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Hydrothermal synthesis of zirconia nanoparticles from commercial zirconia

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Abstract

Recently, it was observed that nanostructured zirconia (ZrO_2) powder exhibits enhanced performance in many applications. In this study, a hydrothermal method was used for the synthesis of nano-crystalline ZrO_2 powder from a fully monoclinic commercial zirconia. The products were characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results of SEM showed that after hydrothermal treatment under alkali condition, a different morphology from the commercial zirconia was obtained and XRD results showed that moreover to monoclinic phase (28%), cubic and tetragonal phases (72%) formed. According to TEM observations and XRD analysis, it was found that the nano-sized zirconia has an average particles size of 15-30 nm.

Keywords: Nano-crystalline ZrO_2;Commercial zirconia;Hydrothermal synthesis;Alkali treatment

1. Introduction

Zirconia has three thermodynamically stable crystalline phases under atmospheric pressure: monoclinic phase (up to 1170 ºC), tetragonal phase (1170–2370 ºC), and cubic phase (2370–2680 ºC) [1-5]. Recently, a high-pressure allotropic form of zirconia (orthorhombic) has been reported, this phase is metastable at atmospheric pressure and reverts to the monoclinic phase [1]. Tetragonal and cubic phases

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are unstable in pure coarse-grained zirconia at ambient temperature, which is unfortunate because they are more valuable for the technological applications than the monoclinic phase. Consequently, many divalent and trivalent cations (such as Mg^{2+}, Ca^{2+}, and rare-earth ions including Y^{3+} and Sc^{3+}) have been doped into zirconia to stabilize the metastable cubic and tetragonal phases at room temperature [6]. Zirconia is an important ceramic with a wide range of applications including electrochemical

Devices, structural ceramics, catalytic systems, etc [7]. Cubic phase (CZ), among the three crystalline phases of zirconia, possesses high oxygen ionic conductivity and chemical stability over a wide range of temperature and oxygen partial pressure. Therefore, It is a well-known candidate for applications such as manufacturing of oxygen sensor [5], development of solid oxide fuel cell [8] and catalytic applications (catalyst [9] and catalyst support (such as: Ni/ZrO_2 [10], Co/ZrO_2 [11], Cu/ZrO_2 [12]), promoter [13]) and finally membrane making for separation of oxygen [8]. In other hand, the tetragonal ZrO_2 polycrystal (TZP) ceramics have attracted special attention because of their good mechanical and electrical properties [14]. Therefore, owing to their high oxygen ion conductivity, the high temperature phases (tetragonal and cubic) of ZrO_2 are useful as chemical engineering applications at lower temperatures [15]. Also, the decrease of the grain size below 100 nm leads to the formation of attractive nanostructured ceramics having superior electrical, thermal, optical and mechanical properties [8].

Interest in synthesis and sintering of nano-crystalline ceramics have recently grown due to the significant improvement in their properties as compared to the conventional coarser grain compacts. In order to prepare zirconia nano-crystalline powders, many methods such as sol–gel, chemical vapor synthesis (CVS), combustion synthesis, precipitation and hydrothermal processing are well known [16,17]. These methods are divided into two groups:

Liquid phase techniques (usually called wet-chemical synthesis) such as sol-gel or hydrothermal method, and on the other hand, various gas phase processes for examples: inert gas condensation, laser ablation, microwave plasma synthesis and chemical vapor synthesis [18]. The crystalline structures and catalytic properties of zirconia are generally dependent on its synthesis method and thermal treatment [19]. Hydrothermal synthesis (HS) refers to the synthesis of a compound in a hydrothermal solution under the effect of temperature >100 °C and pressures above 1 atm. In this method, ceramic sols are produced by chemical reactions in an aqueous or organo-aqueous solution under the simultaneous application of heat and pressure in the presence of an alkali or acid that has a pseudo-catalytic effect upon the reaction [20]. Hydrothermal process was found most preferable because in this method crystal size can be controlled and miniaturized by altering the process conditions. The reaction such as hydrolysis, co-precipitation, oxidation, decomposition, complexion can be performed using hydrothermal method [17,21]. Hydrothermal synthesis is reported to be a soft chemical route with an important advantage like the formation of phase pure products at low temperature [17,22]. Fig. 1 shows the major differences in the products obtained by conventional techniques and by the hydrothermal method [23].

In the present work, we investigate a hydrothermal process to prepare nano-crystalline zirconia powder in cubic and tetragonal phases by alkali treatment of commercial zirconia. Also, this paper presents some results on production of cubic (C-ZrO_2) or tetragonal phase (T-ZrO_2) of zirconia from commercial zirconia which its main phase is monoclinic (M-ZrO_2). Cubic and tetragonal phases of zirconia are very important for chemical engineering applications. The structural study of the feed and the product was performed using X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM).

2. Experimental

2.1. Material and Processing

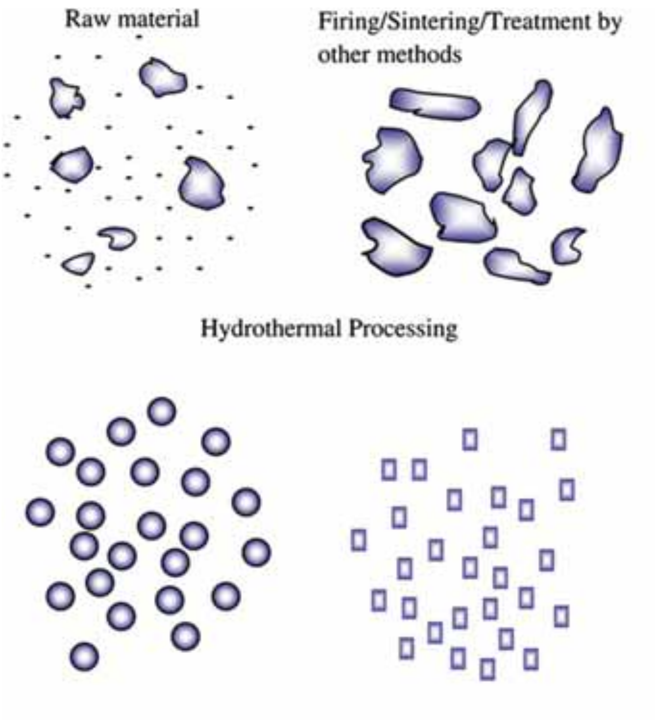

Fig. 1. Difference in particle processing by hydrothermal and conventional techniques [23].

The starting reagents were commercial zirconia (ZrO_2, China) and NaOH (Merck, Germany) aqueous solution. The used water in this work was doubly distilled and deionized. At first, 0.085 g of the yellow powder, commercial zirconia, was mixed with 75 ml of 10 molar NaOH aqueous solution. The specimen was stirred by a magnetic mixer (Heidolph, MR Hei-Tec) for 3 h with a stirring rate of 850 rpm. Finally, the mixture was transferred into a 100 ml teflon-lined high pressure reactor (BERGHOF, BR–100) and maintained at 150 ºC for 85 h. Temperature regulation was done by means of a temperature probe in a submersion tube to measure the internal reactor temperature which was connected to a temperature controller system (Cole Parmer, Digi–Sense®). The experimental setup is shown in Fig. 2.

2.2. Washing, Ultrasonic Deagglomeration and Drying

After hydrothermal treatment of the commercial zirconia, the product which was between sol and gel state (concentrated sol), was obtained. It took around 5-10 h for the whole precipitate to settle down. Subsequently, the product was separated from the liquid phase by centrifugation (5000 rpm for 5 min).

The semisolid phase was washed several times with dilute HCL (pH = 4-5) and deionized water to remove the hydroxide ions and then dried at 110 ºC for 6 h. Afterward, the dried powder was redispersed in acrylonitrile (Merck, Art.800834) using an ultrasonic device (Sounopuls, Bandelin, HD2200, Germany). Microtip ultrasonication with a frequency of 20 kHz and power of 120 W was used to break up the powder agglomerations in the suspension [14].

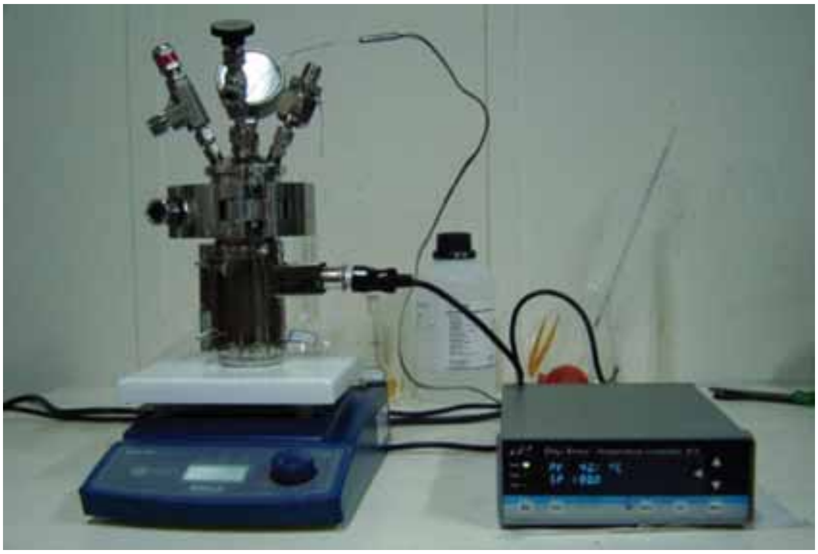

Fig. 2. The hydrothermal experimental setup.

2.3. Materials Characterization

A Philips PW1800 instrument with Cu Kα radiation was used to obtain the XRD patterns for determination of crystalline phases and particles size of the zirconia powders. The morphology observation and aggregates size distribution was studied using a SEM (TESCAN, VEGA II) and a TEM (Zeiss EM900). Also, X-ray fluorescence (XRF) analysis was performed using a Philips PW1480 instrument in order to determine the composition of commercial zirconia before hydrothermal treatment.

3. Result and Discussion

X-ray fluorescence (XRF) analysis of the commercial zirconia reveals that ZrO_2 (pure zirconia) with 99.45 wt.% is the major component of commercial zirconia and also SiO_2 with 0.11 wt.% is another important material.

XRD is of great importance in the microstructure characterization of complex, multiphase and single phase materials. The application of XRD enables not only qualitative and quantitative phase analysis but also microstructure characterization (crystallite size, lattice distortions, dislocation densities, stacking faults and twins probability) [4]. The XRD spectrums of the commercial zirconia and the product are shown in Fig. 3(a) and Fig. 3(b), respectively. X-ray diffractogram corresponding to commercial zirconia (Fig. 3(a)) reveals the occurrence of monoclinic phase while X-ray diffractogram corresponding to hydrothermally treated zirconia (Fig. 3(b)) shows cubic and tetragonal phases in addition to monoclinic phase. The monoclinic and tetragonal contents can be calculated using the intensities of their corresponding peaks in the XRD patterns.

The tetragonal and cubic phases are difficult to distinguish by XRD patterns, due to their similar lattice parameters and the line broadening of XRD peaks in these patterns [24]. XRD peaks of cubic or tetragonal phase of nano-crystalline zirconia (Fig. 3(b)) were observed at $2\theta = 30.485°$, $35.165°$, $50.644°$, $60.285°$ and $63.156°$.

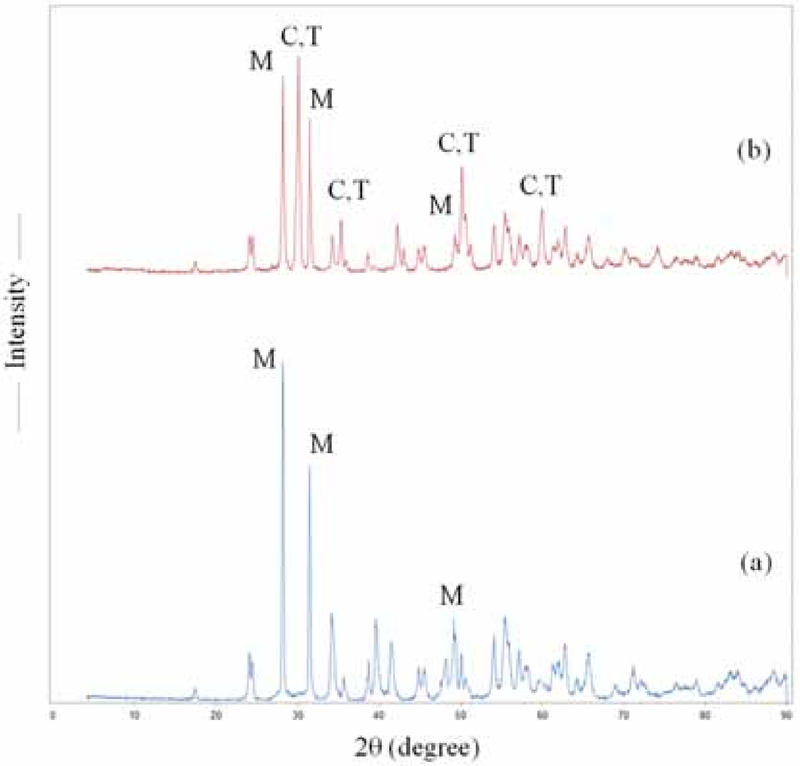

Fig. 3. XRD patterns of (a) the commercial zirconia and (b) the nano-sized zirconia (M–Monoclinic phase and T,C–Tetragonal and Cubic phases).

The monoclinic, tetragonal and cubic structures were defined with monoclinic, tetragonal and cubic unit cells with the symmetry described by space groups P21/c, P42/nmc and Fm3m, respectively. The average crystallite sizes after alkali treatment of zirconia in hydrothermal reactor were estimated by the Scherrer equation using the full width at half maximum (FWHM) of the most intense peak (2θ= 30.485°). As reported in the literature [23-25], the Scherrer's equation is described as follows:

$$d=(k*\lambda)/(B*\cos\theta) \qquad (1)$$

Where D is the average crystallite size (nm), λ is the X-ray wavelength (0.1540593 nm), θ is the Bragg angle, k = 0.9 is a correction factor to account for particle shapes and B is the FWHM. The intensity data were collected over a 2θ range of 4-90°. The crystallite sizes of the alkali treated zirconia calculated from the most intense XRD peaks were found to be approximately in the range of 15–33 nm which are given in Table 1. Overall, it shows that hydrothermal treatment of zirconia (ZrO_2) by highly concentrated NaOH solution (10 molar) lowers the particles size and increases the content of cubic phase which is very important in chemical engineering applications (e.g. production of catalyst and membrane for solid oxide fuel cells). In cubic phase of zirconia, vacancies increase improves diffusion of oxygen ions as the primary charge carriers which elevates the electrical conductivity [26]. Molar fractions of monoclinic, tetragonal and cubic phases of zirconium oxide in product powder (Xi) were estimated using the equations proposed by Toraya [24]:

$$X_m=(I_m(111)+I_m(-111))/(I_m(111)+I_m(-111)+I_t(101(\text{or } I_c(111)))) \quad (2)$$

$$X_{c,t}=I_t(101)/(I_m(111)+I_m(-111)+I_t(101)) \quad (3)$$

where Im(111) and Im(-111) are the integral intensities of (111) and (-111) zirconia monoclinic phase peaks (at 2θ= 28.037°, 31.362°), respectively, and It(101) (or Ic(111)) is the integral intensity of (101) (or (111)) tetragonal (or cubic) zirconia phase peak (at 2θ= 30.485°).

Table 1. Characterization of the hydrothermally nano-sized zirconia by XRD analysis.

Phase formed	Phase content (%)	Crystallite size (nm)
Cubic or Tetragonal (C,T- ZrO_2)	72	15
Monoclinic (M- ZrO_2)	28	33

Fig. 4 is the SEM image of the commercial zirconia particles used in this work which shows that the average size of particles (after an hour dispersing in acrylonitrile) is 0.5 to 3 μm. Following the hydrothermal treatment, the product was dispersed in acrylonitrile for an hour and then a drop of dispersed liquid was dried on a sample holder for SEM analysis. Fig. 5 shows the SEM image of the alkali treated zirconia in hydrothermal reactor. The SEM photographs of commercial ZrO_2 (Fig. 4) and the product (Fig. 5) show different morphology. This indicates that hydrothermal treatment of commercial zirconia under alkali condition declines the particles size.

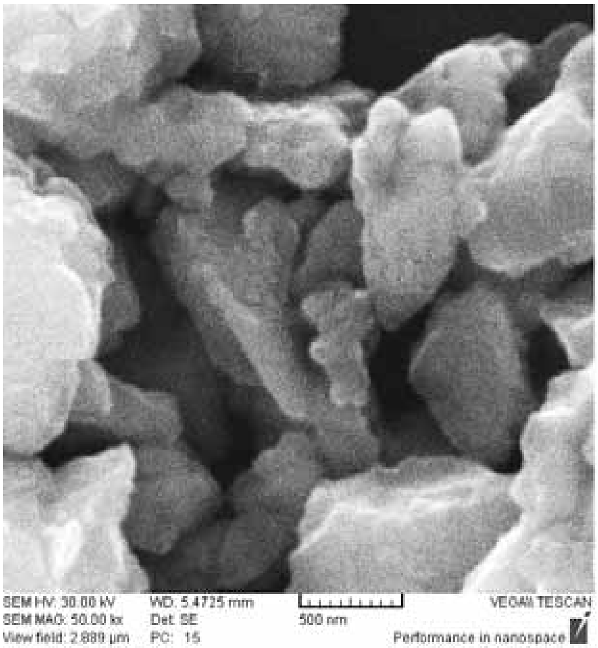

Fig. 4. SEM micrograph of commercial zirconia before hydrothermal treatment as precursor.

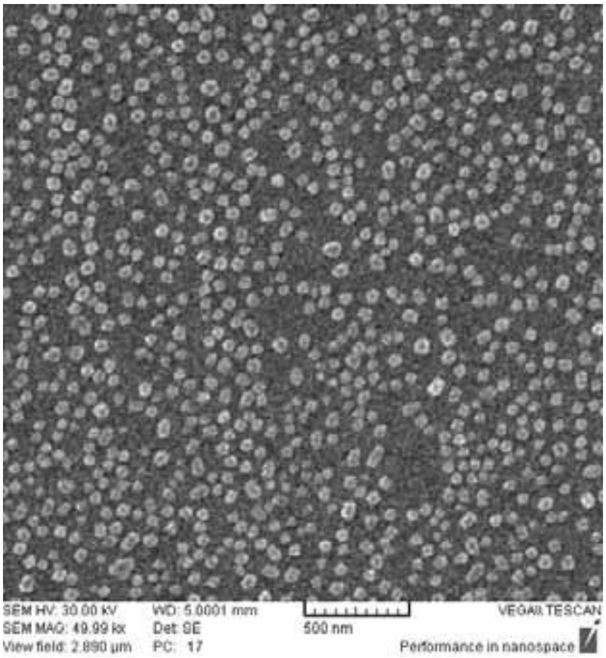

Fig. 5. SEM micrograph of nano-size zirconia after hydrothermal treatment.

The TEM micrograph of the product in Fig. 6 and the histogram of particles size in Fig. 7 reveal that the size of the well-dispersed particles is in the range of 15–30 nm, which is in accordance with the results of XRD pattern (Fig. 3). As shown in Fig. 7, the histogram of nano-size zirconia powder demonstrates that the average particles size of zirconia nanoparticles is 23.55 nm.

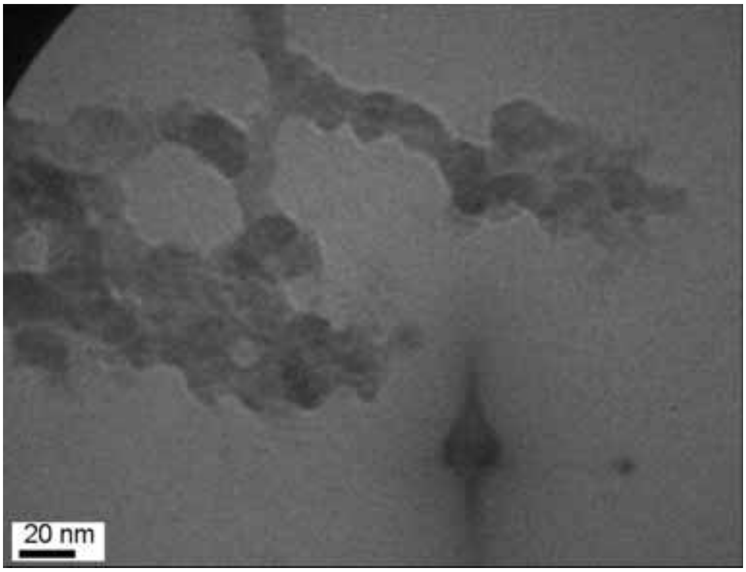

Fig. 6. TEM micrograph of the hydrothermally nano-sized zirconia.

The synthesis parameters affect differently the disperse and phase composition of ZrO_2. No exhaustive theory has been developed to predict quantitatively the formation and growth of nano-crystals with a definite crystal structure as influenced by parameters of a hydrothermal synthesis [27]. Presumably, the decisive factor governing the structure of nanocrystals is the structural similarity of the nucleation centres and growing nano-crystals. This assumption is supported by the fact that the hydroxide of the polymeric hydroxo complex $[Zr_4(OH)_8 .(H_2O)_{16}]^{8+}$, which was the ZrO_2 precursor in the hydrothermal synthesis (Fig. 8), has a structure similar to that of cubic (or tetragonal) ZrO_2 [19,27].

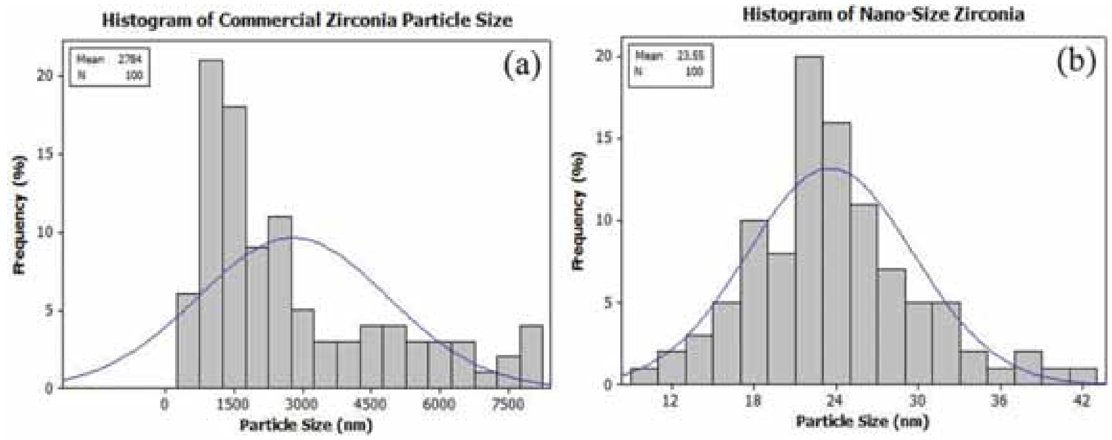

Fig. 7. Particles size histograms of (a) the commercial zirconia and (b) the hydrothermally nano-sized zirconia.

When the concentration of oligomers reaches the critical level, crystal nuclei of ZrO_2 are generated and primary particles of ZrO_2 form by growth of these nuclei. Also, when pH of the reaction solution is strongly basic (For example in 10 M solution of NaOH), hydrolysis occurs easily. The concentration of oligomers could reach the critical level and form crystal nuclei [28]. The formation of nanoparticles in the crystalline structure is reported to be associated with the hydroxyl ions inserted in the hydrothermal solution. The mechanism of this process is not completely realized and when the raw material (commercial zirconia) is treated with NaOH in concentrated solution, some of the Zr–O–Zr bonds may be broken and then the complexes can be formed like the one shown in Fig. 8. This complex may change into the nano-size zirconia particles by the hydrothermal treatment.

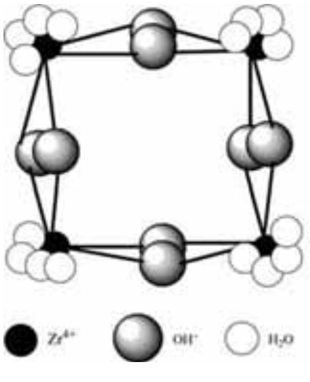

Fig. 8. Schematic of the complex formed from ZrO_2 and NaOH solution [28].

4. Conclusions

In summary, ZrO_2 nano-powder was successfully obtained by alkali treatment of commercial zirconia powder in hydrothermal process at a temperature of 150 ºC with a duration of 85 h. The XRD showed that the ommercial zirconia crystalline phase was fully monoclinic while after hydrothermal treatment, the molar phase fractions of the product were 72% cubic and tetragonal versus 28% monoclinic. The results of XRD, TEM and SEM analyses showed that the particles size of the product was around 15-30 nm.

References

[1] Srinivasan R, Angelis RJD, Ice G, Davis BH. Identification of tetragonal and cubic structures of zirconia using synchrotron x-radiation source. *J Mater Res* 1991;**6**:1287-1292.

[2] Bokhimi X, Morales A, Novaro O, Portilla M, Lo T, Tzompantzi F et al. Tetragonal Nanophase Stabilization in Nondoped Sol–Gel Zirconia Prepared with Different Hydrolysis Catalysts. *J Solid state chemistry* 1998;**135**:28-35.

[3] Sayılkan F, Asilturk M, Burunkaya E, Arpac E. Hydrothermal synthesis and characterization of nanocrystalline ZrO_2 and surface modification with 2-acetoacetoxyethyl methacrylate. *J Sol-Gel Science and Technology* 2009;**51**:182-189.

[4] Dercz G, Prusik K, Pająk L. Structure investigations of commercial zirconia ceramic powder. *J Achiev Mater Manuf Eng* 2006;**18**:259-262.

[5] Nakamura T, Sakamoto Y, Saji K, Sakata J. NOx decomposition mechanism on the electrodes of a zirconia-based amperometric NOx sensor. *J Sensors Actuators* 2002;**93**:214-220.

[6] Xu G, Zhang YW, Liao CS, Yan CH. Tetragonal-to-Monoclinic Phase Transitions in Nanocrystalline Rare-Earth-Stabilized Zirconia Prepared by a Mild Hydrothermal Method. *J Am Ceram Soc* 2004;**87**:2275–2281.

[7] Chang H, Shady P, Shih W. The effects of containers of precursors on the properties of zirconia powders. *J Micropor Mesopor Mater* 2003;**59**:29–34.

[8] Mazaheri M, Valefi M, Razavi Hesabi M, Sadrnezhaad SK. Two-step sintering of nanocrystalline 8Y2O3 stabilized ZrO_2 synthesized by glycine nitrate process. *J Ceram Int* 2007;**35**:13-20.

[9] Su C, Li J, He D, Cheng Z, Zhu Q. Synthesis of isobutene from synthesis gas over nanosize zirconia catalysts. *J Appl Cat A: General* 2000;**202**:81-89.

[10] Liu Q, Dong X, Mo X, Lin W. Selective catalytic methanation of CO in hydrogen-rich gases over Ni/ZrO_2 catalyst. *J Natural Gas Chem* 2008;**17**:268-272.

[11] Panpranot J, Taochaiyaphum N, Praserthdam P. Glycothermal synthesis of nanocrystalline zirconia and their applications as cobalt catalyst supports. *J Mater Chem Phys* 2005;**94**:207-212.

[12] Ma ZY, Yang C, Wei W, Li WH, Sun YH. Catalytic performance of copper supported on zirconia polymorphs for CO hydrogenation. *J Mol Cat A: Chem* 2004;**231**:75-81.

[13] Therdthianwong S, Siangchin C, Therdthianwong A. Improvement of coke resistance of Ni/Al_2O_3 catalyst in $CH4/CO_2$ reforming by ZrO_2 addition. *J Fuel Proc Tech* 2007;**89**:160-168.

[14] Vasylkiv O, Sakka Y. Synthesis and Colloidal Processing of Zirconia Nanopowder. *J Am Ceram Soc* 2001;84:2489–2494.

[15] Shukla S, Seal S. Mechanisms of room temperature metastable tetragonal phase stabilisation in zirconia. *J Int Materials Reviews* 2005;**50**:1-20.

[16] Widiyastuti W, Balgis R, Iskandar F, Okuyama K. Nanoparticleformationinspraypyrolysisunderlow-pressureconditions. *J Chem Eng Sci* 2009;**65**:1846-1854.

[17] Kanade KG, Baeg JO, Apte SK, Prakash TL, Kale BB. Synthesis and characterization of nanocrystallined zirconia by hydrothermal method. *J Mats Rese Bull* 2008;**43**:723–729.

[18] Srdic VV, Winterer M. Comparison of nanosized zirconia synthesized by gas and liquid phase methods. *J Eur Ceram Soc* 2006;**26**:3145–3151.

[19] Wang JA, Valenzuela MA, Salmones J, Vázquez A, Garc A, Bokhimi X. Comparative study of nanocrystalline zirconia prepared by precipitation and sol–gel methods. *J Cat Today* 2001;**68**:21-30.

[20] Kaya C, He JY, Gu X, Butler EG. Nanostructured ceramic powders by hydrothermal synthesis and their applications. *J Micropor Mesopor Mat* 2002;**54**:37–49.

[21] Miya SS, Roy R. Hydrothermal synthesis of fine oxide powders. *J Bull Mat Sci* 2000;23:453–460.

[22] Piticescu R, Monty C, Millers D. Hydrothermal synthesis of nanostructured zirconia materials: Present state and future prospects. *J Sensors Actuators B* 2005;**109**:102–106.

[23] Esmaeilifar A, Yazdanpour M, Rowshanzamir S, Eikani MH. Hydrothermal synthesis of Pt/MWCNTs nanocomposite electrocatalysts for proton exchange membrane fuel cell systems. Int *J Hydrogen Energy* 2011;**36**:5500-5511.

[24] Tahmasebpour M, Babaluo AA, Razavi Aghjeh MK. Synthesis of zirconia nanopowders from various zirconium salts via polyacrylamide gel method. *J Eur Ceram Soc* 2007;**28**:773-778.

[25] Szepesi CJ, Adair JH. High Yield Hydrothermal Synthesis of Nano-Scale Zirconia and YTZP. *J Am Ceram Soc* 2011;**94**:4239–4246.

[26] Indarto A, Choi JW, Lee H, Song HK. A review of C1 chemistry synthesis using yttrium-stabilized zirconia catalyst. *J Rare Earths* 2008;**26**:1-6.

[27] Pozhidaeva OV, Korytkova EN, Romanov DP, Gusarov VV. Formation of ZrO_2 Nanocrystals in Hydrothermal Media of Various Chemical Compositions. *J General Chem* 2000;**72**:910-914.

[28] Qin D, Chen H. The influence of alcohol additives on the crystallization of ZrO_2 under hydrothermal conditions. *J Mater Sci* 2006;**41**:7059–7063.