

Powdered titanium oxide, processes for preparing the same and the use thereof

The invention relates to powdered, inorganically post-processed titanium oxide, processes for preparing the same, and the use thereof in preparing catalysts, particularly for application as a photocatalyst and as a support for refinery catalysts.

A number of titanium dioxides, and also $\text{TiO}_2\text{-SiO}_2$ materials, are known in the related art and used as catalyst and/or support for catalytically active materials.

In the field of photocatalysis, many TiO_2 -based photocatalysts are offered commercially. These are usually in the form of anatase, anatase-rutile mixtures or doped titanium dioxides with a wide range of application possibilities. When exposed to UV irradiation during photocatalysis, gas-phase or dissolved materials are converted to titanium dioxide, most often anatase, in a free radical reaction or charge carrier transfer. Titanium dioxides with large surface areas such as the commercially marketed products "HOMBIKAT UV100" or "HOMBIKAT M211" are known to have good photocatalytic properties. However, it is still desirable to further enhance the photocatalytic activity.

It has long been known to use titanium dioxide as a support material in the production of hydrotreating catalysts for hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN). For example, US6419889B1 describes the use of a titanium dioxide support with a specific surface area of $70 - 99 \text{ m}^2/\text{g}$ and a bimodal pore distribution, wherein 90% of the pores have a diameter of at least 100 nm. However, the thermal stability of pure titanium dioxide is not good enough for hydrotreating applications, which typically take place at 400°C , which results in ageing effects and loss of catalytic activity.

It is generally known that $\text{TiO}_2/\text{SiO}_2$ materials can also be used as catalysts or catalyst supports in a variety of catalytic applications, particularly as supports for selective catalytic reduction in the reduction of nitrogen oxides in exhaust gases from furnaces, incineration plants, gas turbines, industrial installations, internal

combustion engines, and as V-SCR catalysts. In this context, SiO_2 is typically introduced to increase thermal stability. However, when SiO_2 is added, a portion of the catalytically active titanium dioxide surface is covered with SiO_2 , which limits its catalytic properties.

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A number of processes are known for preparing $\text{TiO}_2/\text{SiO}_2$ materials of this kind. Some methods for producing such $\text{TiO}_2/\text{SiO}_2$ materials are based on precipitation from Ti-containing solutions (Ti-alkoxides, titanyl sulphate, titanium oxychloride etc.) with bases, with or without the addition of Si- containing solutions.

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For example, EP668100A1 describes a process for preparing a $\text{TiO}_2/\text{SiO}_2$ catalyst by adding an acid solution containing a silicon compound and a titanium compound dissolved therein to the solution of a basic compound to initiate coprecipitation.

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In DE3619337A1, production of a $\text{TiO}_2/\text{SiO}_2$ powder by mixing an aqueous solution of titanium sulphate with an ammonium-containing, aqueous SiO_2 sol is described. The precipitate is washed, dried and calcined, and used to manufacture a catalyst material.

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Besides the above, many sol-gel processes for preparing nano- TiO_2 from titanium-organic precursor stages are described in the literature: one example of such is described in EP 1719737A1.

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The $\text{SiO}_2/\text{TiO}_2$ materials obtained by precipitation and the $\text{SiO}_2/\text{TiO}_2$ materials prepared with sol-gel processes are both almost amorphous, that is to say, signals are only very weakly detectable, if at all by X ray diffractometry. These amorphous $\text{TiO}_2/\text{SiO}_2$ materials typically have very poor catalytic properties. In order to create active $\text{TiO}_2/\text{SiO}_2$ particles according to the prior art, thermal treatments such as hydrothermal treatments and/or calcination are necessary. These steps serve to increase crystallinity, but they also reduce the specific surface area of the hydroxy group content. This reduction is unfavourable for the catalytic applications.

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Besides the option of mixing solutions containing Ti with solutions containing Si and then initiating precipitation as described above, the prior art also includes descriptions of processes for precipitating Si compounds onto particulate titanium dioxide.

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Accordingly, US6956006 relates to a composite material containing silicon and titanium dioxide in which the pore structure exhibits improved thermal and hydrothermal resistance. The composite material can be obtained by precipitating titanium hydroxide from an aqueous solution containing sulphate salts and urea,
10 followed by hydrothermal treatment in the mother liquor and then reacting the precipitate with a basic colloidal silica.

Furthermore, WO0114054A1 describes a process for preparing mesoporous $\text{TiO}_2/\text{SiO}_2$ material in powder form, in which titanium dioxide in the form of a
15 titanium hydroxide is first precipitated out and then a SiO_2 component is added.

US 7125536B2 describes a process for preparing nanostructured particles with high thermal stability by precipitation of zirconium or titanium salts with a base, adding a stabilising agent such as fumed silica, hydrothermal aging, washing,
20 drying and calcining.

In the process according to US8545796B2, a titanium dioxide suspension is mixed with a source of Si, and the pH value is then adjusted to < 8.5 , so that SiO_2 is precipitated onto the TiO_2 particles. The products prepared in this way have
25 specific surface areas of $< 400 \text{ m}^2/\text{g}$ and pore volumes of $< 0.4 \text{ cm}^3/\text{g}$.

In the processes cited above for precipitating SiO_2 onto particulate titanium dioxide it was found that the addition of SiO_2 has the effect of covering part of the catalytically active titanium dioxide surface, diminishing its catalytic properties.

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There are no titanium dioxides known in the prior art that combine good thermal stability with very large specific surface areas, high pore volumes and marked crystallinity, and so have excellent properties as catalysts or precursor materials

even at elevated application temperatures.

Summary

5 In one aspect, the present invention is directed to a powdered catalyst material on titanium oxide basis, having a combined content of at least 90% by weight hydrated titanium oxide having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ with $0 < x \leq 1$, particularly $0.1 < x \leq 1$ (calculated as TiO_2) and silicon dioxide including hydrated precursors thereof (calculated as SiO_2), which has a specific surface area of $> 300 \text{ m}^2/\text{g}$ and an
10 isoelectric point in the range from 4.5 - 5.9, wherein the $\text{TiO}_2/\text{SiO}_2$ weight ratio, determined respectively for TiO_2 and SiO_2 is at least 3, preferably at least 5, and less than 30, preferably less than 25, and the percentages by weight are relative to the total weight of the catalyst material after it has been dried at 105°C for at least 2 hours. In another aspect, the present invention is directed to a process for preparing
15 the powdered catalyst material on titanium oxide basis according to the present invention, in which: a. an aqueous suspension of titanium oxide hydrate particles having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ with $0 < x \leq 1$, particularly $0.1 < x \leq 1$, preferably with average particle sizes from 20 – 500 nm is reacted with an Si-containing compound while stirring vigorously, wherein the pH value can be maintained in the
20 range from pH = 3 to 9, particularly 4 to 7 by the optional addition of an acid or alkaline solution, b. optionally the pH value is adjusted if necessary to the range between 4 and 7, c. the suspension obtained is filtered off, and d. the filter cake obtained is washed with water until the filtrate has a conductivity not more than $500 \mu\text{S}/\text{cm}$. In still another aspect, the present invention refers to the use of the powdered
25 catalyst material according to the present invention for preparing shaped bodies, particularly for catalytic application or as a support for catalytically active metals for application in the field of catalysis such as photocatalysis, Claus catalysis, Claus-Tail-Gas-treatment, SCR, Hydrotreating, Gas-to-Liquid-Process, Fischer-Tropsch-Process. In yet another aspect, the present invention refers to shaped bodies on a titanium
30 oxide basis with content of powdered catalyst material according to the present invention with a specific surface area of $> 80 \text{ m}^2/\text{g}$, particularly $> 100 \text{ m}^2/\text{g}$, preferably $> 120 \text{ m}^2/\text{g}$, particularly preferably $> 150 \text{ m}^2/\text{g}$, most particularly preferably $> 200 \text{ m}^2/\text{g}$.

Detailed Description

The inventor has now discovered that the inorganically post-processed, powdered titanium oxide according to the invention has significantly enhanced catalytic properties as well as good thermal stability, thus overcoming the disadvantages of the prior art.

The inorganically post-processed, powdered titanium oxide as the inventive product is characterised particularly by the following properties:

- 10 - a combined content of at least 90% by weight hydrated titanium oxide having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ wherein $0 < x \leq 1$, particularly $0.1 < x \leq 1$, (calculated as TiO_2) and silicon dioxide including hydrated precursor forms thereof (calculated as SiO_2), wherein the $\text{TiO}_2/\text{SiO}_2$ weight ratio, in which TiO_2 and SiO_2 are each determined as described in the method, is at least 3,
 - 15 preferably at least 5, and less than 30, preferably less than 25, and the % by weight is relative to the total weight of the catalyst material after it has been dried at 105 °C for at least 2 hours; wherein the remainder to 100% by weight consists of chemically bound water and traces of by-elements as explained below;
 - the specific surface area of the dried product is $> 300 \text{ m}^2/\text{g}$, particularly
 - 20 preferably $> 350 \text{ cm}^2/\text{g}$;
 - the isoelectric point is in the pH range from: 4.0 – 7.0, preferably 4.5 – 5.9, particularly preferably 4.7 – 5.9;

When the material is dried at 105 °C for at least 2 hours, the directly prepared inorganically post-processed, powdered titanium oxide as the product according to the invention undergoes a loss of weight of up to 10%, wherein most of the weight loss is accounted for by water. Besides the water that is then still chemically bound in the inorganically post-processed, powdered titanium oxide which has been dried as before, which can account for up to 7% by weight of the product dried at 105 °C and can only

30 be driven off at higher temperatures from about 200 to 800 °C, traces of by-elements such as Na, K, Ca, Mg, Cl, sulphates, nitrates, Nb, Zr, Fe, Cr, V, Li, Al may be contained as constituents of the product in a combined total amount not exceeding 3%. Thus, the total content of TiO_2 plus SiO_2 in the

directly prepared inorganically post-processed, powdered titanium oxide as the product is at least 90 % by weight after drying at 105 °C as described. Regardless of the degree of drying, the $\text{TiO}_2/\text{SiO}_2$ weight ratio in the inorganically post-processed titanium oxide according to the invention is between 3 and 30, which is
5 also unaffected by other components.

Accordingly, the inorganically post-processed titanium oxide according to the invention may also be described as a powdered catalyst material containing titanium oxide having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ with $0 < x \leq 1$, particularly 0.1
10 $< x \leq 1$ and silicon dioxide including precursor forms thereof, with a $\text{TiO}_2/\text{SiO}_2$ weight ratio of at least 3, preferably at least 5, and less than 30, preferably less than 25, having a specific surface area of $> 300 \text{ m}^2/\text{g}$ and an isoelectric point in the range from 4.0 - 7.0, wherein the total content of TiO_2 plus SiO_2 in the directly prepared powdered, inorganically post-processed titanium oxide is at least 80% by
15 weight and the rest up to 100% by weight is made up of bound water and traces of by-elements as described in the preceding, which originate from the production process and the starter material, such as ilmenite.

In this context, the powdered, inorganically post-processed titanium oxide may
20 advantageously also have at least one of the following properties:

- a particle size not exceeding 1 mm, as classified by sieving;
- the specific surface area of the product after thermal treatment for 1 h at 500°C in a normal atmosphere is still at least $80 \text{ m}^2/\text{g}$, particularly at least $100 \text{ m}^2/\text{g}$, preferably more than $150 \text{ m}^2/\text{g}$;
- 25 • a photocatalytic activity - measured by a degradation rate of chloroform -of more than $0.3 \text{ mmol}/(\text{h} \cdot \text{m}^2)$, particularly more than $0.5 \text{ mmol}/(\text{h} \cdot \text{m}^2)$, most particularly more than $0.6 \text{ mmol}/(\text{h} \cdot \text{m}^2)$ and particularly preferably more than $0.7 \text{ mmol}/(\text{h} \cdot \text{m}^2)$, measured according to the process described in the method section
- 30 • pore volume (N_2 desorption, total) $> 0.3 \text{ cm}^3/\text{g}$, preferably $> 0.5 \text{ cm}^3/\text{g}$, particularly preferably $> 0.7 \text{ cm}^3/\text{g}$;
- an anatase phase with crystallite sizes from 5 – 15 nm;
- a pore distribution with a maximum in the range from 10 – 35 nm, particularly

in the range from 10 – 30, preferably 20 – 30 nm.

When reference is made to titanium oxide or a titanium oxide suspension according to the present invention, it is understood to mean a titanium-oxygen
5 compound according to the invention with formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ ($0 < x \leq 1$) and also as a titanium dioxide hydrate which can also be described as TiO_2 and $\text{TiO}(\text{OH})_2$ side by side or the aqueous suspension thereof.

Oxides in contact with electrolytes develop electrical charges on their surfaces due
10 to dissociation processes, and the magnitude and polarity of these charges at a certain pH value are characteristic of the oxide concerned. The pH value at which the surface does not carry a charge is called the isoelectric point (IEP). With pH values above the IEP, the surface is always negatively charged, below the IEP it is always positively charged. The isoelectric point of pure titanium dioxide or titanium
15 oxide hydrate is at about pH 6. The isoelectric point of SiO_2 is at pH = 2 to 3. Accordingly, this "isoelectric point" (IEP) can be used as a measurement of the degree to which the surface area of titanium dioxide particles is covered with SiO_2 . The coverage of the titanium dioxide/titanium oxide hydrate surface area with SiO_2 causes the isoelectric point to shift in the range from pH 5 to 2, depending on the
20 percentage of the titanium dioxide surface area that is covered with SiO_2 . When 100% of the titanium dioxide surface area is covered with SiO_2 , the IEP of the $\text{SiO}_2/\text{TiO}_2$ is at about pH = 3 to 2. The less the IEP is shifted towards pH = 2 due to the treatment of the titanium dioxide surface areas with SiO_2 , the lower the percentage of the surface area that has been covered with SiO_2 . Conversely, this
25 increases the percentage of the particle surface area that consists of titanium dioxide, which in turn leads to an increase in catalytic activity. At the same time, the percentage of the titanium dioxide surface area that is covered with SiO_2 depends not only on the SiO_2 content, but also by the Si treatment process. It follows that the catalytic performance is determined not only by the structural
30 properties (5-point BET, pore volume) and the absolute SiO_2 content, but also by the method by which the SiO_2 is spread over the TiO_2 surface.

The inventors have made use of this discovery when developing the present

inventive process and the powdered inorganically post-processed titanium oxide prepared according to said process. Accordingly, the inventors have prepared such a powdered, inorganically post-processed titanium oxide with defined crystalline regions mainly with anatase modification, in which a part of the surface area is covered with SiO₂ or hydrated precursor stages or mixtures thereof, wherein the product as a whole is called a Si-containing compound, and is thus able to lend the material increased thermal stability after drying while its catalytic activity is practically unchanged. According to discoveries made by the inventors, these properties may be obtained due to the fact that SiO₂ and hydrated precursors thereof precipitated onto the individual titanium oxide particles with general formula TiO_(2-x)(OH)_{2x}, in which $0 < x \leq 1$ keeps the individual TiO₂ particles "apart" during drying, so that individual crystalline TiO₂ regions are not able to coalesce, with the result that a surface area with sufficient catalytic activity is preserved.

According to the invention, the inorganically post-processed, powdered titanium oxide is thus obtained by treating a suspension of titanium oxide particles having formula TiO_(2-x)(OH)_{2x} ($0 < x \leq 1$) with the one or more Si containing compounds in suspension, so that some of the surface area of said titanium oxide particles is coated therewith.

Accordingly, the process according to the invention is a process for preparing a catalyst material on a titanium oxide basis in powder form, in which:

- an aqueous suspension of titanium oxide hydrate particles and/or hydrated titanium oxide having general formula TiO_(2-x)(OH)_{2x} wherein $0 < x \leq 1$, particularly $0.1 < x \leq 1$, or mixtures thereof, called "titanium oxide suspension" in the following, with medium sized particles from 20 – 500 nm, is mixed by intensive stirring and/or dispersion with a solution of a Si-containing compound, preferably while maintaining a pH at pH values from pH = 3 – 9, particularly 4 to 7,
- optionally the pH value is re-adjusted to the range between 4 and 7 if necessary,
- the suspension obtained is filtered,

- the filter cake obtained is optionally washed with water until the filtrate has a conductivity not exceeding 500 $\mu\text{S}/\text{cm}$, and
- the product obtained is dried.

5 The pH value of the titanium oxide suspension may be adjusted to pH values from 3.0 to 9.0, particularly 4.0 to 8.5, preferably 4.0 to 7.5, particularly preferably 4.0 to 7.0 by adding an acid or a base before the Si-containing solution is added. The pH value may be maintained at the previously set pH value while the Si-containing solution is being added.

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In this context, the quantities of titanium oxide-containing suspension and of the solution of Si-containing compound are selected such that after drying at 105 °C for at least 2 hours as described above, the product according to the invention has a total content of at least 90% by weight TiO_2 plus SiO_2 .

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In one embodiment, the suspension of titanium oxide particles having formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ ($0 < x \leq 1$) may be metatitanic acid with formula $\text{TiO}(\text{OH})_2$, which is precipitated as an intermediate product in the sulphate process used to prepare titanium dioxide.

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In other manufacturing processes, the suspension of titanium oxide particles with formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ ($0 < x \leq 1$) may also be obtained from Ti-containing solutions, particularly from hydrolysable compounds such as TiOSO_4 - or TiOCl_2 -containing solutions by precipitation, hydrolysis or sol-gel processes, although the titanium
25 oxide particles with formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ ($0 < x \leq 1$) are preferably obtained by the sulphate process.

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This used "titanium oxide suspension", which represents this suspension of titanium oxide hydrate and/or hydrated titanium oxide particles with general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ wherein $0 < x \leq 1$, particularly $0.1 < x \leq 1$, or mixtures thereof, preferably has the following properties:

- a Ti content calculated as titanium dioxide of 50 – 400 g TiO_2/l ,

- an average particle size of 20 nm – 1000 nm, preferably 20 nm – 500 nm, particularly preferably 50 nm – 200 nm, most particularly preferably 50 – 150 nm,
- a specific particle surface area of 200 – 500 m²/g, preferably 200 – 400 m²/g, particularly preferably 300 – 400 m²/g (measured by N₂ porosimetry, 5-point BET after drying at 105 °C for at least 120 min)
- a total pore volume of the particles of > 0.3 cm³/g, preferably > 0.5 cm³/g, particularly preferably > 0.7 cm³/g (measured by N₂ porosimetry, 5-point BET after drying at 105 °C for at least 120 min)
- after drying at 105 °C for at least 120 min, most of the crystalline phases of the particles exist in the anatase phase, that is to say, after deduction of a linear subsurface, the ratio of the height of the most intense reflex of the anatase structure (reflex (101)) to height of the most intense reflex of the rutile structure (Reflex (110)) is at least 5:1, preferably at least 10:1. An XRD analysis conducted according to the description in the "Methods" section of this document, preferably involves only reflexes of an anatase structure.

The metatitanic acid used contains titanium-oxygen compounds and may also contain free and bound sulphuric acid, wherein the crystalline fractions of the titanium-oxygen compound are present in the anatase modification, as mentioned earlier, and have a typical crystallite size of about 5-15 nm. The titanium-oxygen compounds may be described with the general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ wherein $0 < x \leq 1$. The metatitanic acid is precipitated as an intermediate product when TiO_2 is prepared according to the sulphate process. In the sulphate process, ilmenite and/or slag is digested with 90% H_2SO_4 , the digestion cake thus obtained is dissolved in water and the solution is allowed to settle. The addition of scrap iron converts the trivalent dissolved iron to its bivalent form, because Fe^{3+} would be precipitated as $\text{Fe}(\text{OH})_3$ together with the metatitanic acid and would then be adsorbed on it, which would be undesirable. Depending on the Fe content of the solution $\text{FeSO}_4 \cdot x \text{H}_2\text{O}$ is precipitated after the solution cools and is removed from the system. During the subsequent hydrolysis, the TiOSO_4 is converted into metatitanic acid. Other hydrated forms such as orthotitanic acid are converted into metatitanic acid and H_2O is released.

According to the invention, the (sulphuric acid) metatitanic acid may be neutralised particularly with a base, preferably selected from NaOH, ammonia, calcium carbonate, calcium hydroxide, or also $\text{Ba}(\text{OH})_2$, particularly preferably with NaOH.

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The neutralised metatitanic acid obtained thereby is preferably washed with water until it reaches a conductivity of not more than 500 $\mu\text{S}/\text{cm}$ in the filtrate, and the washed digestion cake is then placed in suspension or dispersed, preferably with a stirrer, particularly preferably with a dissolver.

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The intensive stirring or dispersion of the "titanium oxide suspension" carried out preferably with the aid of a turbine stirrer, dissolver, torus mill, mill pump, gradient pump, batch bead mill or rotor-stator disperser (e.g., ULTRA-TURRAX manufactured by IKA).

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The percentage by weight figures given in this description refer according to the invention to the total weight of the powdered, inorganically post-processed titanium oxides according to the invention after it has been dried at 105 °C for at least 120 minutes, and when added together are equal to 100% by weight of the total weight of the material, wherein the optional components are included.

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The titanium oxide particles of the material according to the invention are irregularly shaped, and may be described approximately as spherical. The material is not in the shape of tubes, rods or platelets.

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The Si-containing compound may particularly be a Na_2SiO_3 solution with a SiO_2 concentration of 50– 500 g SiO_2/l , particularly 100 – 500 g SiO_2/l , preferably 200 – 400 g SiO_2/l . The Si-containing compound is preferably added as follows: a Si-containing solution, e.g., in the form of Na_2SiO_3 solutions with concentrations of $\text{SiO}_2 = 50 - 500 \text{ g SiO}_2/\text{l}$, is added to the titanium oxide suspension having formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ ($0 < x \leq 1$) during dispersion at a pH value from 3 – 9, preferably pH 4 – 8.5, particularly 4 to 7.5, particularly preferably pH = 4 – 7, most particularly 4.5 to 7, to obtain a $\text{TiO}_2/\text{SiO}_2$ weight ratio of at least 3.

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The powdered titanium oxide-SiO₂ catalyst materials according to the invention obtained thereby may be used according to the invention to manufacture shaped bodies according to the invention with the following process:

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1. Preparing an aqueous titanium oxide-SiO₂ paste from:

- Powdered titanium oxide-SiO₂ catalyst material according to the invention, coated with extrusion aid(s),
- Peptising agents, preferably hydrochloric acid, sulphuric acid, nitric acid, acetic acid, oxalic acid,
- Water, preferably demineralised water, and as optional constituents
 - i. Plasticisers such as cellulose, clay, polyvinyl alcohols, polyethylene glycol, preferably cellulose, particularly preferably tylose
 - ii. Binding agents such as TiO₂ sols, TiOSO₄ solution, alumina, SiO₂-sols or clays, preferably TiO₂ sol, TiOSO₄ solution or AlO(OH) (boehmite or pseudoboehmite)
 - iii. Bases, preferably ammonia or amine-containing compounds
 - iv. Lubricants such as glycerine
 - v. Pore generators such as starch or carbon black

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In this context, the water content in the paste is preferably selected such that the paste can be forced through a nozzle with an outlet cross section from 1 – 5 mm by an extruder (dual auger) at pressures from 1 to 100 bar or up to 200 bar if necessary;

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2. Kneading the paste obtained thereby, e.g. in a double z kneader, typically for 30 – 60 min;

3. Shaping, e.g., extruding the paste to produce shaped bodies such as ropes having a diameter from e.g. 1-5 mm and a length typically of 10 – 25 mm;

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4. Drying the shaped bodies such as extrudates initially at 20 to 30 °C, particularly at 25 °C, for a period of more than 1 hour, particularly more than 6, quite particularly more than 12 hours, then at 80 – 120 °C, preferably at 90 °C, for 60 to 120 min and then calcining at 300 to 600 °C, particularly 350 to 600 °C, particularly preferably 350 °C to 450 °C, particularly at 400 °C, for 1-4 hours.

One or more compounds for coating the surface of the $\text{TiO}_2\text{-SiO}_2$ particles, which compounds evaporate, sublime or decompose, preferably without residue, at temperatures below the conversion temperature from anatase into rutile (915 °C),
5 preferably to below 600 °C, particularly preferably to below 400 °C, may be used as auxiliary shaping agents. The extrusion aid supports shaping and can be left between and/or on the particles of the powdered catalyst material, and have a beneficial effect during a kneading step, and preferably help to keep the particles in the powdered catalyst materials separate. In this way, substances may be
10 added as extrusion aids which primarily promote the formation of a plastic mass during kneading and then also support the mechanical stability of the moulded body when it is shaped. These extrusion aids are removed during calcining, and it is preferable if they are removed completely.

15 The extrusion aid may preferably be an organic hydrocarbon compound which may contain at least one functional group selected from hydroxy, carboxy, amino, imino, amido, ester, sulfonyl, keto, and the thioanalogues thereof or several different substances from said groups, and which evaporates, decomposes or sublimates at temperatures below the temperature at which anatase is converted
20 into rutile (915 °C), preferably to below 600 °C, particularly preferably to below 400 °C, for example during production of the titanium dioxide shaped body according to the invention. A low-molecular organic hydrocarbon compound with at least one functional group and containing one or more oxygen atoms, for example hydroxy, carboxy is preferred. For the purposes of the present invention, a low-molecular
25 organic hydrocarbon compound is understood to be a hydrocarbon compound having one to twelve carbon atoms, and which has one of the substituent groups selected from hydroxy, carboxy, amino, imino, amido, imido, ester, sulfonyl, keto, and thioanalogues thereof, particularly hydroxy and carboxy.

30 Accordingly, the extrusion aid may be an acid, a base, an alkanol amine or some other substance which evaporates, decomposes or sublimates during calcining of the titanium dioxide shaped body according to the invention at temperatures below

the temperature at which anatase is converted into rutile (915 °C), preferably to below 600 °C, particularly preferably below 400 °C.

The extrusion aid is preferably an organic acid, particularly preferably a carboxylic acid, particularly having one to six carbon atoms, including a di- and tricarboxylic acid, particularly preferably acetic acid, oxalic acid, tartaric acid, maleic acid or citric acid, particularly oxalic acid. Nitric acid, ammonia, alkanol amine or an ammonia-releasing compound may also be used preferably as an extrusion aid. Equally, carbohydrates such as cellulose, cellulose ether, tylose, glucose, polyacryl amine, polyvinyl alcohol, stearic acid, polyethylene glycol or mixtures thereof may also be used as extrusion aids. After the evaporation, sublimation or decomposition of the extrusion aid, the shaped body according to the invention has a residual carbon content of less than 2 % by weight, preferably less than 1% by weight, relative to the weight of the shaped body after calcining.

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The shaped bodies produced from the catalyst materials according to the invention typically have the following properties:

- Crushing strength of > 5 N/mm, particularly > 8 N/mm, preferably > 10 N/mm, particularly preferably > 15 N/mm, most particularly preferably > 25 N/mm;
- 20 - Spec. surface area of > 80 m²/g, particularly > 100 m²/g, preferably > 120 m²/g, particularly preferably > 150 m²/g, most particularly preferably > 200 m²/g;
- N₂ pore volumes of > 0.2 cm³/g, preferably > 0.3 cm³/g, particularly preferably > 0.6 cm³/g;
- A specific total surface area per volume of more than 100,000 m²/l, preferably
25 more than 120 000 m²/l.

The shaped bodies according to the invention produced from the catalyst materials according to the invention may be used according to the invention as catalysts or catalyst supports for catalytically active metals such as V, W, Co, Mo, Ni, Fe, Cu, Cr, Ru, Pd, Pt, Ag, Zn for applications in the field of

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- photocatalysis
- Claus catalysis
- Claus Tail gas treatment

- SCR-, hydrotreating-, gas-to-liquid-, Fischer-Tropsch process etc..

Such a loaded titanium oxide-containing shaped body according to the invention typically has a content of 10 – 35% by weight Mo, 0 to 6% by weight Co and/or Ni, each calculated as the metal oxide (MoO_3 , CoO and NiO), and a content of titanium oxide having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ with $0 < x \leq 1$, particularly $0.1 < x \leq 1$, and SiO_2 , up to 100% by weight, and a specific surface area of at least $80 \text{ m}^2/\text{g}$, particularly at least $100 \text{ m}^2/\text{g}$ and a pore volume of more than $0.25 \text{ cm}^3/\text{g}$ preferably more than $0.27 \text{ cm}^3/\text{g}$, wherein the percentages by weight are relative to the total weight of the loaded titanium oxide-containing shaped body. The MoO_3 content of such a loaded titanium oxide-containing shaped body according to the invention may particularly be 18 – 30% by weight. The average pore size of such a loaded titanium oxide-containing shaped body according to the invention may be 7 to 15 nm.

The present invention will be explained in greater detail in the following experimental section, including the production examples according to the invention and comparison examples.

Methods

Determination of average particle size

In order to determine the average particle size of titanium oxide having the general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ wherein $0 < x \leq 1$, the aqueous "titanium oxide suspension" is first diluted in a solution of 1 g calgon/l deionised water to obtain a concentration of approximately 0.4 g TiO_2 in 60 ml solution. The "titanium oxide suspension" diluted in this way is then dispersed by stirring for 5 min in an ultrasonic bath (e.g., Sonorex Super RK106, manufactured by Bandelin) and then dispersing for 5 min with an ultrasonic probe (Sonifier W-450 manufactured by Branson with gold booster for amplitude amplification and 3/4 inch high-performance resonator). The particle size distribution is determined using a photon correlation spectrometer with Zetasizer Advanced Software, e.g., Zetasizer 1000HSa, manufactured by Malvern. A measurement with multimode calculation is taken at a measurement

temperature of 25 °C. The d_{50} value for the volume distribution, corresponding to the mass distribution taking into account the density is given as the average particle size d_{50} .

5 Determination of phase and crystallite size according to Scherrer

An X-ray diffractogram is recorded to determine the crystal modification (phase identification). For this, the intensities of the X-ray beams diffracted according to Bragg's law at the lattice planes of a crystal are measured against diffraction angle 2θ . The X-ray diffraction pattern is typical for a phase.

10

Performance and evaluation

The material to be investigated is spread on the preparation support with the aid of an object support. The powder diffractometry data is evaluated using the JCPDS powder diffractometry database. The phase is identified when the measured
15 diffraction diagram matches the stored line pattern.

The measurement conditions are typically: $2\theta = 10^\circ - 70^\circ$, measured in increments of $2\theta = 0.02^\circ$, measurement time per stop: 1.2 s.

The size of the crystallites is determined from the peak width at half height of the
20 anatase reflex at 2θ of 25.3° using the Scherrer method according to the following formula:

$$D_{\text{crystallite}} = K \cdot l / (S \cdot \cos(\theta))$$

wherein:

D crystallite: Crystallite size [nm]

25 K: Shape constant = 0.9

θ : Angular position of the measurement reflex $2\theta/2$

S: Peak width at half height of the measurement reflex

l: Wavelength of the X-ray beam used.

30 Determination of silicon calculated as SiO_2

Weighing in and digestion of the material with sulphuric acid/ammonium sulphate, followed by dilution with distilled water, filtration and washing with sulphuric acid. Then, incineration of the filter and gravimetric determination of the SiO_2 content.

Determination of titanium calculated as TiO_2

Digestion of the material with sulphuric acid/ammonium sulphate or potassium sulphate. Reduction with Al to Ti^{3+} . Titration with ammonium iron-III-sulphate.

5 (Indicator: NH_4SCN)

Calculation of the $\text{TiO}_2/\text{SiO}_2$ ratio

The concentrations of Ti and Si, calculated as TiO_2 and SiO_2 , in the sample are determined as described above. Then, the $\text{TiO}_2/\text{SiO}_2$ ratio is determined by
10 dividing the calculated TiO_2 content by the calculated SiO_2 content.

Determination of the specific surface area (multipoint method) and analysis of the pore structure using the nitrogen – gas sorption process (N_2 porosimetry)

The specific surface area and the pore structure (pore volume and pore diameter)
15 are calculated by N_2 porosimetry using the Autosorb 6 or 6B device manufactured by Quantachrome GmbH. The BET surface area (Brunnauer, Emmet and Teller) is determined in accordance with DIN ISO 9277, the pore distribution is measured in accordance with DIN 66134.

20 Sample preparation (N_2 porosimetry)

The sample weighed into the measurement cell is pre-dried in a vacuum at the baking station for 16 h. Then it is heated up in a vacuum to 180 °C in about 30 min. The temperature is then maintained for one hour, still in a vacuum. The sample is considered to be sufficiently degassed when a the degasser records a
25 steady pressure of 20 – 30 millitorr and the needle of vacuum display remains stable for about 2 minutes after the vacuum pump has been disconnected.

Measurement / evaluation (N_2 porosimetry)

The entire N_2 isotherm is measured using 20 adsorption points and 25 desorption
30 points. The measurements were evaluated as follows:

Specific Surface area (multipoint BET)

5 measurement points in the evaluation range from 0.1 to 0.3 p/p0

Evaluation of total pore volume

Determination of the pore volume according to the Gurvich rule

(Determination using the last adsorption point)

5

The total pore volume is determined in accordance with DIN 66134 on the basis of the Gurvich rule. According to the Gurvich rule, the total pore volume of a sample is determined from the last pressure point during the adsorption measurement:

p. Pressure of the sorption agent

10 p0. Saturation steam pressure of the sorption agent

Vp. Specific pore volume according to the Gurvich rule (the total pore volume at $p/P_0 = 0.99$) Practically the last adsorption pressure point reached during measurement.

15 Evaluation of average pore diameters (hydraulic pore diameter)

For this calculation, the relationship $4V_p/A_{\text{BET}}$ is used, corresponding to the "Average Pore Diameter". A_{BET} specific surface area according to ISO 9277.

Method for determining photocatalytic activity

20 Photoactivity can be determined from the photocatalytic decomposition of organic substances in the gas phase, such as methanol or chloroform, and the determination of photoactivity is carried out for exemplary purposes in 90 mm diameter dishes. 50 mg of the powder sample and 100 mg barium sulphate blanc fixe XR-HN (commercial product manufactured by Sachtleben Chemie GmbH) are
25 dispersed by ultrasound with stirring in 40 ml purified water in a beaker and poured all at once into the petri dish. The suspension is evaporated to complete dryness at 50 °C in a vacuum. After the drying, an evenly distributed layer of powder must remain. The powder sample prepared in this way is conditioned for 10 hours under UV light with an irradiance value of about 10W/m².

30

To determine photocatalytic activity, the powder sample is placed in the gas reactor of a gas photocatalysis unit (e.g., by Ansyco) with a UV lamp ($E = 5 - 40 \text{ W/m}^2$) and a connected gas chromatograph (with split/splitless injector and FID

and PDD detector, control unit and amplifier, for example "Trace GC Ultra"). The illumination strength has been set to 7 W/m² beforehand and checked using a UV measuring instrument (e.g., PCE-UV34). After the sample has been installed, an overpressure of 0.6 bar is set, and the system is flushed with synthetic air (50% rel. humidity) for 10 min. After flushing, a gas flow of 100 l/h is set, the overpressure is lowered to 0 bar, and the system is left for 5 minutes to stabilise at this setting. Afterwards, 1.0 µl chloroform (equivalent to 12.4 µmol) is injected through the heated septum. The chromatogram measurement is carried out every 7 minutes. Irradiation is not started immediately, to allow the test gas to reach adsorption/desorption equilibrium, i.e. until the content of the test gas deviates from the average by not more than 0.2 µmol for four consecutive measurements. After this equilibrium has been established, irradiation with the UV lamp is begun. Then, a GC measurement of the chloroform content in the reactor is taken every 7 minutes. The GC was calibrated for chloroform beforehand.

The specific photocatalytic decomposition rate in mmol/(h*m²) is determined by means of a linear regression based on the data for 0 and 7 min. The specific decomposition rate is calculated as follows:

$$spec.decomp.rate = \frac{\Delta n(Substance)}{\Delta t \cdot A(sample)}$$

Method for determining the isoelectric point

The isoelectric point of particles is defined as the pH value at which the zeta potential is zero. In this context, the zeta potential is the electrical potential (also called Coulomb potential) at the interfacial layer of a moving particle in a suspension. The electrophoretic mobility is measured in a "PA Field ESA device" with titration unit. The pressure amplitude of ultrasound waves that are created when electrostatically charged particles are exposed to an electrical alternating field in a frequency range of about 0.8 – 1.2 MHz is measured.

The following equation applies: $ESA = c \cdot \phi \cdot \Delta p \cdot \mu$

wherein:

ESA = Electrokinetic Sonic Amplitude (Signal pressure amplitude)

c = Speed of sound in the solution

ϕ = Volume fraction of the particles
 $\Delta\rho$ = Density difference between particles and solution
 μ = Electrophoretic mobility

5 To prepare the sample, the powder is first mixed with demineralised water by vigorous shaking in a flask (2% by vol. powder). The PA Field ESA device is used to measure the ESA signal of the suspended particles as a function of the pH value of the suspension. For this, the suspension is titrated with hydrochloric acid ($c(\text{HCl}) = 1 \text{ mol/l}$) and ($c(\text{NaOH}) = 1 \text{ mol/l}$). The zeta potential can be calculated
10 from the electrophoretic mobility. For aqueous and solvent-containing systems, this is done by the "PA Field ESA Software". Electrophoretic mobility is plotted against the pH value. The isoelectric point corresponds to the pH value at which electrophoretic mobility is equal to zero.

15 Examples

Comparison example 1 (VB1):

Titanium dioxide in the anatase modification with a specific surface area of about $330 \text{ m}^2/\text{g}$, a pore volume of about $0.3 \text{ cm}^3/\text{g}$ and a sulphate content of about 1.5% by weight/ TiO_2 .

20

Comparison example 2 (VB2)

833 mL metatitanic acid (from Sachtleben Chemie GmbH) with a titanium dioxide content of $300 \text{ g TiO}_2/\text{l}$ was placed in a 2 l glass beaker. 67.6 mL water glass ($360 \text{ g SiO}_2/\text{L}$) was added at a metered rate of 2.0 mL/min while stirring. Then, the pH
25 value was determined at $4.5/21^\circ\text{C}$. The suspension was stirred for 5 min longer and neutralised to $\text{pH } 6.5/24^\circ\text{C}$ with caustic soda, wherein 400 ml partially demineralised water was added at $\text{pH} = 5.0$. The suspension was heated to 60°C and allowed to mature at this temperature for 1 hour with stirring. The suspension was filtered through a Büchner funnel and washed. In the last wash filtrate, a
30 conductivity of $40 \mu\text{S/cm}$ was measured. The washed filter cake was dried at a temperature of 150°C for four hours in a drying cabinet with forced air convection and then ground in the IKA laboratory mill for 10 s.

Comparison example 3 (VB3)

500 mL partially demineralised water was provided in a 5 L glass beaker and stirred with a dissolver, Dispermat LL30, and a dissolver disc with a diameter of 6 cm. To bring about precipitation, the educts 1.92 L titanyl sulphate solution (HOMBITYL, $c(\text{TiO}_2) = 112 \text{ g/L}$), 108 mL Na-silicate solution ($c(\text{SiO}_2) = 200 \text{ g/L}$) and 2.47 L ammonia solution ($w(\text{NH}_3) = 15 \%$) were added to the water feed while stirring within 190 minutes, and the pH value was maintained in the range $\text{pH} = 5\text{-}6$ during precipitation. Precipitation was begun with a rotating speed of 700 rpm and increased to 1000 rpm as the volume of precipitate rose. At the end of the precipitation, a pH value of 5.4 was measured at 45°C in the precipitation suspension. The precipitation suspension was heated to 80°C with stirring and allowed to mature for 1 hour at this temperature for 1 h. The pH value of the precipitation suspension was then determined at $4.8/80^\circ\text{C}$ and adjusted with dilute sulphuric acid (20%) to $\text{pH } 4.25/80^\circ\text{C}$. The suspension was filtered through a Büchner funnel and the filter cake was washed. After washing, a conductivity of $342 \mu\text{S/cm}$ was found in the filtrate. The washed filter cake was dried overnight at a temperature of 150°C in the drying cabinet then ground in the IKA laboratory mill for 10 s.

Example according to the invention 1 (EB 1):

A "titanium oxide suspension" with an average particle size of 50 nm and a TiO_2 content of $50 \text{ g TiO}_2/\text{l}$ was used as the feedstock. 6 l of the "titanium oxide suspension" was dispersed for 15 minutes using a dissolver. The pH value of the suspension was adjusted to $\text{pH} = 6.5$ with dilute caustic soda. Then, 34 ml of a Na-silicate solution with ($350 \text{ g SiO}_2/\text{l}$) was added to the titanium oxide suspension within 15 minutes while the dissolver dispersion continued. The suspension was matured for 60 min at 60°C with vigorous stirring. Then, the suspension was filtered, washed and spray dried.

Example according to the invention 2 (EB 2):

A "titanium oxide suspension" with an average particle size of 50 nm and a TiO_2 content of $50 \text{ g TiO}_2/\text{l}$ was used as the feedstock. 6 l of the "titanium oxide suspension" was dispersed for 30 minutes in a torus mill (manufacturer Getzman). The pH value of the suspension was adjusted to $\text{pH} = 7.5$ with dilute caustic soda.

Then, 68 ml of a Na-silicate solution with (350 g SiO₂/l) was added to the titanium oxide suspension within 30 minutes while dispersion continued. The suspension was matured for 60 min at 60 °C with vigorous stirring. Then, the suspension was filtered, washed and spray dried.

5

Example according to the invention 3 (EB 3):

A "titanium oxide suspension" with an average particle size of 50 nm and a TiO₂ content of 50 g TiO₂/l was used as the feedstock. 6 l of the "titanium oxide suspension" was dispersed for 15 minutes in a rotor-stator dispersion unit (ULTRA-TURRAX by IKA). The pH value of the suspension was adjusted to pH = 7.5 with dilute caustic soda. Then, 100 ml of a Na-silicate solution with (350 g SiO₂/l) was added to the titanium oxide suspension within 20 minutes while dispersion continued. The suspension was matured for 60 min at 60 °C with vigorous stirring. Then, the suspension was filtered, washed and spray dried.

15

Example according to the invention 4 (EB 4):

A "titanium oxide suspension" with an average particle size of 50 nm and a TiO₂ content of 100 g TiO₂/l was used as the feedstock. 1.5 l of the "titanium oxide suspension" was dispersed for 15 minutes using a dissolver. The pH value of the suspension was adjusted to pH = 6.0 with dilute caustic soda. Then, 15.9 ml of a Na-silicate solution with (378 g SiO₂/l) was added to the titanium oxide suspension within 15 minutes while dissolver dispersion continued. The suspension was matured for 30 min at 60 °C with vigorous stirring. Then, the suspension was filtered, washed and spray dried.

25

Example according to the invention 5 (EB 5):

A "titanium oxide suspension" with an average particle size of 50 nm and a TiO₂ content of 100 g TiO₂/l was used as the feedstock. 1.5 l of the "titanium oxide suspension" was dispersed for 15 minutes using a dissolver. The pH value of the suspension was adjusted to pH = 6.0 with dilute caustic soda. Then, 31.8 ml of a Na-silicate solution with (378 g SiO₂/l) was added to the titanium oxide suspension within 15 minutes while dissolver dispersion continued. The suspension was

30

matured for 30 min at 60 °C with vigorous stirring. Then, the suspension was filtered, washed and spray dried.

The structural properties as well as the thermal stability and photocatalytic activity of the powders according to the invention and of the comparison examples are listed in Table 1.

According to the prior art, SiO₂-stabilised titanium dioxides are known which have (acceptable) specific surface areas of about 200 m²/g after thermal aging (see e.g., comparison examples 2 and 3). However, the photocatalytic activity of these products is very low (chloroform decomposition rate not more than 0.1 mmol/h*m²). The poor photocatalytic activity is presumably due to the fact that the surface of the photocatalytically active titanium dioxide is covered by inactive SiO₂ and at the same time associated with relatively low IEPs (3.8 – 4.4).

Pure titanium dioxide such as the commercially available product used for VB1 demonstrates acceptable photocatalytic decomposition rates, but these titanium dioxides are not thermally stable. The specific surface area of these products is in a range of just 80 – 100 m²/g after 1 hour at 500 °C. Consequently, such materials cannot be used as catalysts or catalyst supports for applications with elevated temperatures.

Only the materials according to the invention combine very high photocatalytic activity (chloroform decomposition rates of > 0.7 mmol/h*m²) with good thermal stability, i.e., specific surface areas equal to or greater than 130 m²/g after thermal treatment for 1 h at 500 °C.

Tab. 1: Powder properties

No.	Material	TiO ₂ /SiO ₂ -ratio	IEP	BET [m ² /g]	BET after aging* [m ² /g]	Pore volume [cm ³ /g]	Avg. pore diameter [nm]	Photocatalytic chloroform Decomp. [mmol/h*m ²]:
VB1	Titanium dioxide in	n.a.	6	350	80	0.3	3.4	0.6

	anatase modification							
VB2	Titanium dioxide in anatase modification, treated with Na-silicate solution	10	4.4	295	222	0.3	4.1	<0.1
VB3	Coprecipitation from TiOSO ₄ , NH ₄ OH, Na-silicate solution	10	3.8	435	197	0.4	3.8	0.1
EB1	Titanium oxide with SiO ₂	25	5.6	350	~ 160	0.8	9.1	2.0
EB2	Titanium oxide with SiO ₂	12.5	5.3	350	~ 220	0.8	9.1	0.9
EB3	Titanium oxide with SiO ₂	8.5	4.8	350	~ 240	0.8	9.1	0.8
EB4	Titanium oxide with SiO ₂	25	5.7	304	~195	0.75	9	n.a.
EB5	Titanium oxide with SiO ₂	12.5	5.4	311	~190	0.7	9	n.a.

*Aging for 1 h at 500 °C

Production of catalyst supports by extrusion

The materials produced in the preceding examples and comparison examples were used to prepare catalyst supports, wherein an extrusion process was implemented using an extrusion aid. Accordingly, a coated powdered catalyst material can be obtained by treating a suspension of particles according to the invention with the extrusion aid or mixtures of several extrusion aids in solution or suspension, and as a result the surface area of the particles according to the invention is coated with the extrusion aid(s) and the coated particles are subsequently extruded to produce shaped bodies.

VB1-E

400 g Hombikat M211 (titanium dioxide, commercial product manufactured by Sachtleben) and 64 g of an aqueous 2.5% tylose solution are placed in the mixing trough of the double z kneader and mixed for about 1 min. Then 60 g of 10% by weight hydrochloric acid is added, and also demineralised water until the kneading mass has a plastic consistency. This mixture is then kneaded for 30 minutes. Subsequently, 20 g ammonia water (25%) and 20 ml demineralised water are

added and the mixture is kneaded for 30 min. The kneading mass is then extruded under pressure of 40 - 70 bar through a 1.8 mm die ("Quadrilobe" shape) and cut to the desired length (approx. 15 – 20 mm). The extrudates produced in this way are air dried and then heated to 90 °C for 60 min, then to the calcining temperature of 400 °C over the course of several hours and maintained at this temperature for 120 min, then cooled to room temperature.

VB2-E

400 g of example 2 and 64 g of an aqueous 2.5% tylose solution is placed in the mixing trough of the double z kneader and kneaded for about 1 min. Then 60 g of 10% by weight hydrochloric acid is added, and also demineralised water until the kneading mass has a plastic consistency (about 70 ml). This mixture is then kneaded for 30 minutes. Subsequently, 20 g ammonia water (25%) and 20 ml demineralised water are added and the mixture is kneaded for 30 min. The kneading mass is then extruded under pressure of 40 - 70 bar through a 1.8 mm die ("Quadrilobe" shape) and cut to the desired length (approx. 15 – 20 mm). The extrudates produced in this way are first air dried and then tempered as described in Example 1.

EB1-E

400 g of the powder of EB1 and 64 g of an aqueous 2.5% tylose solution are placed in the mixing trough of the double z kneader and kneaded for about 1 min. Then the pH value of the kneading mass is adjusted to pH = 1.5 by the addition of hydrochloric acid, and demineralised water is also added until the kneading mass has a plastic consistency. This mixture is then kneaded for 30 minutes. Subsequently the pH value of the kneading mass is adjusted to pH = 5 for the addition of ammonia water (25%) and kneaded for a further 30 minutes. The kneading mass is then extruded under pressure of 20 - 40 bar through a 1.8 mm die ("Quadrilobe" shape) and cut to the desired length (approx. 15 – 20 mm). The extrudates produced in this way are first air dried and then tempered as described in Example 1.

EB2-E and EB3-E

The production of extrudates from the powders of EB2 and EB3 was carried out in similar manner to the extrusion of powder EB1 (EB1-E) described above.

Table 2: Extrudate properties

Example	Spec. surface area (5 point BET) [m ² /g]	Pore volume (Total) [cm ³ /g]	Avg. pore diameter [nm]	Phase	SCS [N/mm]	TBD [g/l]	Total surface area per volume [5 point BET x TBD] [m ² /l]
VB1-E	142	0.3	8	Anatase	30	675	95850
VB2-E	n.b.	n.b.	n.b.	Anatase	n.b.	n.b.	
EB1-E	215	0.59	11	Anatase	13	505	108575
EB2-E	255	0.55	9	Anatase	12	617	157335
EB3-E	260	0.58	9	Anatase	15	576	149760

5

Impregnation

The extrudates produced for extrusion in the examples were intended for impregnation with active metals such as NiMo- and CoMo. For this purpose, in a first step CoMo- and NiMo-containing impregnation solutions were prepared as follows:

10

Preparation of CoMo- or NiMo impregnation solutions

The impregnation solutions were prepared in aqueous solution using corresponding metal compounds such as salts or oxides in the presence of phosphoric acid and the pH thereof was adjusted with nitric acid.

15

Impregnation of the extrudates

For the impregnation 100 g of each of the extrudate were placed in a rotating vessel (e.g., rotary evaporator). The impregnation solution was added slowly (0.5 ml/min) to the extrudates. After the metered addition of the impregnation solution, the impregnated extrudates were aged for 24 h and then first dried at 120 °C and then tempered at 350 °C. After this calcining process, the catalysts are finished. The sulphiding of the Mo species is then carried out in the hydrotreating reactor as part of the "activation procedure".

20

Examination of hydrotreating activity

The catalytic performance of the catalysts with regard to "hydrodesulphurisation" (HDS) and hydrodenitrogenation (HDN) was tested using the example of a vacuum gas oil (VGO) in a 16 chamber "trickle-bed reactor" built by HTE.

Sample preparation

The catalysts were tested as whole extrudates without being reduced in size. For this purpose extrudates with a length of 2-4 mm were selected and placed in reactors with internal diameters of 5 mm. After the reactors were filled with the respective catalyst materials, silicon carbide SiC (size 125 – 160 µm) was added in a catalyst / SiC volume ratio of 1 / 0.65. This bulk catalyst material filled with SiC particles was compacted. The catalyst quantity was selected such that after compacting a reactor volume of 2 ml was filled in each case. The catalyst mass was calculated from the tapped bulk density (TBD) of the catalysts (see Table 3). In all, the reactor has three zones, the upper and lower zones are filled exclusively with SiC particles (125 – 160 µm), the middle zone is filled with the mixture of SiC and catalyst extrudates described above.

Raw materials

A Vacuum Gas Oil (VGO) (*raw material for a mild hydrocracker*) with the following properties was used as the raw material:

Sulphur content: 27075 mg S /kg

Nitrogen content: 968 mg N / kg

Density at 15 °C: 0.9273 g/ml

Density at 70 °C: 0.8919 g/ml

In order to activate the catalysts, a LGO feed (Light Gas Oil) was reacted with dimethyl disulphide (DMDS). The resulting LGO/DMDS mixture had the following properties:

Sulphur content: 24418 mg S /kg

Nitrogen content: 116 mg N / kg

Density at 15 °C: 0.8589/ml

Activation procedure

Before the extrudates coated with metal were investigated with regard to their catalytic properties, they were activated in the test unit described above. The
5 objective of activation is the sulphidisation of the Mo compounds to form catalytically active molybdenum sulphide. To this end, the reactors filled with the catalysts were installed on the test bench and exposed to the LGO/DMDS mixture. In this process, a pressure of 60 bar and a liquid hourly space velocity (LHSV) of 2 h^{-1} were used. The gas-to-oil ratio (H_2 to LGO/DMDS mixture) was 200 standard
10 litres / (h l). For activation, the following temperature profile was used:

1. Wetting with LGO at about 35 °C: 24 h
2. Temperature increase from 35 °C to 150°C in steps of 25°C/h
3. Temperature increase from 150 °C to 250°C in steps of 15 °C/h
4. T = 250 °C for 14 hours until H_2S signal stable
- 15 5. Temperature increase from 250 °C to 320°C in steps of 10 °C/h
6. T = 320 °C for 11 Hours until H_2S signal stable

Test conditions

To investigate the hydrotreating performance of the catalysts, the following test
20 conditions were selected:

1. Pressure: p = 80 bar,
Gas-to-oil ratio: H_2/VGO : 600 NI(H_2)/h/l(VGO),
Liquid hourly space velocity (LHSV): 1.0 [1/h],
Temperature: T = 370 °C , 380 °C, 390 °C
- 25 2. Pressure: p = 120 bar,
Gas-to-oil ratio: H_2/feed : 600 NI(H_2)/h/l(VGO).
Liquid hourly space velocity (LHSV): 1.0 [1/h],
Temperature: T= 400 °C and 385 °C

The various settings were each kept constant for at least three days. The
30 temperature changes were made in increments of 10 °C/h.

Analysis of the vacuum-gas-oil after catalytic treatment

The volatile organic products (C1-C7) and the permanent gases (H₂, H₂S, TCD) were analysed by online gas chromatography. To determine sulphur and nitrogen contents as well as densities, product samples were drawn and analysed offline. The results of the catalytic tests are shown in Table 3.

5

The results shown in Table 3 show that the inventive catalysts result in significantly lower sulphur contents in the treated vacuum-gas-oil. This therefore demonstrates that the catalyst materials according to the invention and the supports coated with active metal produced with the aid thereof and thus also the

10 CoMo- and NiMo catalysts according to the invention exhibit significantly improved catalytic performance in terms of HDS- and HDN activity than the prior art.

Tab. 3: Catalyst properties and catalytic performance

Sample		Metal load			Physical Properties of the Catalysts				Catalytic Performance				
									(Properties of the VGO after "catalytic treatment")				
									390 °C, LHSV 1 h ⁻¹ , 80 bar	400 °C, LHSV 1 h ⁻¹ , 120 bar			
Powder from Example	Charge	MoO ₃ [wt. %]	CoO [wt. %]	NiO [wt. %]	Spec. surf. area (5- pt. BET) [m ² /g]	Pore volume (Total) [cm ³ /g]	Avg. pore size [nm]	TBD [g/l]	S Content in the product [mg/kg]	N Content in the product [mg/kg]	S Content in the product [mg/kg]	N Content in the product [mg/kg]	Product density
VB1	CoMo	24	4.3	-	55	0.14	9	1060	583	127	76	3	0.8333
VB2	CoMo.	24	4.3	-	65	0,09	6	1180	462	109	60	2	0.8313
EB1	CoMo.	24	4.3	-	110	0.36	13	943	70	27	24	1	0.8257
EB2	CoMo.	18	3.6	-	182	0.39	9	871	71	23	24	2	0.8238
EB2	CoMo.	24	4.3	-	119	0.32	11	1008	85	31	25	1	0.8256
EB2	NiMo.	27.0	-	4.7	96	0.28	12.0	1014	64	11	22	0	0.8217
EB3	CoMo.	24	4.3	-	122	0.33	11	950	63	23	21	1	0.8239

Patent claims

1. Powdered catalyst material on titanium oxide basis, having a combined content of at least 90% by weight hydrated titanium oxide having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ with $0 < x \leq 1$, particularly $0.1 < x \leq 1$ (calculated as TiO_2) and silicon dioxide including hydrated precursors thereof (calculated as SiO_2), which has a specific surface area of $> 300 \text{ m}^2/\text{g}$ and an isoelectric point in the range from 4.5 - 5.9, wherein the $\text{TiO}_2/\text{SiO}_2$ weight ratio, determined respectively for TiO_2 and SiO_2 is at least 3, preferably at least 5, and less than 30, preferably less than 25, and the percentages by weight are relative to the total weight of the catalyst material after it has been dried at 105°C for at least 2 hours.
2. Powdered catalyst material on titanium oxide basis according to claim 1, wherein the material has a photocatalytic chloroform decomposition rate of more than $0.3 \text{ mmol}/(\text{h} \cdot \text{m}^2)$, preferably more than $0.5 \text{ mmol}/(\text{h} \cdot \text{m}^2)$.
3. Powdered catalyst material on titanium oxide basis according to claim 1 or 2 having a total pore volume (N_2 desorption) of at least $0.3 \text{ cm}^3/\text{g}$, preferably more than $0.5 \text{ cm}^3/\text{g}$, particularly preferably more than $0.7 \text{ cm}^3/\text{g}$.
4. Powdered catalyst material on titanium oxide basis according to any one of claims 1 to 3, which has a specific surface area of at least $80 \text{ m}^2/\text{g}$, particularly at least $100 \text{ m}^2/\text{g}$, preferably at least $150 \text{ m}^2/\text{g}$ after thermal treatment for 1 h at 500°C under normal atmosphere.
5. Powdered catalyst material on titanium oxide basis according to any one of claims 1 to 4, wherein the isoelectric point is in the range from 4.7 to 5.9.
6. Powdered catalyst material on titanium oxide basis according to any one of claims 1 to 5, wherein the ratio of the height of the most intensive reflex of the anatase structure (reflex (101)) to the height of the most intensive reflex of the rutile structure (Reflex (110)) the height of the most intensive reflex of is at least 5:1, preferably at least 10:1 after deduction of a linear subsurface.

7. Process for preparing the powdered catalyst material on titanium oxide basis according to any one of claims 1 to 6, in which:
- a. An aqueous suspension of titanium oxide hydrate particles having general formula $\text{TiO}_{(2-x)}(\text{OH})_{2x}$ with $0 < x \leq 1$, particularly $0.1 < x \leq 1$, preferably with average particle sizes from 20 – 500 nm is reacted with an Si-containing compound while stirring vigorously, wherein the pH value can be maintained in the range from pH = 3 to 9, particularly 4 to 7 by the optional addition of an acid or alkaline solution,
 - b. Optionally the pH value is adjusted if necessary to the range between 4 and 7,
 - c. The suspension obtained is filtered off, and
 - d. The filter cake obtained is washed with water until the filtrate has a conductivity not more than 500 $\mu\text{S}/\text{cm}$.
8. Process according to claim 7, in which a Na_2SiO_3 solution with a SiO_2 concentration of 100 – 500 g SiO_2/l , preferably 200 – 400 g SiO_2/l , is used as the Si-containing compound.
9. Process according to claim 7 or 8, in which the pH value of the titanium oxide suspension is adjusted to pH values from 4.0 to 8.5, preferably 4.0 to 7.5, particularly preferably 4.0 to 7.0, by the optional addition of an acid or alkaline solution before the addition of the Si containing solution, and is preferably maintained at the previously set pH value during the addition of the Si containing solution.
10. Use of the powdered catalyst material according to any one of claims 1 to 6 for preparing shaped bodies, particularly for catalytic application or as a support for catalytically active metals for application in the field of catalysis such as photocatalysis, Claus catalysis, Claus-Tail-Gas-treatment, SCR, Hydrotreating, Gas-to-Liquid-Process, Fischer-Tropsch-Process.

11. Shaped bodies on a titanium oxide basis with content of powdered catalyst material according to any one of claims 1 to 6 with a specific surface area of > 80 m²/g, particularly > 100 m²/g, preferably > 120 m²/g, particularly preferably > 150 m²/g, most particularly preferably > 200 m²/g.
12. Shaped bodies according to claim 11 with a pore volume (N₂, Total) of more than 0.2 cm³/g, preferably more than 0.3 cm³/g, particularly more than 0.5 cm³/g, more preferably more than 0.55 cm³/g, most particularly preferably more than 0.6 cm³/g.
13. Shaped bodies according to claim 11 or 12 with a specific total surface area per volume of more than 100 000 m²/l, preferably more than 120 000 m²/l.
14. Use of the titanium oxide-containing shaped bodies according to any one of claims 11 to 13 as a catalyst or support for catalytically active metals for application in the field of catalysis such as photocatalysis, Claus catalysis, Claus-Tail-Gas-treatment, SCR, Hydrotreating, Gas-to-Liquid-Process, Fischer-Tropsch-Process.
15. Titanium oxide-containing shaped bodies according to any one of claims 11 to 13, having a content of 10 – 35 % by weight Mo, 0 to 6 % by weight Co and/or Ni, calculated as metal oxide (MoO₃, CoO and NiO), and the rest up to 100% by weight of titanium oxide with the general formula TiO_(2-x)(OH)_{2x} wherein 0 < x ≤ 1, particularly 0.1 < x ≤ 1 and SiO₂, and which have a specific surface area of at least 80m²/g, particularly at least 100 m²/g and a pore volume of more than 0.25 cm³/g preferably more than 0.27 cm³/g, wherein the percentages by weight are relative to the total weight of the charged titanium oxide-containing shaped bodies.
16. Titanium oxide-containing shaped bodies according to claim 15 wherein the MoO₃ content is 18 – 30 % by weight.

17. Titanium oxide-containing shaped bodies according to claim 15 or 16, wherein the average pore size is 7 – 15 nm.