COMPARATIVE STUDY OF SOL–GEL DERIVED PURE AND Nd-DOPED TiO₂ NANOPODERS

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ABSTRACT

The present study reports on the synthesis of pure and Nd-doped TiO₂ nanopowders using the sol–gel technique. A comparison of their thermal stability and phase formation upon heating is made as well. It is found, on the ground of XRD analysis, that the prepared powdered samples are amorphous up to 300°C while the doping with 2% Nd preserves the mixed organic-inorganic amorphous structure at higher temperatures (400°C). It is also found that TiO₂ (anatase) is the dominating crystalline phase in the temperature range of 400°C - 600°C. At 700°C, TiO₂ (rutile) appears in the pure samples, while it is not detected at this temperature in the presence of Nd. The average crystallite size of TiO₂ (anatase) is about 10 nm at 400°C. The doping with Nd results in obtaining particles of a lower size - 5 nm at 500°C. It is found by DTA that the decomposition of the organics is accompanied by a significant weight loss proceeding in the temperature range of 200°C - 300°C.

Keywords: sol-gel, heat treatment, phase transformations, thermal stability.

INTRODUCTION

Nanostructured materials still provoke scientific interest due to their special chemical, physical and mechanical properties [1 - 3]. It is known that the fundamental properties, especially of titanium dioxide (TiO₂) are extensively studied. Nanosized titanium dioxide materials (films and powders) are still in the researchers’ focus because they exhibit modified physico-chemical properties in comparison with the bulk ones [4 - 7]. But their applications is strongly influenced by their crystalline structure, morphology and particles size [4 - 6]. It is known that anatase is a metastable titania polymorph and it transforms into rutile upon calcination. According to the literature data [8], the anatase preservation in wider temperature range requires a careful control of the microstructures (the surface area, the crystal phase, the crystallite size and the morphology of the particles). On the other hand, the doping with transition or lanthanide metal ions improves significantly the properties (optical, electronic, thermal, photocatalytic) of the obtained materials [9, 10]. Amongst the few lanthanides (Pr³⁺, Nd³⁺, and Dy³⁺), that exhibit absorption in the visible light region, Nd³⁺ has maximum absorption due to 4f electron transition [10]. Thus, the Nd doping of TiO₂ could improve the efficiency of the catalyst by reducing the band gap of TiO₂ and thereby facilitating strong electronic transitions in the visible region [11]. This explains the increased scientific interest to Nd doping of TiO₂. Up to now, the majority of studies of TiO₂, with respect to improvement of the optical absorption and the photocatalytic performance have focused on anatase modification by cation and/or anion doping [12 - 14]. Compared to other methods, sol-gel processing has proven to be an excellent technique to prepare metal oxide thin films and powders. It allows the production of a wide range of compositions using a vari-
Samples characterization

The powder XRD patterns were registered at a room temperature with a Bruker D8 Advance diffractometer using Cu-Kα radiation. The thermal behavior of the gels dried at a room temperature was determined by a differential thermal analysis (LABSYSTM EVO apparatus) with Pt-Pt/Rh thermocouple at a heating rate of 10 K/min in an air flow, using Al₂O₃ as a reference material. The accuracy of the temperature maintenance was determined ± 5°C. Gases evolved (EGA) during the thermal treatments were analyzed by mass spectrometry (MS) with a Pfeiffer OmnistarTM mass spectrometer. Mass spectra recorded for TTIP and TTIP/i-PrOH (Fig. 2) show m/z of 14, 15, 18 and 44 ascribed to CH₄, CH₃, H₂O and CO₂, respectively. The morphology of the selected samples (pure and Nd doped TiO₂) heated at 400°C-500°C was conducted on a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with ultrahigh resolution scanning system (ASID - 3D) in regimes of a secondary electron image (SEI) and a backscattered electron contrast (BEC). The accelerating voltage was 20 kV, I of ca 65 μA, while the pressure was of the order of 10⁻⁴ Pa.

RESULTS AND DISCUSSION

Phase transformations and thermal stability

Transparent TTIP, TTIP/i-PrOH and TTIP/i-PrOH-2 % Nd gels are obtained. It is worth noting that no gels are formed in the system Ti(IV) isopropoxide – isopropanol (1:1) due to the absence of a chelating agent. The XRD patterns of the gels and the heat treated samples in the temperature range of 200°C-700°C are shown in Fig. 1. Neodymium phases are not registered by X-ray diffraction analysis. It is seen that the amorphous phase is dominant up to 300°C in both samples (TTIP and TTIP/i-PrOH), while it is preserved up to 400°C in TTIP/i-PrOH-2 % Nd. Obviously, the doping with Nd suppresses the earlier crystallization of TiO₂ (anatase). At 400°C the first crystals of TiO₂ (anatase) (JCPDS 78-2486) are registered in samples TTIP and TTIP/i-PrOH, while this phase is detected at 500°C in the third sample TTIP/i-PrOH-2 % Nd. The anatase phase is stable up to 500°C in all samples studied. It is worth noting that the phase transition TiO₂ (anatase) – TiO₂ (rutile) occurs at different temperatures in the samples. For pure TTIP the rutile phase (JCPDS 21-1276) appears at 600°C. Very weak peaks of rutile are registered at 700°C in TTIP/i-PrOH sample, while this phase is not registered in the third sample TTIP/i-PrOH-2 % Nd. Thus, the Nd...
The dopant does not stimulate anatase to rutile phase transformation. Fig. 1 shows that the calcination temperature increase leads to an increase of anatase peak intensity. The main diffraction peak becomes narrow which indicates enhanced crystallization. At 400°C the average crystallite size (calculated using the Sherrer’s equation) of TiO$_2$ (anatase) is ca 10 nm (Fig. 1) in all samples. The crystallite size increases at a higher temperature value (500°C) and it is ca 15 nm. It is ca 5 nm in sample TTIP/i-PrOH-2 % Nd. The crystal size in samples containing no Nd increases at 600°C and reaches a value of ca 20 nm. But the Nd dopant preserves the smaller particles size dimensions (5 nm). Our results concerning the calcination temperature effect on the phase formation are in good agreement with those reported in the literature [12, 14, 19, 20].

The thermal stability of gels aged at a room temperature is investigated by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA). The DT/A/TG curves are presented in Fig. 2 (a,b,c). Several stages can be identified on DT/A/TG curves of all samples (TTIP, TTIP/i-PrOH and TTIP/i-PrOH-2 % Nd). The presence of a weak endothermic effect near 100°C referring to the first decomposition step of the gels (Fig. 2 (a,b,c)) is a common feature. This step could be assigned to the evaporation of water adsorbed physically and/or an organic solvent as isopropanol in TTIP/i-PrOH sample. The average mass loss after dehydration is ca 10 %. The first exothermic peak on the curve of pure TTIP gel (Fig. 2(a)) is at ca 235°C. It is accompanied by a mass loss of ca 23 % related to the combustion of alkoxide groups bonded to Ti-atom. The next exothermic effects are at ca 400°C, 580°C and 680°C. The first one at about 400°C could be assigned to the crystallization of TiO$_2$ (anatase), while this at 580°C is related to the beginning of TiO$_2$ (anatase) to TiO$_2$ (rutile) phase transition. According to the XRD analysis (Fig. 1), TiO$_2$ (anatase) is a dominating phase up to 500°C. The exothermic effect at 680°C is connected to the complete crystallization of TiO$_2$ (rutile).

The thermal behavior of the other two samples (TTIP/i-PrOH and TTIP/i-PrOH-2 % Nd) (Fig. 2(b)) is very similar. The first exothermic effect in both gels curves is shifted to a higher temperature value (ca 270°C and 245°C, respectively) in comparison to the previous one (235°C). It is also accompanied by mass loss of ca 10 % for each sample. Obviously, the presence of a chelating agent (AcAc), a solvent (i-PrOH) as well as Nd in the last gel increases the thermal stability of the samples. These exothermic effects (at 270°C, 245°C) could be related to the beginning of combustion of organic groups building AcAc and i-PrOH. The second exothermic effect is observed at 340°C - 350°C. It is at-
Fig. 2. DTA - TG analysis of: a) TTIP, b) TTIP/i-PrOH and c) TTIP/i-PrOH – 2 % Nd.
tributed to an intensive combustion process related to the decomposition of organic compounds, residual hydroxyl groups and AcAc ligands. The total mass loss of these two steps in both gels is 24 % and 27 %, respectively. Probably, the higher amount of organic groups due to presence of a solvent and a chelating agent results in the stepwise release of the organics. A small exothermic effect around 440°C can be also distinguished in the DTA curve of TTIP/i-PrOH sample. No mass loss is observed. A similar peak appears in the curve of the other gel TTIP/i-PrOH-2 % Nd but at a slightly higher temperature of 460°C. These maxima are assigned to the beginning of TiO₂ (anatase) crystallization. This interpretation is confirmed by the XRD data (Fig. 1). The last exothermic effects (530°C, 580°C) are very strong and they could be associated with the intensive crystallization of anatase as well as with the residual carbon oxidation accompanied by CO₂ release. A weight loss of 9 % and 11 % for undoped and Nd doped sample, respectively (Fig. 2b) is observed. The higher weight loss (11 %) could be related to the presence of Nd [21]. The total mass loss in the samples TTIP/i-PrOH and TTIP/i-PrOH-2 % Nd is ca 43 % and 46 %, respectively, which is higher when compared to that of pure TTIP (about 23 %). The DTA results obtained are in correspondence with the XRD data reported.

Undoped and Nd-doped TiO₂ morphology

Two samples (TTIP and TTIP/i-PrOH-2 % Nd, treated at 400°C and 500°C, respectively) are selected for SEM observations (Fig. 3) aiming to verify the effect of Nd doping on the microstructure. These are the temperatures values (400°C and 500°C) where the first TiO₂ (anatase) crystals are detected. As indicated, both micrographs reveal that the particles of undoped and Nd-doped samples exhibit a spherical shape with an average size of 5 nm - 10 nm. In both cases a strong tendency of agglomeration is found. Our investigations are in good agreement with those reported by other authors [8, 10]. It is pointed out there that doping with Nd of a low content (1 %) results in formation of spheres of almost identical particle size. Some authors [12] claim that the higher amount of Nd (5 %) leads to larger particles formation.

The microprobe analysis shows that the composition includes 74,13 mass % of Ti, 1,81 mass % of Nd and 24,05 mass % O. Thus, the presence of Nd in the samples obtained is confirmed. The values pointed above correspond well to the initial samples composition.

CONCLUSIONS

Titania gels are prepared from Ti(IV) isopropoxide in presence of air moisture only. The key role of the chelating agent (AcAc) for obtaining gels on the ground of Ti(IV) isopropoxide and isopropanol is confirmed. Neodymium doping hinders the anatase-to-rutile phase transition and enhances the stability of the anatase phase at higher temperature values (700°C). The particles size increases up to 20 nm with temperature increase (above 400°C) in case of undoped compositions. It is found that Nd doping stimulates the formation of spherical particles of nanosized dimensions (5 nm - 10 nm) even at 600°C. It is indicated by DTA that the organics combustion occurs at higher temperatures (of 250°C) in presence of neodymium when compared to that of the undoped samples (of 230°C). It is suggested that the nanosized powders obtained could be successfully used for various environmental applications.
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REFERENCES