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Crystallite size and phase transition demeanor of ceramic steel

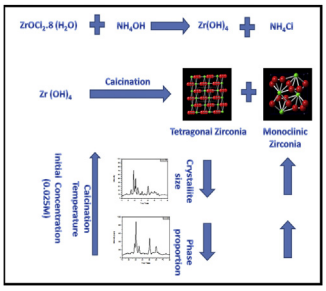
Deepak Gusain [a], Varsha Srivastava [a], Vinay K. Singh [b], Yogesh Chandra Sharma [a,*]

[a] Department of Chemistry, Indian Institute of Technology (Banaras Hindu University) Varanasi, Varanasi 221 005, India
[b] Department of Ceramic Engineering, Indian Institute of Technology (Banaras Hindu University) Varanasi, Varanasi 221 005, India

HIGHLIGHTS

- Highest proportion of tetragonal phase at lowest precursor concentration.
- Tetragonal phase's crystallite size decreased with rise of temperature.
- Average particle size of all samples lies in the range of 13 nm–20 nm.

GRAPHICAL ABSTRACT



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ABSTRACT

Zirconia is an important oxide of zirconium used in variety of field ranging from dentistry, fuel cells, and thermal barrier coatings. Phase transition of zirconia is an important phenomenon controlling its fracture strength, low temperature degradability and ion conductivity. In the present study, effect of molar concentration of precursor and calcination temperature on phase transition and crystallite size of zirconia was investigated. All the samples were characterized by X-ray diffractometry (XRD), Differential Thermal Analysis/Thermogravimetric Analysis (DTA/TGA), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). In sample having lowest precursor concentration crystallite size of monoclinic zirconia was found to be lower than that of tetragonal zirconia, simultaneously with the higher proportion of tetragonal zirconia (67.62%) as compared to all other samples (42.75%–58.04%). In all cases, monoclinic to tetragonal phase transition occurs with raise of temperature but in the sample with lowest precursor concentration, tetragonal to monoclinic phase transition occurred on raising the temperature.

1. Introduction

Zirconia is known as "ceramic steel" due to its excellent mechanical strength which is similar to stainless steel [1]. Zirconia is oxide of element zirconium and has several applications in industries because of its excellent thermal stability, chemical inertness [2], and appreciable electrical, optical, and catalytic properties [3]. Zirconia and its composites are used in catalysis and biomedical applications, solid oxide fuel cells, semiconductors, anticancer drug delivery [3], oxygen pump, and thermal barrier coatings [4].

Nano zirconia is synthesized by number of methods such as precipitation, sol gel synthesis, ball milling, hydrothermal and ultra sound assisted precipitation [5]. Atomic layer deposition, mechano chemical synthesis, chemical vapour synthesis, glyco thermal, inert gas condensation and reactive plasma synthesis [6] are the other methods reported for the synthesis of zirconia. Zirconia is known to exist in three phases namely monoclinic, cubic and tetragonal. Monoclinic form is thermodynamically stable at room temperature

* Corresponding author. Tel.: +91 542 6701865; fax: +91 542 2368428.
E-mail address: ysharma.apc@itbhu.ac.in (Y. Chandra Sharma).

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while tetragonal form is reversibly formed from monoclinic zirconia with a volume shrinkage of 3–5% above 1170 °C and cubic structure is stabilized above 2370 °C [7]. Phase transition of zirconia is affected by number of factors i.e. stabilizer concentration [8], grain size and oxygen vacancy [9]. The phase transition affects the properties, and is helpful in the development of dentistry implants, thermal barrier coating, oxygen sensor and fuel cell applications.

Mechanical treatment of zirconia is reported to give a pure monoclinic phase from polymorphs containing a mixture of tetragonal and monoclinic phase [10]. Tahmasebpour et al. [11] have reported the phase transformation using various precursor salts like oxychloride and nitrate. The effect of oxygen vacancies on phase transition, effect of synthetic parameters on structural, textural and catalytic properties [22,23] has been reported. Current study focused on the role of initial concentration and calcination temperature simultaneously on the phase transition and crystallite size of nano crystalline zirconia. Though not part of this work, the authors have used nano zirconia as an adsorbent for the removal of Cr from its aqueous solutions.

2. Materials and methods

Nano zirconia was synthesized by precipitation method. The $ZrOCl_2 \cdot 8H_2O$ and NH_4OH, used for the synthesis were procured from Himedia, Mumbai, India. $ZrOCl_2 \cdot 8H_2O$ was weighed according to molar concentration (0.025 M–0.075 M) and was subsequently dissolved in 1000 ml of water. Afterwards, $ZrOCl_2$ solution was precipitated by 25% ammonia solution by continuous stirring on a magnetic stirrer at controlled agitation speed. While stirring, the pH of the solution was maintained in the range of 10–10.5 and this resulted in formation of precipitate of zirconium hydroxide. The precipitate was filtered and subsequently washed with distilled water many times until traces of chloride were completely removed from the filtrate. To audit the complete removal of chloride from filtrate, it was titrated with 0.1414 N $AgNO_3$ using potassium chromate as indicator. Zirconium hydroxide, so formed was dried in a hot air oven at 80–90 °C for 24 h. The dried zirconium hydroxide was crushed and sieved to get uniform sized particles. Finally, zirconium hydroxide obtained at three different molar concentration of precursor (0.025, 0.05, 0.075) was calcined at 500 °C and 600 °C for 3 h by keeping the heating rate at 10 °C min^{-1}. After calcination, all samples were again sieved through 65 μm sieve. In the aforementioned method, six samples were prepared with different parameters i.e. molar concentration and calcinations temperature. The details of all samples are given in Table 1 with their sample IDs, molar concentration and calcination temperatures.

After synthesis, all the samples were characterized by Powder X-ray Diffractometer (RIGAKU, MINIFLEX II, Desktop XRD) employing Cu-Kα radiation, Differential Thermal Analysis/Thermogravimetric Analysis (SETARAM, Labsys™ TG–DTA 16, France), Scanning Electron Microscopy (FEI, Quanta 200 f, Netherland), Transmission Electron Microscopy (FEI, Morgagni 268D) and Fourier Transform Infrared Spectroscopy (PerkinElmer Spectrum Version 10.03.05). The samples for X ray diffraction were scanned in the angular regime of 10–80° at a step rate of $0.4\theta\ s^{-1}$. Crystallite size of the tetragonal and monoclinic phases was calculated from the characteristic peak for tetragonal at 30.2° (101), 50.2° (112) and 60.2° (211) (JCPDS card no. 79- 1769) 2θ and monoclinic at 28.1° (11), 31.4 (111) (JCPDS card no. 78- 1807) angle using Scherrer formula [12]:

$$\text{Crystalline size} = K\lambda/W\cos\theta \tag{1}$$

here K is shape factor(0.9), λ is wavelength of X ray used, $W = (Wb - Ws)$ is line broadening measured at half of height (FWHM) and θ is angle of reflection. The quantification of tetragonal and monoclinic phases present in the zirconia was done by comparing the areas of characteristics peaks of both the phases. The percentage composition is calculated as follows [13]:

$$\%\text{Tetragonal} = \left[\sum(\text{peak area})\text{tetragonal}/\sum(\text{peak area}) \times \text{tetragonal and monoclinic}\right] \times 100 \tag{2}$$

$$\%\text{Monoclinic} = \left[\sum(\text{peak area})\text{monoclinic}/\sum(\text{peak area}) \text{tetragonal and monoclinic}\right] \times 100 \tag{3}$$

3. Results and discussion

All six samples were prepared by precipitation of $ZrOCl_2 \cdot 8H_2O$ by ammonia. The precipitation occurred as follows:

$$ZrOCl_2 \cdot 8H_2O + 2NH_4OH \rightarrow Zr(OH)_4 + NH_4Cl \tag{4}$$

On calcination, zirconium hydroxide gave tetragonal and monoclinic zirconia. The ratio of these two phases depends upon the calcination temperature and molar concentration of precursor.

$$2Zr(OH)_4 \rightarrow Zr(O)_2(\text{Tetragonal}) + Zr(O)_2(\text{monoclinic}) + H_2O \tag{5}$$

3.1. XRD analysis

X ray diffraction (Fig. 1.) was used to determine the crystallinity and crystalline phase of samples at various molar concentration and calcination temperature. The effect of molar concentration of precursor and calcination temperature on the product are shown in Fig. 1. The proportion and crystallite size of tetragonal and monoclinic phases are given in Table 2.

3.1.1. Impact on phase

On raising the temperature, monoclinic phase decreased and tetragonal phase increased in two sets of samples (1 and 2). This suggests the significant phase transformation of monoclinic zirconia to tetragonal phase on raising the temperature (Table 2). The role of anionic vacancies created by the foreign anions (ammonium hydroxide and water) has been reported as an important factor in the transformation of tetragonal to monoclinic zirconia [14]. Adsorption of water and oxygen into these anionic vacancies causes the difference in surface energy between tetragonal and monoclinic zirconia. Lowering of surface free energy of zirconia nano particles results in destabilization of tetragonal zirconia towards monoclinic zirconia [14]. With rise of temperature, surface energy has been found to increase leading to increased stability range of tetragonal zirconia [15]. However in case of sample (3A) tetragonal phase is higher in composition which gets decreased on raising calcination temperature to 600 °C (3B). This can be accredited to slow rate of

Table 1
Detail of experimental conditions for the synthesis of various samples.

S. no.	Sample ID	Molar concentration of $ZrOCl_2 \cdot 8H_2O$ (M)	Calcination temperatures (°C)
1	1A	0.075	500
2	1B	0.075	600
3	2A	0.05	500
4	2B	0.05	600
5	3A	0.025	500
6	3B	0.025	600