

The zirconia phase transformation in the preparation of nano zirconia by calcining a gel-emulsion precursor

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Nano-ZrO₂ was successfully prepared by calcining a precursor of a zirconium gel-emulsion in oleic acid. The gel-emulsion process was started with the preparation of a gel zirconium hydroxide. The hydroxide gel was then mixed with oleic acid at various ratios and heated at 200 °C to give zirconia precursors. These precursors were successfully calcined at 800 °C, 1000 °C, and 1200 °C, to give zirconia powder. The crystal structure and the particle morphology of the calcined powder were identified using XRD, SEM, and TEM. The XRD results show that monoclinic zirconia is formed dominantly with crystallite sizes ranging from 46.2 to 55.3 nm at 800 °C. Meanwhile, the SEM micrographs of the zirconia calcined at 800 °C show particles with a homogenous morphology having sizes below 100 nm. The TEM results indicate that the individual grain diameters of ZrO₂ were less than 60 nm. A lower oleic acid concentration leads to a more alkaline condition and more monoclinic zirconia formed; and a higher calcination temperature leads to a larger size of crystallites.

Keywords: Zirconia, Gel-emulsion precursor, Oleic acid, Phase transformation.

Introduction

Extensive researches have been made to synthesize ultra fine particles of nano crystalline zirconia (ZrO₂). The most common methods used to prepare nano zirconia are the "Sol-Emulsion-Gel" and the "Sol-Gel" techniques [1, 2]. Roy [3], synthesized tetragonal zirconia using polyacryl amide as a gelling agent and a matrix, and the final product investigated had a particle size of about ~20 nm. Shukla *et al.* [4], prepared nano powder zirconia through a sol gel process involving hydrolysis and condensation of zirconium (IV) n-propoxide in an alcohol solution using hydroxyl propyl cellulose (HPC) polymer as a steric stabilizer to prevent the agglomeration of molecules; and calcination was successfully conducted at 400 °C for 2 hours to give tetragonal zirconia having a crystallite size of about 65 nm. Joo, *et al.* [5], used a nonhydrolytic solgel reaction between zirconium (IV) isopropoxide and zirconium (IV) chloride at 340 °C to generate 4 nm sized zirconia nanoparticles.

Synthesis and control of materials of nano dimensions would give novel new materials with superior properties. Controlled structures, large interfacial areas, power density and other unique characteristics are examples of the superiority of the properties of nanomaterials so that they can access new and improved properties and functionalities. Also, nanopowder will have characteristics such as a

particle size ranging of about 10-100 nm, a narrower grain size distribution, will be more homogenous chemically and physically, the chemical composition and the purity of materials can be controlled, the morphology also can be controlled, and a lower sintering temperature.

Therefore, nano-ZrO₂ exhibits much better chemical and physical properties as compared to normal or coarse ZrO₂ powder, due to the small particle diameter which will result in better sintering ability [6-8].

Zirconia (ZrO₂) is an oxide material that shows excellent properties, such as high mechanical strength (compressive strength 1000-1800 MPa), fracture toughness 8-13 Mpa m^{1/2}, hardness (Vickers hardness 13-24 GPa), is thermally stable (m.p. 2680 °C), and is chemically inert. Therefore, these characteristics enable zirconia to be used in structural applications and for electrical purposes [1, 2].

In these experiments, oleic acid was used as an emulsifier to bind molecules of zirconium cations either on their salts or hydroxide compounds through chemisorption. Oleic acid has been used as an emulsifier in the preparation of nanocrystalline and nanoparticle oxides, such as α -alumina synthesis by Lee *et al.* [9], Lin *et al.* [10,11], etc. The objectives of this study are to evaluate the zirconia phase transformation under various ratios of a zirconium hydroxide gel to oleic acid; and the alterations of the crystal structure and size by altering the calcination temperature. An XRD analysis was conducted to identify the crystalline phase and the crystallite size of calcined powders using an X-Ray Phillips Pan Analytical instrument. SEM, JEOL JSM-35C, was performed to observe the particle morphology and to estimate the particle size in general. TEM, Tecnai G² 20 Twin, was performed to establish the grain form and size.

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Experimental Procedures

Materials and Instruments

Materials used in this work were ZrCl_4 , 21% ammonia solution, and oleic acid. All materials were obtained from Merck Inc.; whereas instruments used were a dual speed mixer maximum 2000 rpm, a Heraus electrical furnace, a Nabertherm electrical furnace, an X-Ray Phillips PANalytical EMPYREAN instrument with an *X'Celerator* detector, a scanning electron microscope JEOL JSM-35C, and a transmission electron microscope Tecnai G² 20 Twin.

Methods

The preparation of nanoparticle zirconia

A certain amount of zirconium chloride was dissolved in water, then 21% ammonia solution was added appropriately and stirred to give a gel of $\text{Zr}(\text{OH})_4$. The gel was reacted slowly with oleic acid and stirred at ± 800 rpm to produce a homogenous emulsion. The zirconium salt to oleic acid ratios were varied at 1 : 2 (ZAO_02), 1 : 1.4 (ZAO_01), and 1.4 : 1 (ZAO_10). The pH condition of each composition was measured and recorded. The emulsions were continuously heated slowly and stirred simultaneously until the water evaporated completely. The residue obtained was then dried in an oven at 200 °C to produce black charcoals; then they were oxidized at 480 °C for 5 hours, and successfully calcined at the temperatures of 800 °C, 1000 °C, and 1200 °C in an electric furnace. The final products were identified using XRD, SEM, dan TEM.

The characterization of the synthesized nanoparticle zirconia

A qualitative analysis on identification for the crystalline phase of nano zirconia was conducted using an X-Ray Phillips PANalytical instrument in PANalytical *APR Application Laboratory Unit 102*, Shanghai, R.R.China, with software support of X'Pert HighScore Plus and the database references of ICDD PDF4+ and PDF2. Meanwhile, a quantitative analysis for the mineral phases applied the *Rietveld* method and used software of X'Pert HighScore Plus; the crystallite size was identified and determined with *Williamson-Hall plots* and *line profile analysis* using the software.

Result and Discussion

The zirconia phase transformation based on XRD identification

The results of XRD identification on the zirconia phase transformation of the ZrO_2 samples coded (ZAO_02), (ZAO_01), (ZAO_10) and calcined at 800-1200 °C are presented in Figs. 1-3.

Fig. 1 shows XRD patterns of the ZrO_2 samples coded (ZAO_02), (ZAO_01), (ZAO_10) that were calcined at 800 °C. According to the XRD patterns, two phases of zirconia in all the samples were identified as t- ZrO_2 and m- ZrO_2 . The analytical results are based on identification

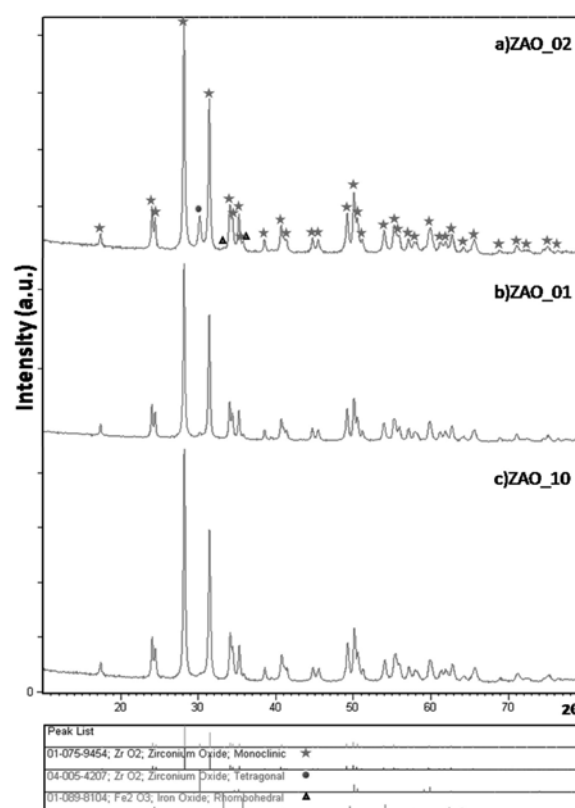


Fig. 1. XRD patterns of the zirconia samples coded (ZAO_02), (ZAO_01), (ZAO_10) at 800 °C.

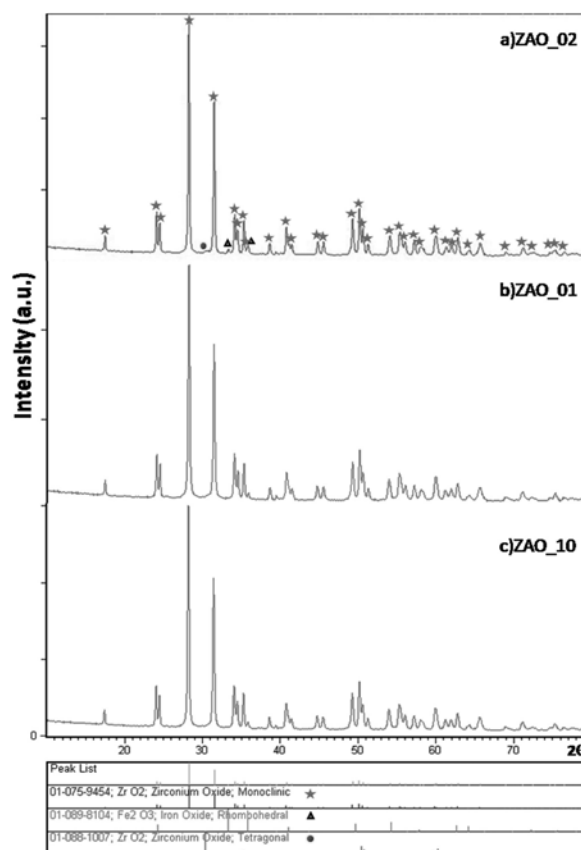


Fig. 2. XRD patterns of the zirconia samples coded (ZAO_02), (ZAO_01), (ZAO_10) at 1000 °C.

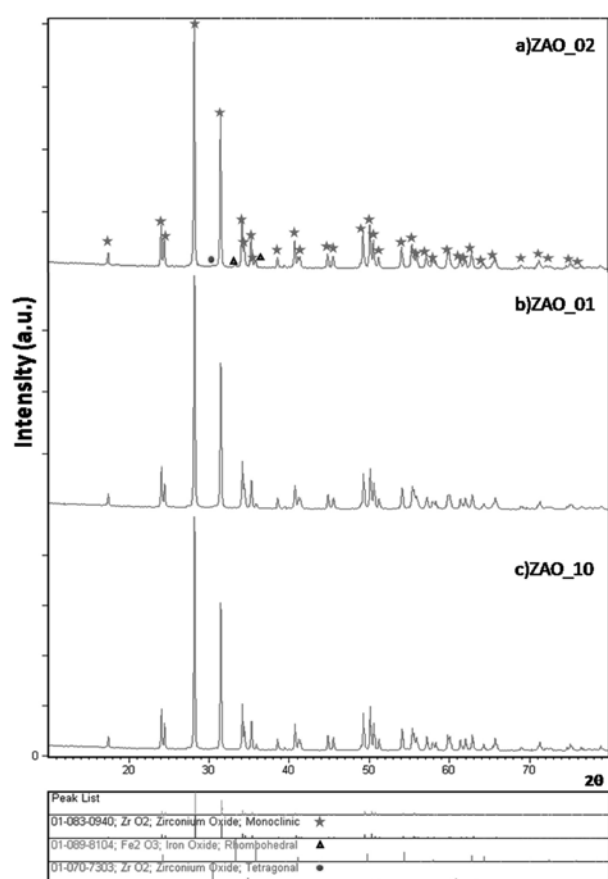


Fig. 3. XRD patterns of the zirconia samples coded (ZAO_02), (ZAO_01), (ZAO_10) at 1200 °C

using software X'Pert HighScore Plus and the database references of ICDD PDF4+ and PDF2; and are summarized in Table 1.

The concentration of t-zirconia in the ZrO_2 samples coded (ZAO_02), (ZAO_01), (ZAO_10) at 800 °C decreases with a lowering of the oleic acid content used. This is probably caused by the pH difference in each precursor emulsion which tends to a basic condition, with the pH values of 3, 4 and 6 for ZAO_02, ZAO_01 and ZAO_10, respectively. A decrease of the oleic acid content in the

preparation of nanoparticle zirconia has influenced the binding process of zirconium by the active functional group of oleic acid ($-\text{OH}$, hydroxyl group). The concentration of Zr^{4+} will be higher in the emulsion when the concentration of oleic acid emulsion is decreased; thus the distance between zirconium cations is getting closer and they would combine quickly with each other to produce larger crystals. By contrast, when the concentration of oleic is increased, more zirconium cations will be bound to oleic acid; thus the distance between zirconium cations is getting wider and far from agglomeration, therefore crystal growth would be slower in thermodynamic terms. The presence of t-zirconia in the ZrO_2 samples coded (ZAO_02), (ZAO_01), and (ZAO_10) is very small in quantity, this is in agreement with the very low intensity peak at a diffraction angle 2θ of 30.25° that refers to t-zirconia. The intensity is lower when the oleic acid concentration is decreased and the calcination temperature is increased. The main phase of all the zirconia samples is m-zirconia, which is indicated by the appearance of two main peaks at diffraction angles 2θ of 28.21° and 31.45° . Both peaks present plane orientations in the crystal of $(\bar{1}11)$ and (111) respectively. The peak intensity of t-zirconia declines as the calcination temperature is increased, because the t-zirconia phase theoretically forms at 400–600 °C [12]. However, above this temperature range, the t-zirconia will slowly transform to m-zirconia. The transformation occurs very well when the temperature reaches to equal or is above 1000 °C [3]. This is in accordance with the diffraction patterns shown from all the zirconia samples calcined at 1200 °C; whose the crystalline phase formed is pure m-zirconia. Hematite was identified in a very small concentration in the sample coded (ZAO_02) after calcining at 800 °C, 1000 °C and 1200 °C. This was probably caused by small quantity of impurities of ultrafine iron which stuck to the reagent container in the earlier synthesis process of the gel-emulsion zirconium-oleate.

A Rietveld refinement was also carried out on the zirconia samples for a quantitative analysis using X'Pert High Score Plus. The Rietveld method is a full-pattern fitting method in which a measured diffraction profile and a calculated profile are compared and, by varying a range of parameters,

Table 1. More information of reference patterns

Reference Code	Compound Name	Mineral Name	Chemical Formula	Crystal System	Space Group
01-075-9454	Zirconium Oxide	Baddeleyite	ZrO_2	Monoclinic	P21/c
04-005-4207	Zirconium Oxide		ZrO_2	Tetragonal	P42/nmc
01-089-8104	Iron Oxide	Hematite	Fe_2O_3	Rhombohedral	R-3c
01-088-1007	Zirconium Oxide		ZrO_2	Tetragonal	P42/nmc
01-072-7115	Zirconium Oxide	Zirconia	ZrO_2	Tetragonal	P42/nmc
01-083-0940	Zirconium Oxide	Baddeleyite	ZrO_2	Monoclinic	P21/c
01-070-7303	Zirconium Oxide		ZrO_2	Tetragonal	P42/nmc
83-0944(PDF 2)	Zirconium Oxide	Baddeleyite	ZrO_2	Monoclinic	P21/c
80-2156(PDF 2)	Zirconium Oxide	Zirconia	ZrO_2	Tetragonal	P42/nmc

Table 2. The quantification results, an agreement index of the Rietveld and the line profile results

Samples	Concentration (%)		Fe ₂ O ₃	Agreement Index		Line Profile Results	
	ZrO ₂ (Monoclinic)	ZrO ₂ (Tetragonal)		Rp	Rwp	grain size (Å)	Micro Strain (%)
800 °C(ZAO_02)	89.1	10.1	0.8	2.66	3.39	467	0.18
800 °C(ZAO_01)	98.0	2.0	-	3.13	3.96	553	0.13
800 °C(ZAO_10)	98.6	1.4	-	2.81	3.67	463	0.18
1000 °C(ZAO_02)	96.0	0.9	3.1	3.35	4.37	1123	0.13
1000 °C(ZAO_01)	100.0	-	-	-	-	972	0.17
1000 °C(ZAO_10)	100.0	-	-	-	-	1031	0.17
1200 °C(ZAO_02)	96.7	0.5	2.8	4.56	5.90	1529	0.09
1200 °C(ZAO_01)	100.0	-	-	-	-	1239	0.09
1200 °C(ZAO_10)	100.0	-	-	-	-	1733	0.05

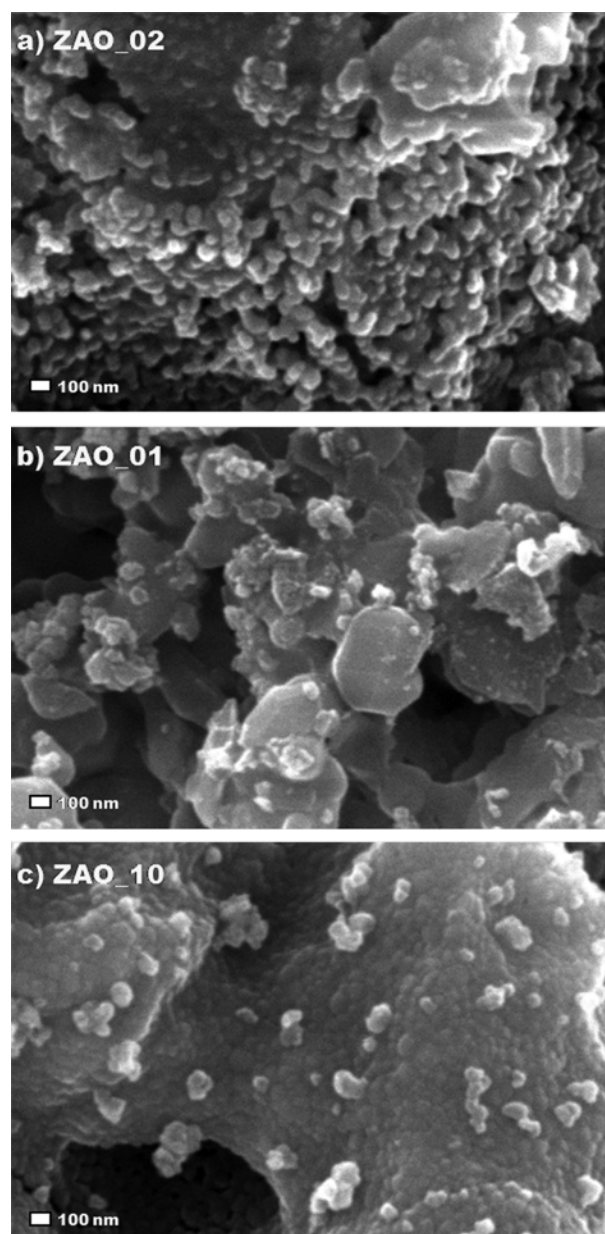
the difference between the two profiles is minimized. Only the crystal structure data of all phases in the samples are needed for this method. Table 2 presents the quantification results of these ZrO₂ samples and agreement index (Rp and Rwp values) of the Rietveld refinement. Line profile analysis was also implemented on the monoclinic zirconium oxide phase in all the samples. X'Pert HighScore Plus 3 uses the classical linear Williamson-Hall plot for line profile analysis. This way a straight line is fitted through the data (structural broadening and peak position) from multiple peaks. The slope of the line gives a micro-strain value while the offset is used to calculate the crystallite size. In order to get accurate results of crystallite size and micro-strain, a crystalline standard sample which has a little of or no line broadening itself must be measured to correct for the instrumental broadening to calculate the correct structural broadening; and the NIST standard SRM 1976a (α -Al₂O₃) is used in this case. The results are also listed in Table 2.

Morphology

SEM micrographs for all the zirconia samples at 800 °C (Fig. 4) show the particle morphology having homogenous irregular grains of 100 nm size. TEM and electron diffraction (ED) patterns of the representative ZrO₂ products are shown in Fig. 5. TEM images of the ZrO₂ coded (ZAO_02) with pH = 3 and (ZAO_10) with pH = 6 at 800 °C are shown as ED patterns in Fig. 5(a1,a2) and Fig. 5(b1,b2), respectively. TEM results revealed that the individual grain diameters of ZrO₂ were less than 60 nm.

The effect of oleic acid on nano zirconia phase transformation

A gel-emulsion technique using oleic acid as an emulsifier in the preparation of nanoparticle zirconia is known as *the calcination control of chemical additives* (CCCA) [11]. This technique has been developed to prepare some oxide materials such as BaTiO₃ [13], Al₂O₃ [14], dan ZrO₂ [15]. By this technique, an aqueous solution of the ceramic precursors is emulsified with an organic fluid that contains an organic surfactant to disperse the aqueous droplets into

**Fig. 4.** SEM micrographs for all the zirconia samples at 800 °C.

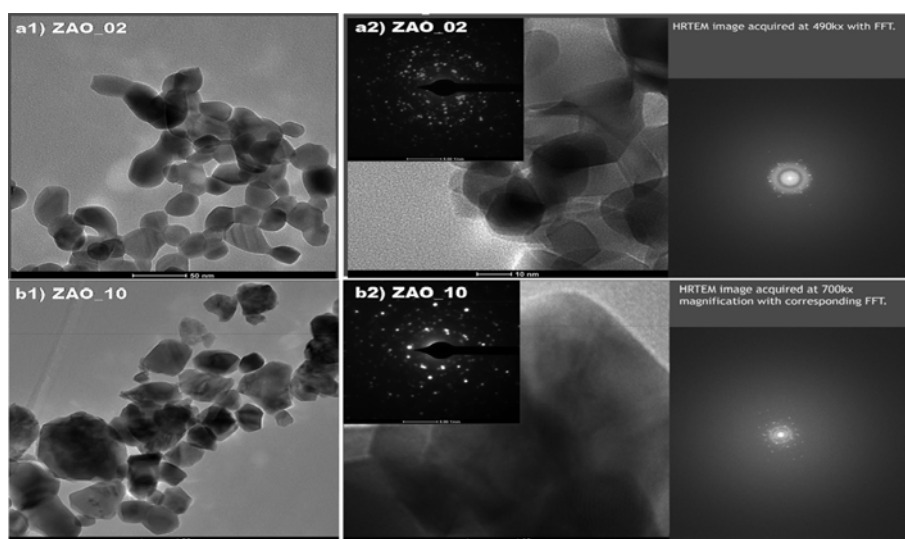
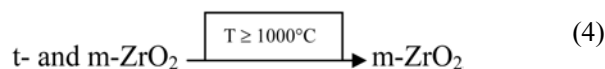
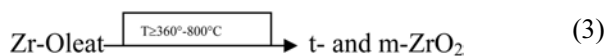
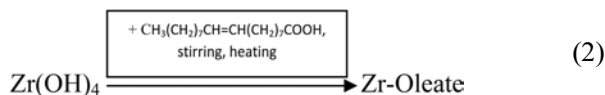
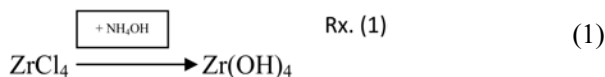


Fig. 5. TEM images and electron diffraction patterns for the zirconia samples coded (ZAO_02) with pH = 3 and (ZAO_10) with pH = 6 at 800°C.

an almost uniform size. The resultant emulsion is pyrolyzed in an oven at a defined temperature, under an air atmosphere, to convert the emulsion into fine particles isolated by an amorphous char. The char is calcined under controlled conditions, to burn off the generated carbon, thus forming the ultrafine powders [11]. During calcination, different types of zirconia may appear through the normal low-temperature to high-temperature progression of the phase transformation, the zirconium that reacted with oleic acid by a chemisorption process transforms to t-zirconia; and it transforms to m-zirconia at a higher calcination temperature.



A nuclear growth during the transformation from Zr(OH)_4 to t-zirconia occurs rapidly before m-zirconia formed. To prevent this effect, coating the hydroxide precursor is proposed with a surfactant to obstruct crystal growth during t-zirconia formation. Therefore, oleic acid was selected as the surfactant because a fatty acid coated onto ZrO_2 , and zirconium modifies the surface properties of those materials. The oleic acid strengthens the layers and isolates the ZrO_2 transformation. The structure of the intermediate ZrO_2 depends on surface reactions, as well as on the phase transformation. Some variations in the mechanism of the phase transformation of Zr(OH)_4 with organic compounds such as oleic acid under a heating and a calcination process have been studied [11]. As Zr(OH)_4 was mixed with oleic

acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ by vigorous stirring and slow heating, the chemisorption process of oleic acid onto Zr(OH)_4 gel was undergone to produce zirconium-oleate (equation 2). When the oleic acid was heated, it helped the oleic acid chars to form carbon, rather than burning out, after they had reached the boiling point of the oleic acid at 360 °C. However, the carbon would isolate and coat onto zirconia which starting to form, thus obstructing crystal growth and preventing the agglomeration of zirconia at the time of the phase transformation on calcinations at over 400 °C [11, 12].

Conclusions

The present investigation studies the zirconia phase transformation through a gel-emulsion of zirconium-oleate in the preparation of nanozirconia and in coexistence with the carbon generated during heating, to obstruct agglomeration during the formation of ZrO_2 . First, the gel precursor of Zr(OH)_4 was mixed with oleic acid at certain ratios to form an emulsion by stirring and heating. After an appropriate time period, the mixture was dried, oxidized and calcined under a controlled atmosphere, at different temperatures. Finally, the products were identified by XRD and SEM, as well as by TEM, which indicated individual grain diameters < 60 nm. XRD was used to analyze the phase changes of the powder particle and crystallite size. SEM was performed to observe the particle morphology and to estimate the particle size in general.

The XRD analysis identifies that monoclinic zirconia is predominantly formed at 800 °C and has crystallite sizes of about 46.2–55.3 nm. Meanwhile, SEM images at 800 °C show particles with a homogenous morphology having sizes below 100 nm. A lower oleic acid concentration leads to a more alkaline condition and more monoclinic zirconia formed; and a higher calcination temperature leads to a larger crystallite size.

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