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Nanocrystalline thoria powders via glycine-nitrate combustion

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Abstract

Nanocrystalline thoria powders were prepared by the combustion technique using glycine as a fuel and nitrate as an oxidizer. The technique involves the exothermic decomposition of viscous liquid prepared by thermal dehydration of the aqueous solution containing thorium nitrate and glycine. Thoria powders of different crystallite sizes, surface areas and sinterabilities were prepared by starting with two different fuel-to-oxidant molar ratios. The exothermic decomposition of viscous liquid, at about 200°C, containing thorium nitrate-to-glycine in molar ratio 1:1.2 yielded the well-crystalline nano-sized ThO_2 powder. Thoria powders prepared by this technique were shown to have a higher surface area (> 50 m^2/g) and could be sintered to highly dense pellets ($\geqslant 93\%$ th.d.) at relatively low sintering temperature of 1300°C for 3 h. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium and its compounds are used in catalysis, nuclear industry and as solid electrolytes (e.g., yttria doped thoria) [1–3]. The thoria pellets with high bulk-density are used as a blanket material in nuclear reactors. Thoria powders prepared by conventional routes [4] require sintering temperatures higher than 1600°C to get dense pellets. Chandramouli et al. [5] used the polyvinyl alcohol aided microwave synthesis and also combustion synthesis [6] using citric acid and urea as fuels for producing nanocrystalline thoria powders. Vaidya et al. [7] had prepared thoria microspheres using the sol–gel process.

The combustion technique has been successfully used for preparation of the ultra-fine powders of a variety of oxide ceramics at a relatively low calcination temperature [8–10]. The technique involves the exothermic decomposition of a fuel (e.g., citric acid, urea, etc.) and an oxidizer (e.g., nitrates). The powders obtained by this synthesis route generally have a higher surface area and better sinterability [11,12]. The combustion technique is of significant interest due to its overall ease and less energy-intensive steps. The combustion synthesis is advantageous over the solid state synthesis in terms of better compositional homogeneity and purity of the final product. The exothermicity, initiated by an external temperature for a particular range of fuel-to-oxidant ratio, sometime appears in the form of a flame, the temperature of which can be in excess of 1000°C [13]. The large volume of gases generated during such type of auto-ignition processes rapidly cools the product leading to nucleation of crystallites without any substantial growth. The gas evolution disintegrates large particles or agglomerates during the process and hence, the resultant product consists of very fine particulates of friable agglomerates. However, only a few efforts have been made to correlate the effect of the fuel-to-oxidant ratio with powder characteristics. Recently, Roy et al. [18] correlated the effect of the citrate-to-nitrate ratio with powder characteristics of Y_2O_3. Any kind of selective precipitation or phase separation during the evaporation of excess solvent in the combustion synthesis is a major failure in achieving the required phase and compositional homogeneity [14]. The nature and amount of the fuel, and the pH of the starting solution are important parameters in preventing the selective precipitation or phase separation.

In this paper, we report the combustion synthesis of nanocrystalline thoria powders using glycine, for the

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first time in case of thoria, as a fuel and nitrate as an oxidizer. The effect of the fuel-to-oxidant molar ratio on the powder characteristics like crystallite size, surface area and sinterability are described.

2. Experimental

Nuclear grade thorium nitrate $Th(NO_3)_4 \cdot 5H_2O$, obtained from M/s. Indian Rare Earth, Mumbai, India, and A.R. grade glycine were used. Glycine and thorium nitrate were mixed, in a required molar ratio, in minimum amount of deionized water to get a clear solution. The thermal dehydration of these solutions on a hot plate at (80 ± 5)°C resulted in viscous liquids. As soon as these viscous liquids were formed, the temperature of the hot plate was raised to about 200°C. The viscous liquid swelled and auto-ignited with the evolution of a large volume of gases in different fashion, depending on the fuel-to-oxidant ratio. Two particular starting fuel-to-oxidant ratios were selected in the present work. In case, where the amount of fuel was adjusted according to the principle of propellant chemistry (i.e., thorium nitrate-to-glycine molar ratio = 1:2.22) a greyish powder was obtained with a considerable carbonaceous residue. The fuel-deficient ratio having a thorium nitrate-to-glycine molar ratio as 1:1.2, upon auto-ignition resulted in a white voluminous product identified by XRD as well-crystalline thoria. Each product obtained by auto-ignition was calcined at 500°C for 4 h before sintering. Simultaneous TG/DTA of each precursor was carried out in flowing air up to 600°C at a heating rate of 10°C/min using a SETARAM simultaneous TG/DTA instrument, model 92-16.18 to study the decomposition behavior and nature of the combustion reaction. The XRD patterns were recorded using Cu-Kα radiation on a Philips X-ray diffractometer, model PW 1927 to know the phase formation and for estimation of the crystallite size. Silicon was used as a standard material for correction due to instrumental broadening. The specific surface area of the powder was measured by a conventional BET technique with N_2 adsorption using a Sorptomatic 1990 CE instrument. The carbon analysis of the uncalcined product obtained by auto-ignition of fuel-deficient ratio was carried out using a carbon analyzer, model EA 1110 CE. ThO_2 powders were cold pressed into cylindrical pellets of 10 mm diameter and about 6 mm height using an uniaxial hydrolic press at a compaction pressure of 187 MPa and sintered in static air at 1300°C for 3 h. Steric acid was used as a lubricant. The sintered densities were determined by the Archimedes principle.

3. Results and discussion

One of the cheapest amino acids, glycine (NH_2CH_2COOH) is known [13] to act as a complexing agent for a number of metal ions as it has a carboxylic acid group at one end and an amino group at the other end. Such type of zwiterionic character of glycine molecule can effectively complex metal ions of varying ionic sizes which help in preventing their selective precipitation to maintain the compositional homogeneity among the constituents. On the other hand, glycine can also serve as a fuel in combustion reactions, being oxidized by nitrate ions. According to Chick et al. [13] glycine-nitrate combustion produces N_2, H_2O and CO_2 as the gaseous products. As per the principle of propellant chemistry [15,16], to generate maximum heat (or flame temperature) during the combustion, the net oxidizing valency of metal nitrates to net reducing valency of fuel should be unity. The net oxidizing and reducing valency of thorium nitrate and glycine are: −20 and +9, respectively. Thus for the complete combustion of 1 mole of thorium nitrate, 2.22 moles of glycine are required as shown in the following stoichiometric redox reaction:

$$\begin{aligned}&Th(NO_3)_4 + 20/9(NH_2CH_2COOH)\\&\quad \rightarrow ThO_2 + 40/9CO_2 + 28/9N_2 + 50/9H_2O\end{aligned}$$

However, the auto-ignition of viscous liquid with a fuel-to-oxidant ratio adjusted according to the concept of propellant chemistry resulted in a greyish powder containing considerable amounts of a carbonaceous residue which indicates the incomplete combustion probably due to less time existing for auto-ignition. Hence, this greyish powder needs calcination at a higher temperature to be converted into pure thoria powder. The auto-ignition exists for a particular range of the fuel-to-oxidant ratio above and below the ratio determined by the concept of propellant chemistry i.e., thorium nitrate-to-glycine molar ratio 1:2.22 (or glycine-to-nitrate ratio 0.555) in present case. It was experimentally observed that below the thorium nitrate-to-glycine molar ratio ≈1:1.2 (or glycine-to-nitrate ratio ≈0.3) auto-ignition ceases to occur. The auto-ignition of this fuel-deficient precursor at about 200°C resulted in well-crystalline thoria powders as characterized by XRD. This product was found to contain a contamination of (0.3–0.4%) carbon. A similar kind of behavior was also observed by Roy et al. [18] in the synthesis of nanostructured yttria powders. In addition, the auto-ignition of a fuel-deficient ratio is safer as it is less violent due to the relatively smaller enthalpy of combustion associated. The calcined powders obtained by using the concept of propellant chemistry and fuel-deficient ratio will be hereafter denoted as PC and FD products, respectively.

The simultaneous TG/DTA of dried precursors are shown in Fig. 1. The exothermic behavior of auto-ignition can be clearly seen at about 200°C. The maximum weight loss occurs in a very narrow temperature range in both the cases which corresponds to the auto-ignition step. The expected weight losses corresponding to the

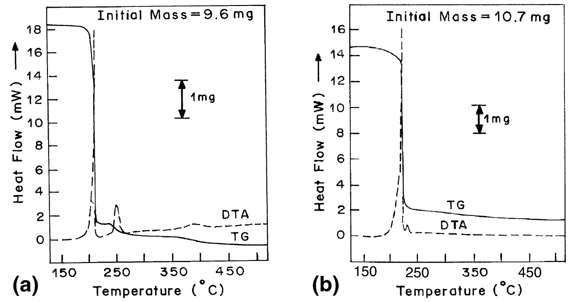

Fig. 1. Simultaneous TG-DTA curves of precursor of (a) the PC product and (b) the FD product.

complete conversion of the precursor to ThO_2 in case of PC and FD precursors are 59.2% and 53.7%, respectively. The observed weight losses during auto-ignition in case of PC and FD precursors were 56.4% and 53.3%, respectively. The difference in expected and observed weight losses explains well, why a greyish product with a considerable carbon contamination was obtained from the PC precursor. However, the observed and expected weight losses almost matched in case of FD precursor, which gave rise to the formation of ThO_2 without any calcination with a negligible carbon contamination of about (0.3–0.4%). In case, where the fuel was adjusted according to the concept of propellant chemistry, a multi-step decomposition of precursor was observed which is likely to produce unwanted intermediates whereas the decomposition of the precursor with a fuel-deficient composition is very near to the single step as described by Gallagher et al. [17] and Roy et al. [18]. Hence, the single-phase thoria with (0.3–0.4%) carbon contamination could be obtained after an auto-ignition. The XRD pattern of the uncalcined FD product is shown in Fig. 2. This observation shows that the nitrate-rich ratio facilitates the decomposition of the precursor to the final product.

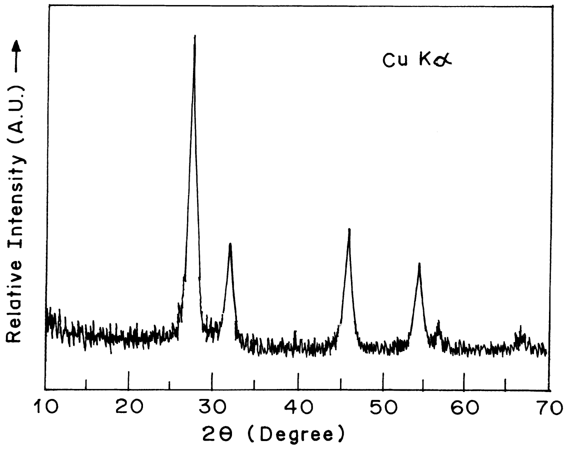

Fig. 2. XRD pattern of the uncalcined FD product.

The XRD patterns of the calcined PC and FD products were found to be due to single-phase well-crystalline thoria. The crystallite sizes, calculated by a X-ray line broadening using the Scherrer formula, for the PC and FD products were found to be about 23 and 15 nm, respectively. The crystallite size of the PC product is larger than that of the FD product probably due to higher crystal growth assisted by a high enthalpy or flame temperature of the combustion reaction in this case. The specific surface areas of the PC and FD products were found to be about 53 and 90 m^2/g, respectively. These surface areas are highest among those reported earlier in the literature [5,6] for ThO_2. In general the glycine-nitrate combustion produces powder with high surface area as compared to the citrate-nitrate combustion process [13]. The substantial reduction of the surface area in case of the PC product as compared to the FD product is due to the very high flame temperature generated in this case which might have facilitated hard agglomeration among active primary crystallites produced in the process. In addition to low exothermicity associated with the auto-ignition of the FD precursor, another crucial factor is the fast cooling due to a near single-step evolution of the gases during auto-ignition. It helps in preventing the formation of a dense structure and results in a higher surface area. The pore volume of the PC and FD products were estimated to be about 0.04 and 0.02 cm^3/g, respectively. It implies that the FD product has a more porous structure as compared to the PC product.

The sintered density for the PC and FD product at 1300°C for 3 h was found to be about 93% and 97% of their theoretical density (th.d.) (i.e., 10 g/cm^3). The higher sintered density in case of the FD product as compared to the PC product is due to the lower possibility of the formation of hard agglomerates in case of the FD product, which results in better packing at the green stage of the pellet. The higher surface area of the FD product further facilitates sintering at a relatively lower temperature.

4. Conclusions

A chemical process has been developed with an overall simplicity for producing nanocrystalline thoria powder at a relatively lower calcination temperature. The process is shown to have a considerable potential for producing thoria powders with high surface area which subsequently can be sintered at relatively lower temperature and in shorter time. It has been observed that the fuel-to-oxidant ratio bears a great influence on the powder characteristics. The fuel-deficient ratio yielded a product with desired powder characteristics.

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