



A hydrothermal peroxo method for preparation of highly crystalline silica–titania photocatalysts



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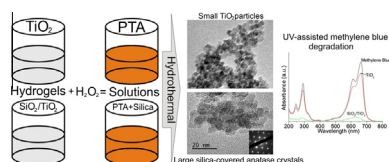
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GRAPHICAL ABSTRACT



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ABSTRACT

A new completely inorganic method of preparation of silica–titania photocatalyst has been described. It has been established that the addition of silica promotes crystallinity of TiO₂ anatase phase. Relative crystallinity and TiO₂ crystal size in the silica–titania particles increase with the silica content until SiO₂/TiO₂ molar ratio of 0.9, but at higher molar ratios they start to decrease. The single-source precursor containing peroxo titanic (PTA) and silicic acids has been proved to be responsible for high crystallinity of TiO₂ encapsulated into amorphous silica. It has been proposed that peroxo groups enhance rapid formation of crystalline titania seeds, while silica controls their growth. It has been concluded from the TEM that the most morphologically uniform anatase crystallites covered with SiO₂ particles are prepared at SiO₂/TiO₂ molar ratio of 0.4. This sample, according to ²⁹Si NMR, also shows the high content of hydroxylated silica Q³ and Q² groups, and it is the most photocatalytically active in UV-assisted decomposition of methylene blue among the tested materials. It has been determined that the increase in the amount of the condensed Q⁴ silica in the mixed oxides leads to the decrease in photocatalytic performance of the material, despite its better crystallinity. High crystallinity, low degree of incorporation of Ti atoms in SiO₂ in the mixed oxide and adsorption of methylene blue in the vicinity of photoactive sites on the hydroxylated silica have been considered as the main factors determining the high degradation degree of methylene blue in the presence of silica–titania.

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1. Introduction

Titania is an excellent photocatalyst, whose applications, properties, structural and morphological features are well known and summarized in the number of comprehensive reviews [1–12]. However, the search for the procedures able to ensure TiO₂ with better qualities for photocatalytic applications is still a key issue. Recently, the industry and researchers have turned towards

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“green” and more economically reasonable technologies. In the field of oxide materials it means that alternative ways for preparation of oxides have to be found, instead of the most widespread alkoxide-based procedures. As a consequence, several reviews on the utilization of peroxy complexes of transition metals [13] and titanium in particular [14,15] have been published. Water-soluble peroxy complexes of transition metals are considered as “green” and inexpensive sources of nanostructured metal oxide catalysts, since application of toxic alkoxides or solvents and organic ligands is not needed. Aqueous titanium peroxy complexes can exist in the wide range of pH values in low-nuclear forms, which allows controlling their phase composition, obtaining 100% pure anatase, rutile or brookite phases [16,17]. Also the peroxy route of TiO_2 synthesis is found to be flexible enough to control shape, sizes and preferential orientation of titania crystals [18–22]. In spite of the fact that this method is inexpensive and allows controlling various titania properties, it has seldom been applied for preparation of mixed silica–titania oxides, which could possess improved photocatalytic properties. The information on application of the peroxy route to $\text{SiO}_2/\text{TiO}_2$ synthesis is scarce; being limited to the thin film preparation or impregnation of the preformed silica colloidal particles with titanium peroxy complex [23]. However, modification of titanium oxide with silica is a widespread method [24] aiming to increase the thermal stability of its most photocatalytically active polymorph anatase [25], tune the sizes of its crystals [26], increase the surface area [27], improve adsorption properties [26], and introduce mesoporosity to the mixed $\text{SiO}_2/\text{TiO}_2$ material [28]. This modification can be achieved by preparation of a highly homogeneous mixed oxide [29], by covering the preformed crystalline titania particles with silica layer [30], or making it otherwise, crystallizing anatase on the surface of colloidal SiO_2 spheres [31]. Sol–gel technique is found to be the most applicable to the abovementioned purposes. Hydrothermal method, on the other hand, is less common for $\text{SiO}_2/\text{TiO}_2$ particles preparation; only several reports on the application of this procedure were published [26,32,33].

Besides the obvious advantages that silica contributes to the mixed silica–titania, it also gives a significant drawback. As a rule, silica in the mixed oxide causes formation of defects and suppresses the growth of TiO_2 crystals [29,34–37]. However, it is known that high crystallinity is an important feature, as the electron pairs recombination takes place on the crystalline defects; this reduces the activity of the photocatalyst [38–40]. In spite of a common view attributing the enhancement of the photocatalytic activity to the decrease of the anatase particles [41,42], it might be supposed that the increase of the TiO_2 crystal sizes could favor lowering recombination rate and improve its catalytic properties. The benefit that silica introduces to the mixed oxide is difficult to combine with high crystallinity of TiO_2 . In order to achieve reasonable crystallinity in silica–titania, heat treatment at temperatures up to 800 °C is applied [25]. However, we have not found any reports on the preparation of highly crystalline $\text{SiO}_2/\text{TiO}_2$ oxides under mild conditions. In the present study we describe a new method of silica–titania particles synthesis and the unusual effect that silica has on the crystallization of TiO_2 under hydrothermal conditions, as it promotes titania crystallinity rather than suppresses it. The test of the prepared materials in the photocatalytic degradation of methylene blue dye shows their high activity.

2. Experimental

2.1. Chemicals

Non-volatile and stable under ambient conditions titanium oxysulfate hydrate ($\text{TiOSO}_4 \cdot \text{H}_2\text{O}$), containing not more than 17 wt% of

sulfuric acid, and 27 wt% solution of sodium silicate ($\text{Na}_2\text{Si}_3\text{O}_7$) in water were purchased from Aldrich and used as the sources of titania and silica, respectively. Sodium hydroxide (Prolabo, 99% purity) was used as precipitation agent, 20% ammonia solution in water (Prolabo) and nitric acid (Prolabo) were applied for pH correction. Hydrogen peroxide 30 wt% solution was obtained from Aldrich. Methylene blue was of analytical grade.

2.2. Synthesis

On the first stage of the synthesis, 50 mL of sodium silicate solution with concentrations: 0.0, 0.025, 0.05, 0.1, 0.14 and 0.18 mol/L was added to 50 mL of 0.1 M solution of TiOSO_4 . The samples were designated as OTS, 0.1TS, 0.4TS, 0.9TS, 1.3TS, and 1.6TS (where the numbers indicate $\text{SiO}_2/\text{TiO}_2$ molar ratio in the synthesized samples, determined by elemental analysis). Then the mixtures were hydrolyzed with 1.5 M solution of sodium hydroxide, the addition of NaOH ended when the pH value reached 3.2 (4.0 for OTS and 0.1TS). The gel-like precipitates obtained after alkali addition were centrifuged at 3000 r.p.m. and thoroughly washed with deionized water eight times, until the negative reaction on sulfate ions. On the next stage, 0.5 mL of 3 M ammonia was added to the precipitate following by ultrasonication in 50 mL of distilled water. Then to the dispersed precipitates 4 mL of H_2O_2 solution was added and the pH of the reaction mixtures was adjusted to 7.0 by the addition of ammonia solution in order to obtain water-soluble titanium peroxy complexes. Soon, the clear transparent yellow solutions of titanium peroxy complex and silicic acid were formed. The findings concerning dissolution of silica–titania hydrogel in hydrogen peroxide were described elsewhere [43,44]. The pH of the solution was adjusted to 7.0 with ammonia. After that, 3 M nitric acid was dropwise introduced to the solution until pH reached the value of 2.0. It is worth mentioning that after the addition of acid all solutions stayed clear with an exception of the samples OTS and 0.1TS, where the formation of sol was observed. Then the volume of the prepared mixtures was adjusted to 80 mL by deionized water and they were transferred to Teflon-lined stainless steel autoclaves having total volume of 140 mL for hydrothermal treatment. Hydrothermal treatment was carried out under autogenic pressure at 180 °C during 48 h. In order to establish the role of the precursor, silica–titania materials with the equimolar $\text{SiO}_2/\text{TiO}_2$ composition in the reaction mixture, were also synthesized under conditions of pH not being controlled by ammonia and nitric acid addition (PTA– SiO_2), by hydrothermal treatment of the gel in the absence of hydrogen peroxide after ammonia and nitric acid were added (GelTS), and using separately prepared titanium peroxy complex and sodium silicate solution ($\text{NH}_3\text{PT–SiO}_2$). When the treatment was over, the precipitates were isolated by centrifugation at 3000 r.p.m., washed with deionized water eight times and dried at 60 °C for 24 h. In order to eliminate adsorbed water, the samples were calcined in static air at 400 °C for 2 h, but a part of each sample was left as-synthesized as well.

2.3. Characterization

X-ray diffraction patterns were registered using Rigaku Ultima IV diffractometer, operating at Cu K_α radiation ($\lambda = 0.15418$ nm) at voltage of 30 kV with a help of high-speed DTEX detector. Scherrer equation was applied to estimate the mean crystallite size of TiO_2 by the (101) reflection, the uncertainty of the estimation is near 5%. Unit cell parameters for anatase crystals were refined using GSAS software [45]. Relative crystallinity was estimated from the ratio of anatase peak intensity of (101) reflection to that of the OTS sample calcined at 400 °C [46,47]. Scanning electron microscope Jeol JSM 7001F with Oxford Instruments EDS-attachment was used to investigate morphology and to determine elemental

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