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(54) **Title:** METHOD FOR PRODUCTION OF PHOTOCATALYTICALLY ACTIVE TITANIUM OXIDE FOR UV AND VISIBLE REGION O LIGHT SPECTRUM

(57) **Abstract:** The method for production of photocatalytically active titanium oxide consisting in hydrolyses of titanyl sulphate by thioacetamide, urea or hydroxymethylamine in a water environment at temperatures of 40 - 100°C and drying of the acquired product at temperatures up to 120°C; the dried product is annealed up to a temperature of 1,000°C in an oxygen atmosphere. During hydrolysis, dopants with soluble salts of components selected from groups Sc, Zn, Y, Zr, Nb, Cd, Al, Ta and lanthanides can be used.

Method for production of photocatalytically active titanium oxide for UV and visible region of light spectrum

Technical field

The patent regards the method for production of photocatalytically active titanium oxide for the UV and visible region of light spectrum.

Background art

At the moment, the most common photocatalyzer is titanium oxide. After UV radiation illumination, a hole-electron pair originates on the surface and the consequence of this excitation is the origination of highly reactive OH radicals, which are able to break down organic compounds into the final products of mineralization – water and carbon dioxide. Commercially available titanium oxide for photocatalysis is currently produced by hydrolysis of $TiCl_4$. This process is very demanding in terms of cost and technical process. For applications of photocatalysis, cheap forms of titanium oxide have to be found, which, by means of dopants, increase photo-activity in the UV region or move photo-activity in the visible region of the light spectrum.

Disclosure of the invention

The aim of this patent is a simple method for production of price-available photocatalytically active titanium oxide; the principle of this method for production is that, in a water environment, titanyl sulphate ($TiOSO_4$) is hydrolyzed by thioacetamide or urea at a temperature of 40 – 100 °C and the acquired product dries at temperatures up to 120 °C. The dried product is further annealed at temperatures up to 1000 °C in oxygen atmosphere or air. Titanyl sulphate can be also hydrolyzed by hexamethyltetramine.

The method with use of dopants during hydrolysis can be used. As dopants, soluble salts of scandium, zinc, yttrium, zirconium, niobium, tantalum, cadmium, aluminum or lanthanides can be used.

Examples

The patent is further explained by means of examples for its realization.

Example 1

100 g of titanyl oxide ($TiOSO_4$) was dissolved in a 5-liter beaker with 3 liters of distilled water acidified with concentrated sulphuric acid. The solution was diluted to a total volume of 4 liters and 100 g of thioacetamide was added. The solution was boiled under continuous stirring and maintained at this temperature for 6 hours. Afterward, the product was decanted by water, filtered and dried at 120 °C. The acquired product was annealed in a furnace in an oxygen atmosphere at 700 °C. The acquired product is a white, very fine, loose powder; according to X-ray powder diffraction, it is anatase modification of titanium oxide, active in the UV region.

Example 2

100 g of titanyl oxide ($TiOSO_4$) was dissolved in a 5-liter beaker with 3 liters of distilled water acidified with concentrated sulphuric acid. The solution was diluted to a total volume of 4 liters and 100 g of thioacetamide was added. The solution was boiled under continuous stirring and maintained at this temperature for 3 hours. Furthermore, 200 g of urea was added to the reaction mixture and the reaction solution was maintained at boiling temperature until a weak alkaline reaction (pH = 7 – 7.5). Afterward, the product was decanted by water, filtered and dried at 120 °C. The acquired product was annealed in a furnace in an oxygen atmosphere at 600 °C. The acquired product is a white, very fine, loose powder; according to X-ray powder diffraction, it is anatase modification of titanium oxide, active in the UV region.

Example 3

100 g of titanyl oxide ($TiOSO_4$) and 20 g of zinc sulphate ($ZnSO_4$) were dissolved in a 5-liter beaker with 3 liters of distilled water acidified with concentrated sulphuric acid. The solution was diluted to a total volume of 4 liters and 100 g of thioacetamide was added. The solution was boiled under continuous stirring and maintained at this temperature for 3 hours. Furthermore, 200 g of urea was added to the reaction mixture and the reaction solution was maintained at boiling temperature until weak alkaline reaction (pH = 7 – 7.5). Afterward, the

product was decanted by water, filtered and dried at 120 °C. The acquired product was annealed in a furnace in an oxygen atmosphere at 500 °C. The acquired product is a white, very fine, loose powder; according to X-ray powder diffraction, it is anatase modification of titanium oxide doped with zinc oxide. Zinc oxide doping increases photo-activity in the UV region.

Example 4

100 g of titanyl oxide ($TiOSO_4$) and 1 g of cerium sulphate ($Ce_2(SO_4)_3$. were dissolved in a 5-liter beaker with 3 liters of distilled water acidified with concentrated sulphuric acid. The solution was diluted to a total volume of 4 liters and 100 g of thioacetamide was added. The solution was boiled under continuous stirring and maintained at this temperature for 3 hours. Furthermore, 200 g of urea was added to the reaction mixture and the reaction solution was maintained at boiling temperature until weak alkaline reaction (pH = 7 – 7.5). Afterward, the product was decanted by water, filtered and dried at 120 °C. The acquired product was annealed in a furnace in an oxygen atmosphere at 500 °C. The acquired product is a white, very fine, loose powder; according to X-ray powder diffraction, it is anatase modification of titanium oxide doped with cerium oxide. Cerium oxide doping moves the photo-activity to the visible region.

Example 5

100 g of titanyl oxide ($TiOSO_4$) and 1 g of neodymium oxide was dissolved in a 5-liter beaker with 3 liters of distilled water acidified with concentrated sulphuric acid. 1 g of neodymium oxide was dissolved in a minimum quantity of diluted hydrochloric acid (1:1) and added to the reaction solution. The solution was diluted to a total volume of 4 liters and 100 g of thioacetamide was added. The solution was boiled under continuous stirring and maintained at this temperature for 3 hours. Furthermore, 200 g of urea was added to the reaction mixture and the reaction solution was maintained at boiling temperature until weak alkaline reaction (pH = 7 – 7.5). Afterward, the product was decanted by water, filtered and dried at 120 °C. The acquired product was annealed in a furnace in an oxygen atmosphere at 500 °C. The acquired product is a white, very fine, loose powder; according to X-ray powder diffraction, it is anatase modification of titanium oxide doped with neodymium oxide. Neodymium oxide doping moves the photo-activity to the visible region.

Industrial applicability

The method for production of photocatalytically active titanium oxide, according to the patent, can be used for the production of pigments used in self-cleansing paints or as a refill for AC units for air-cleansing or for volume-cleansing of water.

CLAIMS

1. The method for production of photocatalytically active titanium oxide for the UV and the visible region of the light spectrum characterized in that titanyl sulphate ($TiOSO_4$) is hydrolyzed in a water environment at a temperature of 40 – 100 °C and the acquired product is dried at temperatures up to 120 °C.
2. The method for production according to claim 1 characterized in that titanyl sulphate is hydrolyzed by thioacetamide.
3. The method for production according to claim 1 characterized in that titanyl sulphate is hydrolyzed by urea.
4. The method for production according to claim 1 characterized in that titanyl sulphate is hydrolyzed by hexamethyltetramine.
5. The method for production according to claims 2, 3 or 4 characterized in that soluble salts of components from groups Sc, Zn, Y, Zr, Nb, Cd, Al, Ta and lanthanides are added during hydrolysis.
6. The method for production according to claims 2, 3, 4 or 5 characterized in that the dried product is annealed up to a temperature of 1000 °C in air or an oxygen atmosphere.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2008/000150

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01G23/053 B01J21/06 B01J35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01G B01J

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, WPI Data, EMBASE, INSPEC, COMPENDEX, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	paragraphs [0006], [0009], [0015], [0017], [0026], [0027], [0037]; examples 1,2	4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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