The Effect of Sulphate Anions on the Ultrafine Titania Nucleation

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Abstract

The phenomenological model of sulphate anions effect on the nanodispersed titania synthesis during hydrolysis of titanium tetrachloride was studied. It was proposed that both chelating and bridging bidentate complexes formation between sulphate anions and octahedrally coordinated \([\text{Ti(OH)}_3\text{(OH}_2)_6-\text{(H}_2\text{O})]^\text{(3+)}\) monomers is the determinative factor for anatase phase nucleation.

Keywords: Hydrolysis, Polycondensation, Nucleation, Anatase, Sulphate anions

Background

Ultrafine TiO₂ has wide range of highly promising applications in many different fields—from the environmental oriented photocatalytic system, such as degradation of hazardous organic compounds [1], waste water cleaning [2], direct decomposition of NOₓ, SOₓ and air purification [3] to novel fields of industry—sensor materials [4] and solar cells [5]. Phase composition, particle size and surface state are the most important characteristics that determine catalytic reactivity, photosensitivity and adsorption properties of TiO₂. For example, the decrease of particle size of titania leads to the rapid increase of catalytic activity [6]. At the same time, the photocatalytic properties of titania are very sensitive to phase composition of TiO₂ polymorphs such as anatase, brookite and rutile [7].

Choice of titania synthesis method with the control of its physical and chemical parameters is crucially important determinants of resulted compositions. The preparation of nanosized TiO₂ is possible by sol-gel [8], chemical precipitation [9], microemulsion [8] and hydrothermal [10] methods. The sol-gel method is the most flexible technique for nanosized oxide preparation. The variations of primary precursor types, hydrolysis conditions, temperature and pH of the reaction medium allow the control of nanoparticle nucleation and growth. The sol-gel method of titania obtained is typically based on the reactions of titanium alkoxides Ti(OR)₄ hydrolysis. The change of these expensive chemicals to the cheaper precursor such as TiCl₄ is very promising for a large scale manufacture of nanosized TiO₂. A promising advantage of TiCl₄ application is the possibility of polycondensation reactions controlled by additive ions with the use of the predicted nucleation of the specified phase of titania.

The aim of this paper was to investigate the effects of SO₄²⁻ anions on the oligomer polycondensation and oxide network formation during titania nucleation for the sol-gel process based on TiCl₄ hydrolysis.

Methods

Titanium tetrachloride TiCl₄ (Merck, 99.9%: specific density 1.73 g/cm³ at 20 °C) was cooled to 0 °C and hydrochloric acid (36.0% aqueous solution) was added with further hydrogen chloride evaporation. The TiCl₄ to hydrochloric acid ratio was 2:1. Aqueous solution of sodium hydrosulphate was added dropwise to sol of titanium oxychloride TiOCl₂ to get pH of 5.0–5.5 under vigorous stirring. Gel formation was observed during all pH increasing process. The suspension of nanoparticles was kept at 80 °C for 3 h with the further washed with distilled water to remove Na⁺ and Cl⁻ ions. Precipitated TiO₂ was dried at the 150 °C, and obtained xerogel was marked as S1. The S2 material synthesis process was carried out likewise, but crystalline-dried Na₂SO₄ was
added directly to titanium tetrachloride on the stage of TiCl₄ hydrolysis.

Diffraction patterns were obtained with the diffractometer DRON-4-07 equipped with an X-ray tube BSV28 (Cu Kα, radiation, 40 kV, 30 mA), a Bragg-Brentano geometry-type and a Ni Kα-filter. A qualitative analysis was carried out with the use of ICSD structural models. The structural models for anatase and rutile were based on the ICSD #92363 and ICSD #24780, respectively. Copper powder annealed in vacuum (850–900 °C for 4 h) with an average grain size of about 50 μm was used as a reference sample to determine instrumental peak broadening. Full width at half maximum (FWHM) for a diffraction peak of this reference sample at the 2θ = 43.38° was 0.129°; therefore, it made it possible to distinguish anatase and brookite phases. The size of the coherently scattering domains was calculated by the Scherrer equation: $D = \frac{Kλ}{β\cosθ}$, with $K$ is the Scherrer constant ($K = 0.9$), $λ$ is the wavelength (0.154 nm), $β$ the FWHM (in radians), and $θ$ is the peak angular position. We used the combination of Gauss and Cauchy (dominated) functions as a profile shape.

Infrared spectra were recorded with Thermo-Nicolet Nexus 670 FTIR spectrometer in the 4000–400 cm⁻¹ region. The TiO₂/KBr mixture after vibrating milling was pressed into pellets and measured in the transmission mode.

The morphology of sample powders was studied by transmission electron microscopy (TEM) with a 100-kV microscope JEOL JEM-100CX II. The microscopic copper grid covered by a thin transparent carbon film was used as a specimen support for TEM researches.

**Results and Discussion**

The presence of sodium sulphate in the reaction medium significantly affected the phase composition of the obtained materials (Fig. 1). The material synthesized in the absence of Na₂SO₄ additive (S1) was a mixture of anatase and rutile with the relative phase contents of 65 ± 4 and 35 ± 5 wt %, respectively. The average size of the coherently scattering domains (CSD) was about 14 nm for anatase and 9 nm for rutile, so both phases are good crystallized. Meanwhile, the part of the material is close to amorphous state as the presence of the halo on XRD pattern for 2θ = 16–32° is evident. According to synthesis conditions, the formation of non-titania phase is unlikely to occur. As a result, the material consists of separated regions with different crystallinity degrees. The specific surface area of S1 sample was about 152 m² g⁻¹. The material S2 was close to amorphous ultrafine titania with clear structural features of anatase. The halo on XRD pattern is also observed in this case but it is relatively narrowed and shifted to larger 2θ values. The average size of CSD was about 4–5 nm (the analysis is complicated by low crystallinity of the material). The specific surface area for S2 sample was increased to 328 m² g⁻¹.

TEM images of S1 sample (Fig. 2a) do not allow to make clear conclusions about its morphology but the observed agglomerates consisted of the lamellar-like primary particles with the sizes of 10–15 nm. Furthermore, there is no evidence of crystalline area boundaries (Fig. 2b). The S2 sample had bubble-like morphology of the agglomerates (Fig. 2c, d). HR TEM showed high crystallinity of some grains of this material (Fig. 3) with the interplanar distances of 0.34–0.37 nm. The obtained interplanar spacing corresponds to the (101) plane of anatase (0.352 nm). This indicates that the preferred growth direction of CSD (crystallites) is [010] crystallography axis. This result led to conclusions that the anatase nanocrystals with oxygenated surfaces have developed facets in the (010) direction [11].

More information about synthesized materials was obtained by FTIR spectroscopy. The broad absorption area around 3400 cm⁻¹ indicates the presence of chemisorbed OH-groups on the surface of titania particles (v-OH modes) (Fig. 4) [12]. The shift of the v-OH bands from typical 3700–3600 to about 3400 cm⁻¹ can be caused by the presence of hydrogen bonding [13]. The band around 1600 cm⁻¹ demonstrates the presence of molecularly adsorbed water (δ-H₂O modes) [14]. The higher crystallinity degree for S1 sample causes the formation of relatively more distinct absorption bands in the titania characteristic area (400–700 cm⁻¹) [15].

The additional absorbance band on the FTIR patterns for S2 materials at 1139 and 1060 cm⁻¹ corresponds to chemisorbed SO₄²⁻ ions [16]. A sharp low intensity band 1384 cm⁻¹ is typical for the metal oxides modified by sulphate ion bands and assigned to S=O stretching frequency. Meanwhile, S=O–H coordination is unlikely
because the absorption band will shift in low-frequency area up to 1325 cm\(^{-1}\) in this case. There are two different variants of SO\(_4^{2-}\) immobilization on the titania surface—a chelating bidentate complex formation with coordination to one metal ion through two oxygens or bridged bidentate complex formation using bonding through two metal ions; both complexes belong to C\(_2\) point group. Bridged bidentate SO\(_4^{2-}\) anions coordinated to Ti\(^{4+}\) have characteristic stretching frequencies in the 930–1200 cm\(^{-1}\) range, and major absorption peak at 1148 cm\(^{-1}\) is attributed to asymmetric stretching
vibrations [17]. The bands in the 1300–900 cm\(^{-1}\) region were observed for SO\(_4^{2-}\)/TiO\(_2\) system, and the peaks at 1217, 1134, 1044, and 980 cm\(^{-1}\) were identified in [18] as characteristic frequencies of a bridge bidentate SO\(_4^{2-}\) coordinated to metals. According to [19], bridged bidentate complex has four absorption bands at 1195–1160, 1110–1105, 1035–1030 and 990–960 cm\(^{-1}\), which are assigned to the asymmetric and symmetric stretching frequencies of the S=O and S–O bonds.

The conclusion about energetic favorability of chelating complex formation where SO\(_4^{2-}\) anions are coordinated to Ti atoms through two oxygen was made on the base of sulphated titania investigation with the use of DFT calculation [20]. The formation of chelate sulphate complex corresponds to skeletal FTIR band at 1201 cm\(^{-1}\) [21] as chelating bidentate complex has four bands at 1240–1230, 1125–1090, 1035–995 and 960–940 cm\(^{-1}\) which are assigned to the asymmetric and symmetric stretching frequencies of S=O and S–O bands [19].

Deconvolution of the 1200–1000 cm\(^{-1}\) region of S2 material FTIR spectra revealed the presence of four bands at 1182, 1140, 1086 and 1060 cm\(^{-1}\). The absorption band at 1086 cm\(^{-1}\) is quite close to that of the chelating bidentate complex. Two bands of chelating and bridging bidentate complexes overlap each other so band at 1182 cm\(^{-1}\) can correspond to both types of complexes. The bands at 1060 and 1140 cm\(^{-1}\) imply that bridged bidentate complex is formed on the surface of the S2 sample.

We can suggest the following model of SO\(_4^{2-}\) impact on titania nucleation at the stage of olation interaction between primary hydrocomplexes taking into account the results shown in [22]. The hydrolysis of TiCl\(_4\) leads to [Ti(OH)\(_2\)]\(^{3+}\) formation where Ti\(^{4+}\) ions are in the octahedral coordination with the next transformation to [Ti(OH)\(_2\)(OH\(_2\))\(_{6-}\)]\(^{4-}\)\(^{h+}\) monomers as a result of deprotonation. The hydrolysis ratio h is a function of pH and is determined by partial charge theory [23]. In these monomers, OH\(^-\) groups have thermodynamic advantages of the location in the octahedron equatorial planes, and H\(_2\)O molecules primarily occupy the “vertex” position [24]. The products of hydrolysis are [Ti(OH)\(_2\)(OH\(_2\))]\(^{3+}\) and [Ti(OH)\(_2\)(OH\(_2\))]\(^{2+}\) monomers when pH of reaction medium is close to 1. At pH = 3, the [Ti(OH)\(_2\)(OH\(_2\))]\(^{2+}\) and [Ti(OH)\(_2\)(OH\(_2\))]\(^{3+}\) complexes coexist in solution. At pH = 4, the hydrolysis leads to the formation of the [Ti(OH)\(_2\)(OH\(_2\))]\(^{3+}\) complexes, and in the range of pH = 6–8, the [Ti(OH)\(_4\)(OH\(_2\))]\(^0\) monomers are formed. The possibility of the titania polymorph formation is defined by the spatial organization of [Ti(OH)\(_2\)(OH\(_2\))]\(^{h+}\) primary monomers. [Ti(OH)\(_4\)(OH\(_2\))]\(^0\) monomers (in which OH groups occupy octahedron equatorial planes and H\(_2\)O molecules are in the vertexes) form in neutral or alkaline mediums [20, 25]. Dimers are formed as a result of olation reaction between two primary monomers for which the octahedron coordination has a common edge outside the octahedron equatorial plane. After further polycondensation, the zigzag-like or spiral chain of [Ti\(_n\)(OH)\(_{4n}\)(OH\(_2\))]\(^0\) polyhedrons are formed and the conditions for the anatase phase nucleation are created. The [Ti\(_{mn}\)O\(_{mn}\)(OH)\(_{2mn}\)(OH\(_2\))]\(^0\) polymer is formed resulting from m linear structures of [Ti\(_n\)(OH)\(_{4n}\)(OH\(_2\))]\(^0\) olation interaction. The nucleation of anatase phase is the result of octahedron merger by lateral planes of faces [26]. At the same time, the hydroxium ions of the reaction medium interact with hydroxyl groups in the octahedron equatorial plane. If the hydroxium ion concentration in the reaction medium increases, [Ti(OH)\(_h\)(OH\(_2\))]\(^{4-}\)\(^{h+}\) monomers will form under h < 2 condition. Olation interaction between them leads to the polymer chain formation where monomers are linked by joint edges in octahedron equatorial planes, thus defining the precondition for rutile phase nucleation [25].

The presence of SO\(_4^{2-}\) ions in the reaction medium at pH about 5.5 will cause both Ti(SO\(_4\))(OH)\(_2\)(H\(_2\)O)\(_2\) chelating and Ti\(_2\)(SO\(_4\))(OH)\(_3\)(OH\(_2\))\(_2\) bridging bidentate complexes formation (Fig. 5). There are two different pathways of olation interaction between these complexes. Two monomers connect with each other by sharing apical edges (chelating complexes influence) or in equatorial plane (bridging bidentate complexes influence) with the dehydrating of water molecule. At the
next stage in both cases, the formation of skewed zigzag-like tetranuclear titanium complexes with the dehydrating of two water molecules takes place and the nucleation of anatase structure starts.

Conclusions

The effect of SO$_4^{2-}$ anions on the titania nucleation during hydrolysis of titanium tetrachloride was studied. We concluded that the nucleation process is mainly controlled by pH of the reaction medium and SO$_4^{2-}$ anion presence. Sulphate anions form both chelating Ti(SO$_4$)(OH)$_2$(H$_2$O)$_2$ and bridging bidentate Ti$_2$(SO$_4$)(O-H)$_3$(OH)$_2$ complexes at the stage of titanium tetrachloride hydrolysis. We suggested the model with two pathways of olation interaction between titanio-sulphate complexes when SO$_4^{2-}$ ligands stimulate screw polymer chains formation and the nucleation of TiO$_2$ anatase phase.

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Authors’ Contributions

VOK offered the general concept of the effect of SO$_4^{2-}$ Sciences Faculty at Vasyl Stefanyk Precarpathian National University. SVF is a researcher of Natural Sciences Faculty at Vasyl Stefanyk Precarpathian National University. VLCh is a researcher of Department of Organic and Analytical Chemistry, Natural Sciences Faculty at Precarpathian National University. IFM is a Doctor of Chemistry, Head of the Materials Science, Physical and Technical Faculty at Vasyl Stefanyk Ivano-Frankivsk 76018, Ukraine. 2Institute of Materials Science I.M. Frantsevich, Kotsyubynsky

Competing Interests

The authors declare that they have no competing interests.

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