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ScienceDirect
Journal of the European Ceramic Society 28 (2008) 773–778
www.elsevier.com/locate/jeurceramsoc

Synthesis of zirconia nanopowders from various zirconium salts via polyacrylamide gel method

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Received 21 March 2007; received in revised form 13 August 2007; accepted 1 September 2007
Available online 22 October 2007

Abstract

Pure monoclinic zirconia nanopowders were synthesized via a simple, fast and low cost method; *polyacrylamide gel* method. Also, the effect of initial salt precursor on thermal behavior of gel network and structure of the synthesized nanoparticles was studied with thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. The XRD results showed that the presence of nitrate ions not only retarded the crystallization, but also delayed the tetragonal to monoclinic phase transformation of zirconia nanoparticles which resulted in smaller particle sizes in comparison with the chloride samples. However, TG-DTA analysis confirmed accelerator role of nitrate ions on degradation of polymeric network. Thus, it was expected that zirconia nanopowders synthesized by nitrate samples have bigger sizes than the chloride base powders. Therefore, the presence of nitrate ions affects the synthesized nanoparticle size via two different mechanisms: the retarded crystallization and polymeric network degradation. But, TEM images revealed that the controlling mechanism is the former one.

Keywords: Nanostructures; ZrO_2; Polycrylamide gel; Grain growth; Phase transitions

1. Introduction

Due to possessing a combination of unique properties such as excellent refractoriness and chemical resistance, good mechanical strength, high ionic conductivity, low thermal conductivity at high temperature together with relatively high thermal expansion coefficient and good thermal stability, ultrafine zirconia (ZrO_2) particles have attracted much interest recently. Based on the above mentioned properties, they have found a broad industrial applications including: fabrication of dense ceramics, sensors, batteries, capacitors, corrosion-resistant and thermal-barrier coatings, fuel cells, solid electrolytes, catalysts, etc.[1,2] It is well known that using nanocrystalline structure of zirconia improves its functional properties.[3]

Zirconia exists in three crystalline forms of monoclinic, tetragonal and cubic structures at atmospheric pressure. The martensitic transformation from the tetragonal to the monoclinic structure has great importance in ceramic and catalytic applications of zirconia. 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.[1]

Ultrafine zirconia particles have been synthesized via various methods such as sol–gel processing,[4–6] chemical vapor synthesis,[7] precipitation from inorganic salt solutions,[1,6,8] microwave plasma synthesis,[9] inert gas condensation,[10] combustion synthesis,[11] ultrasonically assisted hydrothermal synthesis[12] and laser ablation.[13]

Sol–gel method is mostly used in order to obtain high purity, homogeneity and well controlled properties. The complex sol–gel process, a modified Pechini method, is a polymerized

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doi:10.1016/j.jeurceramsoc.2007.09.018

complex method.[14] This method is based on the formation of a solid polymer resin with cations chelated on it in a homogeneous manner. Cations in solution with a hydroxycarboxylic acid (e.g. citric acid) as chelating agent mixed with a polyhydroxy alcohol (e.g. ethylene glycol) causes to polyesterification at medium temperatures.[15] The product is then heated to elevated temperatures to remove organic residuals and the desired stoichiometric compounds are formed during the pyrolysis. This method has been previously applied for the preparation of different zirconia based powders such as yttria-stabilized zirconia[16,17] and ZrO_2:Eu nanopowders using EDTA as complexing agent.[14]

Polyacrylamide gel method is a new improvement of the previous synthetic routes, in which a solution of the respective cations is soaked. In this method, direct pyrolysis of polymeric network without separate drying step yields very fine and highly dispersed powders.[18–20] This method is time-saving in comparison with the Pechini method because in this method the formation of the artificial gel at low temperatures is more rapid than the Pechini method.[15] On the other hand, the original materials used in the polyacrylamide gel method are the aqueous solutions of inorganic salts. This allows avoiding use of the expensive metal alkoxides, unlike the other sol–gel methods.[20] Although, this method has been successfully applied in the synthesis of a considerable number of ultrafine powders, but it has not yet been used in the synthesis of zirconia nanoparticles. Therefore, regarding to this method benefits, synthesis of zirconia nanoparticles via polyacrylamide gel method would be a novel and simple process.

The main objective of the present work was synthesis of the zirconia nanoparticles via polyacrylamide gel method. In addition, the effect of zirconium source on properties of zirconia calcined at different temperatures was investigated and characterized by using X-ray diffraction (XRD), thermogravimetric and differential thermal analysis (TG-DTA) and transmission electron microscopy (TEM) techniques.

2. Experimental

2.1. Materials

The characteristics of the used materials are given in Table 1.

2.2. Synthesis procedure

AM and MBAM monomers with molar ratio of 22[21] as polymerization agents were added in an aqueous solution of zirconium oxychloride or zirconium oxynitrate. In all experiments, total concentration of the prepared solution and the weight ratio of monomers to salt were kept constant 50% (w/v) and 2/1, respectively. The mixture was stirred up to the transparent solution was observed. The free-radical crosslinking copolymerization of AM and MBAM was initiated by adding the initiator system (APS and TEMED) to the mixture. In this state, a transparent gel was rapidly obtained. The obtained xerogel was homogenized in a ceramic mortar and submitted to one subsequent thermal treatment. The xerogel was heated in a laboratory furnace (Ex.1200-2LA) and calcined at different temperatures (300–1000 °C). The thermal treatment was applied in a heating rate of 5 °C/min up to the desired holding temperature during 3 h, followed by the same cooling rate.

2.3. Characterization

Thermal decomposition behavior of the xerogels was evaluated with thermogravimetric and differential thermal analysis (RAS Diamond TG-DTA high temperature). The crystallite size, size distribution, structure and morphology of the zirconia powders were investigated from transmission electron microscopy images obtained with a Philips CM-200 FEG microscope. TEM samples were prepared by suspending the powder in ethanol and evaporating a droplet onto a carbon-coated copper grid. XRD data collection on the synthesized powders was carried out for phase identification and crystallite size determination using a Philips X-ray diffractometer, Model TW3710 using Cu Kα radiation in the range of $2\theta = 20–70^\circ$ with a 2θ step of 0.02 for 0.2 s per point. The monoclinic and tetragonal contents can be calculated using the intensities of their corresponding peaks in the XRD patterns. The tetragonal and cubic phases are difficult to distinguish by XRD patterns, due to their similar lattice parameters and the line broadening of XRD peaks in these patterns.[11] Molar fraction of m-ZrO_2 and t-ZrO_2 phases in zirconia samples (x_m and x_t) was estimated using equations proposed by Toraya[12]:

$$x_m = \frac{I_m(\bar{1}\,1\,1) + I_m(1\,1\,1)}{I_m(\bar{1}\,1\,1) + I_m(1\,1\,1) + I_t(1\,1\,1)} \quad (1)$$

Table 1
Characteristics of materials

Materials	Function	Molecular formula	Supplier
Acrylamide (AM)	Monofunctional monomer	$C_2H_3CONH_2$	Merck[a]
N,*N*′-Methylene bis acrylamide (MBAM)	Difunctional monomer (crosslinker)	$(C_2H_3CONH_2)_2CH_2$	Merck[a]
Ammonium persulfate (APS)	Initiator	$(NH_4)_2S_2O_8$	Merck[a]
N,*N*,*N*′,*N*′-Tetramethyl ethylene diamide (TEMED)	Accelerator	$C_6H_{16}N_2$	Merck[a]
Zirconium oxychloride	Initial salt	$ZrOCl_2{\cdot}8H_2O$	Merck[a]
Zirconium oxynitrate	Initial salt	$ZrO(NO_3)_2{\cdot}2H_2O$	BDH[b]
Water	Solvent	H_2O	Ghazi[c]

[a] E. Merck, D 6100 Darmstadt, Germany.
[b] BDH Laboratory Supplies Poole, BH151TD, England.
[c] Shahid Ghazi Pharmaceutical Co., Tabriz, Iran.

$$x_t = 1 - x_m \quad (2)$$

where I_m and I_t are the integrated intensities of the monoclinic and tetragonal phases, respectively. Furthermore, the crystallite size of the zirconia nanopowders was estimated using the standard Scherrer's formula[22]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

where D is the crystallite size (nm), λ is the radiation wavelength (0.15406 nm), θ is the diffraction peak angle and β is the corrected half-width at half-maximum intensity (FWHM).

3. Results and discussion

3.1. Thermal analysis

TG and DTA curves of the pure polyacrylamide gel together with the same results for nitrate and chloride base xerogels are presented in Fig. 1. As it can be clearly seen in Fig. 1(a), degradation of polymeric network is a multi-step process, which is completed at temperatures about 600 °C. The weak endothermic effect associated with a weight loss about 10% for temperatures below 250 °C, was attributed to departure of trapped moisture. Considering that the elimination of organics through oxidation is an exothermic reaction, two strong exothermic peaks appeared at about 330 °C (step I) and 500 °C (step II) were assigned to the oxidative decomposition of organic residues. In addition, the results show that the presence of nitrate ions accelerates the degradation of polymeric network, while chloride ions effect on the thermal stability of polyacylamide gel is not significant in comparison with nitrate ions. It is interesting to note that the loss of approximately 40% of the original mass for the former sample has occurred at temperature about 280 °C, while for the later sample the same weight loss has occurred at temperature about 480 °C. This is supported by the presence of an exothermic peak at about 280 °C in the DTA curve of the nitrate sample (Fig. 1(b)). Knowing that the thermal stability of polymeric network can effectively inhibit the aggregation of powders at high temperatures of calcination, it would be expected that zirconia nanopowders synthesized by nitrate samples have bigger sizes in comparison with the chloride base powders.

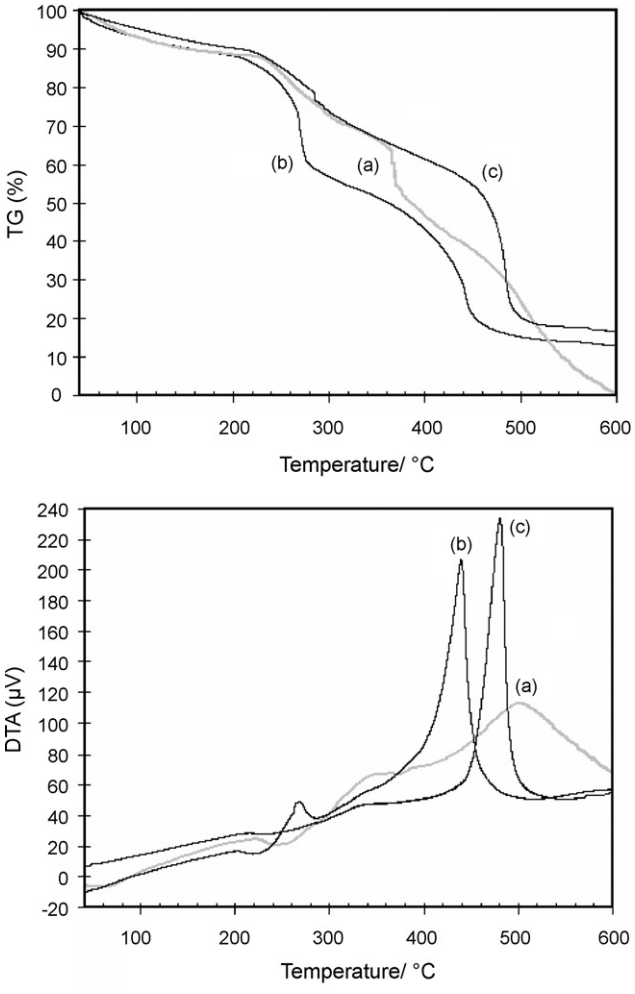

Fig. 1. TG (top) and DTA (bottom) curves under air flow at a heating rate of 5 °C/min for: (a) pure gel; (b) oxynitrate salt xerogel; (c) oxychloride salt xerogel.

3.2. Crystallization

XRD patterns of the synthesized product with oxynitrate salt are shown in Fig. 2. As can be seen, the synthesized zirconia powders have amorphous structure at 300 °C. By rising the calcination temperature, a semicrystalline structure (only tetragonal phase) is formed at 400 °C. As the calcination temperature increases to about 600 °C, both monoclinic and tetragonal phases are detected. Further increasing of the temperature, causes an increase in the proportion of monoclinic phase and at temperature 800 °C the transformation to monoclinic phase is completed. Using oxychloride salt precursor results in different trend of phase transformation in the zirconia crystallinity structure. As shown in Fig. 3, crystallization initiates at lower

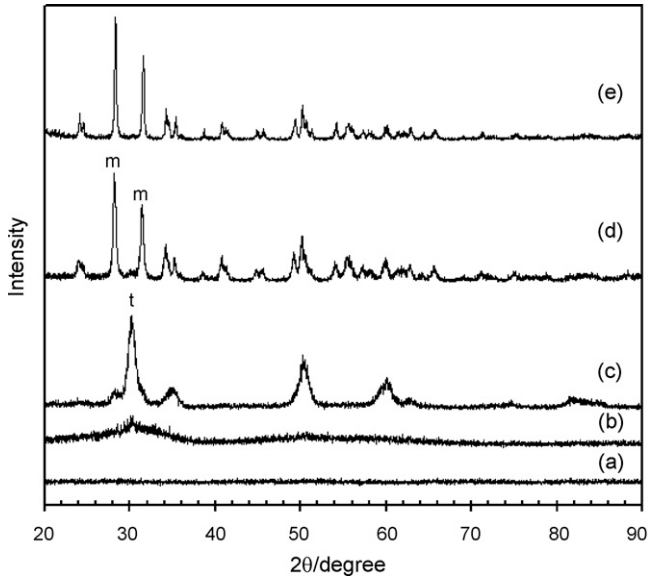

Fig. 2. XRD patterns of nano-ZrO_2 prepared by oxynitrate salt calcined at: (a) 300 °C; (b) 400 °C; (c) 600 °C; (d) 800 °C; (e) 1000 °C.

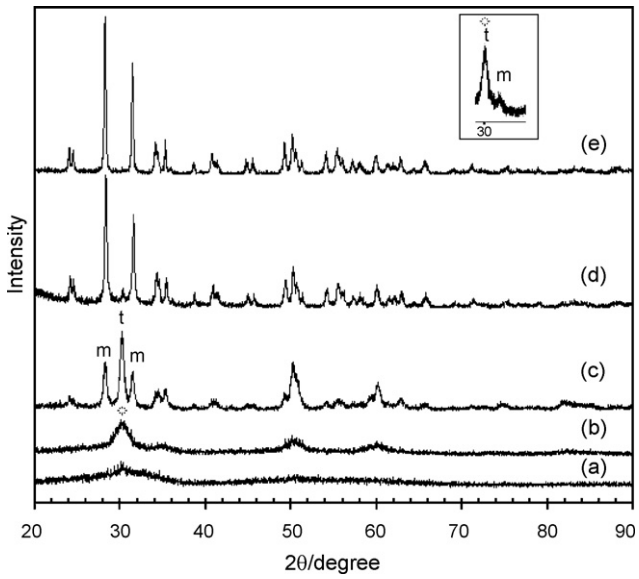

Fig. 3. XRD patterns of nano-ZrO_2 prepared by oxychloride salt calcined at: (a) 300 °C; (b) 400 °C; (c) 600 °C; (d) 800 °C; (e) 1000 °C. The inset picture corresponds to a magnification of the XRD pattern in the range between 29 and 35 (m: monoclinic phase).

temperatures (300 °C) unlike the oxynitrate salt. Appearance of a weak hump near 2θ 31.4° observed in the XRD pattern of (Fig. 3b) implies the presence of small amount of monoclinic ZrO_2 at temperature 400 °C. The presence of monoclinic phase can be exactly clarified at temperature 600 °C, while from 800 °C to higher temperatures two salt precursors show the same behavior and the samples are comprised of nearly pure m-phase.

Fig. 4 illustrates the variation of the monoclinic phase content as a function of calcination temperature for two different salts. As mentioned before, increasing of calcination temperature causes to increase the monoclinic phase content dramatically. However, the formation of monoclinic phase in oxychloride salt is initiated at lower temperatures than that of oxynitrate salt. It can be concluded that the presence of nitrate ions delays tetragonal to monoclinic phase transformation of zirconia. Also, chloride ions affect the crystallization temperatures, so that the crystallization shifted to a lower temperatures and transition rate of t → m phase increased. These results are in good agreement with the literature.[23–26]

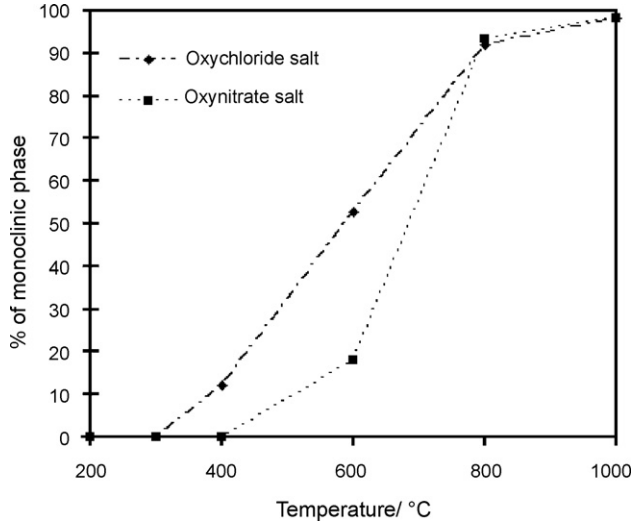

Fig. 4. Variation of the monoclinic phase amount as a function of the calcination temperature for two salts.

3.2.1. *Effect of impurities*

Nitrate and chloride ions were the only high concentration impurities in our precursor solutions. The suggested structure for zirconium oxynitrate precursor made up parallel cations chains, with the repeating unit $[Zr(OH)_2(OH_2)_2(NO_3)]^+$, in which zirconium atoms are eightfold coordinated by four OH groups, two water molecules and one chelating nitrate. These chains are held together by hydrogen bonds through additional water molecules and non-complexing nitrate groups located between the chains. Thus, half of the present nitrate groups are directly (covalently) coordinated to the zirconium atoms and the other half are ionically bound in the crystal lattice between the chains. But anions such as Cl^- do not give complexes with zirconium. In zirconium oxychloride aqueous solution, the structure of the cyclic tetramer species, $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$ existed in solution, in which zirconium atoms are eightfold coordinated by four bridging OH groups and four terminal water molecules. Thus there is no Zr–Cl bond in this system.[27,28]

There has been a wide range of effective parameters on the nucleation and stabilization of the tetragonal phase, such as lattice defects, oxygen vacancies, structural similarity with the amorphous precursor, retention of various anions or water, strain, surface energy, etc. The structure of the precursor material may well influence the size, strain defect density and surface energy of the calcined crystals, all of which have been suggested to determine the stability of the tetragonal phase. It has been suggested that nitrate ions, remaining from the original solution, could retard the nucleation and growth of monoclinic domains. This impurity may act as point defects which inhibit the martensitic t → m transformation.[27] Also, in other experiments,[26] the stabilization of tetragonal phase of ZrO_2 by nitrate ions has been confirmed.

Although chloride is apparently not present as a bulk impurity in ZrO_2, the presence of chloride in precursor solution during processing, does have a major influence on the crystalline structure. As mentioned in the literature, increasing of t → m phase transformation rate in the presence of chloride ions, may be explained by two mechanisms. The first is the effect of crystallite size on transformation pointed out by Garvie,[29] which probably the presence of chloride has lowered the critical crystallite size because of easier evolving of HC1 to the gas phase in compare to H_2O. The second is the effect of oxygen vacancies, which may play an important role in the stabilization of tetragonal zirconia. It can be suspected that chloride also affects the oxygen vacancies density, i.e. by increasing chloride impurity content, oxygen vacancies density decreases significantly.[25] The possibility remains that oxygen vacancies may act as point defects, inhibiting the martensitic t → m transformation.[27]

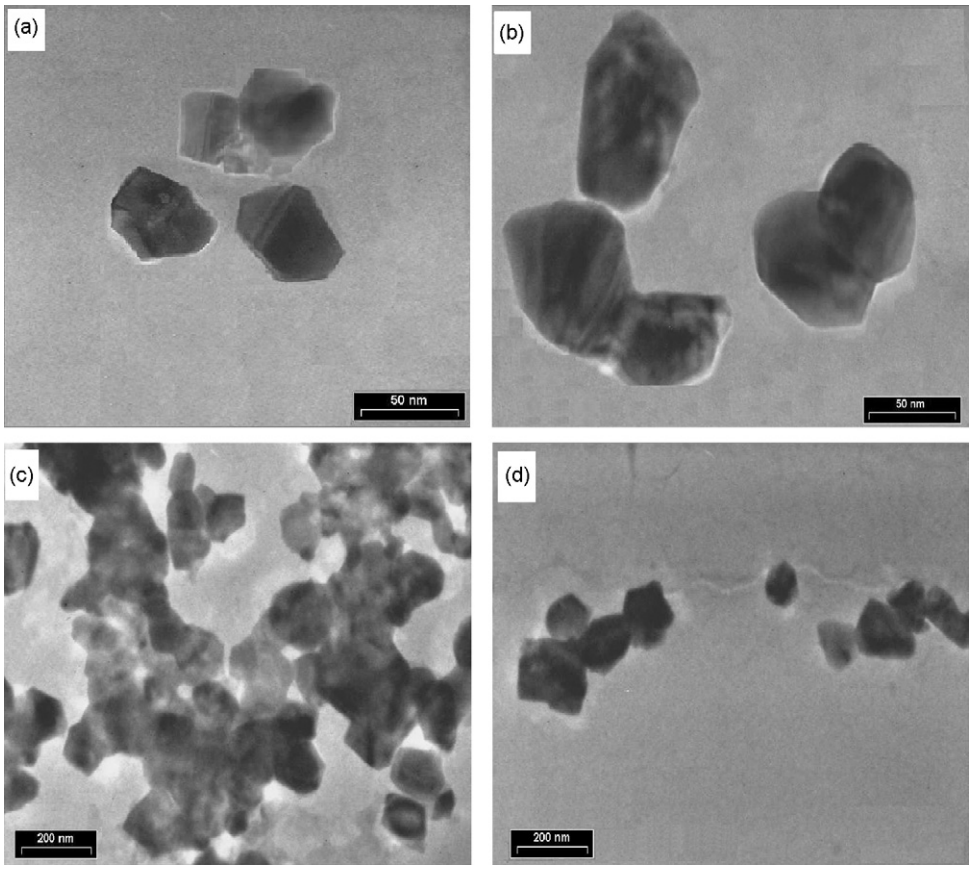

Fig. 5. TEM micrographs of monoclinic zirconia nanopowders obtained by different salts and calcination temperatures: (a) oxynitrate salt, 800 °C; (b) oxychloride salt, 800 °C; (c) oxynitrate salt, 1000 °C; (d) oxychloride salt, 1000 °C.

3.3. Particle size and morphology

To determine the mean crystallite size of the monoclinic phase, we selected the two strongest peaks assigned to the monoclinic phase (28.19, indexed as $\bar{1}\,1\,1$, and 31.49, indexed as 1 1 1). The obtained results (Table 2) show that the crystallite size of monoclinic phase is growing with increasing heat-treatment temperature. Unlike the thermal analysis results, the crystallite size of zirconia nanopowders synthesized from oxychloride salt is bigger than the oxynitrate one which can be due to the formation of monoclinic crystals at lower temperatures with oxychloride salt precursors. The calculated crystallite sizes are 42 nm for the nitrate sample and 56–60 nm for the chloride sample calcined at 800 °C. But for both samples heated at 1000 °C the mean sizes of the crystallites is estimated about 70 nm. In other words, the zirconia nanopowders prepared from oxynitrate salt in the temperature region 800–1000 °C grow faster than another salt.

Table 2
Average crystallites size of m-zirconia (nm) as a function of temperature determined from XRD patterns

Calcination temperature (°C)	ZrON[a]		ZrOCl[b]	
	$D_{\bar{1}\,1\,1}$	$D_{1\,1\,1}$	$D_{\bar{1}\,1\,1}$	$D_{1\,1\,1}$
400	–	–	–	–
600	–	–	35	37
800	42	42	60	56
1000	72	65	72	68

[a] Zirconia prepared from oxynitrate salt.
[b] Zirconia prepared from oxychloride salt.

Typical TEM images of ZrO_2 powders synthesized by various salts at 800 and 1000 °C of calcination are presented in Fig. 5. The mean diameter of the particles as measured is about 45 nm for nitrate sample and 60 nm for chloride sample calcined at 800 °C. Both samples calcined at 1000 °C are comprised of particles with 85 nm sizes. These results are in good agreement with that of estimated by X-ray line broadening. Also, the synthesized nanopowders are well crystallized without defects, non-agglomerated with narrow size distributions.

4. Conclusion

The polyacrylamide gel method has been successfully employed to obtain pure, homogeneous and nano-sized zirconia powder. TG-DTA analysis confirmed the accelerator role of nitrate ions on degradation of polymeric network. Due to the thermal stability of polymeric network effect on the inhibition of powders aggregation at high calcination temperatures, it was expected that zirconia nanopowder synthesized by nitrate samples have bigger sizes in comparison with the chloride base powder. However, the obtained XRD results showed that the presence of nitrate ions, unlike the chloride ones, retarded the

crystallization and delayed the tetragonal to monoclinic phase transformation of zirconia nanoparticles. This trend can be due to the point defects arised in the presence of nitrate ions, stabilizing the tetragonal phase, while chloride ions decrease point defects (oxygen vacancies), accelerating the martensitic t → m transformation. But, at higher calcination temperatures (approximately 800 °C) only pure monoclinic phase was observed for both of the initial salts. Thus, as a result of the retarded crystallization mechanism, samples calcined at 800 °C and prepared by oxynitrate salt had average particle sizes smaller than the chloride samples. TEM images showed that the mean diameter of nanoparticles as measured was about 45 nm for nitrate sample and 60 nm for chloride sample. These results confirmed that in this case, the retarded crystallization mechanism dominated over the polymeric network degradation.

Acknowledgments

The Authors wish to thank Sahand University of Technology (SUT) for the financial support of this work. Also, thank coworkers and technical staff in the research center for polymeric materials of SUT for their help during various stages of this work.

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