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Synthesis and Characterization of Uniform Zirconia Particles by Homogeneous Precipitation Method

Abstract: Colloidal spherical particles (micrometer size) of zirconia were synthesized at 50°C by homogeneous precipitation method from aqueous solutions, containing appropriate amounts of zirconium chloride, hydrochloric acid, potassium sulphate and urea. Results revealed that reactants concentration significantly affected characteristics of the precipitated solids, which ranged from gel to dispersion of discrete particles. Size uniformity in the resulted particles was obtained only under limited conditions. SEM images revealed that particles of zirconia obtained under the described experimental conditions have spherical morphology, which maintained their original shape after calcination at 700°C. Selected powders were also characterized with XRD, TGA/DTA, and FT-IR techniques. XRD results showed that as-prepared and calcined powders were crystalline. We believe that our method is simple and has the potential for further tailoring of the particles characteristics. Work is in progress in our laboratory in developing Cu-ZrO_2 metal matrix composite coating on steel substrate with better resistant properties than simple Cu electroplating.

Keywords: homogeneous precipitation method, monodispersed system, zirconia particles

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1 Introduction

Uniformity in particle size and shape is desirable in powder-based technological processes, such as pigments, advanced ceramics, catalysis, adsorption, gas sensors, piezoelectric materials, directional delivery drugs, solid lubricants and metal matrix composites [1–4] etc. In this regard, material scientists and powder technologists have been working on developing methods for the production of powder materials, comprised of particles, having reasonable uniformity in their morphological features. To name a few, these methods include sol-gel, laser ablation, forced hydrolysis, and homogeneous precipitation [5–7]. Among these methods, homogeneous precipitation is considered the most versatile method in terms of producing particles in various shapes and sizes [8, 9]. Zirconia is an important material because it has a unique set of excellent mechanical, electrical, thermal and optical properties makes it a best choice for use in industry such as catalysts, fuel cells, batteries, capacitors, electrodeposition and in fabrication of gas sensors [10, 11]. It has an important role in advanced ceramics due to its excellent chemical resistance, ionic conductivity and polymorphic nature [12]. Zirconia particles in different morphologies have been synthesized by using different methods [13–15] but in most of the cases in the presence of various additives and surfactants in organic medium at high temperatures [16–18].

The aim of the present study was to establish a recipe for uniform micron size zirconia particles without any aid of organic or polymeric additives in aqueous medium by homogeneous precipitation method.

2 Experimental

2.1 Materials

Zirconium chloride, Potassium sulphate, Hydrochloric acid and Urea were obtained from the reputed companies and used as received. Solution storage and reactions were carried out in Pyrex glass vessels. All the solutions were filtered through membrane filters before use in order to remove the insoluble impurities, if any.

2.2 Synthesis of ZrO_2 precursor particles

Particles of ZrO_2 were synthesized by the method of homogeneous precipitation. For this system, aqueous solutions

containing known amounts of zirconium chloride, potassium sulphate, urea and hydrochloric acid were heated in a double-walled Pyrex glass container at different temperatures (50–90°C) for various periods of time. Temperature of the reaction vessel was maintained constant at the given value by circulating hot water in the double-walled jacket of the reaction vessel from a circulating thermostated water bath. After predetermined aging time, the resulting dispersions were quenched to room temperature in an ice-water bath and the precipitates were separated from mother liquor through vacuum filtration by using membrane filters. The solids was extensively washed first with doubly distilled water and then with ethanol. The air dried powder was stored in a desiccator for further use.

2.3 Heat-treatment

Samples of the above mentioned synthesized dry powders were heated in a tube furnace (Nabertherm, M7/11 equipped with the programmable controller) up to 700°C at the heating rate of 5°C/min and then kept at this temperature for 1 h. The samples were cooled down to room temperature inside the furnace by turning it off and then stored in a desiccator.

2.4 Characterization

Selected batches of the as-prepared and heat-treated solids were characterized by various physical methods. Particle morphology was analyzed with scanning electron microscope (JSM-5910, JEOL). For this purpose, the sample was prepared by mounting small quantity of the desired powder on aluminum stub with the help of a double-stick conducting tape and then coated with gold in an auto fine coater (JEOL, JFC-1600). IR spectra of the same solids were recorded with FTIR (Schimadzue, IR Prestigue-21) in the range 400–4000 cm^{-1}. Before each run, the sample was thoroughly mixed with KBr in appropriate ratio and then transferred to the sample holder of the diffuse reflectance accessory (DRS-800A), installed in the same instrument. Similarly, the crystallinity of these powder samples was assessed from the XRD patterns, obtained with x-ray diffractometer (JEOL JDX-3532) using Cu-Kα radiation. The accelerating voltage and the applied current were 40 kV and 20 mA, respectively. The sample was scanned in a 2θ range 5–80° with the step angle of 0.02°. Thermal behavior of the samples was evaluated with a simultaneous TGA/DTA analyzer (Diamond TGA/DTA Perkin Elmer) at the heating rate of 5°C/min in the flow of air.

3 Results and discussion

3.1 SEM

Precipitation of zirconia particles was carried out by varying the experimental conditions, such as concentration of the reactants, aging time, temperature, etc. SEM analysis indicated that morphology of the precipitated particles was dependent upon relative amounts of the starting chemicals in the reactant mixtures, and aging time. In fact, the precipitation of the dissolved zirconium ions into precipitated solids was triggered by the products formed in the reaction medium as a result of thermal decomposition of urea according to the following reaction (Eq. 1):

$$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_3.H_2O \quad (1)$$

In most of the cases, irregular shaped particles were obtained. Uniformity in particles shapes and size was achieved under a narrow set of the applied experimental conditions. SEM image shown in Figure 1A is of the zirconia particles obtained under controlled experimental conditions.

The sample shown in Figure 1A was heated at 700°C for 1 h at the heating rate of 5°C/min. The heat-treated solid was examined with SEM and the obtained image is given in Figure 1B. As can be seen, that the sample lost thermally decomposable material and the residue maintained their original morphology to the obvious extent.

3.2 FT-IR

FTIR analysis of the given sample of zirconia particles (Figure 2) shows bands at 3369 and 3393 for OH stretching vibration of adsorbed and structural water molecules respectively. The bands at 1628 & 1642 regions are attributed to OH bending vibration of free water molecules, while the broad band at 900–1250 cm^{-1} was attributed to different vibration modes of carbonate. The spectra also shows band in the region of 600–425 cm^{-1} due to vibration of Zr-O group, and these bands became more intense with increasing calcinations temperature.

3.3 X-ray diffraction study

The particles shown in Figure 1A & B were analyzed by XRD (Figure 3A & B). The XRD spectra shows weak crystal-

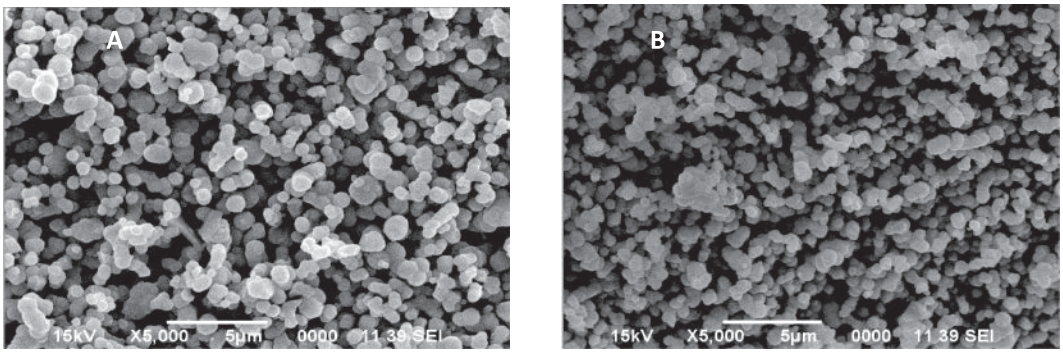

Fig. 1: Scanning electron micrographs (SEM) of zirconia particles obtained by aging at 50°C temperature for 90 min, aqueous solutions containing 0.006 mol/L zirconium chloride, 0.006 mol/L potassium sulphate, 0.15 mol/L hydrochloric acid and 0.2 mol/L urea (A), and remains of the particles shown in A after their calcination at 700°C for 1 h at the rate of 5°C/min (B).

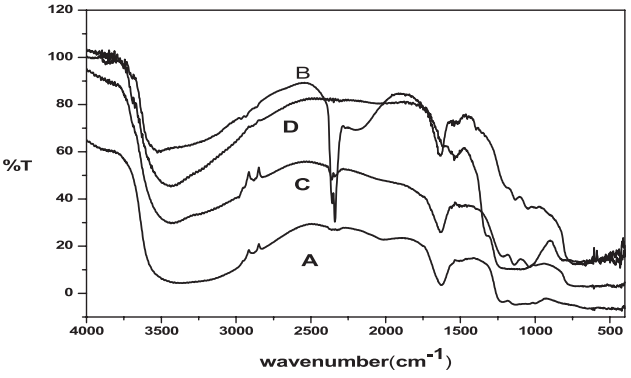

Fig. 2: Fourier Transform Infrared (FTIR) spectra of the particles shown in Fig. 1A (A), and after calcinations at 550°C (B), 700°C (C) and 800°C (D).

line nature of the as prepared sample (Figure 3A) and crystalline tetragonal phase start to transform into monoclinic phase (Fig. 3B) with increase in calcination temperature (700°C). In addition, the reflections observed for the as prepared and calcined particles (Figure 1A & 1B) at the 28 2θ value were employed for the estimation of crystallite sizes, using the under mentioned Scherrer equation [19, 20]:

$$D_p = (0.94\lambda)/(\beta_{1/2} \cos \theta) \quad (2)$$

where D_p = crystallite size, $\lambda = 154°A$, θ = Bragg angle, $\beta_{1/2}$ = the line broadening at half the maximum intensity (FWHM) in radians.

The crystallite sizes came out to be 9.8 nm and 45 nm for the as prepared and calcined particles respectively. This clearly indicated that calcinations temperature affected the crystallite size [21] of the precipitated crystalline solid, obtained in this study.

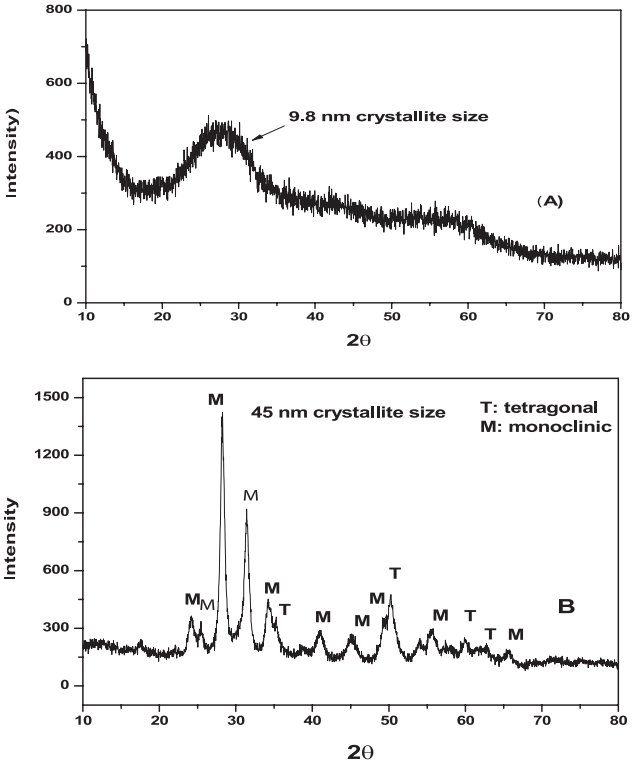

Fig. 3: X-ray diffraction (XRD) patterns of the particles shown in Fig. 1A (A) and Fig. 1B (B).

3.4 Thermal analysis

In order to observe the thermal changes in the properties of precursor particles; sample was analyzed by TG/DTA as shown in Figure 4. Two weight loss regions (22.6% and 16.3%) are prominent in TGA curve in the temperature range of 50–310°C and 656–720°C. The observed steps of weight losses in both cases agreed well with theoretical weight losses, showed by following reactions:

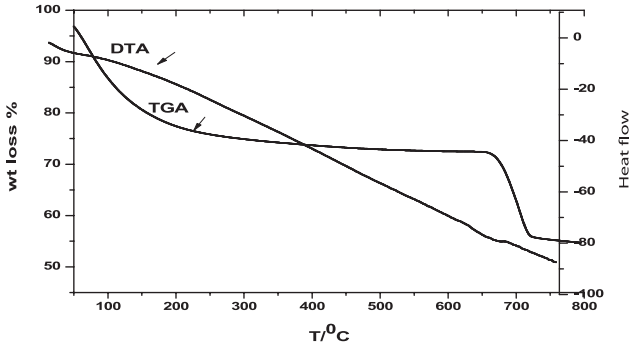

Fig. 4: Thermograms obtained with the particles shown in Fig. 1A.

$$Zr(OH)_2CO_3.2H_2O \xrightarrow{50-310^{\circ}C} ZrO_2.3H_2O + CO_2 \quad (3)$$

$$ZrO_2.3H_2O \xrightarrow{656-720^{\circ}C} ZrO_2.(3-n)H_2O + nH_2O \quad (4)$$

Moreover, activation energies were estimated for the thermally activated reactions of the as prepared zirconia particles, which led to the temperature dependent weight losses, by using the following Coats–Redfern equation [22–25].

$$\ln[-\ln(1-\alpha)/T^2] = -E/RT + \ln[(AR/\beta E)(1-(2RT/E))] \quad (5)$$

where β represents the heating rate, i.e. dT/dt, the term $\ln[(AR/\beta E)(1-(2RT/E))]$ is considered a constant quantity, and α is the mass fraction of the decomposed material which was estimated from the experimental determined weight losses according to the following equation:

$$\alpha = (W_i - W_t)/(W_i - W_f)$$

Using Equation 5, the experimental data was plotted in the form of $\ln[-\ln(1-\alpha)/T^2]$ vs $1/T$ and the estimated activation energies are 19.61 and 179.3 KJ/mol for the above reactions 2 and 3.

Conclusions

Monodispersed micron size spherical particles of Zirconia are synthesized by homgeneous precipitation method.

On heat treatment at 700°C, dry powder of the hydrated zirconia particles converts into ZrO_2 with a change in the surface morphology of the particles due to thermally initiated loss of material but the particles maintained their original morphology to the obvious extent.

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References

[1] J. Widoniak, S. Eiden-Assmann, G. Maret, Synthesis and Characterization of Monodisperse Zirconia Particles. *Eur. J. Inorg. Chem.* **2005**, *15*, 3149–3155.

[2] I. Haq, F. Haider, Synthesis and Characterization of Uniform Fine Particles of Copper Oxalate. *Mater. Lett.* **2009**, *63*, 2355–2357.

[3] A. A. Ismail, A. El-Midnay, E. A. Abdel-Aal, H. El-Shall, Application of Statistical Design to Optimize the Preparation of ZnO Nanoparticles via Hydrothermal Technique. *Mater. Lett.* **2005**, *59*, 1924–1928.

[4] L. Benea, P. Ponthiaux, F. Wenger, Co-ZrO_2 Electrodeposited Composite coatings Exhibiting Improved Micro Hardness and Corrosion Behavior in Simulating Body Fluid Solution. *Surf. Coat. Technol.* **2011**, *205*, 5379–5386.

[5] V. Santos, M. Zeni, C. P. Bergmann, J. M. Hohemberger, Correlation between Thermal Treatment and Tetragonal/ Monoclinic Nanostructured Ziconia Powder Obtained by Sol-Gel Process. *Rev. Adv. Mater. Sci.* **2008**, *17*, 62–70.

[6] X. C. Yang, W. Riehemann, M. Dubiel, H. Hofmeister, Nanoscaled Ceramic Powders Produced by Laser Ablation. *Mater. Sci. Eng., B* **2002**, *95*, 299–307.

[7] J. P. Markovic, S. K. Milonjic, Synthesis of Zirconia Colloidal Dispersions by Forced Hydrolysis. *J. Serb. Chem. Soc.* **2006**, *71*, 613–619.

[8] M. Z.-C. Hu, R. D. Hunt, E. A. Payzant, C. R. Hubbard, Nanocrystallization and Phase Transformation in Monodispersed Ultrafine Zirconia Particles from Various Homogeneous Precipitation Methods. *J. Am. Ceram. Soc.* **1999**, *82*, 2313–2320.

[9] J. L. Shi, J. H. Gao, Preparation of Sperical Zirconium Salt Particles by Homogeneous Precipitation. *J. Mater. Sci.* **1995**, *30*, 793–799.

[10] F. Heshmatpour, R. B. Aghakhanpour, Synthesis and Characterization of Nanocrystalline Zirconia Powder by Simple Sol–Gel Method with Glucose and Fructose as Organic Additives. *Powder Technol.* **2011**, *205*, 193–200.

[11] M. Tahmasebpour, A. A. Babaluo, M. K. R. Aghjeh, Synthesis of Zirconia Nanopowders from Various Zirconium Salts via Polyacrylamide Gel Method. *J. Eur. Ceram. Soc.* **2008**, *28*, 773–778.

[12] M. Z.-C. Hu, E. A. Payzant, C. H. Byers, Sol–Gel and Ultrafine Particle Formation via Dielectric Tuning of Inorganic Salt–Alcohol–Water Solutions. *J. Colloid Interface Sci.* **2000**, *222*, 20–36.

[13] J. M. E. Matos, F. M. A. Júnior, L. S. Cavalcante, V. Santos, S. H. Leal, L. S. S. Júnior, M. R. M. C. Santos, E. Longo, Reflux Synthesis and Hydrothermal Processing of ZrO_2 Nanopowders at Low Temperature. *Mater. Chem. Phys.* **2009**, *117*, 455–459.

[14] M.-H. Lee, H.-Y. Lin, J. L. Thomas, A Novel Supercritical CO_2 Synthesis of Amorphous Hydrous Zirconia Nanoparticles, and Their Calcination to Zirconia. *J. Am. Ceram. Soc.* **2006**, *89*, 3624–3630.

[15] B. B. Nayak, S. K. Mohanty, M. Q. B. Takmeel, D. Pradhan, A. Mondal, Borohydride Synthesis and Stabilization of Flake-like Tetragonal Zirconia Nanocrystallites. *Mater. Lett.* **2010**, *64*, 1909–1911.

[16] M. Rezaei, S. M. Alavi, S. Sahebdelfar, Z.-F. Yan, H. Teunissen, J. H. Jacobsen, J. Sehested, Synthesis of Pure Tetragonal Zirconium Oxide with High Surface Area. *J. Mater. Sci.* **2007**, *42*, 1228–1237.

[17] M. Salavati-Niasari, M. Dadkhah, F. Davar, Synthesis and Characterization of Pure Cubic Zirconium Oxide Nanocrystals by Decomposition of Bis-aqua, Tris-acetylacetonato Zirconium (IV) Nitrate as New Precursor Complex. *Inorg. Chim. Acta* **2009**, *362*, 3969–3974.

[18] K. Geethalakshmi, T. Prabhakaran, J. Hemalatha, Dielectric Studies on Nano Zirconium Dioxide Synthesized through Co-Precipitation Process. *World Acad. Sci. Eng. Technol.* **2012**, *64*, 179–182.

[19] A. W. Burton, K. Ong, T. Rea, I. Y. Chan, On the Estimation of Average Crystallite Size of Zeolites from the Scherrer equation: A Critical Evaluation of Its Application to Zeolites with One-dimensional Pore Systems. *Micropor. Mesopor. Mater.* **2009**, *117*, 75–90.

[20] I. Uslu, T. Tunc, M. K. Öztürk, A. Aytimur, Synthesis and Characterization of Boron-Doped Hafnia Electrospun Nanofibers and Nanocrystalline Ceramics. *Polym. Plast. Technol. Eng.* **2012**, *51*, 257–262.

[21] M. M. Rashad, H. M. Baioumy, Effect of Thermal Treatment on the Crystal Structure and Morphology of Zirconia Nanopowders Produced by Three Different Routes. *J. Mater. Process. Technol.* **2008**, *195*, 178–185.

[22] K. Ada, Y. Sarıkaya, T. Alemdaroglu, M. Onal, Thermal Behaviour of Alumina Precursor Obtained by the Aluminium Sulphate–Urea Reaction in Boiling Aqueous Solution. *Ceram. Int.* **2003**, *29*, 513–518.

[23] E. Oktay, A. Yayli, Physical Properties of Thorium Oxalate Powders and Their Influence on the Thermal Decomposition. *J. Nucl. Mater.* **2001**, *288*, 76–82.

[24] B. B. Parekh, P. M. Vyas, S. R. Vasant, M. J. Joshi, Thermal, FT–IR and Dielectric Studies of Gel Grown Sodium Oxalate Single Crystals. *Bull. Mater. Sci.* **2008**, *31*, 143–147.

[25] Y. Sarikaya, I. Sevinc, M. Akinc, The Effect of Calcination Temperature on Some of the Adsorptive Properties of Fine Alumina Powders Obtained by Emulsion Evaporation Technique. *Powder Technol.* **2001**, *116*, 109–114.