only in FIG. 9. The diffractogram indicates the presence of cubic Pt, cubic Rh, Al₂O₃ and SiO₂. The fact that an alloy is formed leads to widening of the peaks.

25

Compound Name	Chemical Formula	Crystal System	Space Group
Platinum	Pt	Cubic	Fm-3m
Aluminum Oxide	Al ₂ O ₃	Tetragonal	I41/amd
Silicon Oxide	SiO ₂	Hexagonal	P3221

Examples 6 and 7: Route 2 - Atomization

3 kg of an alloy of 77.7 wt% Al, 6.6 wt% Si, 11.6 wt% Pt and 4.1 wt% Rh was prepared. Alloy preparation was done in ZrO₂ crucibles. At first, an Al bath was prepared, and Si was added at 730°C. Pt and Rh in the right ratio were added gradually, to keep the exothermic reaction under control. Because of the lower Pt and Rh content, the liquidus temperature was lower, such that the maximal temperature was about 1000°C. The melt was cast in a steel mold, focusing on smaller pieces for atomization.

Atomization was performed under Ar atmosphere. The D50-value measured with laser diffraction is 12.1 µm with 80% < 20 µm and 90 % <25 µm. The powders obtained were further processed in the same way as described above: Oxidation in boiling water for 10 days, bead milling, calcination for 1 h at 550°C, splitting in 2 fractions. The first fraction was the product of Example 6. The second fraction was bead milled again, dried and calcined for 1 h at 550°C to obtain the product of Example 7.

TEM analysis of the product of Example 7 gave an average size of 4.6 and 3.4 nm, respectively. FIG. 4 shows that alloyed PGM particles were obtained. It can be seen that nanoparticles formed from Pt and Rh are distributed in a matrix from Al, Si and O.

Examples 8 and 9: Route 3 - Melt spinning

3 kg of an alloy of 77.7 wt% Al, 6.6 wt% Si, 11.6 wt% Pt and 4.1 wt% Rh was prepared. Alloy preparation was done in ZrO₂ crucibles. At first, an Al bath was prepared and Si was added at 730°C. Pt and Rh in the right ratio were added gradually, to keep the exothermic reaction under control. Because of the lower Pt and Rh content, the liquidus temperature was lower, such that the maximal temperature was about 1000°C. The melt was cast in a steel mold, focusing on smaller pieces for melt spinning. The material was melt spun on a meltspinning HV system (Edmund Bühler, DE) equipped with a BN crucible, with a 17*0.4 mm slit and a 250*40 mm spinning Cu wheel turning at 29 Hz. The melt temperature was about 1050°C. The ribbons obtained had a thickness of about 30 µm and a width of 15 mm. FIG. 5 shows two XRD graphs of the ribbons (upper graph: from top side of ribbon; lower graph: from bottom side of ribbon). The graphs show that the melt-spun ribbons have a crystalline structure.

The ribbons were cut in pieces of about 5 mm, blended with 10% alumina and milled in a ring mill. This product was further treated in a similar way as described above: oxidation in boiling water for 10 days, bead milling, calcination for 1 h at 550°C, splitting in 2 fractions. The first fraction was the product of Example 8. The second fraction was bead milled again, dried and calcined for 1 h at 550°C to obtain the product of Example 9. For both materials, the D50 was determined to be 2.6 nm.

Examples 10 to 16: Comparison of properties

Catalyst materials with catalyst metal particles, which are Pt-Rh alloys, were prepared according to the inventive method. The average composition and standard deviations from the average composition were determined for each material by TEM EDS measurement (examples 10 to 13). Further, these parameters were determined for conventional catalyst materials comprising Pt-Pd catalytic nanoparticles produced by other methods (plasma, wet chemical precipitation; examples 14 to 16; conventional materials with particles of Pt-Rh were not available). The results are summarized in table 1 below. The results demonstrate that the inventive materials are highly uniform, because the ratio of standard deviation to average composition is very low. Comparable materials produced by conventional methods such as wet precipitation or plasma formation typically comprise catalytic particles having a broader compositional distribution.

Table 1: Summary properties of catalyst materials of examples 10 to 16

	catalyst metals	number	average composition [at.%]	STD [at.%]	STD/average composition
10	Pt-Rh	17	40.4	5.65	0.14
11	Pt-Rh	18	32.3	5.27	0.16
12	Pt-Rh	20	44.1	2.02	0.05
13	Pt-Rh	31	41.8	4.80	0.11
14 comp.	Pt-Pd	109	28.7	8.61	0.30
15 comp.	Pt-Pd	90	9,6	5.32	0.55
16 comp.	Pt-Pd	94	12.1	9.92	0.82

Comparison of catalytic performance

To determine the NH₃ oxidation performance of the Pt-Rh catalysts (examples 4 to 9) six Washcoats were prepared with a precious metal loading of 3 g/ft³ and milled to a medium particle size of d₅₀ from 4 to 5 μm. Cordierite flow through substrates (3.66*3.66*3 inch

5 with 400 cells per square inch) were coated with a washcoat loading of 25 g/l substrate volume, dried at 120°C and calcined at 350°C and tempered at 550°C for 2 hours.

To illustrate the procedure the following composition is given for a washcoat with the powder of example 4

- 10 670 g aluminum oxide, 1387 g water and 31 g Pt-Rh-catalyst powder (example 4) were mixed together and milled to a medium particle size of d₅₀ of 4.7 μm using a bead mill with ZrO₂-beads of 2 mm diameter. The cordierite substrate was coated with the Washcoat to a loading of 25 g/l substrate volume, dried and calcined at 350°C and tempered at 550°C for 2 hours. After calcination catalyst sample parts of 3*1 inch were cut
- 15 out of the substrate and hydrothermally oven-aged at 800°C for 16 hours in nitrogen atmosphere containing 10 Vol% water and 10 Vol% oxygen. The samples with the other Pt-Rh powders were prepared the same way with adjusted amounts of the catalyst powder to achieve the same final precious metal loading of 3 g/ft³.
- 20 The NH₃ oxidation performances of the Pt-Rh catalysts were measured at a model gas bench according the parameters of table 2.

Table 2: Test conditions (GHSV: Gas hour space velocity (Nm³/m³/h))

	concentration
GHSV [1/h]	200000
O ₂ [vol-%]	5
H ₂ O [vol-%]	5
NH ₃ [ppm]	300
N ₂	Reminder

Results of the NH₃ conversion tests for Pt-Rh catalysts samples are summarized in table 3.

Table 3: NH₃ conversion rates and temperature for 50% conversion

Sample	NH ₃ conversion at 350°C [%]	T ₅₀ of NH ₃ conversion [°]
Sample 4	60	334
Sample 5	17	-----
Sample 6	52	345
Sample 7	27	399
Sample 8	37	371
Sample 9	61	335

5

CLAIMS

1. A method comprising the steps of
 - (a) providing an alloy powder, wherein the alloy consists of
 - 5 20% to 98% by weight of at least one carrier element selected from Al, Si, Ti, Zr, Y, La, Ce, Pr, Nd and Mg, and
 - 2% to 80% by weight of at least one catalyst metal selected from Pd, Pt, Rh, Co, Ni, Ru, Os, Ir, Fe and Au,
 - (b) oxidizing the alloy powder in liquid medium, such that at least one carrier
 - 10 element is oxidized,
 - (c) obtaining a catalyst material.
2. The method of claim 1, wherein the alloy in step (a) is an intermetallic compound or comprises an intermetallic compound.
3. The method of at least one of the preceding claims, comprising before step (a) a step:
 - 15 (a0) providing the at least one carrier element and at least one catalyst metal, combining and heating the elements to obtain a melt, solidifying the melt to obtain a solid alloy, and optionally pulverizing the solid alloy.
4. The method of at least one of the preceding claims, wherein in step (b) the oxidation is carried out the presence of an oxidizing agent, which is selected from water, alcohols,
 - 20 hydrogen peroxide and oxygen, and mixtures thereof.
5. The method of claim 4, wherein the oxidizing agent is water.
6. The method of at least one of the preceding claims, wherein in step (b) the oxidation is carried out at a temperature below 200°C.
7. The method of at least one of the preceding claims, wherein an oxide of the at least
 - 25 one carrier element is added to the alloy powder before step (b).
8. The method of at least one of the preceding claims comprising at least as a step:
 - (c) calcining the oxidized product obtained in step (b)
 - and/or

(d) reducing the particle size of the oxidized product obtained in step (b) and/or of the calcined product obtained in step (c).

9. A catalyst material obtainable by a method of any of claims 1 to 8.
10. A catalyst material according to claim 9, comprising
- 5 a carrier, which comprises at least one carrier element in oxidized form selected from Al, Si, Ti, Zr, Y, La, Ce, Pr, Nd and Mg, and catalyst metal particles, which comprise at least one catalyst metal selected from Pd, Pt, Rh, Co, Ni, Ru, Os, Ir, Fe and Au, wherein the catalyst metal is present in metallic or oxide form,
- 10 wherein catalyst metal particles are present on the surface of the carrier, wherein the catalyst metal particles have a medium particle size D50 between 1 nm and 50 nm.
11. The catalyst material of claim 9 and/or 10, wherein the catalyst metal particles comprise at least two different catalyst metals, preferably in the form of an alloy.
- 15 12. The catalyst material of at least one of claims 9 to 11, wherein the catalyst metal particles are crystalline.
13. The catalyst material of at least one of claims 9 to 12, wherein the particle size distribution $(D90 - D10) / D50$ of the catalyst metal particles is below 4, preferably below 3.
- 20 14. The catalyst material of at least one of claims 9 to 13, wherein the catalyst metal particles comprise Pd, Pt and/or Rh, or at least one oxide thereof.
15. The catalyst material of at least one of claims 9 to 14, wherein the carrier comprises aluminium oxide, silicon oxide and/or lanthanum oxide.

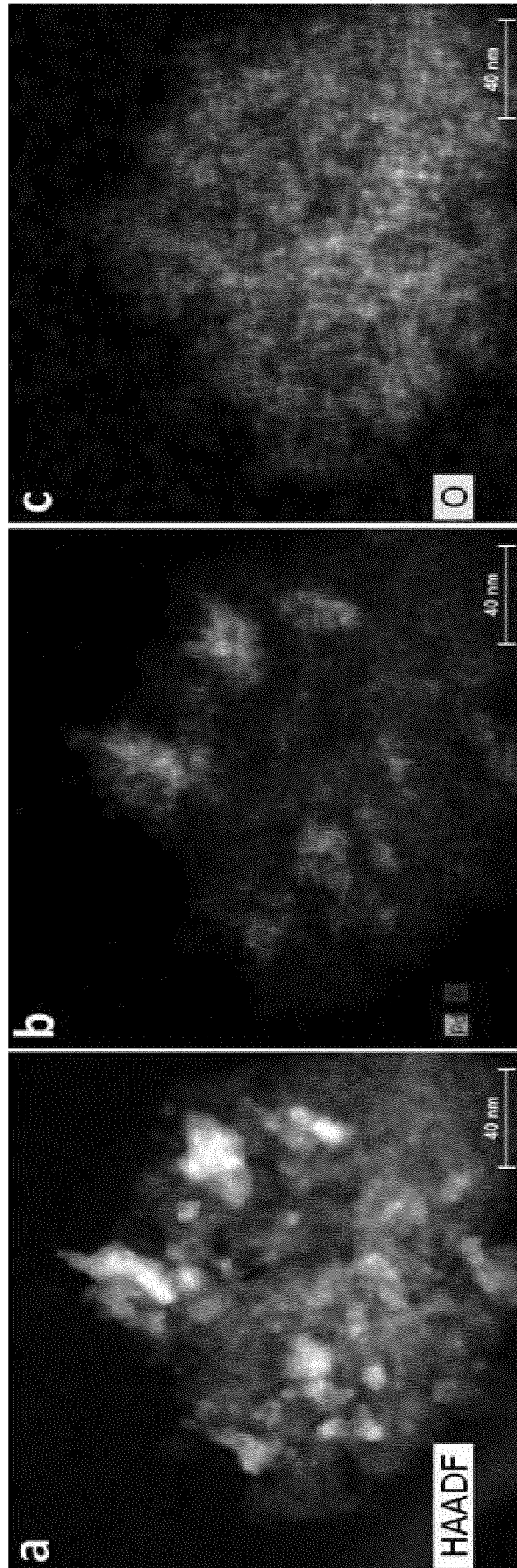


FIG. 1

FIG. 2

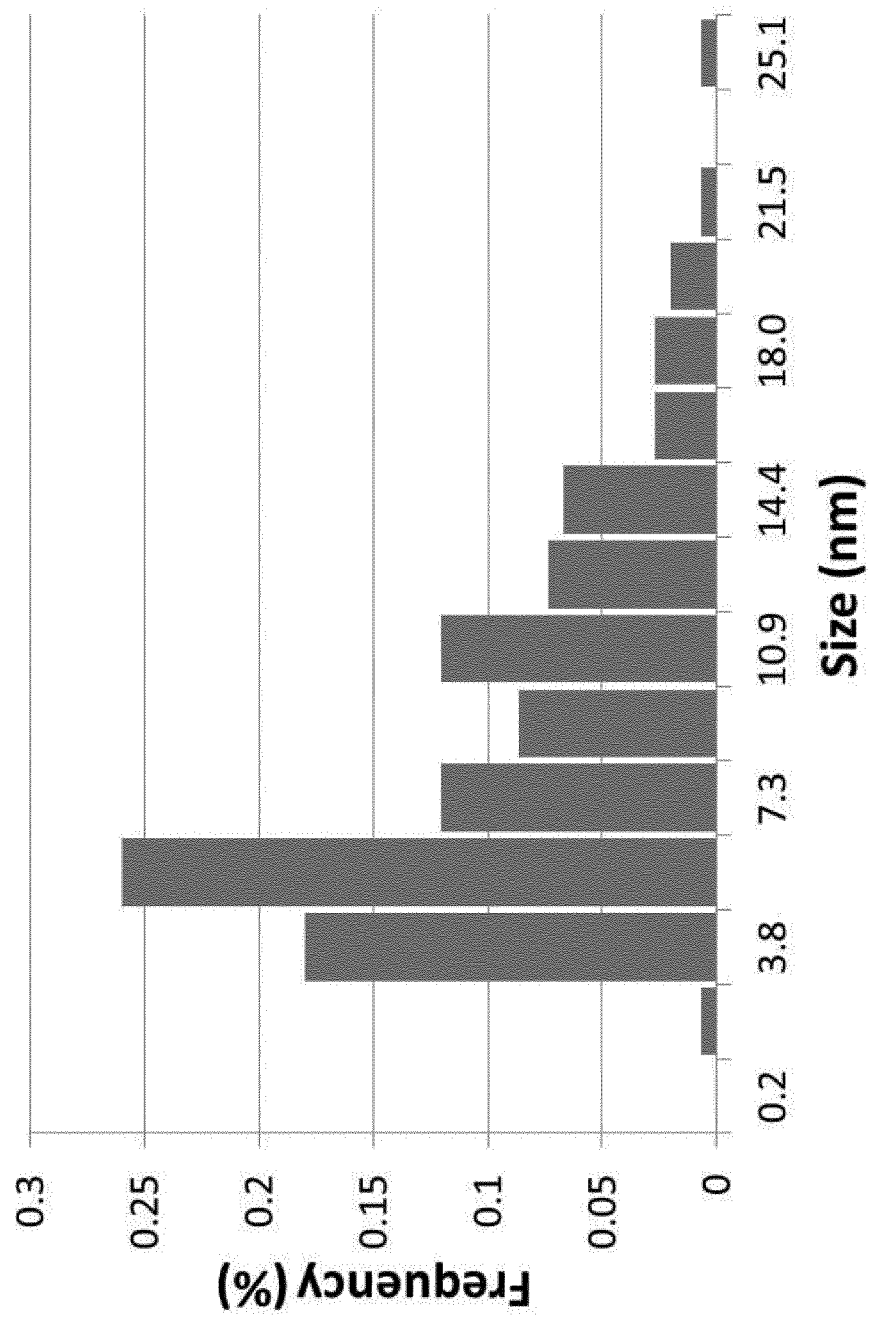
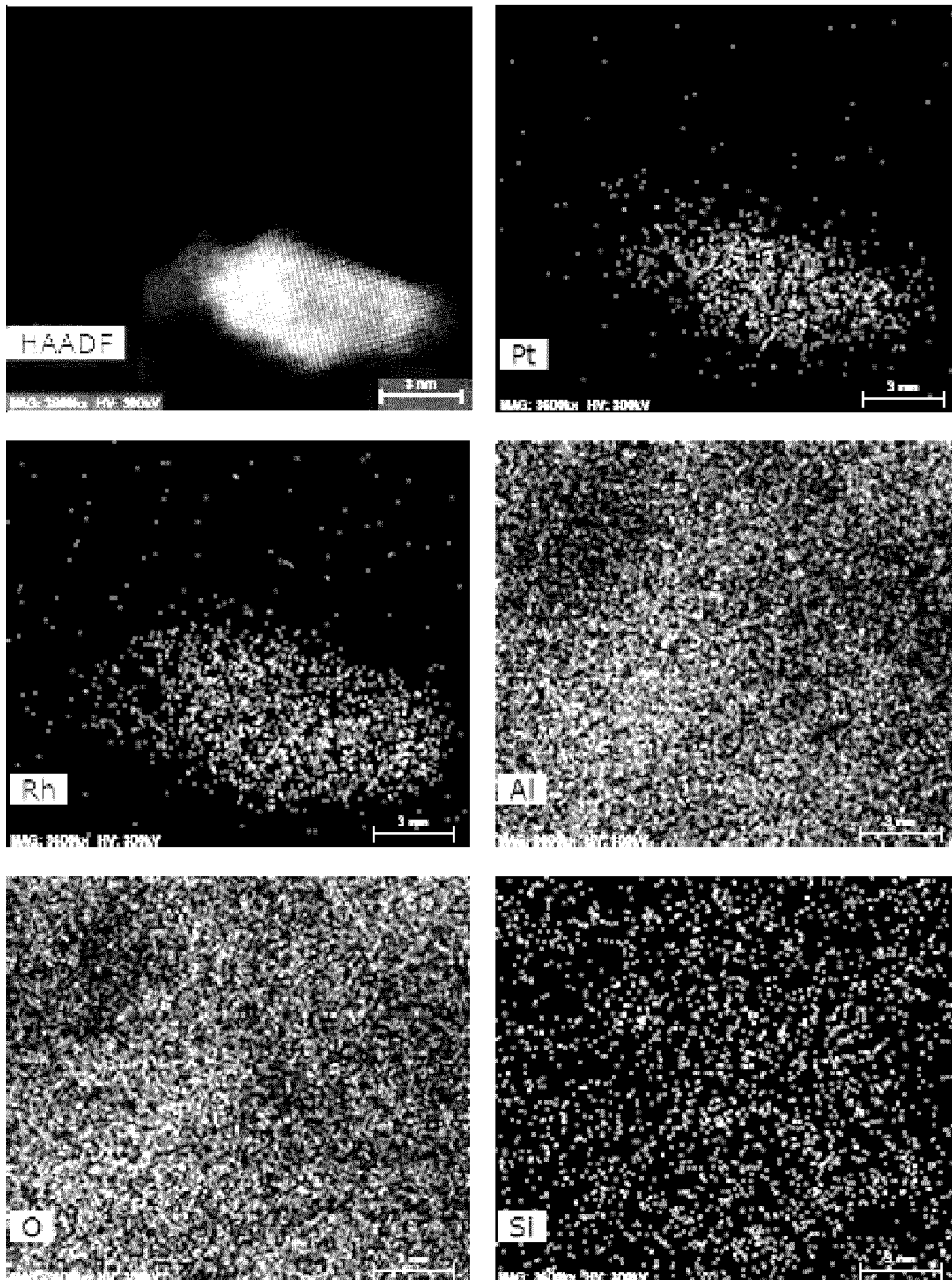


FIG. 3



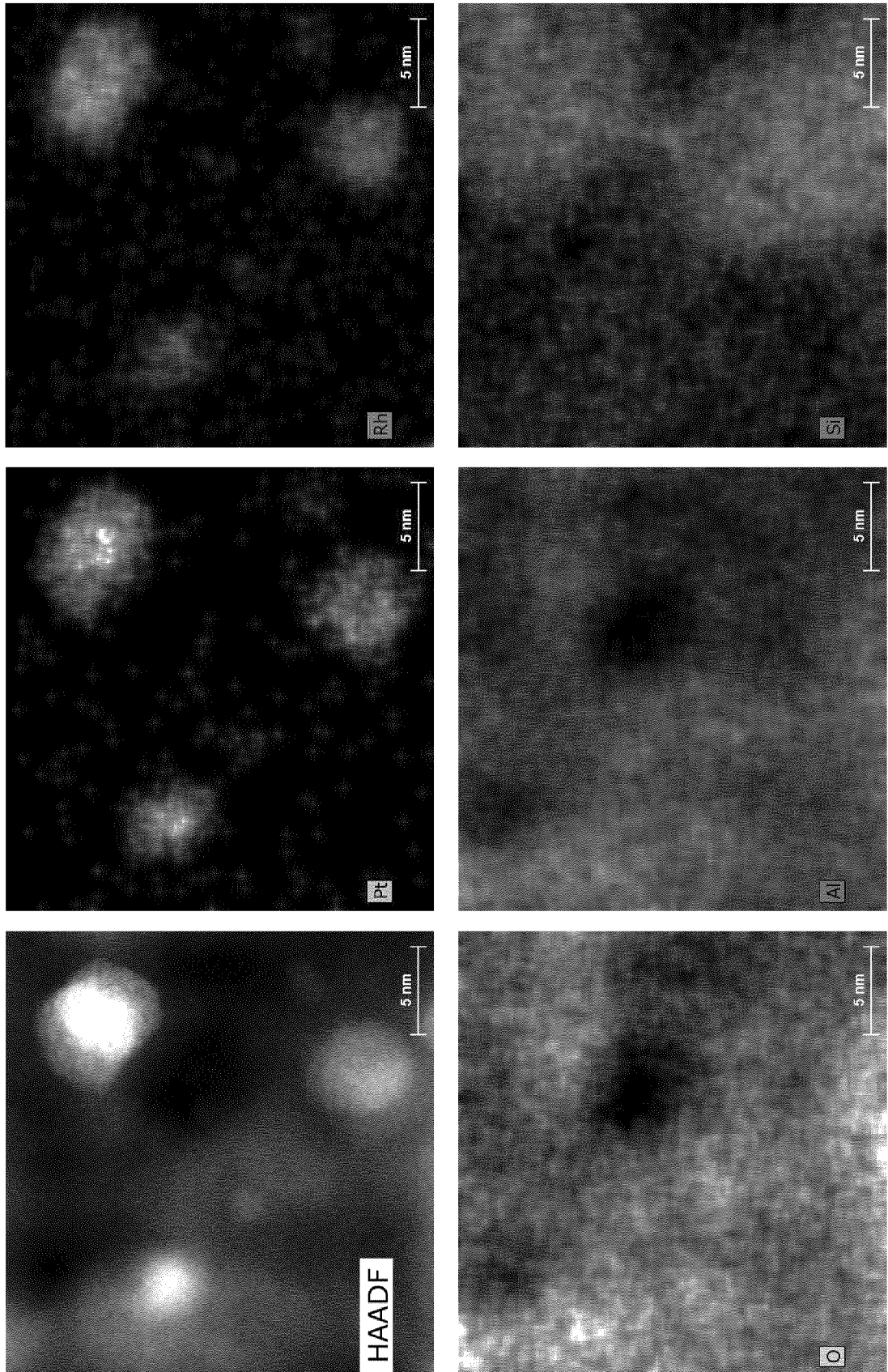


FIG. 4

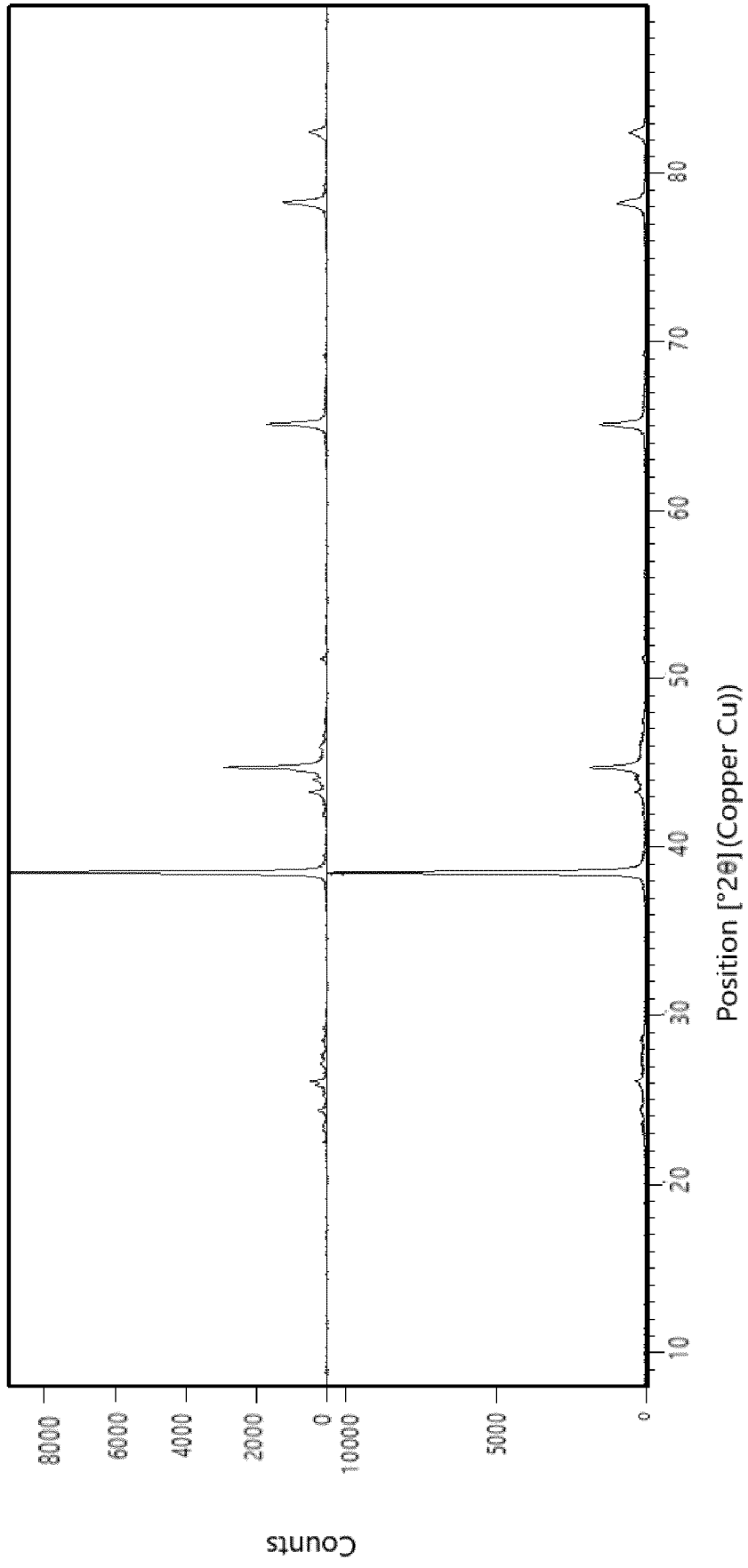


FIG. 5

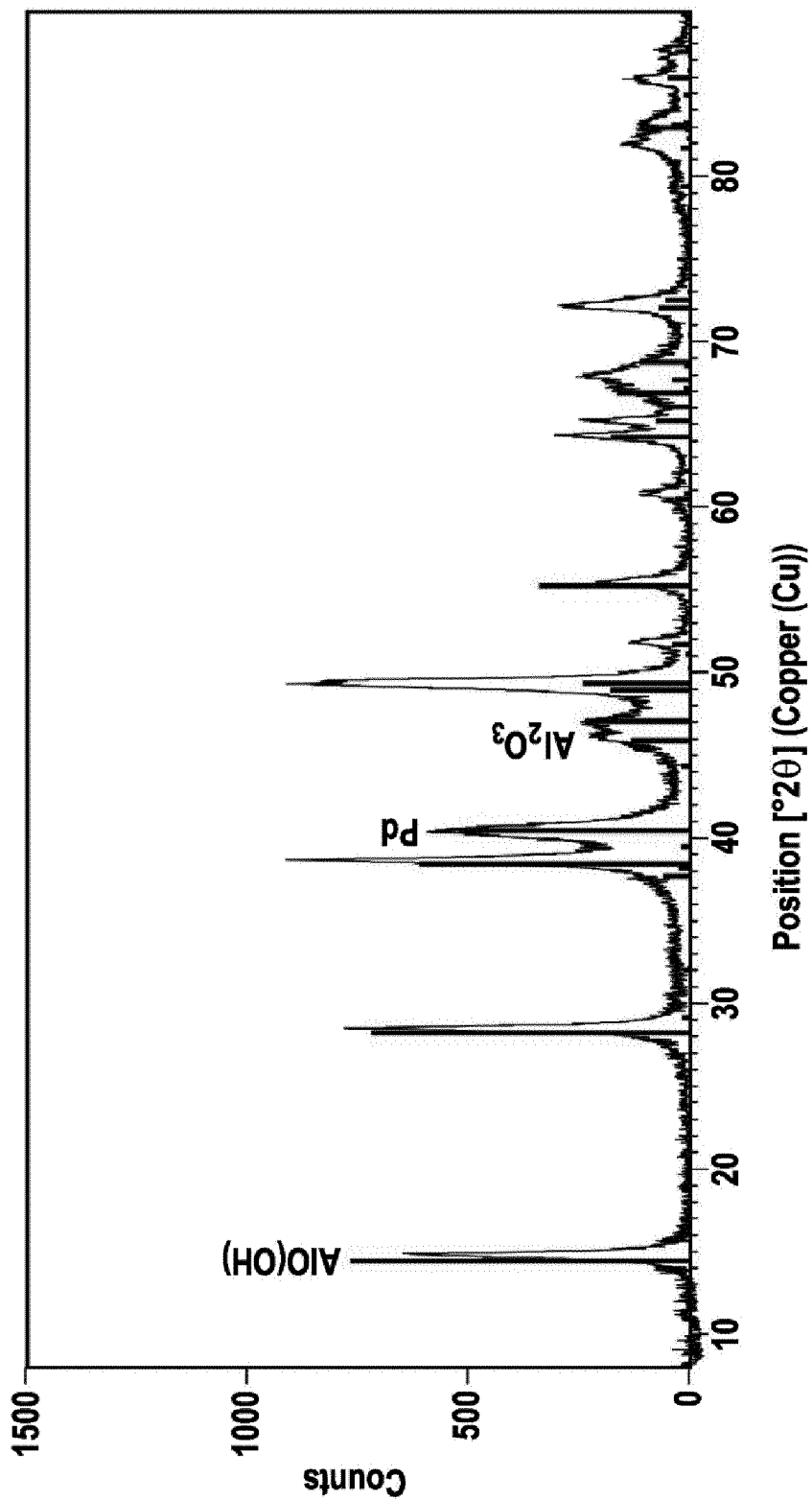


Fig. 6

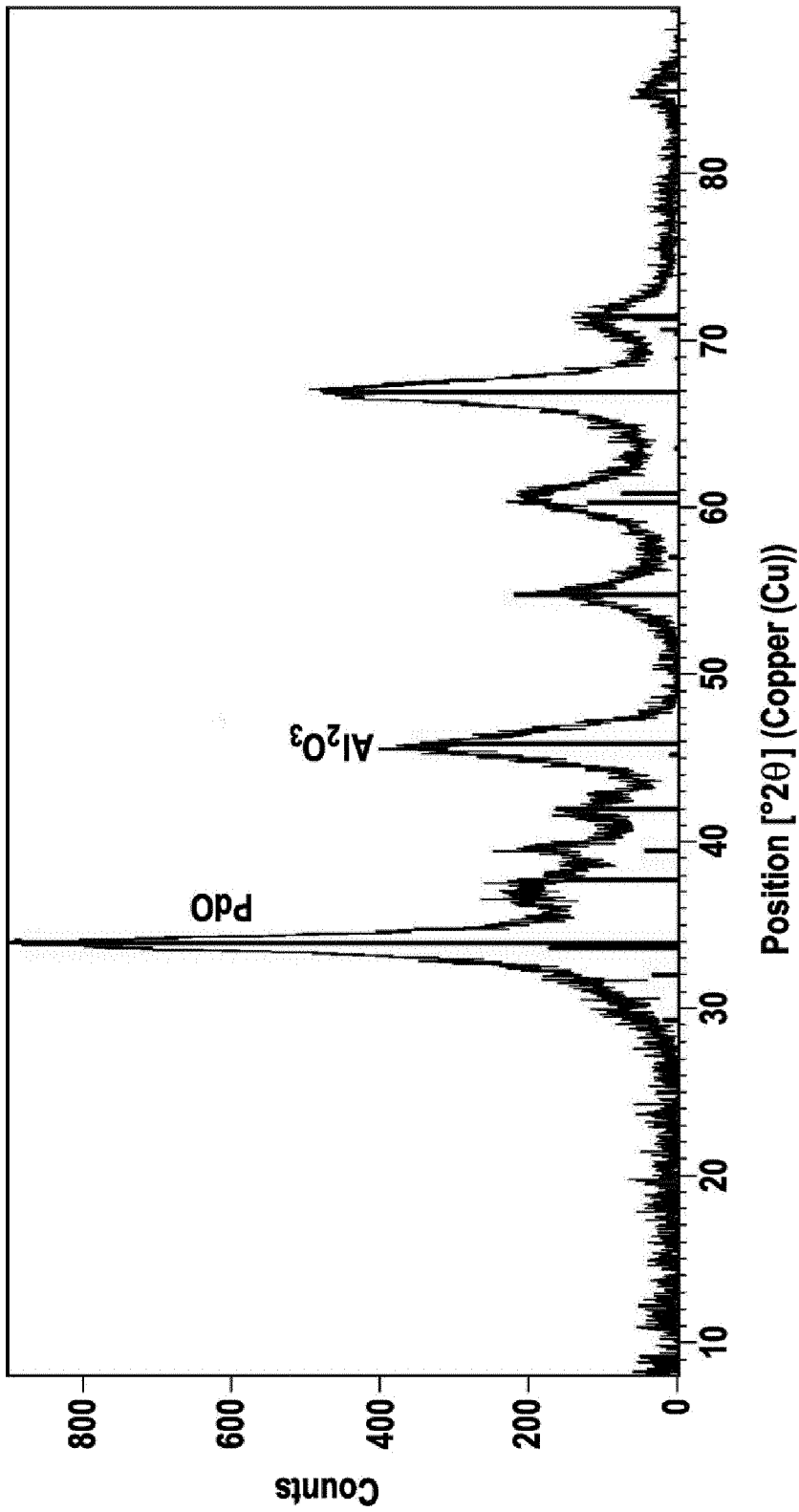


Fig. 7

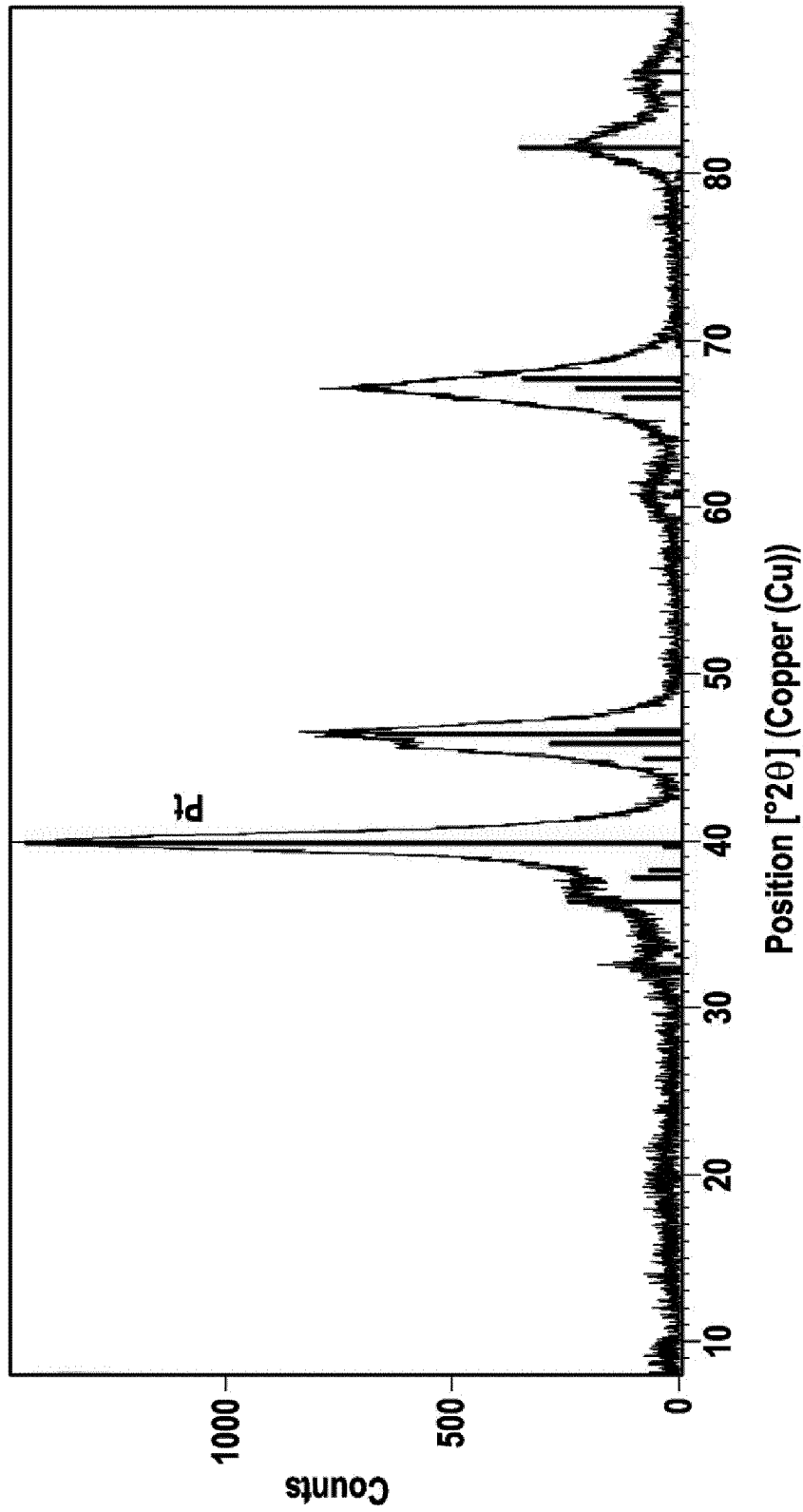


Fig. 8

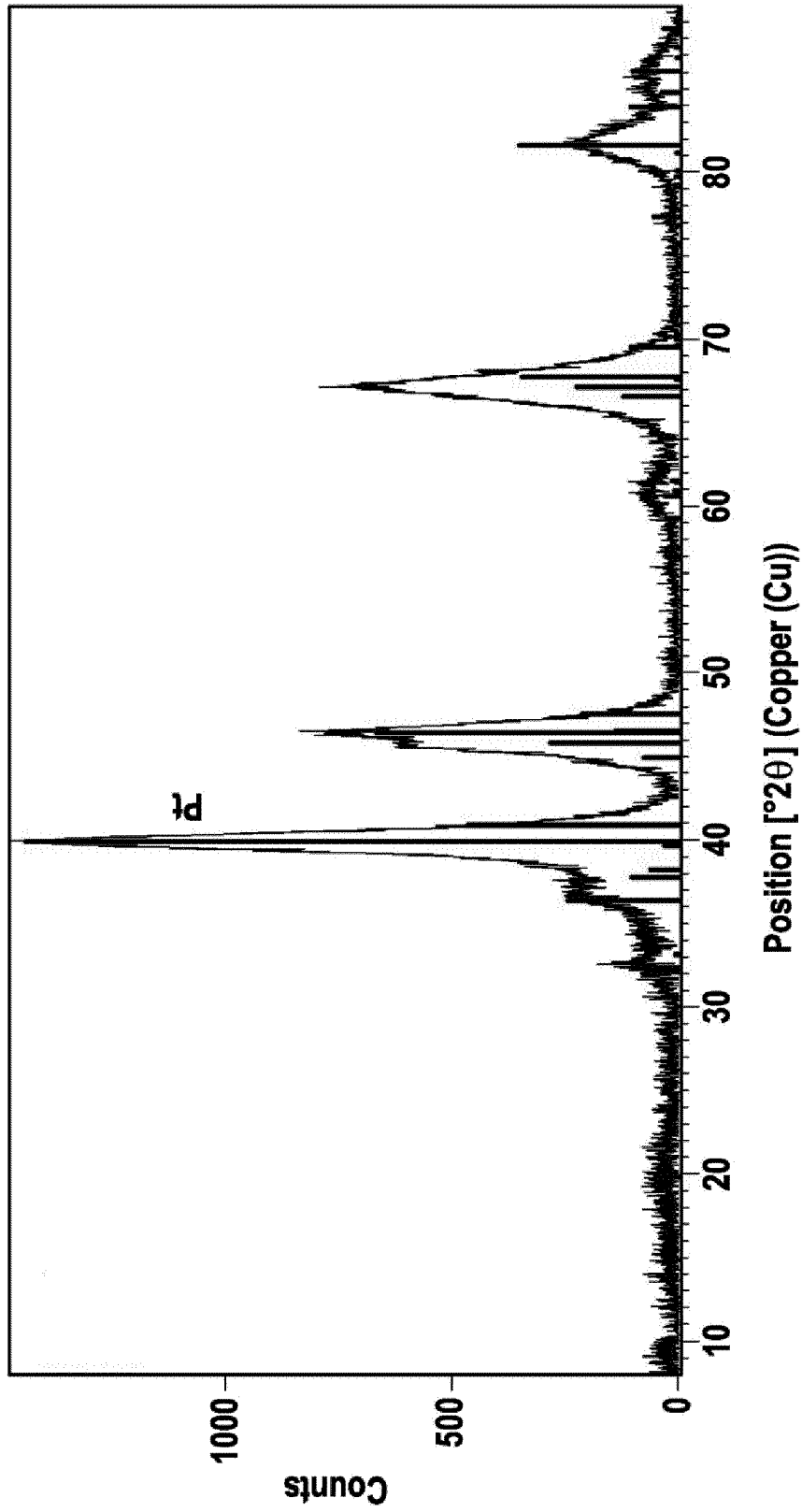


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/054848

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B01J37/00	B01J37/12	B01J37/14	B01J35/02	B01J23/38
	B01J23/74	C22C5/04	C22C19/00	B01D53/94	B01J35/00
	B82Y30/00	B22F1/00			

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 C22C B01D B82Y B22F

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
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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP S64 11642 A (IDEMITSU KOSAN CO) 17 January 1989 (1989-01-17)	9-15
Y	the whole document	1-9
X	EP 3 321 249 A1 (LG CHEMICAL LTD [KR]; KOREA ADVANCED INST SCI & TECH [KR]) 16 May 2018 (2018-05-16)	9-15
A	the whole document paragraphs [0028] - [0043], [0091] examples table 1	1-8
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
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* Special categories of cited documents :	
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
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Date of the actual completion of the international search 9 April 2020	Date of mailing of the international search report 21/04/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Gosselin, Daniel

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/054848

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 671 846 A1 (NAT INST OF ADVANCED IND SCIEN [JP]) 11 December 2013 (2013-12-11)	9-15
Y	the whole document paragraphs [0017] - [0019], [0023] examples figures claims	1-9
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