Enhanced reactivity of peroxo-modified surface of titanium dioxide nanoparticles used to synthesize ultrafine bismuth titanate powders at lower temperatures


ABSTRACT

Bismuth titanate with sillenite structure (Bi₁₂TiO₂₀) was prepared at lower temperatures and shorter times using a modified oxidant peroxide method (OPM). Bi₁₂TiO₂₀ was synthesized utilizing commercial Bi₂O₃ and reactive titanium dioxide nanoparticles having peroxo-modified surfaces. Rather than depending on particle size, the reaction mechanism is related to the highly exothermic decomposition of peroxo groups, regardless the titanium source used, which locally releases a large amount of energy that can accelerate the reaction, similar to self-propagating high temperature routes (SHS).

1. Introduction

There is a growing need for faster and more efficient methods for synthesizing technologically important materials. In the case of nanomaterials, their physical and chemical properties are dependent on their composition and morphology [1], which makes the synthetic route a critical decision. In this context, wet-chemical routes are superior to traditional solid-state reactions [2–4]. Unfortunately, these wet methods are tedious, time consuming and have low batch yields. On the other hand, the synthesis of multi-component oxides through the simple heating of a mixture of oxides or carbonates require additional treatment at high temperatures for long periods to overcome kinetic barriers [5,6], which usually results in large particles of irregular shape, and secondary phases in some instances [7–9]. To solve this problem, new approaches have been proposed that combine the robustness of solid-state reactions with the chemical design of wet-chemical routes, with special attention being paid to self-propagating high temperature routes (SHS) [6,10–14], partial oxalate methods [15], and the oxidant peroxide method (OPM) [4,16].

Bismuth titanates with different composition and structures have attracted considerable interest due their excellent optical, electrical and catalytic properties [17]. For instance, Bi₆Ti₃O₁₂ has potential use in photocatalysis [18] and is a promising ferroelectric material for high-temperature applications [19], while nanstructured Bi₁₂TiO₂₀ shows superior photocatalytic performance [20–22].

In this study, we prepared pure Bi₁₂TiO₂₀ nanoparticles (referred to as BT) as a model compound to evaluate this new OPM approach, which begins with the synthesis of reactive nanoparticles of titanium dioxide modified with peroxo groups on the surface using titanium isopropoxide or titanium metal as precursor. In a second step, these reactive nanoparticles were mixed with commercial bismuth oxide, resulting in single-phase BT at lower temperatures and shorter reaction times than conventional solid-state reactions.

2. Materials and method

2.1. Synthesis of reactive titanium dioxide

Titanium dioxide nanoparticles with peroxo-modified surfaces were synthesized from a yellow gel obtained by heating solutions of peroxo complexes of titanium. In a typical procedure, 250 mg of titanium metal (98% Aldrich, USA) or 5 mL of titanium...
isopropoxide (97% Aldrich, USA) were added to 100 mL of an aqueous solution of hydrogen peroxide (60 mL, 30% Synth, Brazil) and ammonia (40 mL, 28% Synth Brazil). This mixture was left in an ice-water cooling bath until complete dissolution of the titanium precursors (i.e. several hours for the metal and a few minutes for the isopropoxide), which resulted in a transparent yellow aqueous solution of the soluble peroxytitanate ion \([\text{Ti(OH)}_3\text{O}_2]\)^{4-} \[4,16,20\]. In order to obtain titanium dioxide nanoparticles covered by peroxo groups, the solutions were heated to 80°C until a yellow gel formed, and was held at this temperature for several hours to form yellow powders of TiO2-Met (from titanium metal) or TiO2-Iso (from titanium isopropoxide). The control material was obtained by heating TiO2-Met at 250°C for 30 min under H2, which resulted in a white powder of titanium dioxide (TiO2-Red) with reduced surfaces free of peroxo groups, but with the same morphological and structural properties of the original yellow nanoparticles covered with peroxo groups.

2.2. Synthesis of bismuth titanate

Analytical grade Bi2O3 (99.99% Aldrich, USA), commercial TiO2 anatase (99% Alfa Aesar; TiO2-Com) and the as-prepared TiO2-Met, TiO2-Iso, and TiO2-Red were used to prepare bismuth titanate with a selenite phase structure (Bi12TiO20) through a solid-state reaction. Appropriate amounts of the constituent oxides were weighed and mixed in a conventional ball-mill for 24 h using small zirconia spheres and ethanol as milling media. The slurries were dried at 60°C and sieved through 120-mesh sieves. The mixtures were calcinated at different temperatures for 1 h at a heating rate of 10°C min⁻¹ in closed alumina boats.

![Fig. 1.](a) XRD patterns of TiO2-Met, TiO2-Iso and TiO2-Red reactive precursors, in which crystalline structure and particle size were maintained even after removing the peroxo groups from the surface using H2. (b) TEM image 5 nm TiO2-Iso crystalline particles, and (c) XPS profiles of O1s region of TiO2-Met and TiO2-Red showing the elimination of peroxo groups by H2 treatment.

![Fig. 2.](XRD patterns of three different mixtures of Bi2O3 and titanium precursors (TiO2-Met, TiO2-Red and TiO2-Com) calcined at 600°C for 1 h. Note the absence of any secondary phases in the TiO2-Met pattern and the presence of unreacted Bi2O3 in the TiO2-Com and TiO2-Red patterns. Arrows in the pattern of TiO2-Com indicate the presence of Bi12TiO20.)
2.3. Characterization

All powders were characterized at room temperature by X-ray diffraction (XRD) using Cu K\(\alpha\) radiation (Rigaku D/MAX 200 with a rotary anode operating at 150 kV and 40 mA) in the 2\(\theta\) range from 15° to 75°, with a step scan of 0.02°. Powder crystalline structure was characterized by transmission electron microscopy (TEM-FEI/PHILIPS CM120) and by scanning electron microscopy (SEM-FEG, ZEISS model-SUPRA 35). XPS spectra were collected in a XPS VG Microtech ESCA3000 (MgK\(\alpha\) and AlK\(\alpha\) radiations) operating at 3\(\times\)10\(^{-10}\) mbar of pressure. Binding energies were corrected for the charging effect, assuming a constant binding energy for the adventitious O1s peak. Thermogravimetric analysis (TGA) were carried out with a NETZSCH TG 209F1 and differential scattering calorimetry (DSC) measurements were done using a NETZSCH DSC 204. All analysis were collected from 50 to 400 \(^\circ\)C using a heating rate of 10 °C min\(^{-1}\) and under nitrogen atmosphere.

3. Results and discussion

The key idea behind OPM is the substitution of hydrogen peroxide by soluble peroxo complexes, which react with lead or bismuth ions to form a stoichiometric amorphous precipitate that crystallizes in a desired oxide, free of any typical contaminants [4,16]. Peroxo complexes of titanium are commonly prepared by reacting titanium metal with hydrogen peroxide and ammonia [4]. Although this technique has successfully yielded a series of important technological compounds [23–27], titanium metal is an expensive and low reactive chemical that is an obstacle for large-scale OPM syntheses. For example, while approximately 12 h in an ice bath is necessary to dissolve no more than 1 g of titanium metal, a much larger amount of titanium peroxo complexes could be obtained at room temperature by diluting titanium isopropoxide in an aqueous solution of hydrogen peroxide and ammonia [28–31]. For this reason, there are ongoing efforts to find better alternatives to titanium metal.

Titanium isopropoxide was chosen as a starting reagent in order to understand the role played by these reactive nanoparticles during the synthesis of complex oxides, and to minimize reagent costs. Unlike most titanium compounds, titanium isopropoxide is relatively safe and inexpensive, halide-free, and its residual alcohol is easily removed [28–31]. Solutions of titanium peroxo complexes are relatively unstable and spontaneously form yellow gels that are used to synthesize white nanoparticles of titanium dioxide after hydrothermal processing [28–31]. However, unlike previous studies, we preserved the peroxo groups on the surface of the TiO\(_2\) nanoparticles, keeping the gel at 80 °C for a few hours under ambient pressure to obtain a fine yellow powder. For comparison, Fig. 1a shows the XRD patterns of two yellow reactive TiO\(_2\) powders synthesized from different titanium sources. One of them (TiO\(_2\)-Met) was obtained by means of traditional OPM using titanium metal, while the second (TiO\(_2\)-Iso) was obtained using titanium isopropoxide.

**Fig. 3.** XRD patterns of BT synthesized with (a) TiO\(_2\)-Met and (b) TiO\(_2\)-Iso reactive titanium dioxide calcined at temperatures varying from 500 to 800 °C for 1 h. Both series of XRD patterns show crystalline Bi\(_{12}\)TiO\(_{20}\) powders when calcined at 600 °C or higher. Samples calcined at 500 °C show unreacted Bi\(_2\)O\(_3\) and of Bi\(_4\)Ti\(_3\)O\(_7\) (see Supporting Information for phase assignments).
Both powders present a mixture of phases, mainly anatase and rutile, which can be observed by the shoulder at left side of the broad diffraction peak at approximately 27°. However, it is interesting that the amount of each phase seems to be the same, regardless the reagent used. TEM image (Fig. 1b) confirmed crystalline nanoparticles of approximately 5 nm in the sample synthesized with titanium isopropoxide.

A recurring question concerning the effect of particle size emerges during discussions about nanoparticle reactivity. To this end, we exposed a small amount of TiO2-Met to H2 for 30 min at 250 °C in order to remove the peroxo groups from the surface of nanoparticles. This yielded a white powder (TiO2-Red) with a XRD pattern identical to the patterns of our yellow powders (TiO2-Met and TiO2-Iso), indicating that their structure, morphology and particle size were successfully preserved. XPS spectra collected before and after H2 treatment (Fig. 1c) confirmed the elimination of peroxo groups from the particle surfaces.

Fig. 1 We evaluated the reactivity of titanium dioxide nanoparticles to form Bi12TiO20 by solid-state reactions using three different precursors, (i) yellow TiO2-Met with peroxo-modified surfaces, (ii) TiO2-Red with reduced surfaces, and (iii) commercial micrometric titania (TiO2-Com) with anatase structure. Fig. 2 shows XRD patterns after reacting these precursors with Bi2O3 at 600 °C for 1 h. There are evident differences between the pattern of pure BT (PDF 34-0097) obtained using reactive TiO2-Met nanoparticles with peroxo groups and the other two patterns obtained under the same conditions with white micrometric TiO2-Com or nanometric TiO2-Red nanoparticles. These two patterns show unreacted monoclinic Bi2O3 (PDF 71-465) as the main phase with Bi12TiO20 as a secondary phase (most intense peaks are marked with arrows).

Fu and Ozoe [32] reported that BT synthesis using commercial Bi2O3 and TiO2 is diffusion-controlled, and concluded that pure Bi12TiO20 cannot be obtained by this method at temperatures below 780 °C, even after 800 h of reactive TiO2-Met (Fig. 2) at a relatively low annealing temperature of 600 °C for 1 h, suggesting that the peroxide surface may play an important role in the reaction mechanism.

Fig. 2 In principle, the surface of oxide nanoparticles are much more complex than metals due the presence of voluminous oxygen centers [33]. These surfaces are rich in defects or imperfections that lead to charge redistribution [34]. Evidently, the presence of peroxo groups bonded to the surface of TiO2 leads to enhanced reactivity relative to typical white TiO2.

To compare the chemical reactivity of both yellow titanium dioxides (TiO2-Met and TiO2-Iso) covered with peroxo groups, we calcined their mixtures with commercial bismuth oxide at different temperatures with the aim to synthesize Bi12TiO20 while keeping all other conditions fixed (Fig. 3). Both series of XRD patterns showed crystalline Bi12TiO20 powders when calcined at 600 °C or higher. The patterns were quite similar, including

Fig. 4. (a) DSC curves of TiO2-Iso and TiO2-Met samples. The exothermic decomposition of peroxo group occurs between 200 and 250 °C. In this temperature range, there is major weight loss rate as seen on the (b)-(c) TG and dTG curves.

Both powders present a mixture of phases, mainly anatase and rutile, which can be observed by the shoulder at left side of the broad diffraction peak at approximately 27°. However, it is interesting that the amount of each phase seems to be the same, regardless the reagent used. TEM image (Fig. 1b) confirmed crystalline nanoparticles of approximately 5 nm in the sample synthesized with titanium isopropoxide.

A recurring question concerning the effect of particle size emerges during discussions about nanoparticle reactivity. To this

end, we exposed a small amount of TiO2-Met to H2 for 30 min at 250 °C in order to remove the peroxo groups from the surface of nanoparticles. This yielded a white powder (TiO2-Red) with a XRD pattern identical to the patterns of our yellow powders (TiO2-Met and TiO2-Iso), indicating that their structure, morphology and particle size were successfully preserved. XPS spectra collected before and after H2 treatment (Fig. 1c) confirmed the elimination of peroxo groups from the particle surfaces.

Fig. 1 We evaluated the reactivity of titanium dioxide nanoparticles to form Bi12TiO20 by solid-state reactions using three different precursors, (i) yellow TiO2-Met with peroxo-modified surfaces, (ii) TiO2-Red with reduced surfaces, and (iii) commercial micrometric titania (TiO2-Com) with anatase structure. Fig. 2 shows XRD patterns after reacting these precursors with Bi2O3 at 600 °C for 1 h. There are evident differences between the pattern of pure BT (PDF 34-0097) obtained using reactive TiO2-Met nanoparticles with peroxo groups and the other two patterns obtained under the same conditions with white micrometric TiO2-Com or nanometric TiO2-Red nanoparticles. These two patterns show unreacted monoclinic Bi2O3 (PDF 71-465) as the main phase with Bi12TiO20 as a secondary phase (most intense peaks are marked with arrows).

Fu and Ozoe [32] reported that BT synthesis using commercial Bi2O3 and TiO2 is diffusion-controlled, and concluded that pure Bi12TiO20 cannot be obtained by this method at temperatures below 780 °C, even after 800 h of reactive TiO2-Met (Fig. 2) at a relatively low annealing temperature of 600 °C for 1 h, suggesting that the peroxide surface may play an important role in the reaction mechanism.

Fig. 2 In principle, the surface of oxide nanoparticles are much more complex than metals due the presence of voluminous oxygen centers [33]. These surfaces are rich in defects or imperfections that lead to charge redistribution [34]. Evidently, the presence of peroxo groups bonded to the surface of TiO2 leads to enhanced reactivity relative to typical white TiO2.

To compare the chemical reactivity of both yellow titanium dioxides (TiO2-Met and TiO2-Iso) covered with peroxo groups, we calcined their mixtures with commercial bismuth oxide at different temperatures with the aim to synthesize Bi12TiO20 while keeping all other conditions fixed (Fig. 3). Both series of XRD patterns showed crystalline Bi12TiO20 powders when calcined at 600 °C or higher. The patterns were quite similar, including

Fig. 4. (a) DSC curves of TiO2-Iso and TiO2-Met samples. The exothermic decomposition of peroxo group occurs between 200 and 250 °C. In this temperature range, there is major weight loss rate as seen on the (b)-(c) TG and dTG curves.
relative normalized intensities, indicating no differences in the chemical reactivity of yellow titanium dioxide powders prepared from titanium metal (TiO2-Met) or titanium isopropoxide (TiO2-Iso). Similar results could likely be achieved using other titanium sources like chlorides or sulfates. Diffraction peaks were indexed according to the sillenite phase of bismuth titanate (PDF 34-0097) except for the samples calcined at 500 °C, which showed extra peaks related to unreacted monoclinic Bi2O3 (PDF 71-465) and the presence of a Bi2TiO7 (PDF 35-0795) metastable phase (see Supporting Information).

Much attention has been paid to the synthesis of white TiO2 colloids using hydrogen peroxide to control their structure and morphology [28,29,31,35–38], but only a few of these have examined the influence of the peroxo groups on the reactivity of TiO2 nanoparticles. Despite the lack of experimental data regarding this type of nanoparticles in solid-state reactions, some studies about the chemical bond between peroxo ligands and titanium can shed lights on this problem. Peroxides can increase the lability of chemical bonds near central titanium [17], which in turn decreases the energy barrier during the solid-state reaction, favouring the diffusion of atoms at lower temperatures and shorter times. Fig. 3 Some energy-efficient methods employed to synthesize inorganic ceramics and composites, known as self-propagating high temperature routes (SHS), utilize the energy released from exothermic transformations to accelerate reaction in the solid state [6,10–14,39]. In the case of TiO2-Iso and TiO2-Met nanoparticles, peroxo groups bonded to their surface decompose exothermally [30], which means that they can act as an energy source similar to other chemicals in SHS reactions.

Fig. 4a shows differential scanning calorimetry (DSC) curves of TiO2-Iso and TiO2-Met samples with peaks related to the exothermic decomposition of peroxo groups between 200–250 °C, which coincide with the maximum weight loss rates at 235 °C and 285 °C in thermogravimetric (TG) curves of TiO2-Iso and TiO2-Met, respectively (Fig. 4b). Anatase and brookite phases are metastable and transform to stable rutile at temperatures above 350 °C [40,41], much higher than the decomposition of peroxide groups and should not affect the thermal profile in the temperature range shown in Fig. 4.

Figs. 4 and 5 illustrates the differences between the conventional solid-state reaction and a route based on surfaces activated by peroxo groups. Conventional white TiO2 requires a large amount of energy from an external source to overcome the kinetic barrier, which is quite high in solid-state reactions, while a small amount of energy is needed to start the decomposition of peroxo groups bonded to yellow TiO2. Due to short time needed to disperse the energy released during this exothermic decomposition, which is a good approximation of an adiabatic transformation [42], there is enough local energy to activate the nanoparticle surfaces to react faster and at lower temperatures than in conventional solid-state reactions. The SEM images on the right of Fig. 5 show BT particles after treatment at 600 °C for 1 h obtained by traditional solid-state reaction (above) and using TiO2 nanoparticles with the peroxo-modified surfaces (below) that confirm this difference in reactivity.

Fig. 5 This concept of a reactive surface activated by peroxo groups can be extended to other valve metal oxides such as tungsten, niobium or vanadium [43]. These oxides also form peroxo-modified surfaces and are present in the composition of several important technological materials. In addition to the evident energetic advantage of performing such reactions at milder conditions, their syntheses by this new approach can preserve their size scale, morphology and sinterability, which have a positive impact on the performance and quality of resulting devices. It is also important to mention that this new method allows the preparation of large amounts of material using the same apparatus employed in traditional solid-state reactions, which can be easily adopted by the industrial sector to produce high-quality oxides on commercial scales.

4. Conclusions

Peroxo groups on the surface of titanium dioxide (TiO2-Iso or TiO2-Met) create a gentle environment to promote the formation of crystalline Bi2TiO7 powders at lower temperatures and shorter times regardless the titanium source used through a mechanism similar to self-propagating high temperature routes. The reactive properties of peroxidized titanium oxide seem to be related to the highly exothermic decomposition of peroxo groups, which locally releases a large amount of energy that accelerates the reaction. This new OPM approach is a promising way to obtain a huge number of commercial and technological titanates of complex structures, using low calcination temperatures, and this approach can also be used with others elements, mainly other metals that form chemical bonds with peroxo groups such as niobium, tungsten, and zirconium.

Acknowledgments

This study was supported by FAPESP (Grants 2015/139580-3, 2014/09014-7 and 2013/07296-2), CNPq and CAPES.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2016.07.039,

References


