

Synthesis of Nanocrystalline ZrO₂ Powder by the Polyol Route

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Abstract

The polyol route, with zirconium oxychloride as the metal ion source, was used to synthesize nanocrystalline ZrO₂ powder. The complete process for the synthesis of nanocrystalline ZrO₂ was monitored by TG/DTA, FTIR, XRD and TEM. Thermal behavior of the intermediate powder was investigated using TG/DTA analysis. The structural coordination and phase of the intermediate, as well as the synthesized ZrO₂ powder, were investigated by FTIR and XRD respectively. The microstructure of the synthesized nanocrystalline ZrO₂ powder was identified using transmission electron microscopy.

Keywords: Nanocrystalline ZrO₂ Powder; Polyol synthesis; TG/DTA; FTIR; XRD; TEM

1. INTRODUCTION

Zirconium oxide has a wide range of applications, including restorative dentistry, catalysis, high temperature ceramics, etc., due to its properties [1-4]. Recently, it was observed that nanostructured ZrO₂ powder exhibits enhanced performance in many applications [5, 6]. A wide range of wet chemical routes such as sol gel, polyol, combustion, hydrothermal, co-precipitation, etc., have been investigated for the synthesis of nanocrystalline metal oxides, including ZrO₂ powders [7-12]. Among them, ethylene glycol mediated polyol synthesis has been used for the preparation of nanostructured metal and metal oxides because of its strong reducing power as well as high boiling point (~197°C) [13]. In this process, ethylene glycol also acts as a solvent for the precursor chemicals due to its high relative permittivity ($\epsilon = 32$), and leads to hydrolysis reactions under atmospheric pressure [13]. Thus, the polyol route involves hydrolysis and inorganic polymerization carried

out on the salts dissolved in a polyol medium. In the present work, the polyol route was used for the synthesis of nanocrystalline ZrO₂ powder, which was characterized by TG/DTA, FTIR, XRD and TEM techniques.

2. EXPERIMENTAL TECHNIQUES

2.1. Polyol synthesis of nanocrystalline ZrO₂ powder.

The required amount of zirconium oxychloride (AR Grade, S.D-Fine, India) was added to ethylene glycol (S.Q Grade, Qualigens, India) under stirring condition by keeping the total metal ion to ethylene glycol ratio at 1:40. The resulting clear solution was heated at 175°C for 2 h in an erlenmeyer flask. During heating, the clear solution turned to a white, turbid suspension, which may indicate the formation of zirconia intermediates. After cooling to room temperature, colloiddally stable suspensions were obtained. Photographs of the various stages of the reaction mixture are shown in fig. 1. The suspended particles were separated from ethylene glycol by centrifugation at 3000 rpm. Repeated washing was performed on the particles using distilled water and dried in an oven at 100°C for 12 h. The dried intermediate was calcined at 600°C for 6 hours to obtain the nanocrystalline ZrO₂ powder.

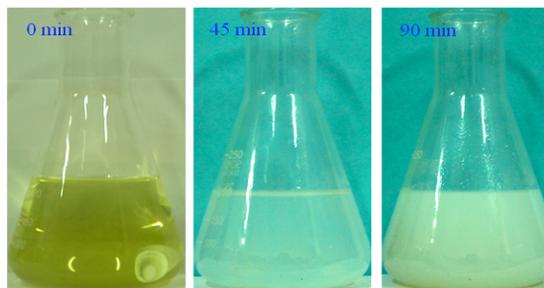


Fig. 1. Photograph of the various stages in the synthesis of nanocrystalline ZrO₂ powder by a polyol route

2.2. TG/DTA, FTIR, XRD and TEM measurements on nanocrystalline ZrO₂ powder.

The thermal behavior of the polymeric intermediates was investigated by simultaneous TG/DTA measurement (Lybsys thermal analyzer, Setaram, France). Approximately, 3mg of polymeric intermediate was heated at a rate of 10°C min⁻¹ between 30 and 600°C. All thermal studies were performed in flowing oxygen. The FTIR spectra were recorded between 400 and 4,000 cm⁻¹ with KBr dilution (Shimadzu FTIR - 8000 spectrometer). Powder XRD patterns were recorded by Cu K_α X-ray powder diffractometer (X' Pert PRO MPD, PANalytical, Philips). The crystallite size of the ZrO₂ powder was calculated using Scherrer's formula [14].

$$L = \frac{0.9\lambda}{\beta_{1/2} \cos \theta_B}$$

where, λ is Wavelength of X-ray radiation used (in Å), θ_B is the Bragg angle (in degrees) and $\beta_{1/2}$ is full width at half maximum (FWHM) in radians. $\beta_{1/2}$ is calculated using the following expression:

$$\beta_{1/2} = (\beta_M^2 - \beta_S^2)^{1/2}$$

where, β_M is full width at half maximum (FWHM) value of the sample and β_S is the FWHM value of the Si standard. A NBS silicon standard was used to estimate instrumental broadening. The microstructure of the polymeric intermediate was identified using transmission electron microscopy (TEM), Jeol, Japan

3. RESULTS AND DISCUSSION

3.1 TG/DTA analysis

A TG/DTA thermogram of the intermediate particle product obtained from the ethylene glycol mediated polyol process is shown in fig. 3. From fig. 3, the observed broad endothermic peak in the DTA curve between

50°C and 150°C with ~3% weight loss is due to the removal of absorbed water. Further heating of the intermediate particles caused the broad exothermic peak between 200 and 350°C, which is attributed to the decomposition of organic derivatives (glycolates), and the respective ~2% weight loss in the TGA curve. The exothermic peak at approximately 455°C corresponds to crystallization of the ZrO₂ phase. There is no significant weight loss observed beyond 500°C, which indicates the complete decomposition of organic derivatives and also the formation of a ZrO₂ phase, as confirmed by FTIR and XRD analyses.

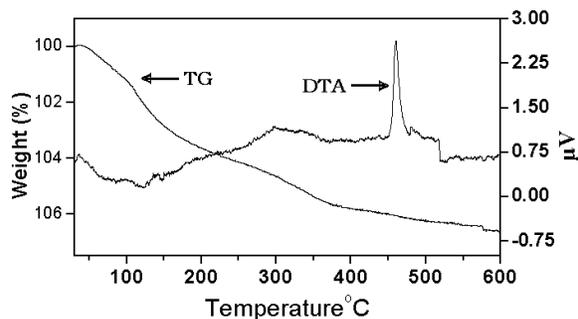


Fig. 3. TG/ DTA Thermogram of the collected suspension (ZrO₂ intermediate)

3.2. FTIR

Fig 4 shows the FTIR spectra of the as-prepared as well as-calcined intermediate powder (at 300°C and 600°C for 6 hours). From fig. 4, the observed broad IR peak at 3377 cm⁻¹ is due to the presence of adsorbed water, which is not observed in calcined samples [15]. The intense IR peaks observed at 2939, 2867, 1093 and 909 cm⁻¹ are attributed to the ethylene glycol based organic derivatives [19]. Also, the observed low intensity peaks at 1644 and 1432 cm⁻¹ are respectively due to the asymmetric and symmetric vibrations of chelated carboxylate, which may be due to the formation of a minimum fraction of metal glycolate. All the IR peaks, which are related to the organic derivatives, begin to disappear at 300°C and are completely removed from the intermediate after being calcined at 600°C, which is consistent with the TG/DTA results. The FTIR peaks at 747-755 cm⁻¹ and 498-502 cm⁻¹ in the intermediate products calcined at 300°C and 600°C are due to the vibrational modes of ZrO₃²⁻ groups, which confirm the formation of the ZrO₂ structure. Further, its phase is confirmed by XRD analysis [15-16].

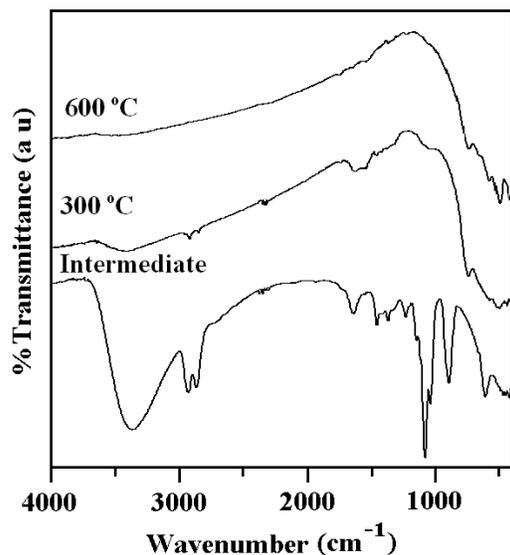


Fig. 4. FTIR spectra of the as-separated as well as suspensions calcined at 300°C and 600°C for 6 hours

3.3. XRD

Fig. 5 shows the XRD patterns of the as-prepared as well as the as-calcined intermediates at 300°C and 600°C. The peaks for the as-prepared as well as as-calcined intermediate at 300°C indicate the formation of a tetragonal (t) ZrO₂ phase only. However, the calcination of polymeric intermediates at 600°C yields a mixture of both metastable t-ZrO₂ and monoclinic (m)-ZrO₂ phases. The XRD patterns indicate that both crystalline phases were independently formed during calcination, since the small intense peak at ~32° 2θ related to the m-ZrO₂ phase is observed in the XRD pattern of the polymeric intermediate calcined at 300°C. The diffraction patterns also show that increasing calcining temperature leads to increasing ZrO₂ crystallinity. FTIR and XRD analyses confirmed the formation of organic-free ZrO₂ powder with t-ZrO₂ and m-ZrO₂ phases at 600°C for 6 hours. The volume fraction and their respective crystallite sizes were calculated using XRD data. The volume fraction for the tetragonal phase and the crystallite size were, respectively, found to be 41.95 % and 18 nm. Also, the calculated crystalline size for the monoclinic phase was found to be 21 nm.

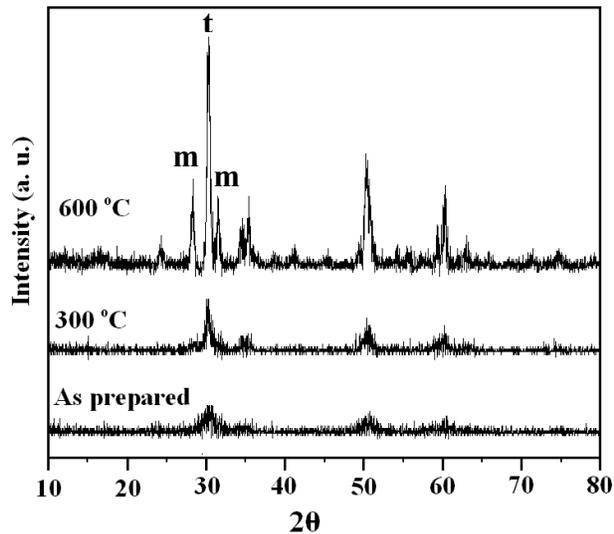


Fig. 5. XRD pattern of the as-separated as well as suspensions calcined at 300°C and 600°C for 6 hours

3. 4. TEM analysis

Transmission electron micrographs of the ZrO₂ powder synthesized by the ethylene glycol mediated polyol route and calcined at 600°C for 6 hours are shown in fig. 6 at various magnifications. The micrographs show the agglomeration of ZrO₂ particles, which are about 25 nm in size. 25 nm is comparable with the crystalline size calculated using XRD data.

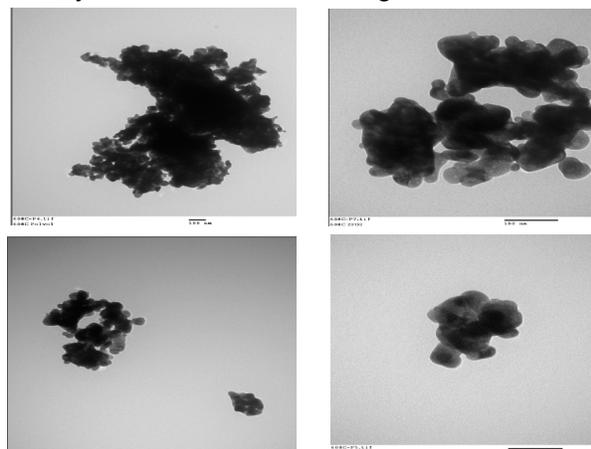


Fig. 6. TEM micrographs of nanocrystalline ZrO₂ powder synthesized at 600°C. (Magnification bars are 100 nm.)

4. Conclusions

Nanocrystalline ZrO_2 powder can be successfully synthesized by employing an ethylene glycol mediated polyol process. From TG/DTA, FTIR and XRD results, it was found that organic-free nanocrystalline ZrO_2 particles can be formed at $600^\circ C$, that consist of both tetragonal and monoclinic phases. Their volume fraction was calculated using XRD data and found to be 42 % for t- ZrO_2 and 48 % for m- ZrO_2 . The average crystallite size of the synthesized ZrO_2 powder was calculated using Scherer's formula and found to be in range of ~18 nm for t- ZrO_2 and ~21 nm for m- ZrO_2 . TEM analysis shows that ~25 nm primary ZrO_2 particles are formed, and agglomerate into larger aggregate particles.

Keywords:

Nanocrystalline ZrO_2 Powder; Polyol synthesis; TG/DTA; FTIR; XRD; TEM

Acknowledgments:

NS gratefully acknowledges CSIR, AICTE, DRDO, DST and UGC for utilizing research facilities available from the major research projects.

SV acknowledges the CSIR, Government of India, for the award of a senior research fellowship (SRF).

HRR gratefully acknowledges support by NIH/NIDCR grant 1P01 DE11688.

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