JOURNALOF

Ceramic Processing Research

Effect of sugar and citric acid as precursors in ZrO₂ nanopowder preparation at low calcination temperatures

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Zirconia nanopowder was successfully prepared using sugar and citric acid by a precursor calcination process, in which sugar was used as a gelling agent and citric acid as a catalyst. The effect of citric acid on this zirconia preparation is found out by the variable time of addition of citric acid on the preparation, namely SZG (before sugar) and SGZ (after sugar). The calcinations were conducted at 600 °C and 800 °C. XRD results show that at 600 °C, t- and m-ZrO₂ phases are identified in SZG, whereas t-ZrO₂ is the only phase in SGZ. XRD analysis finds that both of the zirconia samples having had crystallites below 20 nm. At a high temperature of 800 °C, two phases of zirconia are identified as t- and m-ZrO₂ in both of the samples with different intensities. A Quanta FEG SEM study shows both of the zirconia samples at 800 °C have homogenous microstructures and grain sizes less than 100 nm. A high resolution sophisticated SEM investigation shows that the SZG sample at 800 °C has an average grain size below 50 nm. However, the effect of the citric acid addition time on the zirconia preparation is clearly visible in the zirconia phase transformation. The earlier addition of citric acid on the preparation gives two phases of zirconia in the final product at 600 °C; and by contrast, the later addition of the acid after sugar on the preparation produces only t-ZrO₂ phase.

Key words: Nanopowder, Zirconia, Preparation, Precursor process, Sugar, Citric acid.

Introduction

Zirconium oxide (ZrO_2) is one of the most important ceramic materials because of its outstanding thermal stability, chemical resistance, mechanical characteristics, and ionic conductivity that finds wide applications in thermal barrier coatings, biomaterials, catalysis, gas sensors, automobile engine parts, fuel cell technology, and structural applications [1-4].

Zirconia exhibits three well-defined polymorphs: monoclinic (m), tetragonal (t), and cubic (c) phases [5-7]:

Monoclinic
$$\stackrel{950-1170\,^{\circ}C}{\longleftrightarrow}$$
 tetragonal $\stackrel{1170-2270\,^{\circ}C}{\longleftrightarrow}$ (1)

Cubic
$$\xleftarrow{2270-2680 \,^{\circ}C}$$
 melting point. (2)

The tetragonal-to-monoclinic phase transformation in ZrO_2 has been used to increase the fracture toughness, strength, and hardness of oxides (alumina), using tetragonal- ZrO_2 as a dispersed phase. Tetragonal- ZrO_2 is also used as a catalyst, while cubic- ZrO_2 finds other applications in the automobile industry as an oxygen

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sensor and in the fabrication of fuel cells [7, 8].

Nanostructured materials, with grain sizes of <100 nm, show superior properties such as excellent phase homogeneity, large interfacial areas, enhanced sinterability and densification at a relatively low temperature and microstructures leading to unique electrical, mechanical, dielectric, magnetic and optical properties. Therefore, nanostructured materials exhibit better chemical and physical properties as compared to the material in the normal state or as coarse powder, due to the small particle diameter [9, 10].

Many synthesis methods have been proposed for nano zirconia preparation such as a combustion method [1], sol-gel processing [9, 10], precursor methods [1, 5, 8, 11], colloidal routes [12, 13], and chemical vapour synthesis [14]. The purpose of this paper is to prepare nanopowder zirconia by a precursor process using sugar and citric acid. In this study, sugar was used as a gelling agent that also acted as a templating material and citric acid as a catalyst. The calcinations were conducted at 600 °C and 800 °C. XRD analysis was performed to identify the crystalline phases and the crystal sizes of the calcined zirconia nanopowder using an X-ray Phillips Pan Analytical instrument. Meanwhile a QUANTA FEG scanning electron microscope was used to investigate the morphology and microstructure of the calcined zirconia nanopowder. A

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FEI Nova NanoSEM 650 was used to observe the morphology and the grain sizes of calcined zirconia nanopowder in a very high resolution until 50 nm magnification.

Experimental Procedures

Materials and instruments

High purity grade zirconium (IV) chloride and 25% ammonia solution were obtained from Merck; whereas technical grade sugar and citric acid were obtained from a local market. Instruments used in this research were a dual speed mixer max. 2000 rpm, a Heraus electrical furnace, an X-Ray Phillips PANalytical, a QUANTA FEG scanning electron microscope, and a FEI Nova NanoSEM 650.

Synthesis and calcination of precursor

The appropriate amount of ZrCl₄ was dissolved in sufficient water, and then the appropriate of citric acid was added slowly to the solution and stirred at \pm 800 rpm. After that the appropriate amount of sugar was added to the mixture. Zirconium salt-to-total citric acid and sugar weight ratios were maintained at 6:1. The degree of acidity of the solution mixture was modified by adding 25% ammonia solution drop wise under constant stirring to reach a pH value of about 7 or until a quite alkaline condition, thus giving Zr(OH)₄. The mixture was heated slowly until a concentrated vellowish brown gel was formed at 100 °C. In this step, a reaction between the hydroxide and precursor molecules was assumed to have occurred to form a metal organic of zirconium. The concentrated gel was continuously heated slowly and stirred simultaneously until water evaporated completely and a black concentrated gel formed. The gel was then dried in an oven at 200 °C to produce black charcoal-like precursors. The precursors were milled in a non polar solvent for 24 hours and successfully calcined at 600 °C and 800 °C for 5 hours in a Heraus electric furnace. The final products were identified using XRD, QUANTA FEG SEM, and FEI Nova NanoSEM 650.

A second batch with the same composition and preparation procedure of the previous nanopowder zirconia was conducted. Here, citric acid was added later after the sugar into the mixture. The first batch was coded SZG and the second batch was coded SGZ.

Characterization

All calcined samples, SZG-600 °C, SGZ-600 °C, SZG-800 °C and SGZ-800 °C were characterized by XRD and SEM. XRD analysis was conducted to identify the crystalline phases and the crystal sizes of calcined zirconia nanopowder using an X-ray Phillips Pan Analytical instrument. Meanwhile a QUANTA FEG scanning electron microscope was used to investigate the morphology and microstructure of the calcined zirconia nanopowder. A FEI Nova NanoSEM 650 was used to observe the the morphology and the grain sizes of calcined zirconia nanopowder in a very high resolution until 50 nm magnification.

Results and Discussion

The results of XRD analysis

Zirconia precursor phase transformation

Fig. 1 shows typical XRD patterns of calcined ZrO₂ nanopowder coded SZG and SGZ at 600 °C. According to the XRD pattern of SZG (Fig. 1), when sugar was used as a gelling agent in the water medium which was added later after the addition of citric acid, the zirconium salt was found to transform and to crystallize at a low temperature of 600 °C, having small peaks at 28.21 ° and 31.45 ° (20-CuKa), referring to the crystal planes $(\overline{111})$ and (111) of the monoclinic zirconia structure; whereas the tetragonal zirconia gave a sharp peak at a diffraction angle of 30.25 ° (101). These results seem to be different with the findings in the SGZ sample. The only zirconia phase formed was t-ZrO₂ that was shown by the main sharp peak at a diffraction angle of 30.25 °, from the crystal plane of (101). Generally, the emergence of different zirconia phases in both zirconia samples may be controlled by the specific conditions of the operating process, such as the type of template, conditions in the preparation, etc.



Fig. 1. XRD patterns of ZrO_2 nanopowder calcined at 600 °C, (a) SZG, (b) SGZ.



Fig. 2. XRD patterns of ZrO_2 nanopowder calcined at 800°C, (a) SZG, (b) SGZ.

At a higher temperature of 800 °C (Fig. 2), the main peak intensities of m-ZrO₂ at 28.21° and 31.45° become significantly higher with an elevation of the calcination temperature, whereas the peak intensity of t-ZrO₂ with a sharp peak at 30.25 $^{\circ}$ becomes lower. This phenomenon occurs in both SZG and SGZ. However, the peak intensity of t-ZrO₂ at a diffraction angle of 30.25 ° in the SGZ sample is still higher than the peak intensity of t-ZrO₂ at a diffraction angle of 30.25 ° in the SZG sample. In fact, at a temperature of 800 °C, the peak intensity of the t-ZrO₂ is at a low level because during the thermal treatment of the amorphous zirconia gels at temperatures above 400-600 °C, crystallization occurred to a thermodynamically metastable tetragonal phase, whilst at temperatures above 600 °C, the tetragonal-to-monoclinic phase transformation occurred [15].

The XRD quantitative analysis for measuring crystallite sizes and determining zirconia phase concentrations

A quantitative analysis of difractogram patterns for each sample including composition and crystal sizes of zirconia phases formed was applied and assisted using XRD software. The Scherrer equation was implemented to calculate crystallite sizes of zirconia phases in the samples at both calcination temperatures based on the main peaks of XRD patterns from Figs. 1 and 2 [16]:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

where *D* is the crystal size, *K* is a shape factor with a value of 0.9-1, λ is the wavelength of the X-rays (1.54056 Å), and β is the value of the *full width half maxima* (FWHM). Table 1 presents the quantification results of zirconia nanopowder at both calcination temperatures using the Scherrer method on any phases formed. When the peak in an XRD pattern is more broadened and has a lower intensity, the crystal size is smaller. By contrast, if the peak of an XRD pattern is sharper, the crystal size will be bigger and its crystallinity will be better. This is in conformity with the XRD patterns of the zirconia nanopowder in Figs. 1 and 2.

Table 1. Zirconia phase composition and crsytallite size of the calcined ZrO_2 nanopowder at 600 °C and 800 °C.

Sampel Code	Composition (%)		Crystallite Size (nm)		
	Tetragonal	Monoclinic	t-ZrO ₂ (101)	m <u>-Z</u> rO ₂ (111)	m-ZrO ₂ (111)
SZG600	65.6	34.4	14	11	4
SGZ600	100	-	13	-	-
SZG800	4.6	95.4	4	16	13
SGZ800	7.7	92.3	6	13	10



Fig. 3. SEM images for samples of (a) SZG-800 $^{\rm o}{\rm C}$ and (b) SGZ-800 $^{\rm o}{\rm C}.$



Fig. 4. Nova NanoSEM 650 images for a sample of (a) SZG-800 °C.

Morphology and microstructure

Figs. 3(a) SZG and 3(b) SGZ, show the images obtained from scanning electron microscopy of the zirconia powder where an appreciable formation of agglomerates after thermal treatment at 800 °C can be seen. Nanoscale particles, since they have large surface areas, often agglomerate to form either lumps or secondary particles to minimize the total surface area or interfacial energy of the system. The agglomeration refers to adhesion of the particles to each other because of *van der Waals* forces of attraction, which are significantly higher in nanoparticles. The size of

ZrO₂ powders are found to be less than 100 nm at a calcination temperature of 800 °C [17]. In addition, the morphology and the size of zirconia grains can be seen more clearly when using a more sophisticated SEM such as a FEI Nova NanoSEM 650, which can observe and investigate a material microstructure at a very high resolution of 50 nm magnifition. Therefore, a FEI Nova NanoSEM 650 was used to observe the morphology of SZG samples calcined at 800 °C to get clearer images as can be seen in Fig. 4. The images represent most region of the ZrO₂ powder having an average grain size below 50 nm, as shown in Fig. 4.

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Effect of the citric acid addition into the zirconia phase transformation by sugar precursor method

The rate of a chemical reaction depends on the following: (a) pH, (b) concentration, and (c) solution [5]. When salts are dissolved in the solution, the solution is not always neutral in reaction. This is because some of the salts interact with water; which it is termed hydrolysis. As a result, hydrogen or hydroxyl ions remain in the solution in excess. Therefore, the solution itself becomes acidic or basic respectively. The salt of zirconium tetrachloride, is a type of salts of a strong acid and weak base, when dissolved in water, produce a solution, which reacts acidically. This phenomenon is in agreement with the experimental results, where the pH of the zirconium solution was very acidic [17]. When a salt of ZrCl₄ is hydrolyzed in water, it rapidly gives a salt of zirconium oxychloride in solution; and when the salt is continuously hydrolyzed in water, a tetrameric cation of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is formed in which there is a square of Zr⁴⁺ ions with two hydroxide groups bridging between Zr atoms on each side of the square and with four water molecules attached to each Zr atom [18]. The process of hydrolysis of zirconium solutions was accelerated with the addition of a NH₄OH catalyst. The pH of both the solutions was then adjusted, at ambient temperature, to about 7 or to a quite basic condition by dropwise addition of a 25% concentrated ammonia solution under vigorous stirring, until zirconium hydroxide $(ZrO_2 \cdot 2H_2O \text{ or } Zr(OH)_4)$ was formed. At this point, citric acid plays an important role especially in the reaction of the SZG batch. When citric acid was added earlier than sugar into the zirconium salt solution, the acid inhibited the precipitation of zirconium hydroxide [19].

Another function of the acid is as a catalyst in the inverting process of the sugar to monosachcharides through hydrolysis. The sugar has a sucrose structure, a disaccharide consisting of two monosaccharides of the six-carbon sugars D-glucose and D-fructose joined covalently by an O-glycosidic bond (See in Fig. 5). Sucrose can be considered a polyalcohol, because each monomer unit has hydroxyl groups, which can react to



Fig. 5. The sucrose structure of sugar.

form alcohol derivatives [20]. Therefore, the existence of citric acid in the solution would partially hydrolyze the sucrose to monosachcharides namely glucose (dextrose) and fructose (levulose), which have a melting point, lower than sugar.

The presence of sugar in the preparation significantly reduces the tendency toward agglomeration in the assynthesized zirconia particles. As is the previous explanation, sugar has a sucrose structure, which contains hydroxyl and ether groups, whose hydrogen bonds with the hydroxyl groups from the particle surfaces (Fig. 5). As a result, the surface hydroxyl groups get capped with the sugars. The sugar molecule coating on ZrO_2 particle surfaces results in reduced particle aggregation due to the steric hindrance provided by the sugars. Therefore, the binding distance will increase because sugar restricts the grain contacts among the nucleated ZrO_2 and restrains crystallite growth [17].

According to the XRD results in Figs. 1 and 2, the effect of the citric acid addition before or after sugar addition is clearly visible in the zirconia phase transformation. When the acid was added before the sugar into the zirconium salt solution in the SZG batch, a faster growth rate was detected for the m-ZrO₂ crystallites from 600 °C to 800 °C. By contrast, a slower growth rate was comparatively detected for the m-ZrO₂ crystallites from 600 °C to 800 °C in the SGZ batch. The different crystallite growth rate in case of the m-ZrO₂ for both of the batches could be related to the solubility of zirconium hydroxide and the hydrolysis process of the sugar by the citric acid. For the first batch of SZG, when citric acid was added earlier in the preparation, zirconium hydroxide still remained soluble in the solution and sugar was partially hydrolyzed to monosachcharides. These monosachcharides coating on the ZrO₂ particle surfaces restrict the contact among the nucleated ZrO2 particles. However, the melting points of these monosachcharides are lower than sugar, so that the carbon residue is completely burnt out at a low temperature, and the zirconia phase transformation would occur faster. This is in agreement with the XRD results of the SZG batch, where slightly

more monoclinic zirconia is identified in the zirconia phase composition of SZG at 600 °C. This is slightly different from the results of the SGZ batch. As is clear from Fig. 1, the only t-zirconia phase is identified with a high intensity at 600 °C; however, the late addition of citric acid into the solution after the sugar caused the an incomplete hydrolysis process because most of the sugar molecules reacted with the surface of zirconium hydroxide through hydrogen bonding in the earlier of sugar addition. Sugar or disachcharide are largers molecule than glucose and have higher melting points and more carbon atoms than glucose, thus requiring much more energy or a higher temperature to burn the residual carbon completely after the sugar decomposition from the nucleated zirconia surfaces. Therefore, the rate of zirconia phase transformation from m- to t-ZrO2 in the SGZ batch runs very slowly either at 600 °C or from 600 °C to 800 °C. This phenomenon is also proved by the brownish color of the calcined zirconia powder at

very white color. In the zirconia preparation, citric acid not only acts as a catalyst in the hydrolysis process of sugar but also it can act as a masking compound to zirconium hydroxide because of its chemical structure through a reaction with zirconium producing zirconium citrate $(Zr_3(C_6H_5O_7)_4.4H_2O)$, thus allowing hydrogen bonding from the hydroxyl groups of the citric acid to the hydroxyl group of zirconium hydroxide $(ZrO_2 \cdot 2H_2O)$ or $Zr(OH)_4$) particle surfaces [21]:

600 °C, which differs from the SZG powder having a



$$Zr_{3}(C_{6}H_{5}O_{7})_{4}.4H_{2}O \xrightarrow[-4H_{2}O]{} Zr_{3}(C_{6}H_{5}O_{7})_{4} \xrightarrow[-H_{2}, CO, CO_{2}]{} t-ZrO_{2}$$

$$t-ZrO_{2} \xrightarrow{>600^{\circ}C} x\% t-ZrO_{2} + y\% m-ZrO_{2}$$
(5)

Conclusions

Zirconia nanopowder was successfully prepared using sugar and citric acid by a precursor calcination process, in which sugar was used as a gelling agent and citric acid as a catalyst. The presences of sugar and citric acid produce zirconia in a nanopowder form because the tendency to agglomeration has been reduced in the as-synthesized ZrO_2 particles. However, the effect of citric acid on this zirconia preparation was found to be affected by the addition time of the citric acid on the preparation, namely SZG (before sugar) and SGZ (after sugar). At 600 °C, the tZrO₂ and m-ZrO₂ phases are formed in SZG, whereas the t-ZrO₂ is the only phase in SGZ. Both of the zirconia samples have zirconia crystallite sizes below 20 nm. At a high temperature of 800 °C, the t- and m-ZrO₂ phases are formed in both of the samples with different intensities. A Quanta FEG SEM study shows both of the zirconia samples at 800 °C have homogenous microstructures and grain sizes less than 100 nm. A high resolution sophisticated SEM investigation of the SZG sample at 800 °C gives an average grain size below 50 nm. However, the effect of the citric acid time of addition on the zirconia preparation is clearly visible in the zirconia phase transformation. The earlier addition of citric acid on the preparation gives two phases of zirconia in the final product at 600 °C; and by contrast, the later addition of the acid after the sugar on the preparation produces only the t-ZrO₂ phase.

Acknowledgement

This work was supported by the FEI Company.

References

- K. Boobalan, R. Vijayaraghavan, K. Chidambaram, U. Mudali, K. Mudali, and B. Raj, J. Am. Ceram. Soc., 93 [11] (2010) 3651-3656.
- P. Manivasakan, V. Rajendran, P.R. Rauta, B.B. Sahu, and B.K. Panda, J. Am. Ceram. Soc., 94 [5] (2011) 1410-1420.
- 3. A.K. Bandyopadhyay, in "Nano Materials" (New Age International, 2008) p. 135-141.
- K.C. Patil, M.S. Hedge, T. Rattan, and S.T. Aruna, in "Chemistry of Nanocrystalline Oxide Materials: Combustion synthesis, properties and applications" (World Scientific, 2008) p. 212-224.
- R. Septawendar, B.S. Purwasasmita, Suhanda, L. Nurdiwijayanto, F. Edwin, J. Ceramic Processing Research, 12 [1] (2011) 110-113.
- D. He, Y. Ding, H. Luo, and C. Li, J. Mol. Cat. A:Chem, 208 (2004) 267-271.
- 7. S. Roy, J. Sol-Gel Sci. Tech., 44 (2007) 227-233.
- S. Shukla, S. Seal, R. Vij and S. Bandyopadhyay, J. Nanopart. Res, 4 (2002) 553-559.
- R. Caruso, O. Sanctis, A. Macias-Gracia, E. Benavidez, and S.R. Mintzer, J. Mater. Proc. Tech., 152 (2004) 299-303.
- C.K. Muoto, E.H. Jordan, M. Gell, and M. Aindow, J. Am. Ceram. Soc., 93 [10] (2010) 3102-3109.
- 11. A. Mondal and S. Ram, J. Am. Ceram. Soc., 87 [12] (2004) 2187-2194.
- O. Vasylkiv, Y. Sakka, and V.V. Skorokhod , J. Am. Ceram. Soc., 86 [2] (2003) 299-304.
- O. Vasylkiv, and Y. Sakka, J. Am. Ceram. Soc., 84 [11] (2001) 2489-2494.
- V.V. Srdic, M. Winterer, and H. Hahn, J. Am. Ceram. Soc., 83 [8] (2000) 1853-1860.
- M. Marinsek, J. Macek, and T. Meden, J. Sol-Gel Sci. Tech., 23 (2002) 119-127.
- 16. Y.J. Kwon, K.H. Kim, C.S. Lim, and K.B. Shim, J. Ceramic Processing Research, 3 [3] (2002), 146-149.

- 17. R. Septawendar, A. Setiati, and S. Sutardi, Ceram. Int. 37 [8] (2011) 3747-3754.
- 18. T.C.W. Mak, Can. J. Chem. 46 (1968) 3491-3497.
- G. Shevla, in "Vogel's textbook of macro and semimicro qualitative inorganic analysis", 5th ed. (Longman Inc., 1979) p. 39-48, 535.
- D.L. Nelson, M.M. Cox, in "Lehninger's Principles of Biochemistry", 4th ed., (W.H. Freeman & Co., 2004) p. 246.
- 21. A. Srivastava and M.K. Dongare, Mater. Lett., 5 [3] (1981) 111-115.