Journal of Colloid and Interface Science 342 (2010) 327–332

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Synthesis and characterization of nano-sized zirconia powder synthesized by single emulsion-assisted direct precipitation

Navin Chandra *, Deepesh Kumar Singh, Meenakshi Sharma, Ravi Kant Upadhyay, S.S. Amritphale, S.K. Sanghi

Advanced Materials and Processes Research Institute (CSIR), Habibganj Naka, Hoshangabad Road, Bhopal 462 064, MP, India

ARTICLE INFO

Article history:
Received 23 October 2009
Accepted 24 October 2009
Available online 29 October 2009

Keywords:
t-ZrO_2
Phase transformation
Reverse microemulsion
X-ray diffraction (XRD)

ABSTRACT

For the first time, single reverse microemulsion-assisted direct precipitation route has been successfully used to synthesize tetragonal zirconia nanoparticles in narrow size range. The synthesized powder was characterized using FT-IR, XRD and HRTEM techniques. The zirconia nanoparticles obtained were spherical in shape and has narrow particle size distribution in the range of 13–31 nm and crystallite size in the range of 13–23 nm.

1. Introduction

Zirconia (ZrO_2) is a widely used ceramic material exhibiting excellent properties such as low thermal conductivity, high coefficient of thermal expansion, high thermal stability, high oxygen ion conductivity, high strength, high fracture toughness and high thermal shock resistance enabling it to be used as thermal barrier coating, cutting tools, refractory material, as catalyst/catalyst support (stable under a reducing atmosphere and photo irradiation). Moreover, owing to their high oxygen ion conductivity, the high temperature phases (tetragonal and cubic) of ZrO_2 are useful as solid electrolytes in oxygen sensors and solid oxide fuel cells [1,2]. ZrO_2 is also used as ball heads for total hip replacement because of its good chemical and dimensional stability, mechanical strength, toughness and Young's modulus [1]. About 95% of ferrules used in optical fiber connectors are made of zirconia [3]. Because of amphoteric nature, it can be used to modify the inner surface of fused silica capillary, which can be applied in separation science (capillary electrophoresis) to obtain switchable electro-osmotic flow [4]. Zirconia is stable over a wide pH range and has higher thermal stability, so surface modifications using zirconia nanoparticles may increase options in the development of analytical methods. The isoelectric point of ZrO_2 depends on the nature of its crystallographic phase, which in turn decides the pH of the background electrolyte [5].

At atmospheric temperature and pressure, zirconia exists in monoclinic form, but with increase in temperature, it transforms to tetragonal at 1170 °C and cubic phase above 2370 °C. The application of pressure also causes phase transformation in zirconia; at ~3 GPa, a Pbca-type orthorhombic phase occurs, which converts to Pnam at ~16–22 GPa [6,7]. Orthorhombic structure is considered to be an intermediate structure between monoclinic and tetragonal. Transformation of tetragonal to monoclinic phase is accompanied by 3–5% increase in volume [8]. High temperature polymorphs (tetragonal and cubic) have to be stabilized at lower temperature because of their application in various fields, either by adding stabilizers such as Y_2O_3, MgO and CaO or by reduction in grain or particle size into nanometer regime [9].

Zirconia particles in the nano-size range have been synthesized using various routes such as sol–gel [1,10], co-precipitation [11,12], ball milling [13], hydrothermal process [14,15], gas phase synthesis and microemulsion methods [16–18]. Due to the possibility of controlling reactor (droplet) size, the emulsion method yields nanopowders with a narrow size range. Reverse microemulsion is a transparent, isotropic and thermodynamically stable dispersion of nano-sized aqueous droplets dispersed in a continuous oil phase, in the presence of interfacial film of surfactant molecules. The microemulsion methods reported in literature for the preparation of nano-sized zirconia powder may either involve preparation of a single emulsion followed by precipitation or preparation of two separate emulsions and their mixing followed by hydrolysis. For example, Feng et al. [19] used single as well double microemulsion system to synthesize zirconia particles. The former method produced larger particles with a mixture of tetragonal and monoclinic phases, while the latter yielded finer zirconia particles with tetragonal phase. Following two emulsions, dopant/stabilizer

* Corresponding author. Fax: +91 755 2587042/2488323.
E-mail addresses: navinchandrarrl@yahoo.com (N. Chandra), nit_d7@yahoo.com (D.K. Singh), meenakshirrl@yahoo.com (M. Sharma), rkupadhyay85@gmail.com (R.K. Upadhyay), ssamritphale@hotmal.com (S.S. Amritphale), sksanghi@ampri.res.in (S.K. Sanghi).

0021-9797/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2009.10.065

was used by Yang et al. to stabilize tetragonal phase taking Isooctane/AOT/water. Tai et al. [17] as well as Duan et al. [20] prepared two emulsions of zirconia precursor and ammonia separately, mixed them and allowed hydrolysis to proceed to obtain nano-sized zirconia particles.

The present work for the preparation of nano-sized zirconia powder involves emulsion-assisted direct precipitation technique using Isooctane/AOT/water system to form amorphous hydroxyl precipitate such as $Zr(OH)_4$ or $[ZrO(OH)_2]_n{\cdot}xH_2O$ followed by calcination at 800 °C. Low water-to-surfactant ratio (Rw = 8) in the emulsion leads to the formation of tetragonal phase, but with increasing Rw, monoclinic phase appears, and at Rw > 30, almost pure monoclinic phase was formed. The results of the studies are presented later.

2. Materials and methods

$ZrOCl_2{\cdot}8H_2O$ of LR Grade and Isooctane of AR Grade, both from CDH (India), were used as zirconia precursor and oil phase, respectively, and AOT (Dioctyl sodium sulfosuccinate Assay-98%) procured from Loba Chemie was used as surfactant. All the chemicals were used as received. For synthesis, 0.1 M sodium bis (2-ethyl hexyl) sulfosuccinate was dissolved in Isooctane in a round bottom flask using a Teflon-coated magnetic bit where after required quantity of water was added under continuous stirring to prepare dispersed phase, which served as nanoreactors. To this microemulsion, aqueous solution of zirconyl chloride was added drop wise using a burette. Precipitation was done by adding 3–5% liquid ammonia to the above solution drop wise at a rate of 0.2 ml/min. The precipitate so obtained was dried in a petridish where the organics were allowed to evaporate, and later the obtained material was dried as such at 80 °C. The oven-dried material was made free of agglomeration using agate mortar and pestle and calcined at 800 °C for 1 h in muffle furnace, and phase identification was done using X-ray diffraction (XRD). However, as the samples were dried as such without washing, NaCl peak was observed in the combination with the other phases of zirconia. Therefore, calcined samples were washed with distill water and subjected to XRD analysis.

The identification of phases in the synthesized zirconia powder sample was carried by X-ray diffraction studies (Bruker – Model D8) using Cu Kα radiation (1.54 Å), operated at 40 kV and 40 mA at a scan rate of 1° 2θ/s in the 2θ range 5–70° and comparing the interplanar distances and intensity values with those of the corresponding standard peaks using JCPDS files. The crystallite size of the nano-sized zirconia was evaluated from X-ray diffraction data using Debey–Scherrer formula for the most intense peak (1 1 1) plane of zirconia crystal using the equation: $D = k\lambda/(\beta \cos\theta)$, where D, the crystallite size; $k = 0.9$, a correction factor to account for particle shape; β, the full width at half maximum (FWHM) of the most intense diffraction plane; λ, the wavelength of Cu target = 1.54 Å; and θ, the Bragg angle. For HRTEM studies, the synthesized samples were sonicated in acetone for 15 min followed by ambient drying and mounted on carbon-coated copper grids. The particle morphology was recorded using high-resolution transmission electron microscope (HRTEM) (JEOL 3010 operating at 300 keV), and the particle size was estimated. FT-IR spectrum of the powder (400–4000 cm^{-1}) has been studied in a KBr pellet with Perkin Elmer spectrum GX Spectrophotometer.

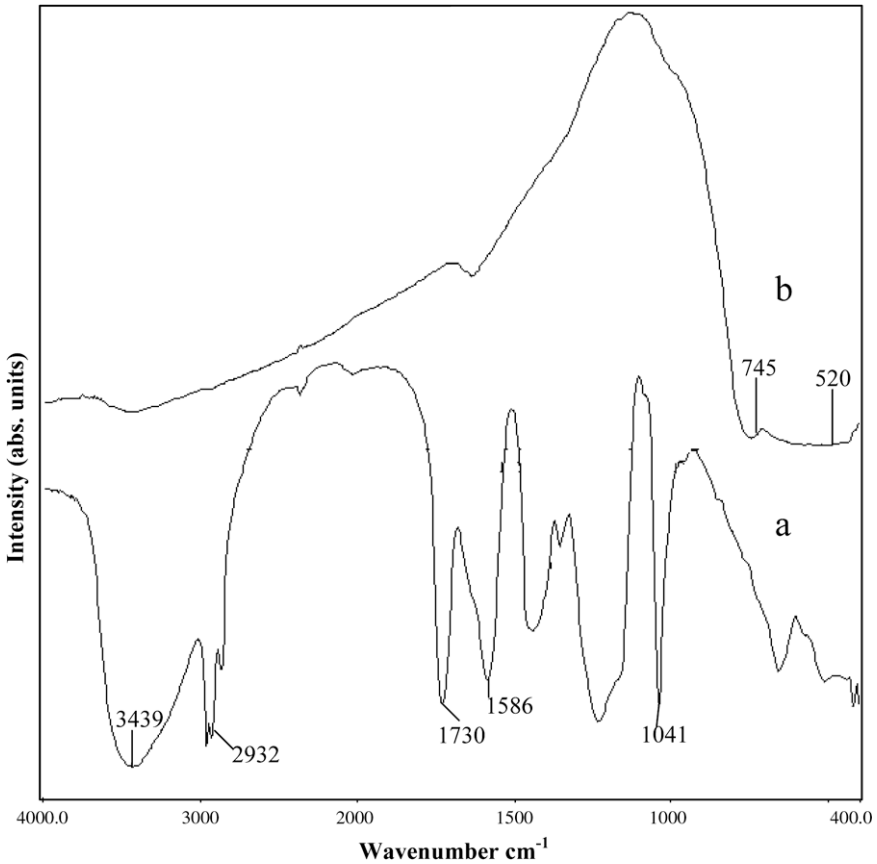

Fig. 1. FT-IR absorption spectra of (a) uncalcined amorphous zirconia sample and (b) calcined sample at 800 °C for 1 h (Rw = 20).