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Combustion synthesis and properties of nanocrystalline zirconium oxide

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ABSTRACT

Nanocrystalline tetragonal zirconia powders have been synthesized by aqueous combustion using glycine (Gly) as a fuel and zirconyl nitrate (ZN) as an oxidizer. The effect of the fuel-to-oxidant molar ratio on the structural and morphological properties of nanocrystalline zirconia powders was studied. Thermodynamic modeling of the combustion reaction showed that the increase in the Gly:ZN molar ratio leads to the increase in theoretical combustion temperature, heat of combustion and amount of produced gases. Powder properties were correlated with the nature of combustion and results of thermodynamic modelling. The increase in the Gly:ZN molar ratio produces more agglomerated powders characterized by a lower degree of uniformity, a lower specific surface area and a slightly bigger crystallite size. On the other hand, the presence of hard agglomerates suppresses the volume expansion, stabilizing tetragonal zirconia, as confirmed by Rietveld refinement. The absence of cubic zirconia was confirmed by FTIR and Raman Spectroscopy. The increase in the calcination temperature led to more agglomerated, compact and less uniform powders. The nanocrystalline nature of zirconia is the reason for the formation of bigger crystallites, the increase in the relative amount of monoclinic phase and sample sintering after calcination at high temperature. The highest measured specific surface area of zirconia was 45.8 $m^2 \cdot g^{-1}$, obtained using a fuel-lean precursor.

1. Introduction

Nanocrystalline zirconium oxide (zirconia, ZrO_2) is one of the most important ceramic materials, shock- and corrosion-resistant, with wide variety of potential applications such as a structural and biomaterial, solid-state electrolyte, gas sensor and thermal barrier coating [1]. It also attracts a great attention as a catalyst or as a support

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for many reactions [2,3]. Moreover, the application of the nanosized metastable tetragonal zirconia particles, as a dispersed phase in ceramic materials, leads to the increase in their fracture toughness, strength and hardness [4]. Those unique properties of ZrO_2 have become a driving force for the development of alternative techniques for its preparation, among them the aqueous combustion synthesis [5]. It is a versatile, simple, safe, energy- and time-saving process, with capability to produce homogeneous, high purity and nanocrystalline ceramic powders [6]. The aqueous combustion synthesis involves the formation of a homogeneous oxidant-fuel precursor and its redox exothermic reaction, accompanied with a quick evolution of large volume of the gaseous products. The nature of the combustion and the properties of the resulting powder depend on the type and the amount of the fuel used in the process. According to Toniolo et al. [7], a good fuel should react non-violently, produce non-toxic gases and act as complexing agent to form metal cations. Glycine, one of the cheapest amino acids, is known to act as a complexing agent due to its carboxylic acid group at one end and amino group at the other. Such types of zwitterionic character of a glycine molecule can effectively complex metal ions of different ionic size, which helps in preventing their selective precipitation to maintain compositional homogeneity among the constituents. On the other hand, it can also serve as a fuel in the combustion reaction, being oxidized by nitrate ions [8]. Therefore, glycine was chosen as a fuel for the preparation of nanocrystalline zirconia powders in this study.

Several papers have already discussed the role of the fuel in controlling the morphology of the synthesized powders [7–11]. A zirconia nanosized single crystal has already been prepared by the combustion of an aqueous solution of metal nitrate and glycine [12]. Zirconia nanocrystalline powders were also synthesized using sucrose [13], glycine [9] and citric acid [14] as a fuel. However, in the most of these researches, the amount of the fuel and/or complexing agent has been fixed according to the concept of propellant chemistry [15]. Scarce systematic studies on the effect of the fuel-to-oxidant molar ratio on the nature of combustion and properties of zirconia nanocrystalline powders have been reported. As far as we know, the effect of calcination temperature on zirconia's properties [16,17], obtained by combustion method, has not also been presented. Moreover, in view of beneficial properties of metastable tetragonal zirconia particles, in the area of ceramic materials, we consider important to review its formation by different techniques: XRD, FTIR and Raman Spectroscopy. This is due to the fact that it is very difficult to distinguish between tetragonal and cubic phases of zirconia by a qualitative XRD analysis, as a result of both (400) and (004) lines splitting and (112) line broadening, as made by the most of researches.

Here, the combustion synthesis of nanocrystalline zirconia powders using glycine as a fuel and zirconyl nitrate as an oxidizer is reported. The study is focused on the effect of:

- the fuel-to-oxidant molar ratio on the properties (such as: specific surface area, crystalline structure, crystallite size, extent and nature of agglomerates) of nanocrystalline zirconia powders;
- sample morphology on tetragonal zirconia stabilization;
- calcination temperature on the microstructural evolution of zirconia powders.

For these purposes, the synthesized powders have been characterized by: TGA, specific surface area measurements, SEM-EDS, XRD, FTIR and Raman Spectroscopy. The thermodynamic modeling of the combustion reaction was carried out in order to study the role of the fuel-to-oxidant molar ratio on the heat of combustion, theoretical combustion temperature, number of moles of gases evolved in the reaction and the nature of combustion process. The results of thermodynamic modeling were correlated with powders properties.

2. Experimental

2.1. Synthesis

Zirconyl nitrate hydrate [$ZrO(NO_3)_2{\cdot}xH_2O$, Aldrich, purity 99%, ZN] and glycine [NH_2CH_2COOH, Mallinckrodt, purity 99.5%, Gly] were used as the starting materials. The different compositions of the redox mixtures (Gly:ZN) for the combustion were calculated using the total reducing (+9) and oxidizing (−10) valences of the starting materials: Gly and ZN, respectively. According to the principle of propellant chemistry [15], for stoichiometric redox reaction, the ratio of the net reducing valency of the fuel net to the oxidizing valency of the metal nitrate should be unity (maximum quantity of energy released in the combustion process). Therefore, the Gly:ZN molar ratio for the stoichiometric combustion should be 1.11. Moreover, fuel-lean (0.5 and 0.75) and fuel-rich (2) Gly:ZN precursors were applied for sample preparation. The studied range of the Gly:ZN molar ratio was chosen experimentally to guarantee the auto-ignition of the combustion process, considering that it takes place only in a limited range of the fuel-to-oxidant molar ratio (above and below the stoichiometric one). The amounts of fuel as well as of oxidant were taken to obtain approximately 3 g of the final product. The required amounts of starting materials were dissolved in the minimum amount of deionized water and mixed to obtain transparent aqueous solution of oxidant-fuel precursor. After its thermal dehydration at ca. 80 °C, as soon as a viscous liquid was formed, the temperature was increased up to ca. 250 °C. It led to the auto-ignited, fast, self-sustaining, flameless and non-explosive combustion of the liquid, accompanied with a rapid evolution of large amount of gases and formation of an amorphous powder (as confirmed by XRD, not shown here), indicating the incomplete combustion. The nature of the ignition and the aspect of the obtained powders depended on the fuel-to-oxidant molar ratio. Henceforth, these samples are indicated as raw powders. Subsequently, they were calcined in air, at 600 °C, with a ramp rate 3 °C·min^{-1}, for 4 hours at atmospheric conditions, in order to remove traces of unreacted starting materials (if any) and/or products of their decomposition and obtain pure and well-crystallized