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Preparation and Characterization of Tetragonal Zirconium Oxide Nanocrystals from Isophthalic Acid-Zirconium(IV) Nanocomposite As a New Precursor

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Abstract:

In this study, isophthalic acid-zirconium(IV) nanocomposite has been prepared from zirconyl nitrate pentahydrate and potassium iodide, with isophthalic acid, ($C_8H_6O_4$=Benzene-1,3-dicarboxylic acid) as a ligand, via sonochemical method in ethylene glycol and methanol as solvents. The crystalline tetragonal ZrO_2 has been produced by thermal decomposition of isophthalic acid-zirconium(IV) nanocomposite as precursor. Characterization of nanocomposite was carried out using element analysis, Fourier transfer infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA) techniques. The results demonstrated that, pure zirconia with particle size of about 49 nm was obtained in which methanol has been used as solvent during the reaction, particle sizes was significantly reduced to about 20 nm, when ethylene glycol used as solvent during formation of the nanocomposite isophthalic acid-zirconium (IV) as precursor.

Keywords: *Zirconium oxide, Sonochemical method, Hydrothermal method, Isophthalic acid, Nanocomposite.*

1. INTRODUCTION

The interest for nanostructured materials, which are synthesized from particles smaller than 100 nm, has been growing in the last decades. It is very well known that materials with nano scale grain size show different properties from the same material in bulk form. The unique properties are related to the large number of surface or interface atoms [1,2]. Zirconia exhibits several crystalline modifications: monoclinic, that is thermodynamically stable at the temperatures below 1172°C, tetragonal, stable at the temperature range 1172–2347°C, cubic, stable above 2347°C, and rhombic, stable at a high pressure. However, tetragonal and cubic zirconia can be prepared at low temperatures (in the range of 550–750°C) in the forms of highly dispersed metastable phases. The martensitic transformation from the tetragonal to the monoclinic structure has great importance in ceramic and catalytic applications of zirconia [3]. Generally, the tetragonal phase of zirconia is preferentially formed relative to the monoclinic phase during the crystallization of amorphous hydrous zirconia. So, upon increasing calcination temperature, most amorphous zirconia precursors convert to the tetragonal phase first and then transform to the monoclinic phase at higher temperatures (~600°C). Above approximately 800°C, transformation is completed [4–6]. Zirconia-based ceramics are found in a remarkable variety of technological and commercial applications such as catalysts [7], oxygen sensors [8], high dielectric constant materials for very large scale integrated circuits, and as gate dielectrics in metal oxide-semiconductor devices [9, 10].

ZrO_2 has been synthesized via different routes, for example by the microwave plasma method [11], chemical vapor synthesis [12], sol–gel method [13–15], precipitation [16], hydrothermal synthesis [17], etc. [18–20]. Several years ago we initiated a research work aimed at the synthesis of metallic [21, 22] and metal oxide nanoparticles [23–25] by thermal decomposition of inorganic complexes as precursors. A major interest at the moment is development of organometallic or inorganic compounds for preparation of nanocrystals. Using novel metal organic nanocomposites compounds as precursor for synthesis nano zirconia can be useful and can open a new way for preparing nano materials with controlling the nanocrystals sizes, shape and distribution size.

A variety of zirconium complexes have been successfully prepared and modified [26–29]. These precursors can be good candidates for the synthesis of ZrO_2 nano materials. In the present work, we discussed the synthesis of isophthalic acid-zirconium (IV) nanocomposite that has been prepared via sonochemical method, and preparation of ZrO_2 nano structures with tetragonal geometry, has been take place by thermal decomposition of the mentioned nanocomposite. Overall, we present a new rout for synthesis of pure t-ZrO_2 with high crystalinity, using a rapid, simple and cost-effective chemical method.

2. EXPERIMENTAL

2.1. Material and characterization

All reagents and solvents were obtained from Merck and Aldrich Chem. Co. and were used without further purification. FT-IR spectra (4000-400 cm^{-1}) were recorded on a Bruker tensor 27 spectrometer in a KBr matrix. Elemental analyses were performed with a Heraeus CHN-O-rapid analyzer apparatus. X-ray powder diffraction (XRD) measurements were performed with graphite monochromatic CuKα (λ=1.54056 Å) radiation using a Philips diffractometer manufactured by X'pert. Crystallite sizes of selected samples were estimated using the Scherrer method. The samples were gold coated for characterization with a scanning electron microscope. Thermo gravimetric analysis was carried out using a pyres diamond instrument. The compound was heated in a static atmosphere of nitrogen from 20-600^oC, with a heating rate of 10^oC/min. A multiwave ultrasonic generator using a Misonix, operating at 20 KHz with a maximum power output of 600 W, equipped with a convertor/transducer and titanium oscillator (horn), 12.5 mm in diameter, was used for the ultrasonic irradiation.

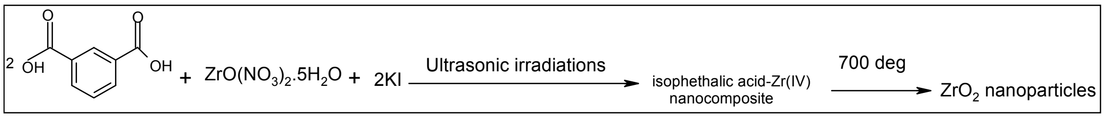
2.2. Synthesis of isophthalic acid-zirconium (IV) nanocomposite

Zirconyl nitrate pentahydrate, $ZrO(NO_3)2.5H_2O$, (0.23 g, 1 mmol) and the solid KI (0.17 g, 1mmol) were mixed in methanol (10 ml). Isophthalic acid (0.17 g, 1mmol) was solved in methanol (10 ml) and both of solutions were mixed together and sonicated for 30 min to obtain homogeneous mixture in an ultrasound vessel with the rated output power of 600 W and frequency 20 KHz. A yellow precipitate was obtained and was separated by centrifugation (4000 rpm, 15 min), washed with double distilled water and acetone. After that, this experiment has been done with ethylene glycol as a solvent. Both of precipitates were decomposed at 220°C. The resulting yellow powder isophthalic acid-zirconium (IV) (0.88 g) was prepared in 72% yield. Elemental analysis showed the following results: Calcd for ($ZrC1_6H_{10}O_9$): Zr, 20.89%; C, 43.91%; H, 2.28%; O, 32.93%. Found: Zr, 21.00%; C, 43.6%; H, 2.24%; O, 33.00%.

0.14 g of the product and 20 ml double distilled water was placed in 50 ml stainless-steel Parr bomb container (autoclave). After 48 h at 180^oC, the autoclave was immersed in 4^oC water. The suspension formed was centrifuged at 4000 rpm for 15 min. The precipitate was washed and dried at room temperature. Based on elemental analysis, FT-IR, and melting point results, the product was the same as isophthalic acid-zirconium (IV) nanocomposite produced by sonochemical method.

***Table 1**: Lattice parameters and size for ZrO_2 nanoparticles*

Sample	Solvent	Lattice constant (Å)		Cell volume	Average size (nm)	
		a=b	c	V (Å^3)	XRD	SEM
1	Methanol	3.617	5.176	67.330	51	49
2	Ethylene glycol	3.592	5.179	67.810	22	20



***Scheme 1:** The synthesis method for the preparation of the ZrO_2 nanocrystals*

2.3. Preparation of tetragonal ZrO_2 nanoparticles

As mentioned above a variety of zirconium complexes were prepared successfully. So these precursors can be good candidate for the synthesis of ZrO_2 nano materials.

ZrO_2 nano structures were synthesized by a simple route. In order to prepare the ZrO_2 nanoparticles, the mentioned nanocomposite was calcinated at 700°C for 4h, under air atmosphere. The resulting powder indicated a 99% yield of ZrO_2 nanoparticles. The product has been characterized with scanning electron microscopy (SEM), FT-IR and X-ray powder diffraction (XRD). FT-IR (KBr pellet, cm^{-1}): 1210(s), 510(w), 470(w), 431(s).

3. RESULTS AND DISCUSSION

Reaction between isophthalic acid ligand, with mixture of zirconyl nitrate pentahydrate and potassium iodide under ultrasonic irradiation in methanol and ethylene glycol as solvents, leads to the formation of a new isophthalic acid-Zr(IV) nanocomposite (Scheme 1) in 72% yield. The resulting product was insoluble in H_2O and DMSO. The most significant features of the FT-IR spectra of nanocomposite and ZrO_2 nanocrystals are recorded in the range of 4000-400 cm^{-1} and the bonding nature of functional groups in ligand with Zr(IV) before and after calcinations were studied by FT-IR spectroscopy (Figure 1, 2 and 3).

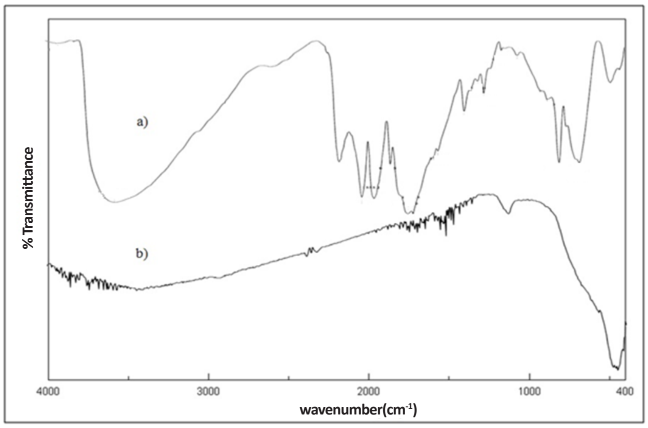


***Figure 1:** FT-IR Spectra for (a) Isophthalic acid- zirconium(IV) nanocomposite prepared by sonochemical method, (b) ZrO_2 nanocrystals (methanol).*

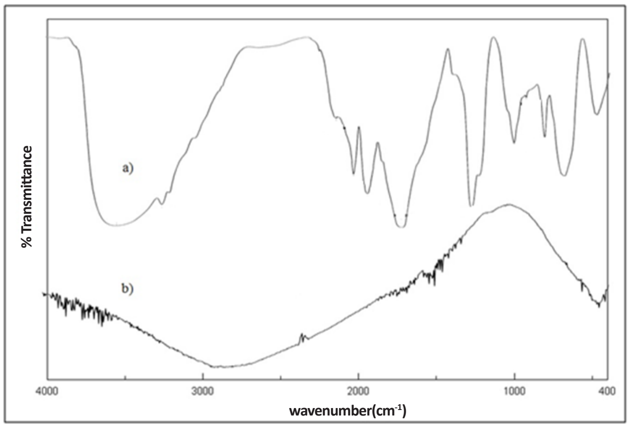


***Figure 2:** FT-IR Spectra for (a) Isophthalic acid- zirconium(IV) nanocomposite prepared by sonochemical method, (b) ZrO_2 nanocrystals (ethylene glycol).*

Comparing the infrared spectra of the prepared nanocomposite and isophthalic acid (ligand) showed that there are slight shifts in the peak position to lower wave numbers due to coordination of carbonyl groups and existence of new vibrational mode due to forming new Zr-O bonds. All these characteristic vibrational frequencies are found to be in good agreement with the proposed structure. It is well known that the FT-IR spectra are very useful technique for the determination of the crystal phase for ZrO_2 [30]. The spectra in Figure 1b and 2b showed bands at 400, 450, 501 and 700 cm^{-1} that can be related to t-zirconia.

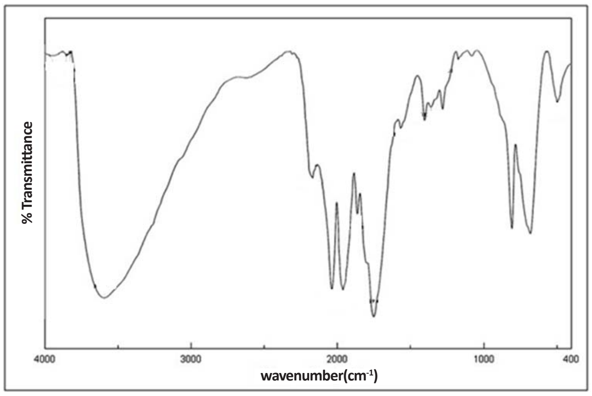


Figure 3: *FT-IR Spectra of Isophthalic acid-zirconium(IV) nanocomposite by hydrothermal method*

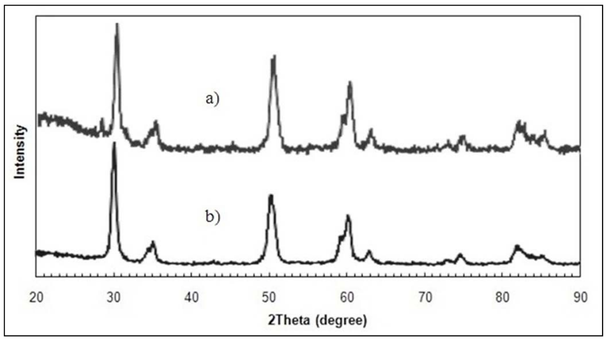


Figure 4: *XRD pattern of ZrO_2 nanocrystals in (a) methanol, (b) ethylene glycol*

The XRD diffraction pattern of the ZrO_2 was recorded for the identification of the product (Figure 4). From the XRD data, the crystallite size (Dc) of the as-prepared ZrO_2 particles was calculated to be 51 nm using the Debye–Scherrer equation [31],

$$D_c = \frac{K\lambda}{\beta\cos\theta}$$

where β is the breadth of the observed diffraction line at its half-intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in the XRD. All of the reflections of the XRD pattern in Figure 4 can be indexed to the standard pattern of the tetragonal phase of ZrO_2, which is in good agreement with the reported data (JCPDS No. 81-1544). This revealed that the ZrO_2 sample produced a single-phase tetragonal structure. Three observed peaks with 2 values of 30.17°, 50.18° and 60.03° correspond to the (1 0 1), (1 1 2) and (2 1 1) diffraction peaks of crystalline zirconia, respectively. The average crystallite size (Dc) and lattice parameters for two samples were reported in Table 1. As seen from Table 1, the average size of nanoparticles prepared in presence of ethylene glycol is smaller than that of obtained for the product prepared when methanol used as the solvent. Also, average size of the products

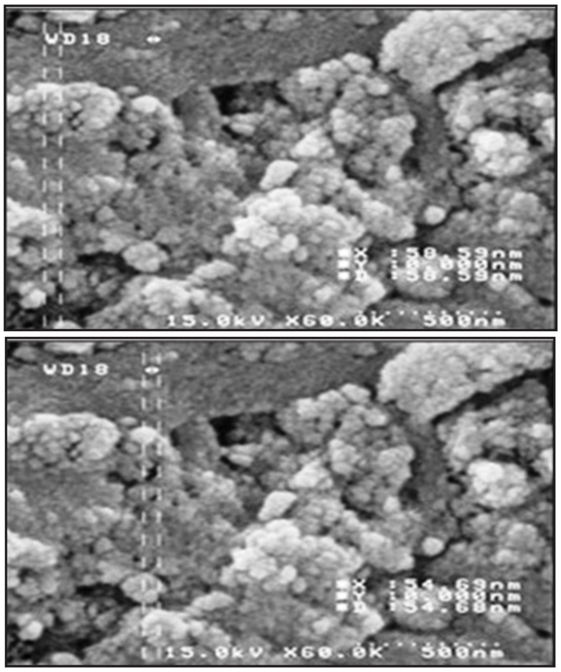


Figure 5: *SEM photograph of isophthalic acid-zirconium(IV) nanocomposite prepared by (a) sonochemical method, (b) hydrothermal method (methanol)*

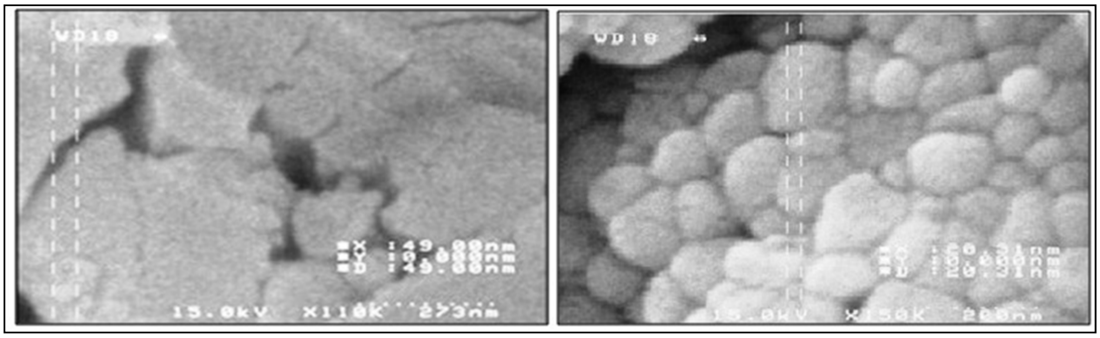


Figure 6: *SEM photograph of ZrO_2 nanocrystals in (a) methanol, (b) ethylene glycol*

is in good agreement with which was observed by scanning electron microscopy.

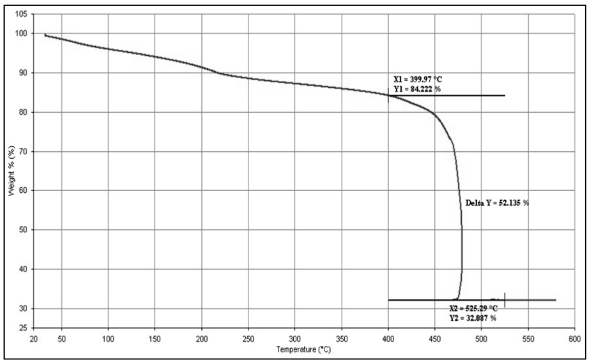


Figure 7: *TG curve of isophthalic acid-zirconium(IV) nanocomposite by sonochemical method in methanol*

The morphology of the isophthalic acid-zirconium (IV) naocomposite was examined by SEM. Typical SEM image is shown in Figure 5a shows nanocrystals with particle sizes about 58 nm. After hydrothermal treatment in an autoclave the particle size reduced up to about 54 nm (Figure 5b). This micrograph reveals that isophthalic acid-Zr (IV) nanocomposite is uniform in shape and size. Also, spherical shaped morphology has been observed for the nanoparticles. As a result, the nanoparticles aggregate randomly to form almost spherical shape. Figure 6a and b shows the SEM photograph of ZrO_2 nanoparticles in presence of methanol and ethylene glycol as solvent, respectively. As a result, when ethylene glycol has been used as solvent, ZrO_2 particles sizes decreased from about 49 nm to 20 nm. The TGA curve for decomposition of isophthalic acid-zirconium (IV) nanocomposite was recorded between 20 to 600°C in a static atmosphere of nitrogen is shown in Figure 7. According to Figure 7, a total of three weight losses were observed.

A weight loss of 8% occurred until 200°C, which is indicative of the loss of existing methanol and H_2O in compound and may be due to crystal lattice. The TG curve of the complex shows a loss of weight around 399°C and a gradual loss of weight of about 52% around 525°C to give a residual mass consisting of about 33%, close to that expected for a complete conversion to ZrO_2.

The weight loss from 399 to 525°C is linked with burning of organic factors (exothermic). There was some organic residue left after 525°C, because complete decomposition needs higher temperature (700°C) as confirmed by the FT-IR spectrum of the residual mass, after calcinations in 700°C.

4. CONCLUSIONS

A new nano structure of isophthalic acid-zirconium(IV) composite has been synthesized by sonochemical and hydrothermal methods in two different solvents methanol and ethylene glycol, in high yield. The compound has been found to be stable and insoluble in water and DMSO. Elemental analysis and FT-IR spectra showed that and thermal gravimetric analysis (TGA) showed that all the products were the same as each other, the particle sizes of the product, decreased in hydrothermal method. Calcination of the complex was produced tetragonal ZrO_2 nanoparticles. The particle size of the nanocrystals estimated between 51-22 nm by

Debye–Scherrer equation and SEM methods. When the solvent of the reaction is ethylene glycol, the produced ZrO_2 showed smaller particle sizes. The importance of this method of synthesis of tetragonal zirconia is production in lower temperature than ordinary methods and it is not only produces good yield in a short time, but also it does not require high temperatures or high pressures. This procedure can be generally approached to synthesize many other metal oxide nanoparticles.

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