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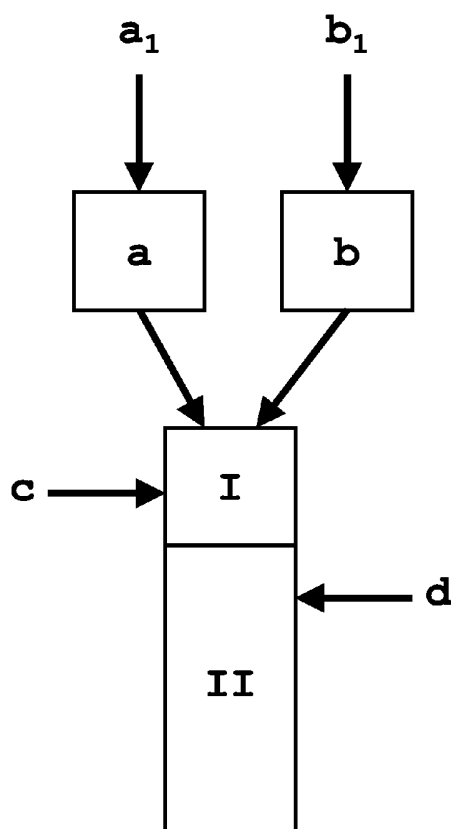
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[Continued on next page]

(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 at least 95 wt.% and a content of zirconium dioxide of not more than 5 wt.%, and the sum of the contents of titanium dioxide and zirconium dioxide is at least 99.7 wt.%, in each case based on the total amount of powder, and which exhibits only reflections of titanium dioxide in the X-ray diffraction diagram. It is prepared by transporting into a mixing chamber a titanium compound in vapour form by means of primary air and a zirconium compound in vapour form by means of an inert gas, mixing the mixture with hydrogen in a mixing chamber burning 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, to its preparation and to its use.

DE-A-3611449 discloses a titanium-zirconium mixed oxide
5 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
a mixing chamber and is there mixed with hydrogen, air and
10 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
analysis. The mixed oxide powder can be used as a catalyst
15 support.

The object of the invention is to provide a titanium-
zirconium mixed oxide powder which exhibits properties that
are at least equally as good as those of catalyst supports
described in the prior art, but which has a lower content
20 of the expensive zirconium dioxide component.

The invention provides a titanium-zirconium mixed oxide
powder in the form of aggregated primary particles, which
powder has a content of titanium dioxide of at least
95 wt.% and a content of zirconium dioxide of not more than
25 5 wt.%, and the sum of the contents of titanium dioxide and
zirconium dioxide is at least 99.7 wt.%, in each case based
on the total amount of powder, and which exhibits only
reflections of titanium dioxide in the X-ray diffraction
diagram.

30 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 in which intimate mixing of zirconium dioxide and titanium 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. In the case of very high contents of titanium dioxide, individual primary particles can even consist completely of titanium dioxide.

- 10 The sum of the contents of titanium dioxide and zirconium dioxide in the titanium-zirconium mixed oxide powder according to the invention is at least 99.7 wt.%. The powder can comprise up to 0.3 wt.% impurities. In general, the content of impurities is less than 0.1 wt.%, and the
- 15 sum of the contents of titanium dioxide and zirconium dioxide is accordingly at least 99.9 wt.%. The impurities can result from the materials that are used or from the preparation process. Chloride is generally the main impurity.
- 20 The titanium-zirconium mixed oxide powder according to the invention exhibits only the reflections of titanium dioxide, in particular the rutile and anatase modification, in the X-ray diffraction diagram. No reflections of zirconium dioxide or zirconium titanate phases are
- 25 detected.

The rutile content of the titanium-zirconium mixed oxide powder according to the invention is not limited. Preference is given to a content of at least 10 wt.%, particularly preferably to a content of at least 20 wt.%,

30 based on the amount of titanium dioxide.

The BET surface area, determined in accordance with DIN 66131, of the titanium-zirconium mixed oxide powder according to the invention is not limited. The BET surface area can preferably be from 10 to 200 m²/g and particularly

35 preferably from 40 to 120 m²/g.

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

- a titanium compound in vapour form is transported by
5 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 titanium and zirconium compounds can be converted into the oxides thereby, corresponding to a
10 $\lambda_{(pr)}$ value of at least 0.5, and
- a zirconium compound in vapour form is likewise transported into the mixing chamber, by means of an inert carrier gas,
- wherein the amounts of the titanium compound and of the
15 zirconium compound that are used are so chosen that the mixed oxide powder has a content of titanium dioxide of at least 95 wt.% and a content of zirconium dioxide of not more than 5 wt.%,
- hydrogen is introduced into the mixing chamber separately
20 from the titanium compound and the zirconium compound, and the mixture of titanium compound, zirconium compound, hydrogen and primary air is ignited in a burner and the flame burns into a reaction chamber,
- the solid is then separated from gaseous substances, and
- 25 - the solid is then freed of chloride to the greatest possible extent by treatment 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
30 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 titanium compound and at least 50 % of the air that is necessary stoichiometrically in order to

convert the titanium compound and the zirconium compound into the mixed oxide powder according to the invention are transported into the mixing chamber together.

5 A further important feature is that the zirconium compound is transported into the mixing chamber by means of an inert gas.

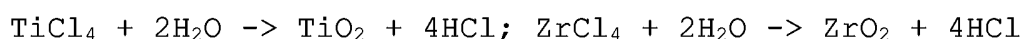
It is also important that, if the air introduced into the mixing chamber is not sufficient to convert the starting compounds completely into the mixed oxide powder according to the invention, secondary air is introduced into the reaction chamber.

It is also important that the gamma value is ≥ 1 , preferably from 1 to 4. Different gamma values permit the preparation of mixed oxide powders according to the invention having (approximately) the same BET surface area and a variable rutile content. A higher rutile content can be obtained by means of a higher gamma value.

Figure 1 shows the process according to the invention in diagrammatic form. In the figure: a = titanium compound in vapour form; a₁ = primary air; b = zirconium compound in vapour form; b₁ = inert gas; c = hydrogen; d = secondary air; I = mixing chamber; II = reaction chamber.

The metal compounds in vapour form are converted into the corresponding metal oxide either by hydrolysis or by oxidation.

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.

5 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 $\lambda_{(pr)}$ is from 0.7
to 4.

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

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

Examples:Example 1:

4300 g/h of TiCl_4 are vaporised. The vapours are transported into a mixing chamber by means of primary air ($14.8 \text{ Nm}^3/\text{h}$).
5 Separately therefrom, 24 g/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, $2.20 \text{ Nm}^3/\text{h}$ of hydrogen are introduced into the mixing chamber. In a central pipe, the
10 reaction mixture is fed to a burner and ignited. The flame thereby burns into a water-cooled reaction chamber. $17 \text{ Nm}^3/\text{h}$ 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
15 air and steam at about 700°C .

Examples 2 to 9 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 9 exhibit only the reflections
20 of titanium dioxide modifications in the X-ray diffraction diagram.

Examples 6 to 8 show that it is possible to obtain mixed oxide powders of approximately equal BET surface area having rutile contents of from 27 % to 42 %.

25 Example 10: Tests with a λ_{pr} value of less than 0.5 generally result in explosion. A powder according to the invention cannot be obtained.

Example 11: analogous to Example 1 but, instead of titanium tetrachloride, zirconium tetrachloride in vapour form is
30 transported into the mixing chamber by means of primary air. A product according to the invention is not obtained. The mixed oxide components in this powder are not

distributed uniformly. In addition, the powder has only low sintering stability.

Table 2 shows the behaviour of the BET surface area of the powders according to the invention of Examples 4, 7 and 8 compared with Aerioxide® TiO₂ P 25, BET surface area 45 m²/g (Degussa) and a zirconium dioxide sample (VP ZrO₂, BET surface area 52 m²/g), on thermal loading.

The Examples show that even a powder according to the invention having a very low zirconium dioxide content results in a high stability of the BET surface area on thermal loading.

Table 1: Substances and amounts used; physico-chemical parameters of the resulting powders

Example		1	2	3	4	5	6	7	8	9
TiCl ₄	g/h	4300	6000	4300	6000	4300	2200	1660	1704	4470
ZrCl ₄	g/h	24	24	25	30	25	25	19	29	19
Hydrogen	Nm ³ /h	2.20	2.20	2.2	2.20	2.20	0.60	0.75	0.30	0.20
Primary air	Nm ³ /h	14.8	11.0	18.0	11.0	14.8	2.80	2.00	3.08	3.70
Secondary air	Nm ³ /h	17.0	17.0	17.0	17.0	17.0	0	0.50	0	0
gamma		2.84	2.04	2.84	2.04	2.84	1.33	2.15	1.30	3.95
lambda _(pr)		2.14	1.59	2.60	1.59	2.14	1.67	0.98	2.46	3.66
Lambda _(pr + sec)		4.59	4.04	5.05	4.04	4.59	1.67	1.23	2.46	3.66
ZrO ₂ content	wt. %	0.07	0.11	0.2	0.48	0.56	1.10	1.40	1.60	4.80
TiO ₂ content	wt. %	99.5	99.5	99.6	99.2	99.2	98.6	98.5	98.1	95.0
Chloride content	wt. %	0.02	0.01	0.1	0.015	0.03	0.04	0.10	0.05	0.05
Rutile content	%	26	41	22	39	27	27	42	24	31
BET	m ² /g	75	47	105	47	73	51	52	53	110
pH		3.92	3.86	3.6	3.72	4.10	2.14	4.18	3.98	2.07

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

		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 4	0.48	45	6
Example 7	1.40	49	13
Example 8	1.60	45	8
VP 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 at least
5 95 wt.% and a content of zirconium dioxide of not more than 5 wt.%, and the sum of the contents of titanium dioxide and zirconium dioxide is at least 99.7 wt.%, in each case based on the total amount of powder, and
 - it exhibits only reflections of titanium dioxide in
10 the X-ray diffraction diagram.
2. Titanium-zirconium mixed oxide powder according to claim 1, characterised in that the rutile content is at least 10 wt.%, based on the sum of rutile and anatase.
3. Titanium-zirconium mixed oxide powder according to
15 claim 1 or 2, characterised in that the BET surface area is from 10 to 200 m²/g.
4. Process for the preparation of the titanium-zirconium mixed oxide powder according to claims 1 to 3, characterised in that
 - 20 - a titanium 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 titanium and zirconium
25 compounds can be converted into the oxides thereby, corresponding to a $\lambda_{(pr)}$ value of at least 0.5, and
 - a zirconium compound in vapour form is likewise transported into the mixing chamber, by means of an inert carrier gas,
 - 30 - wherein the amounts of the titanium compound and of the zirconium compound that are used are so chosen that the mixed oxide powder has a content of titanium

dioxide of at least 95 wt.% and a content of zirconium dioxide of not more than 5 wt.%,

- hydrogen is introduced into the mixing chamber separately from the titanium compound and the zirconium compound, and the mixture of titanium compound, zirconium compound, hydrogen and primary air is ignited in a burner and the flame burns into a reaction chamber,
 - the solid is then separated from gaseous substances, and
 - the solid is then freed of chloride to the greatest possible extent by treatment 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 1.0, and
 - wherein γ is ≥ 1 .
5. Process for the preparation of the titanium-zirconium mixed oxide powder according to claim 4, characterised in that $\lambda_{(pr)}$ is from 0.7 to 4.
6. Process for the preparation of the titanium-zirconium mixed oxide powder according to claim 4 or 5, characterised in that $\lambda_{(pr + sec)}$ is from ≥ 1 to 7.
7. Use of the titanium-zirconium mixed oxide powder according to claims 1 to 3 as a catalyst support.

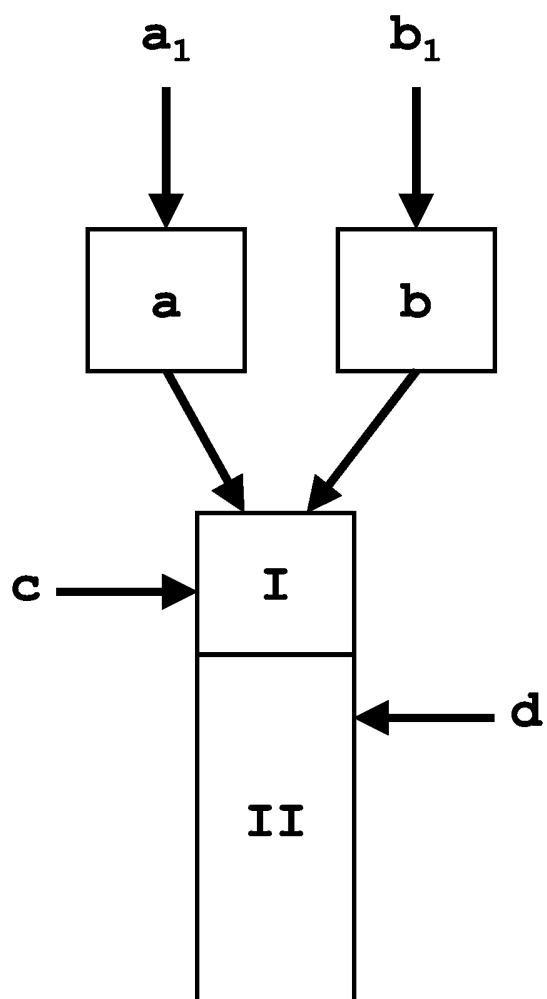


Figure 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2005/056939

A. CLASSIFICATION OF SUBJECT MATTER

C01G23/00 C01G23/07 C01G25/00 C01B13/14

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)

C01G C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 138 632 A (DEGUSSA AG) 4 October 2001 (2001-10-04) examples 1-5	1-7
A	EP 0 241 647 A (DEGUSSA AKTIENGESELLSCHAFT) 21 October 1987 (1987-10-21) cited in the application examples 4-6	1-6
A	US 5 684 116 A (MARTL ET AL) 4 November 1997 (1997-11-04) column 2, lines 1-39; example 2	1-3,7

☐

Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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