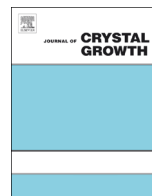




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Influence of thermal treatment on the formation of zirconia nanostructured powder by thermal decomposition of different precursors [☆]



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ABSTRACT

The paper presents some results concerning the preparation of zirconia powders starting from $ZrOCl_2 \cdot 8H_2O$ by using two synthesis methods: (a) precipitation with NH_3 , at $90^\circ C$, and (b) thermal decomposition of carboxylate precursors, obtained in the reaction of zirconium nitrate and two different alcohols, 1,3-propanediol (PD) and poly(vinyl alcohol) (PVA), at $150^\circ C$. The precursors obtained at different temperatures have been characterized by thermal analysis (TG, DTA) and FT-IR spectroscopy. DTA analysis evidenced very clearly the transition temperatures between zirconia crystalline phases. The precursors have been annealed at different temperatures in order to obtain zirconia powders and the as obtained powders have been characterized by means of X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). In case of precipitation method the presence of the tetragonal phase was observed at $400^\circ C$, while the monoclinic phase appears at temperatures higher than $400^\circ C$, becoming major crystalline phase starting with $700^\circ C$. In case of the powders prepared by thermal decomposition of carboxylate precursors, the tetragonal phase was formed at temperatures below $700^\circ C$, when the monoclinic phase begin to crystallize as secondary phase, in a higher proportion for the samples synthesized with 1,3-propanediol. All powders annealed at $1200^\circ C$ are pure monoclinic zirconia. SEM images have evidenced for the zirconia powders annealed at $1000^\circ C$ particles with diameters up to 150 nm, agglomerated in micrometer-sized aggregates, more individualized and homogenous than that obtained in the case of zirconia powder synthesized with poly(vinyl alcohol).

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1. Introduction

Zirconia is an important material because of its use in different fields of chemistry such as ceramics and catalysis. Nano-zirconia applications are based on its unique properties as high refractoriness, corrosion resistance, high fracture toughness and hardness, resistance to thermal shock, etc. [1]. Furthermore, nano-zirconia has interesting catalytic activity for reactions as dehydration or synthesis of alcohols [2].

Zirconia exhibits three different phases: monoclinic ($m-ZrO_2$), tetragonal ($t-ZrO_2$) and cubic ($c-ZrO_2$). The phase structure of zirconia is important for many materials and catalytic reactions;

for example, stabilized *tetragonal* zirconia is considered an important structure for ceramics because of its excellent mechanical properties such as fracture toughness, strength, and hardness. The tetragonal phase may exist as a metastable phase down to ambient temperatures. The transitions between these phases and the corresponding volume changes can represent a real problem [3]; thus, a phase transformation from tetragonal phase to the monoclinic phase of crystalline ZrO_2 prevents its applications over a broader temperature range [4].

Due to the difficulties in the synthesis of a specific nanostructured zirconia crystalline phase, previous literature has reported several synthesis methods for different doped and undoped zirconia phases (sol-gel [5], thermal decomposition of organic precursors [3,6,7], hydrothermal [8]), but the field is far from being exhausted. Practical synthesis methods are still under development in order to obtain pure zirconia crystalline phases with controlled particle size and desired properties [5].

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In order to establish the optimal conditions for obtaining of stabilized pure tetragonal zirconia phase we present a study on the preparation of nanostructured zirconia starting from $ZrOCl_2 \cdot 8H_2O$, by using three different precursors: zirconium hydroxide and respectively two zirconia carboxylates, the last two being obtained by the redox reaction of zirconium nitrate with 1,3-propane diol (PD) and respectively poly(vinyl alcohol) (PVA), respectively. The zirconia powders obtained by thermal treatment of these precursors were characterized by means of differential thermal analysis, thermogravimetric analysis, X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy.

2. Experimental

We have used analytical grade reagents (provided by Merck): $ZrOCl_2 \cdot 8H_2O$, 25% NH_3 solution, 1,3-propanediol and poly(vinyl alcohol).

2.1. Synthesis methods

2.1.1. Precipitation of $Zr(OH)_4$ followed by calcinations

The aqueous solution of $ZrOCl_2$ (0.2 M) was treated with aqueous solution of NH_3 prepared by diluting a 25% solution with distilled water in a 1:1 volume ratio. We used an excess of NH_3 solution of about 30% reported to the stoichiometry necessary for the precipitation of $Zr(OH)_4$. The white precipitate was washed several times with a very diluted NH_3 solution, until no Cl^- was detected through the reaction with $AgNO_3$, then filtered and washed with distilled water under vacuum. The obtained precipitate was dried at 90 °C to constant mass.

The obtained solid product, noted Zrpp was annealed in static air for 3 h at different temperatures (300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 900 °C, 1000 °C and 1200 °C).

2.1.2. Thermal decomposition of carboxylate type precursors, obtained by the redox reaction between zirconium nitrate and a poly-alcohol: 1,3-propane diol and respectively poly(vinyl alcohol)

In this case, we have obtained first an aqueous solution of zirconium nitrate by dissolving the precipitate of $Zr(OH)_4$ obtained according to method (1) with concentrated HNO_3 added drop wise, under stirring, to complete dissolution of the precipitate. To the obtained solution of zirconium nitrate, 1,3-propanediol, corresponding to a Zr: alcohol molar ratio of 1:2, was added. The as-obtained clear solution was magnetically stirred at 120 °C until the solution became almost a gel, then was transferred in an oven and heated at 150 °C, until the redox reaction between NO_3^- ions and the poly-alcohol took place (until no emission of nitrogen oxides was observed). The as obtained solid products, used as precursor for zirconia, were named ZrPD (in case of using 1,3-propane diol) and ZrPVA (in case of using poly(vinyl alcohol)). The precursors ZrPD and ZrPVA have been annealed in the same conditions and at the same temperatures as the first one (Zrpp).

The flowcharts for the synthesis of ZrO_2 by the two methods are presented in Figs. 1 and 2.

3. Characterization techniques

Thermal analysis was performed on a 1500D MOM Budapest Derivatograph. The heating was achieved in static air, up to 600 °C, with a heating rate of 5 °C min^{-1} , on Pt plates using $\alpha-Al_2O_3$ as the inert material. The synthesized powders were characterized by FT-IR spectrometry using a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range 400–4000 cm^{-1} . Phase analysis was achieved at ambient temperature with a Bruker D8 Advance

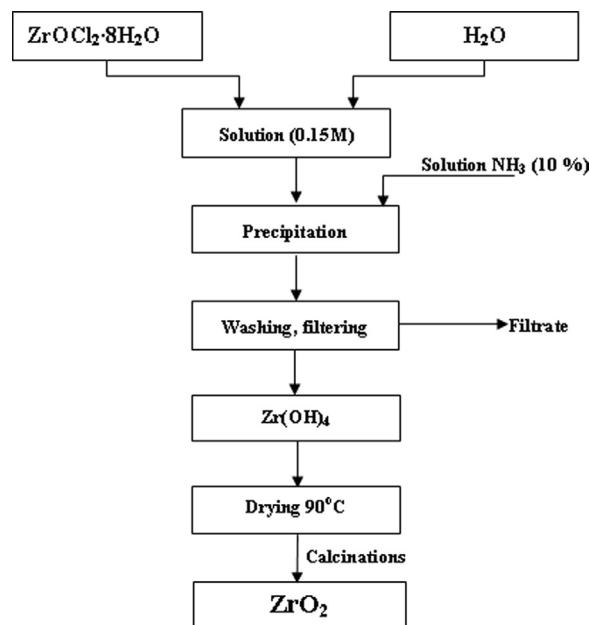


Fig. 1. Flowchart for the synthesis of ZrO_2 by precipitation method.

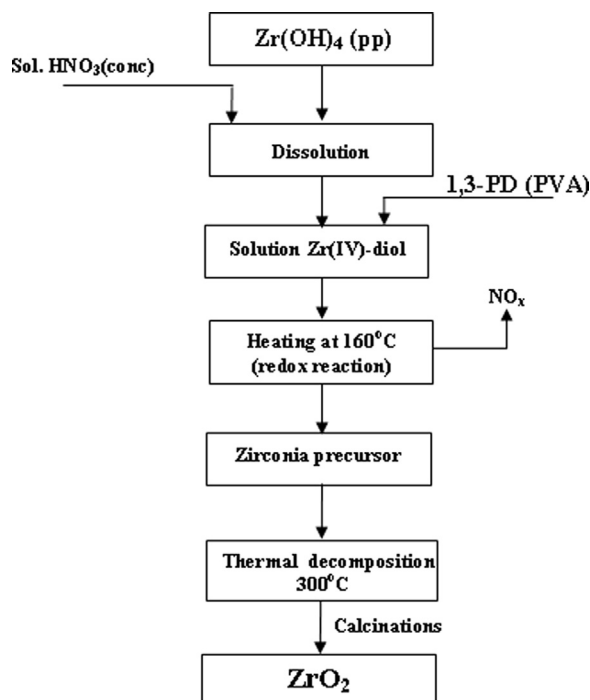


Fig. 2. Flowchart for the synthesis of ZrO_2 by thermal decomposition of carboxylate type precursors method.

diffractometer, using the MoK_α radiation (Zr filter) and respectively CuK_α radiation (Ni filter). SEM images have been recorded on a Quanta 3D FEG (FEI) microscope.

4. Results and discussions

Initially, we have characterized the precursor Zrpp obtained by chemical precipitation of $Zr(OH)_4$ from $ZrOCl_2$ solution with NH_3 , by thermal analysis and FT-IR spectroscopy. The Zrpp was used subsequently for the obtaining of two other precursors.

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