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Research of obtaining TiO_2 by sol-gel method using titanium isopropoxide TIP and tetra-n-butyl orthotitanate TNB

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Abstract. Titanium dioxide crystallises in three polymorphs: anatase, rutile and brookite. Rutile is most stable form of the TiO_2 polymorphs. In this paper we concentrate on obtaining rutile and anatase, both used in various applications. The chosen method is sol-gel, which is a reliable method used for obtaining titanium oxides. We prepared titanium dioxide with using titanium isopropoxide (TIP) with chemical construction ($C_{12}H_{28}O_4Ti$) and tetra-n-butyl orthotitanate (TNB) with chemical construction ($C_{16}H_{36}O_4Ti$). The experiments were carried out in order to compare the results of the samples with similar reaction conditions, but with different precursors, thus concluding which precursor gives best results. Using different analysis techniques as X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Thermogravimetric Analysis (TGA) we characterised the samples morphologically and structurally.

1. Introduction

For obtaining the samples we used one of the most popular methods of oxides preparation the sol-gel method. Titanium oxide has many unique properties as optical, dielectric, catalytic and photocatalytic [1-6]. Sol-gel method is very efficient in obtaining transparent thin layers or multi-component oxide layers on different substrates [7]. Titanium dioxide crystallises in three polymorphs: anatase, rutile and brookite [8]. Rutile is most stable form of the TiO_2 polymorphs [9]. Anatase has a tetragonal centred crystal structure while rutile has a simple tetragonal structure. The temperature of transformation from anatase to rutile depends on many factors like method of preparation, present impurities, oxygen-metal bond length from the precursor and texture and dimensions of anatase particles [10]. The main advantages of sol-gel method are: molecular homogeneity, possibility of using a large variety of precursors, microstructural and properties control, low purity conditions, simplicity of use at relatively low temperatures and low prices [11-12]. Therefore this method is the most suitable for obtaining homogeneous titanium dioxide nanopowders. Titanium dioxide is a well-known semiconductor due to its optoelectronic properties, one of the most important applications from electrochemistry where it is used as semiconductor for gas sensors, in electrochromic devices or solar energy conversion [13]. In this study we propose obtaining TiO_2 using 2 precursors and compare the results.

2. Experiment details

2.1. Materials

We prepared titanium dioxide with the use of titanium isopropoxide (TIP) in chemical construction ($C_{12}H_{28}O_4Ti$), produced by Panreac and tetra-n-butyl orthotitanate (TNB) in chemical construction ($C_{16}H_{36}O_4Ti$), produced by Merck. We also used ethanol (C_2H_6O), nitric acid (HNO_3) 65%, ammonia (NH_3) and sodium hydroxide (NaOH) by Panreac.

2.2 Method description

The first step is to dissolve the precursor to the solvent and keep it under constant stirring a given time. Then dropwise funnel and a solution of nitric acid 65% at pH = 1.5, which causes hydrolysis of titanium is added. Then dropwise too, is added the base until appreciate the stopping agitation gelation whitish (pH = 10). The addition of the base allows greater control of the reaction rate and will thus favours the formation of the nanometric particles in the system, in addition to neutralizing the above reaction. Finally, after mixing the obtained xerogel, we washed and dried them in the oven at 110 °C for 24 hours. The dried gels was grinded and characterized using different analysis techniques.

3. Results and discussion

For comparison we took two different samples with similar reaction conditions but with different precursors, thus concluding which one suits the best obtaining titanium oxide. We used titanium isopropoxide (TIP) with chemical construction ($C_{12}H_{28}O_4Ti$) and tetra-n-butyl orthotitanate (TNB) with chemical construction ($C_{16}H_{36}O_4Ti$) as precursors and analysed the samples using XRD, FTIR, SEM, TEM and TGA. The scanning electron microscope used is a JEOL JSM-6400, and EDX analysis by Oxford Link Pentaflet sensor. By SEM we could observe that the first sample contains agglomerates (figure 1) and also a lot of fibres, which is due to the TIP precursor. On the other side, the second sample is very different, it contains no fibers in figure 2. The TEM used is a JEOL JEM-2100 and can work in accelerating voltage modes 200 kV obtaining a resolution of 0.14 nm between lines and between points of 0.25 nm may reach 1.200.000 increase times. In figure 3 we can observe the titanium dioxide nanoparticles, from the TEM micrographs, in the area belonging to the agglomerates, confirming that the crystallinity is quite low. It confirm crystallographic plans to TIP precursor of that observed images TEM, peaks in analysis XRD tetragonal structure belonging to anatase. The second sample shows that the agglomerates are smaller (figure 4) and that the TiO_2 nanoparticles are also present. By electron diffraction the crystallinity is confirmed.

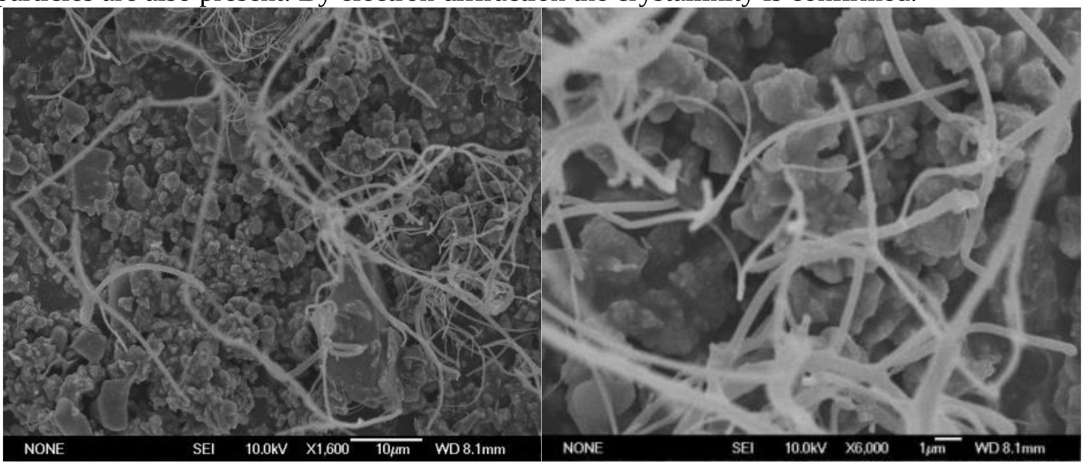

Figure 1. SEM micrographs of the sample obtained with TIP.

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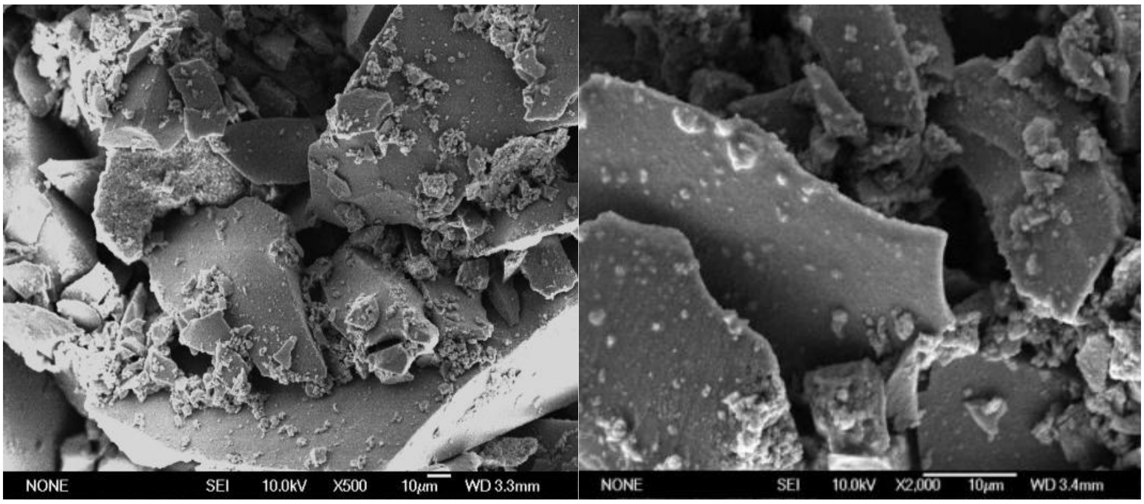

Figure 2. SEM micrographs of the sample obtained with TNB.

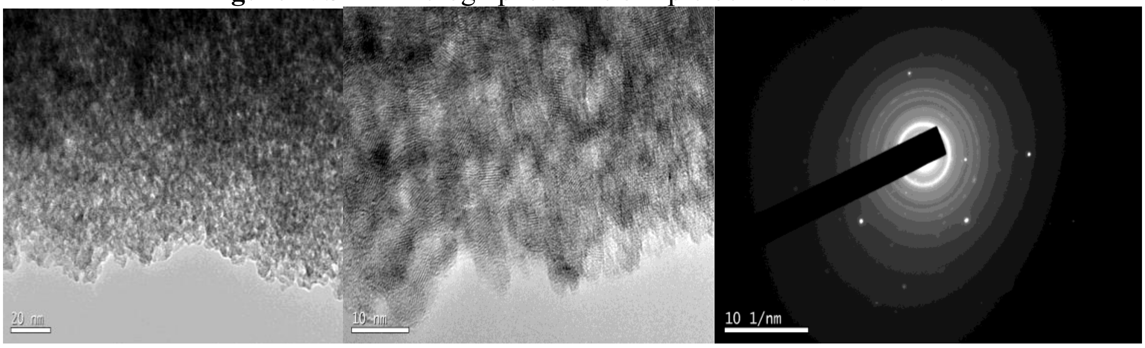

Figure 3. TEM and SAED images of the sample obtained with TIP.

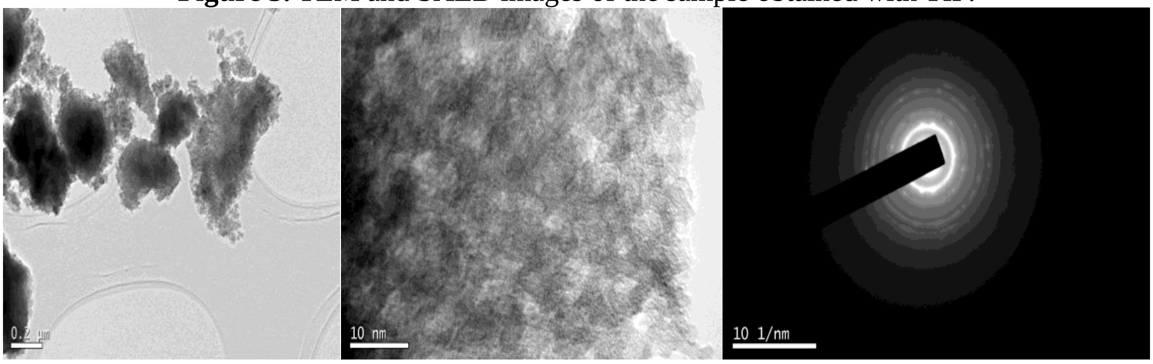

Figure 4. TEM and SAED images of the sample obtained with TNB.

Selected-area electron diffraction (SAED) and TEM studies confirmed that the crystallinity was less developed in the sample TIP as compared to the sample TNB. The diffraction pattern clearly indicates a crystalline structure for this samples. All the diffraction rings can be indexed using anatase. TEM analysis confirmed the appearance of rutile. The Mettler Toledo TC15 TA Controller (thermal analysis) allows TGA measurements from -170 to 1000°C at a heating rate of 10 ^{0}C/ min. The experiment parameters are composed in a PC and sent to the TC15 where the segments of the temperature program are controlled. Using TGA in figure 5 of the two samples after the water loss we can see the water loss initiation and ending and that the calcination takes place at 430 °C for sample TIP and 370 °C for sample TNB. It was found that the onset transformation temperature of anatase to rutile ($A \rightarrow R$) was different in the two gels.

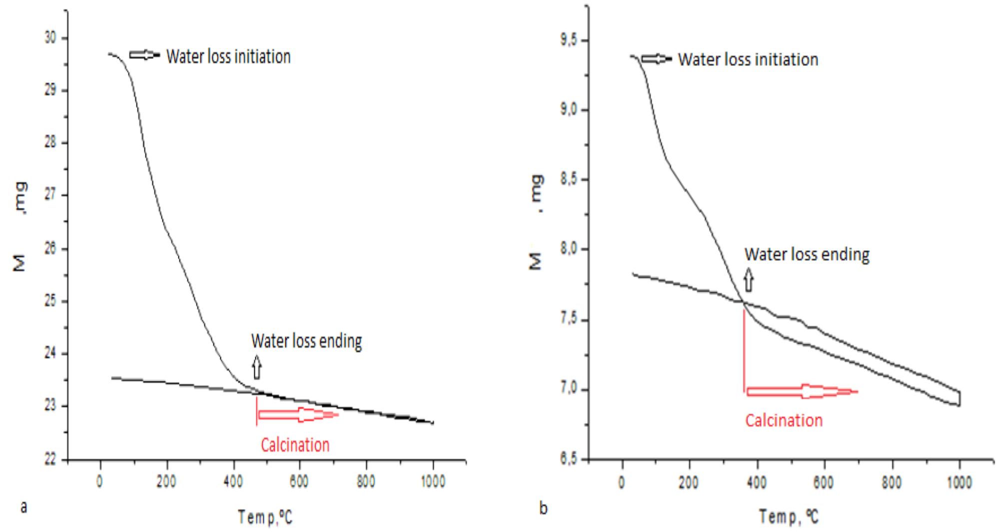

Figure 5. TGA characterisation of the samples.

For structural material characterization XRD method was used. It used a Philips model X`Pert PDP3040 with a source $K_{\alpha 1}$ Cuα, 40 kV and 40 mA, and working with a curved single crystal monochromator copper in order to eliminate the contribution $K_{\alpha 2}$ and $K_{\alpha 1}$ =1.547, $K_{\alpha 2}$ = 1.54439. The program which was used for the analysis of the diffraction patterns is X`Pert HihgScore Plus PANalytical (version 2.0). The XRD analysis shows the corresponding phase peaks, so we can detect the samples state. Most of the peaks belong to anatase phase because the sample is not calcined in figure 6a. In figure 6b we can see the anatase and rutile phase peaks. To outline a conceivable mechanism responsible for the synthesis of TiO_2, FTIR transmission spectra were obtained.

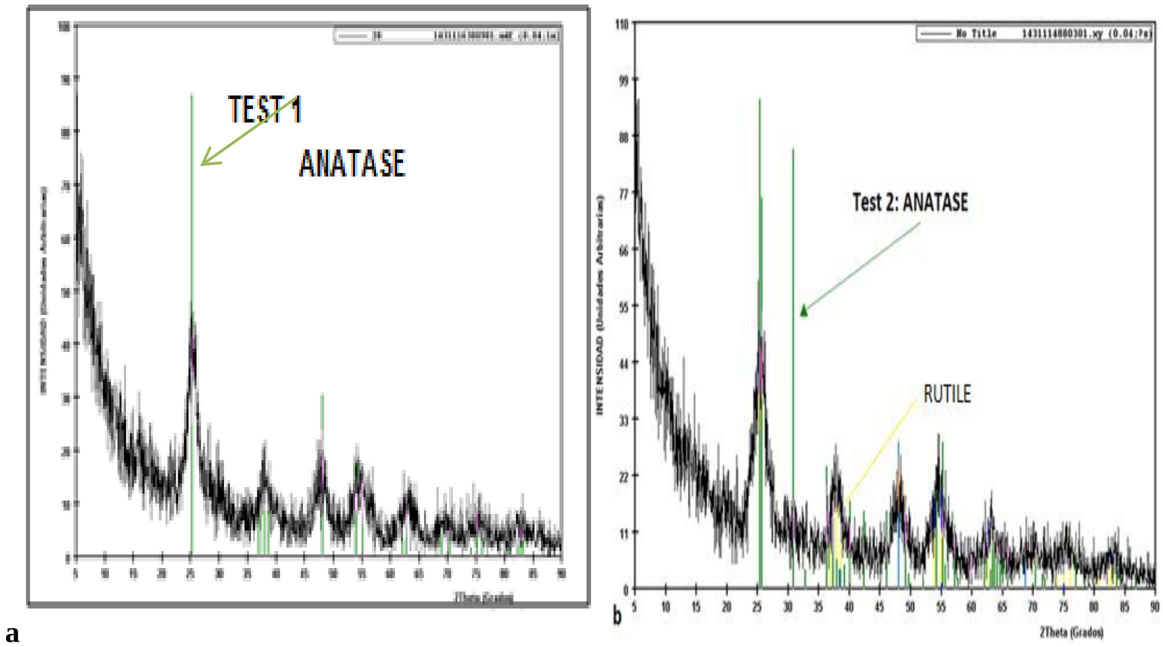

Figure 6. X-ray diffraction of TiO_2, a -sample TIP, b -sample TNB.

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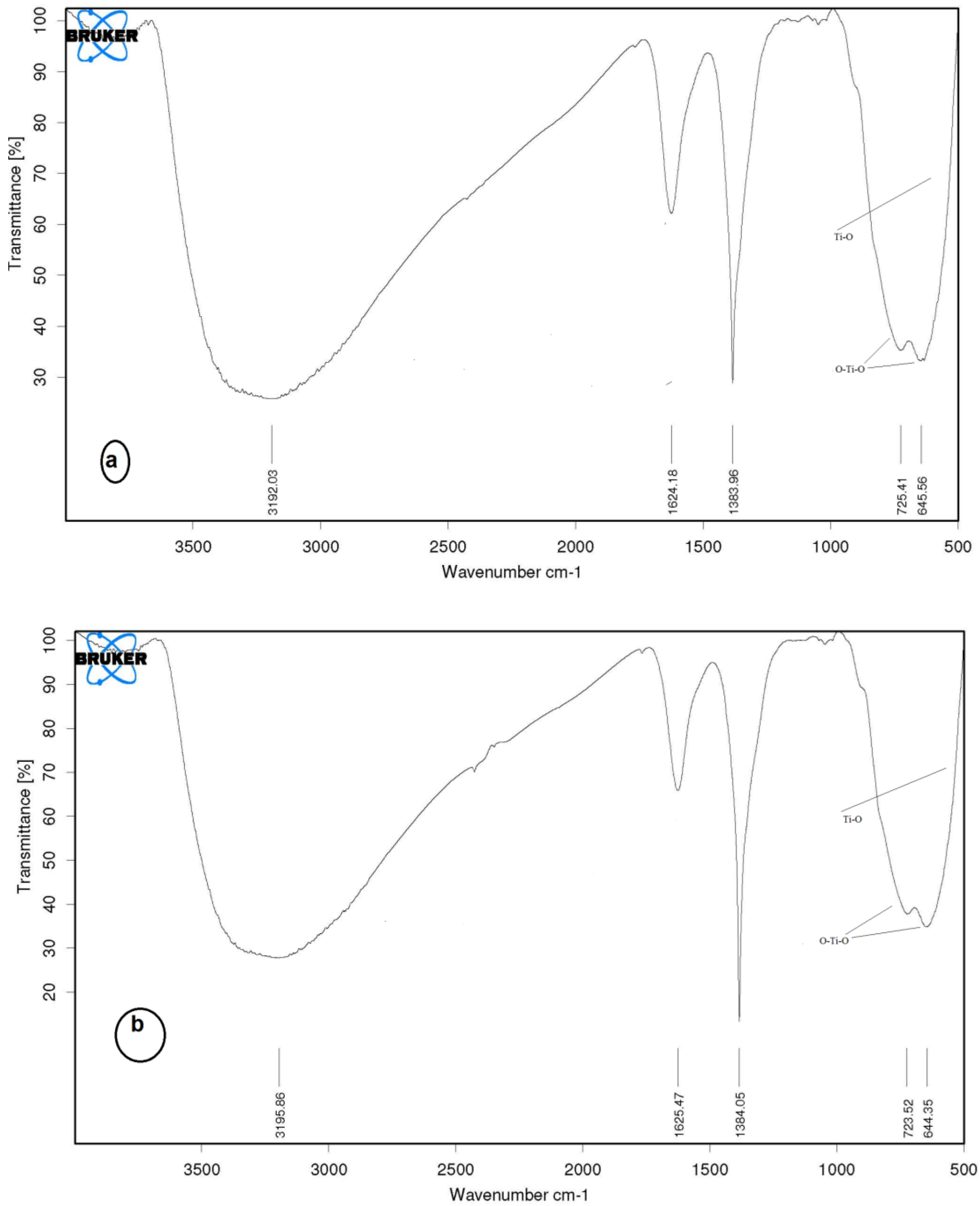

Figure 7. FTIR spectra of the samples, a-sample TIP, b-sample TNB.

Fourier transform infra-red spectra were carried out on a FTIR spectrometer Nicolet Magna 750. FTIR characterisation in figure 7a IR bands be read the peaks 3192 cm^{-1} - assigned to the stretching of OH chemisorbed of on the surface, assigned to hydroxyls for both dissociated water and molecularly adsorbed, 1623 cm^{-1}- pertaining to H-O-H bending for molecular water and at 1383 cm^{-1} – to organic substances, because the sample was not calcined, between 640 and 730cm^{-1} - are observed the O-Ti-O vibrations, that can be also associated to the Ti-O group at 600 cm^{-1}. In figure 7b we can also see the peak at 3195 cm^{-1}- that corresponds to a wide band of the OH groups and deformation vibrations of the H_2O adsorbed protons. At 1625 cm^{-1} - pertaining to H-O-H bending for molecular water and at

1384 cm^{-1} the organic substances traces, and between 635 and 725 cm^{-1} are observed the O-Ti-O vibrations, that can be also associated to the Ti-O group at 600 cm^{-1}.

4. Conclusions

The main objective of this paper was to obtain titanium dioxide nanoparticles using the sol-gel method. Titanium dioxide monocrystalline powder was obtained by the TIP and TNB precursors hydrolysis. To outline a conceivable mechanism responsible for the synthesis of TiO_2, FTIR transmission spectra were obtained. It was found that the onset transformation temperature of anatase to rutile ($A \rightarrow R$) was different in the two gels. We could observe the homogeneous and compact titanium dioxide powder, confirmed by the results of XRD, SEM, TEM, FTIR analysis. The use of TNB precursor leaded to better results, due to the absence of the fibers in the second sample, as seen on the SEM micrographs. The XRD analysis confirms the presence of rutile, so we conclude that TNB precursor is better.

Acknowledgements: Ministry of Economy and Competitiveness. Reference: MAT2013-46755-R, POSDRU/159/1.5/S/137750.

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