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(54) Title: TITANIUM-ZIRCONIUM MIXED OXIDE POWDER

(57) Abstract: Titanium-zirconium mixed oxide powder in the form of aggregated primary particles, which powder has a content of titanium dioxide of from 40 to 97 wt. % and a content of zirconium dioxide of from 3 to 60 wt.%, wherein the sum of the contents of titanium dioxide and zirconium dioxide is at least 99.7 wt.% and wherein the contents are in each case based on the total amount of powder, and which exhibits reflections of titanium dioxide modifications and does not exhibit reflections of monoclinic, tetragonal and cubic zirconium dioxide in X-ray diffraction analysis. It is prepared by transporting into a mixing chamber a starting compound, in vapour form, for the first mixed oxide component by means of primary air and a starting compound, in vapour form, for the second mixed oxide component by means of an inert gas, mixing the mixture with hydrogen in a mixing chamber and burning it into a reaction chamber. It can be used as a catalyst support.



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Titanium-zirconium mixed oxide powder

The invention relates to a titanium-zirconium mixed oxide powder and its use, and to a process for the preparation of titanium-zirconium mixed oxide powders.

5 DE-A-3611449 discloses a titanium-zirconium mixed oxide powder which comprises at least 5 wt.% of a mixed oxide component. The mixed oxide powder is obtained by a process of flame hydrolysis, in which anhydrous zirconium tetrachloride is transported by means of an inert gas into
10 a mixing chamber and is there mixed with hydrogen, air and titanium tetrachloride, and the mixture is burnt in a reaction chamber. The mixed oxide powder so prepared exhibits reflections of zirconium dioxide, titanium dioxide and zirconium titanate phases in X-ray diffraction
15 analysis. The mixed oxide powder can be used as a catalyst support.

The object of the invention is to provide a titanium-zirconium mixed oxide powder which, compared with the prior art, exhibits greater thermal stability than catalyst
20 supports.

A further object of the invention is to provide a process for the preparation of titanium-zirconium mixed oxide powders.

The invention provides a titanium-zirconium mixed oxide
25 powder in the form of aggregated primary particles, which powder

- has a content of titanium dioxide of from 40 to 97 wt.% and a content of zirconium dioxide of from 3 to 60 wt.%, wherein the sum of the contents of titanium dioxide and
30 zirconium dioxide is at least 99.7 wt.% and wherein the contents are in each case based on the total amount of powder,

- exhibits reflections of titanium dioxide modifications and does not exhibit reflections of monoclinic, tetragonal and cubic zirconium dioxide in X-ray diffraction analysis.

5 The titanium-zirconium mixed oxide powder according to the invention is in the form of aggregates of primary particles. The primary particles are not porous. The surfaces of these primary particles have hydroxyl groups.

Mixed oxide powder is to be understood as meaning a powder
10 in which intimate mixing of titanium dioxide and zirconium dioxide at primary particle or aggregate level is to be understood. The primary particles exhibit Zr-O-Ti bonds. In addition, areas of zirconium dioxide can also be present in the primary particles in addition to titanium dioxide.

15 The titanium-zirconium mixed oxide powder according to the invention exhibits rutile and anatase as titanium dioxide modification. The reflections of monoclinic ZrO_2 at 2 theta = 28.2° , tetragonal ZrO_2 at 2 theta = 30.1° , 49.7° and 59.7° and cubic ZrO_2 at 2 theta = 30.5° , 50.6° , 35.1° and 60.4° are
20 not detectable.

The content of the titanium dioxide modification rutile in the titanium-zirconium mixed oxide powder according to the invention can preferably be at least 5 wt.%, particularly preferably at least 20 wt.%, based on the sum of rutile and
25 anatase.

In the case of a zirconium dioxide content of more than 40 wt.%, the X-ray diffraction analysis can exhibit the reflections of titanium-zirconium mixed phases.

The BET surface area, determined in accordance with
30 DIN 66131, can preferably be from 10 to $200 \text{ m}^2/\text{g}$ and particularly preferably from 40 to $120 \text{ m}^2/\text{g}$.

The invention further provides a process for the preparation of titanium-zirconium mixed oxide powders, in which

- as starting compound for the first mixed oxide component,
5 a titanium compound or zirconium compound in vapour form is transported by means of primary air into a mixing chamber, wherein the primary air, which can optionally be enriched with oxygen and/or preheated, is supplied in such an amount that at least 50 % of the starting
10 compounds for the first and second mixed oxide components can be converted into the oxides thereby, corresponding to a $\lambda_{(pr)}$ value of at least 0.5, and
- as starting compound for the second mixed oxide component, a zirconium compound or titanium compound in
15 vapour form is likewise transported into the mixing chamber, separately from the starting compound for the first mixed oxide component, by means of an inert carrier gas,
- wherein the amounts of the titanium compounds and
20 zirconium compounds in vapour form that are used are so chosen that the mixed oxide powder has a content of titanium dioxide of from 40 to 97 wt.% and a content of zirconium dioxide of from 3 to 60 wt.%,
- hydrogen is introduced into the mixing chamber separately
25 from the titanium compounds and zirconium compounds in vapour form, and the mixture of titanium compounds and zirconium compounds in vapour form, hydrogen and primary air is ignited in a burner and the flame burns into a reaction chamber,
- 30 - the solid is then separated from gaseous substances, and
- the solid is then treated with steam at temperatures of from 250 to 700°C,
- wherein, in the case where $\lambda_{(pr)}$ is less than 1.0, an amount of secondary air is added to the reaction chamber
35 to give a value of $\lambda_{(pr+sec)}$ of at least 1.0, and

- wherein γ is ≥ 1 .

An important feature of the process according to the invention is that the starting compound for the first mixed oxide component and at least 50 % of the air that is
5 necessary stoichiometrically in order to convert the starting compounds for the first and second mixed oxide components into the mixed oxide powder according to the invention are introduced into the mixing chamber together.

A further important feature is that the starting compound
10 for the second mixed oxide component is transported into the mixing chamber by means of an inert gas.

It is possible for both the titanium compound and the zirconium compound to be introduced into the burner with the primary air. It has proved advantageous for the metal
15 compound that is greater in terms of amount to be introduced into the mixing chamber with the primary air.

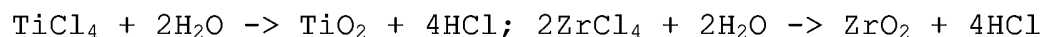
It is also important that, if the air introduced into the mixing chamber is not sufficient to convert the starting compounds completely into the mixed oxide powder according
20 to the invention, secondary air is introduced into the reaction chamber.

It is also important that the γ value is ≥ 1 , preferably from 1 to 6.

Figure 1 shows the process according to the invention in
25 diagrammatic form. In the figure: a = titanium or zirconium compound in vapour form; a_1 = primary air; b = zirconium or titanium compound in vapour form; b_1 = inert gas; c = hydrogen; d = secondary air; I = mixing chamber; II = reaction chamber.

30 The titanium compounds and zirconium compounds in vapour form are converted into the corresponding metal oxide either by hydrolysis or by oxidation. Suitable compounds may be halides, nitrates, alcoholates and/or carboxylates.

Hydrolysis can be illustrated with reference to the compounds titanium tetrachloride and zirconium tetrachloride, which are preferably used, as follows, the water originating from the reaction of the (atmospheric) oxygen with hydrogen:



Gamma and lambda are defined as follows:

gamma = H_2 supplied / H_2 required stoichiometrically,

lambda = O_2 supplied / O_2 required stoichiometrically.

10 Lambda includes the total amount of oxygen introduced from the primary air and the secondary air.

The process according to the invention can preferably be carried out in such a manner that $\lambda_{(\text{pr})}$ is from 0.7 to 2.

In the process according to the invention, secondary air can be introduced into the reaction chamber regardless of whether $\lambda_{(\text{pr})}$ is less than 1. Preferably, $\lambda_{(\text{pr} + \text{sec})}$ is from > 1 to 7, particularly preferably $\lambda_{(\text{pr} + \text{sec})}$ is from 1.2 to 4.

The invention relates also to the use of the titanium-zirconium mixed oxide powder as a catalyst support.

Examples:

Example 1:

1.63 kg/h of TiCl_4 are vaporised. The vapours are transported into a mixing chamber by means of primary air (3.08 Nm^3/h). Separately therefrom, 0.11 kg/h of ZrCl_4 are vaporised and are likewise transported into the mixing chamber, by means of nitrogen. Separately from the titanium tetrachloride and the zirconium tetrachloride, 0.30 Nm^3/h of hydrogen are introduced into the mixing chamber. In a central pipe, the reaction mixture is fed to a burner and ignited. The flame thereby burns into a water-cooled reaction chamber. 0.30 Nm^3/h of secondary air are additionally introduced into the reaction chamber. The powder that forms is separated off in a downstream filter and then treated countercurrently with air and steam at about 700°C.

Examples 2 to 5 are carried out analogously to Example 1. The amounts of the substances used and the physico-chemical values of the powders in each case are shown in Table 1.

The powders of Examples 1 to 3 exhibit only the reflections of titanium dioxide modifications in the X-ray diffraction diagram, but not reflections of zirconium dioxide modifications. The powders of Examples 4 and 5 additionally exhibit reflections of titanium-zirconium mixed phases, namely Ti_2ZrO_6 and ZrTiO_4 .

Table 2 shows the behaviour of the BET surface area of the powders according to the invention of Examples 1, 2 and 4 compared with Aerioxide® TiO_2 P 25, BET surface area 45 m^2/g (Degussa) and a zirconium dioxide sample (VP ZrO_2 , BET surface area 52 m^2/g), on thermal loading.

The Examples show that the powders according to the invention exhibit a high stability of the BET surface area on thermal loading.

Table 1: Substances and amounts used; physico-chemical values of the titanium-zirconium mixed oxide powders

Example		1	2	3	4	5
TiCl ₄	kg/h	1.63	1.65	1.44	0.83	0.96
ZrCl ₄	kg/h	0.11	0.19	0.30	0.68	0.75
Hydrogen	Nm ³ /h	0.30	0.70	0.30	0.70	0.30
Primary air	Nm ³ /h	3.08	2.35	3.08	2.25	3.08
Secondary air	Nm ³ /h	0.30	0	0	0.10	0.10
gamma		1.29	1.88	1.32	2.44	1.42
lambda _(pr)		2.46	1.23	2.46	1.18	2.46
lambda _(pr + sec)		2.69	1.23	2.46	1.23	2.54
ZrO ₂ content	wt. %	7.9	10.0	19.9	45.3	49.6
TiO ₂ content	wt. %	91.9	89.8	80.0	55.0	50.4
Chloride content	wt. %	0.01	0.02	0.01	0.015	0.01
Rutile	%	36	55	39	7	5
BET	m ² /g	62	49	57	52	73
pH		2.10	2.19	5.66	2.20	1.88

Table 2: Stability of the BET surface area on thermal treatment

5

		BET surface area [m ² /g]	
Powder	ZrO ₂ content [wt. %]	after 3h 600°C	after 3h 1000°C
TiO ₂ P 25	0	41	1
Example 1	7.9	56	8
Example 2	10.0	43	4
Example 4	45.3	44	7
ZrO ₂	100	38	13

Patent claims:

1. Titanium-zirconium mixed oxide powder in the form of aggregated primary particles, characterised in that
 - it has a content of titanium dioxide of from 40 to 97 wt.% and a content of zirconium dioxide of from 3 to 60 wt.%, wherein the sum of the contents of titanium dioxide and zirconium dioxide is at least 99.7 wt.% and wherein the contents are in each case based on the total amount of powder,
 - it exhibits reflections of titanium dioxide modifications and no reflections of monoclinic, tetragonal and cubic zirconium dioxide in X-ray diffraction analysis.
2. Titanium-zirconium mixed oxide powder according to claim 1, characterised in that the content of the titanium dioxide modification rutile is at least 5 wt.%, based on the sum of rutile and anatase.
3. Titanium-zirconium mixed oxide powder according to claim 1, characterised in that, in the case of a zirconium dioxide content of more than 40 wt.%, it exhibits the reflections of titanium-zirconium mixed phases in X-ray diffraction analysis.
4. Titanium-zirconium mixed oxide powder according to claim 1 or 2, characterised in that the BET surface area is from 10 to 200 m²/g.
5. Process for the preparation of titanium-zirconium mixed oxide powders, characterised in that
 - as starting compound for the first mixed oxide component, a titanium compound or zirconium compound in vapour form is transported by means of primary air into a mixing chamber, wherein the primary air, which can optionally be enriched with oxygen and/or

- preheated, is supplied in such an amount that at least 50 % of the starting compounds for the first and second mixed oxide components can be converted into the oxides thereby, corresponding to a $\lambda_{(pr)}$ value of at least 0.5, and
- 5
- as starting compound for the second mixed oxide component, a zirconium compound or titanium compound in vapour form is likewise transported into the mixing chamber, separately from the starting compound for the first mixed oxide component, by means of an inert carrier gas,

10

 - wherein the amounts of the titanium compounds and zirconium compounds in vapour form that are used are so chosen that the mixed oxide powder has a content of titanium dioxide of from 40 to 97 wt.% and a content of zirconium dioxide of from 3 to 60 wt.%,

15

 - hydrogen is introduced into the mixing chamber separately from the titanium compounds and zirconium compounds in vapour form, and the mixture of titanium compounds and zirconium compounds in vapour form, hydrogen and primary air is ignited in a burner and the flame burns into a reaction chamber,

20

 - the solid is then separated from gaseous substances, and

25

 - the solid is then treated with steam at temperatures of from 250 to 700°C,
 - wherein, in the case where $\lambda_{(pr)}$ is less than 1.0, an amount of secondary air is added to the reaction chamber to give a value of $\lambda_{(pr+sec)}$ of at least

30

 - 1.0, and
 - wherein γ is ≥ 1 .

6. Process for the preparation of the titanium-zirconium mixed oxide powder according to claim 5, characterised in that the metal compounds in vapour form are titanium tetrachloride and zirconium tetrachloride.
- 5 7. Process for the preparation of the titanium-zirconium mixed oxide powder according to claim 5 or 6, characterised in that $\lambda_{(pr)}$ is from 0.7 to 4.
8. Process for the preparation of the titanium-zirconium mixed oxide powder according to claims 5 to 7,
- 10 characterised in that $\lambda_{(pr + sec)}$ is from ≥ 1 to 7.
9. Use of the titanium-zirconium mixed oxide powder according to claims 1 to 4 as a catalyst support.

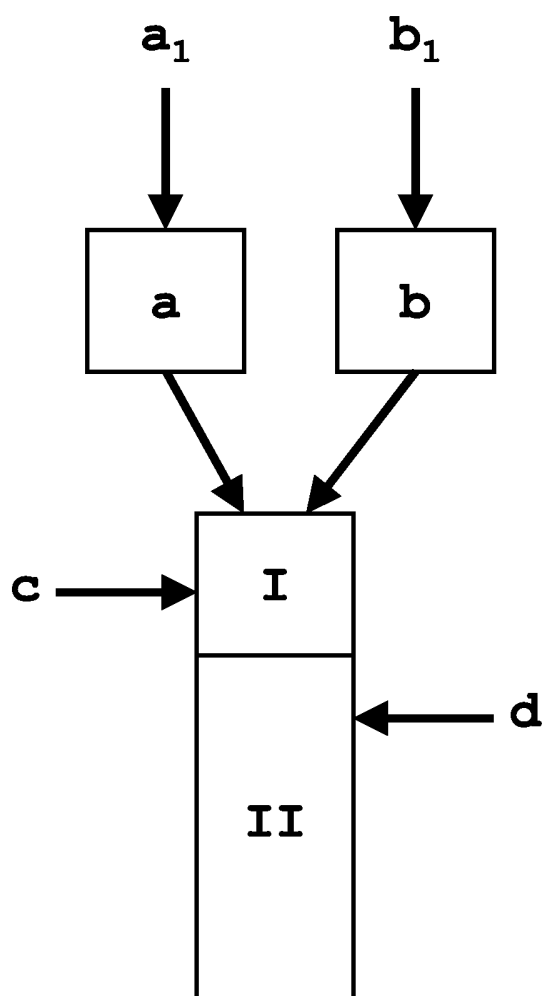


Figure 1