

Ultrasonic-Assisted Co-Precipitation Method of Preparation of Nanocomposites in The $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-ZrO}_2$ System: Characterization and Microstructure

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Abstract

Recently, the $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-ZrO}_2$ system has found valuable applications, particularly, as a support for NOx storage-reduction (NSR) catalysts. Nanocomposite powders were prepared from the co-precipitation method in inorganic precursors. The behaviors of mixed oxide nanoparticles under ultrasonic irradiation, such as dispersion, and crushing were studied. Phase transformations, crystallite size, and microstructure of the mixed oxides were investigated by STA (DTA/TG), FTIR, XRD, and SEM. XRD studies showed that zirconium titanate (ZT) is main phase, and the crystallite size varies with the final calcination temperature, and ultrasonic irradiations. SEM observations revealed that the calcination temperature strongly influences the morphology of prepared mixed oxides. The results showed that the inorganic nanoparticles in the aqueous solution can be redispersed more effectively by ultrasonic irradiation than by conventional stirring. The average crystallite sizes of the ZT particles heat treated at 1200 °C for 2 h were in the range of 47-85 nm.

Keywords: FTIR; Co-precipitation; Ultrasonic

1. Introduction

Nanostructured materials have been intensively studied in recent years because the physical properties of these materials are often quite different from those of the bulk [1]. Aluminium titanate (tialite) shows several interesting properties, such as low thermal expansion coefficient ($(0.2-1)\times 10^{-6}\text{K}^{-1}$), low thermal conductivity ($0.9-1.5\text{ W.m}^{-1}\text{.K}^{-1}$), excellent thermal shock resistance ($\approx 500\text{ W.m}^{-1}$) and high melting point (1860 °C), that suggests the use of this ceramic material in many different industrial applications including parts in explosion engines, metal smelting, thermal barriers and as support material for catalyst [2]. It has been proved that a decreasing in the grain size ($0.5-1\ \mu\text{m}$) helped minimizing the microcracking problem [3]. Eutectoid decomposition in the initial oxides and low mechanical strength limit the well-known properties of aluminum titanate desired in several applications. In order to minimize these limitations new synthesis routes and additives were studied [2]. ZrTiO_4 (ZT) is one of the important materials, which satisfies the requirements for various microwave applications due to its high dielectric constant (38-40), high quality

factor ($\tan \delta \sim 10^{-2}$ to 10^{-3}) and high temperature stability (τ_f value of $\pm 20\text{ ppm}/^\circ\text{C}$) [4].

The favourable inherent properties of alumina and zirconia supports can be explored by combination of both the supports in a mixed oxide. The $\text{Al}_2\text{O}_3\text{-ZrO}_2$ supported catalysts were found to exhibit better catalytic properties than the catalyst supported on pure oxides [5]. In recent times, $\text{Al}_2\text{O}_3\text{-ZrO}_2$ based materials have been employed as catalysts in numerous catalytic applications [5, 6]. The advantages of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ as a catalyst support include more thermal stability, moderate surface area and medium acidity. The activity of supported vanadia catalysts depends mainly on the method of preparation, the nature of the support and dispersion of the active component [5].

Nanocomposite powders can be made by various methods, such as vapor-phase synthesis, sol-gel, co-precipitation, and hydrothermal reaction [7]. Colloid chemical methods generating nanostructured materials were reviewed recently by Fendler and Meldrum [8]. It is very difficult for inorganic nanoparticles to disperse in the matrix at the

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nanoscale through conventional mixing, because nanoparticles have very high surface energy and will agglomerate during mixing. Generally, many approaches have been tried to solve the problem: e.g. ultrasonic irradiation, as a new technology, has been widely used in chemical reactions. When ultrasonic waves pass through a liquid medium, a large number of microbubbles form, grow, and collapse in very short time, about a few microseconds, which is called ultrasonic cavitation. Therefore, ultrasound has been extensively applied in dispersion, crushing, and activation of particles [9]. The use of ultrasound to enhance the rate of reaction has become a routine synthetic technique for many homogeneous and heterogeneous chemical reactions [10].

In the present study, an ultrasonic irradiation technique-assisted co-precipitation which was first employed based on our knowledge, to prepare nanoparticle composites in the Al_2O_3 – TiO_2 – ZrO_2 system. Mixed oxide particles with different crystallite sizes and morphologies are obtained at various calcination temperatures. Enhancing effects ultrasonic irradiation on the crystallite size of nanocomposite powders were discussed. The phase transformation, crystallite size, morphology, and dispersion stability of the ultrasonic irradiated nanoparticles were characterized by means of Simultaneous Thermal Analysis (STA) and Fourier transform infrared (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM).

2. Experimental Details

Nanocomposite powders in the Al_2O_3 – TiO_2 – ZrO_2 system were synthesized by co-precipitation (CP) and ultrasonic-assisted co-precipitation (UCP) methods. Aluminum nitrate (extra pure, Merck), zirconium nitrate (technical, England BDH), and titanium chloride (for synthesis, Merck) were used as precursors. Also, the ammonia solution (%25, GR for analysis, Merck) was used as a precipitant agent. The molar ratios of materials were presented in table 1. In CP method, requisite quantities of aluminum

nitrate and zirconium nitrate were dissolved in distilled water, and then titanium chloride was added dropwise to the mixed solution under vigorous stirring at room temperature. The gained sol showed to be very clear and transparent without any precipitation; white precipitates were obtained by adding dropwise ammonia solution into the sol, of which pH value was adjusted to 12. In the UCP samples, precipitation of particles took place under ultrasonic irradiation in an ultrasonic cleaning bath (Fritsch ultrasonic cleaner, model labortte 17, 20 kHz, 120 W) for 1 h in a continuous mode. The precipitates were washed three times with distilled water till they were free from nitrate ions and once more with commercial ethanol until no Cl ion was detected by the silver-mirror test. Finally, wet cakes were dried at 120 °C for 24 h and the collected powders were heated at various temperatures between 1000 and 1400 °C at a heating rate of 10 °C.min⁻¹.

The thermal patterns of the samples were recorded in a Shimadzu STA-449C apparatus by linearly heating (10 °C/min) the sample in a N₂ atmosphere. The material reference was Alumina. Bonds in as-made and calcined powders were characterized using FTIR (Model Nicolet Nexus 670, Thermo Nicolet, Waltham, MA). XRD (Philips, XRG3100-PW3710) measurements using Cu, K α (λ ~0.154 nm) radiation were employed to identify the crystalline phase of the synthesized materials and to calculate the mean crystallite size based on Scherrer's equation [11] using the FWHM data of each phase after correcting the instrumental broadening [12]. Diffraction intensity was measured between 4 and 120°, with a 2 θ step of 0.04° for 1 s per point. The particle morphology of the calcined powders was observed by means of SEM (TESCAN, VEGAII XMU).

3. Results and Discussion

STA (DTA/TG) curve of the CP sample dried at 120°C for 24 h are shown in Fig. 1. It can be seen in the TG-curve that there is a strong weight loss (%15) between about 80

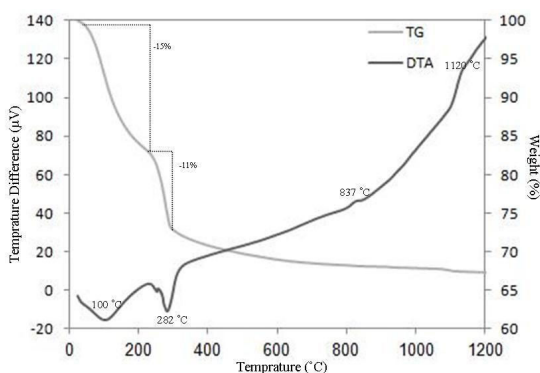
Table 1. The composition for samples and the experimental conditions.

Sample Assign	Molar Ratio (%)			Preparation Method	Calcination Temperatures (°C)
	%Al ₂ O ₃	%TiO ₂	%ZrO ₂		
CP	50	25	25	Co-precipitation	1000,1100,1200,1400
UCP	50	25	25	Ultrasonic-assisted Co-precipitation	1000,1100,1200,1400

Table 2. Crystallite size of CP and UCP samples.

Calcination Temperature (°C)	Crystallite Size of CP Samples (nm)		Crystallite Size of UCP Samples (nm)	
	ZT	corundum	ZT	Corundum
1000	-	-	28	-
1100	-	-	32	86
1200	85	86	47	-

and 220 °C, after which another significant weight loss (%11) between about 220 and 282 °C is observed. The DTA-curve shows a broad endothermic peak at around 100 °C and another relatively small endothermic peak at around 282 °C. Also, two small exothermic peaks were observed at around 837 and 1120 °C, respectively. The weight loss below around 282 °C and the endothermic peak is due to desorption of water and organic solvent. Above 282 °C, the weight loss is attributed to the furthermore burning of the remnant organic compounds [13]. Two exothermic peaks, respectively, can be attributed to crystallization of ZT and corundum (α -Al₂O₃) phases. The following analysis results of XRD data coincide well with it.

**Fig. 1.** STA (DTA/TG) curve of the CP sample dried at 120 °C for 24 h.

FTIR is a very sensitive and well established tool for studying the orientation, transformation and nature of hydroxyl bonds in both alumina and titania hydrogel. The position and intensity of the IR peaks are strongly influenced by the crystallization

behavior, degree of crystallinity, morphology and particle size. Therefore, the FTIR results could well be correlated with the crystallization behavior and phase evolution in the composites [14].

Fig. 2(a–d) shows the FTIR spectra of the samples obtained through CP and UCP. In all the cases the characteristic vibrations due to the molecular water (1550–1650 cm⁻¹) and structural hydroxyl groups (2650–3600 cm⁻¹) are observed. The spectra of (a) and (b) are similar. They present the characteristic modes of vibration for boehmite (494, 600, 1027cm⁻¹) [2]. The band around 3655 cm⁻¹ can be assigned to terminal O–H vibration of the Ti–OH groups [15]. The narrow band around 1630 cm⁻¹ can be assigned to OH (bending modes) of hydroxyl group and surface adsorbed water. A small band at 1095 cm⁻¹ (c) is detected due to the symmetric bending modes of Al–O–Al bonds. The OH torsional mode observed at 775 cm⁻¹ (a,b) overlaps with Al–O stretching vibrations. The broad band in the region of 500–750 cm⁻¹ is assigned to α -AlO₆, whereas the shoulder at 980 cm⁻¹ (a,b) is assigned to α -AlO₄ [16]. The FTIR spectra of the composite samples show a pronounced bands at 3400 and 1620 cm⁻¹ due to the hydroxyl group of the oxides and surface adsorbed water. A broad band centered at 640 cm⁻¹ (a,c) is detected which can assigned to Al–O–Al and Ti–O–Ti [15,16]. In addition, new small bands are detected at 586 and 494 cm⁻¹ which can be assigned to hetero metal–oxygen bonds of Ti–O–Al [17], these bands are probably implying the incorporation of alumina into the framework of titania.

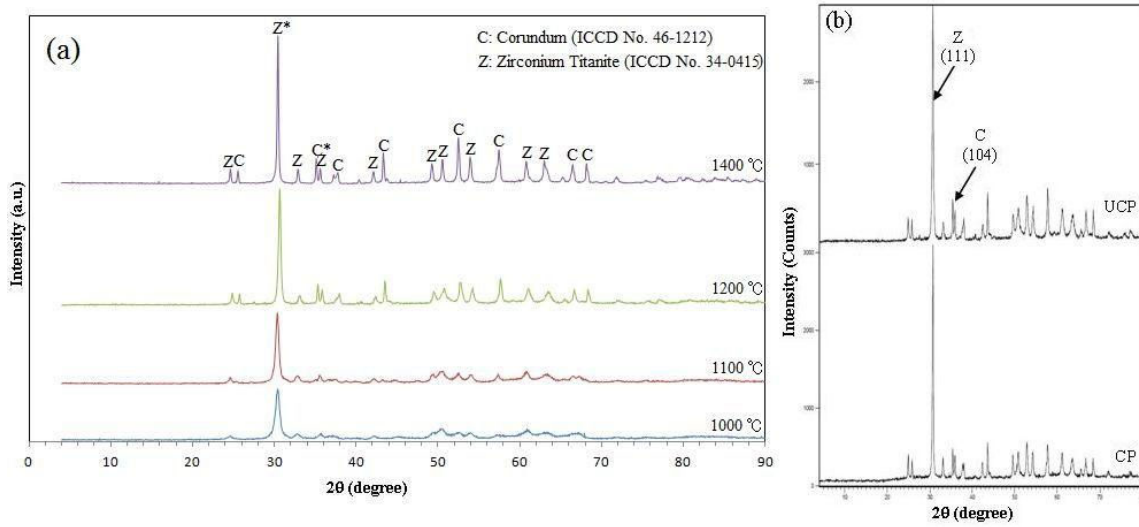


Fig. 3. X-ray diffraction patterns of specimens (a) UCP samples after heat treatment at 1000, 1100, 1200, and 1400 °C, (b) CP and UCP samples were calcined at 1200 °C.

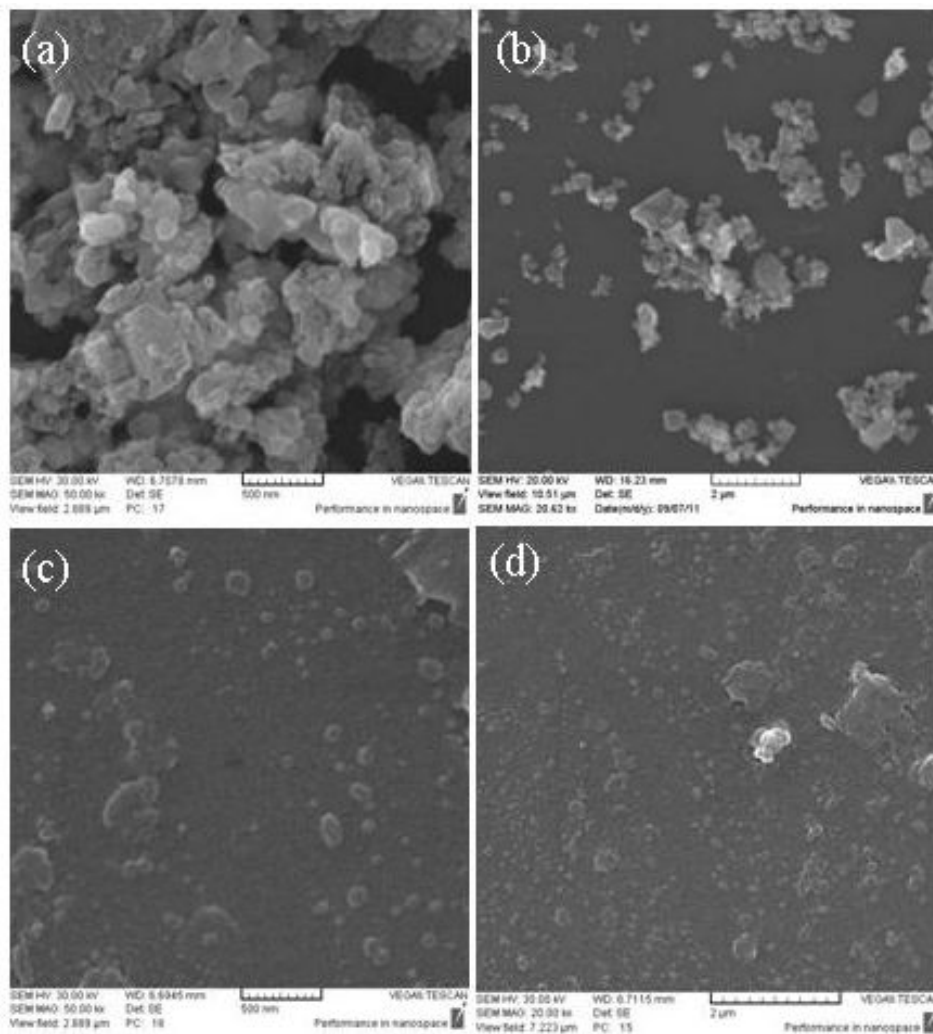


Fig. 4. SEM micrographs of nanocomposites were calcined at 1200°C. (a), (b) CP samples with 50000x and 20000x, respectively, (c),(d) UCP samples with 50000x and 20000x, respectively.

4. Conclusions

This study clearly demonstrates the importance and advantages of ultrasonication technique in the modification and improvement of the particle size, and dispersion of nanocomposite powders in the Al₂O₃-TiO₂-ZrO₂ system via co-precipitation methods. FTIR and SEM confirm that ultrasonic irradiation greatly improves the dispersion, stabilization and composting of nanoparticles in the ceramic matrix, and offering a new way to deal with the challenges encountered in preparing inorganic nanocomposite materials.

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