Available online at www.sciencedirect.com

ScienceDirect

Materials Research Bulletin 41 (2006) 1638–1645

Materials Research Bulletin

www.elsevier.com/locate/matresbu

Effect of acidity on the glycine–nitrate combustion synthesis of nanocrystalline alumina powder

Tianyou Peng [a,b,*], Xun Liu [a], Ke Dai [a], Jiangrong Xiao [a], Haibo Song [a]

[a] *Department of Chemistry, Wuhan University, Wuhan 430072, PR China*
[b] *Centre of Nanoscience and Nanotechnology, Wuhan University, Wuhan 430072, PR China*

Received 23 June 2005; received in revised form 6 February 2006; accepted 20 February 2006
Available online 15 March 2006

Abstract

Nanocrystalline alumina powders were prepared by combustion synthesis using glycine as fuel and nitrate as an oxidizer. The effect of the pH values in the precursor solutions on crystallite sizes, surface areas and morphologies of the synthesized alumina powder has been investigated by X-ray diffractometry, thermal analysis, nitrogen adsorption–desorption, and transmission electron microscopy. With decreasing the pH values in the precursor solutions, the obtained materials could be modified from segregated nanoparticles (pH 10.5) to aggregates of nanoparticles (pH 6.0), and finally to a flaky morphology (pH 2.5). The rates of decomposition, the interaction of coordination as well as the hydrogen bonding of the glycine and the Al-hydroxides species at different pH values were found to be responsible for the generation of flake and/or segregated nanoparticles during auto-ignition reactions. The as-prepared combustion ashes were converted into pure nanocrystalline alumina after calcination at elevated temperatures. The specific surface areas of the products calcined at 800 °C ranged from 96 to 39 m^2/g with the pH decreased from 10.5 to 2.5.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: A. Ceramics; A. Nanostructures; A. Oxides; B. Chemical synthesis

1. Introduction

In recent years, there has been an increasing interest in the synthesis of nanocrystalline metal oxides due to important applications in advanced ceramics and as reinforcement in polymer and brittle matrix composites [1–7]. Nanocrystalline α-alumina (Al_2O_3) has considerable potential for various applications including high strength materials, electronic ceramics and catalysis etc. In particular, high quality nanocrystals of α-Al_2O_3 are used as electronic substrates and in fine precision equipment [2–9]. α-Al_2O_3 powders prepared by conventional methods require high temperatures 1300–1600 °C for solid-state thermally driven decomposition of the hydrates of alumina. The extent of conversion to the α-Al_2O_3 phase depends on the temperature and the time of calcinations [9]. Generally, the following series of phase transformation may occur before conversion to α-Al_2O_3: hydrous alumina → boehmite → γ → δ → θ → α. The average crystallite size increases to larger than 100 nm for α-Al_2O_3 at the high temperature required for almost all *these* salt-derived aluminium hydroxides or hydrated *aluminas* to form α-Al_2O_3 [6,9–11].

---

* Corresponding author. Tel.: +86 27 87218474; fax: +86 27 68754067.
E-mail address: typeng@whu.edu.cn (T. Peng).

0025-5408/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2006.02.026

Also, co-precipitation [10,11], sol–gel [12,13] and combustion synthesis [3–5] methods have been developed for the preparation of nanocrystalline Al_2O_3 powers, but the processing routes of co-precipitation and sol–gel methods are complicated and the duration times are long [14]. The combustion process to prepare the precursor powders of high-tech ceramic materials, particularly the nanocrystalline ceramics, however, is of significant interest due to its overall ease and less energy-intensive steps [3–5,15–21]. Moreover, the solution-based combustion synthesis is advantageous over the solid-state synthesis in terms of better compositional homogeneity and purity of the final product. Therefore, a series of such solution-based combustion decomposition techniques are developed to yield single-phase products of various multi-component ceramics at relatively low temperatures [15,19–22]. This technique involves the exothermic chemical reaction of a fuel (e.g. citric acid, urea, glycine or glycol, etc.) and an oxidizer (e.g. nitrates) [3–5,15–19]. The exothermicity sometime appears in the form of a flame, which temperature can be in excess of 1500 °C [15]. The large amount of gases generated during combustion synthesis rapidly cools the product leading to nucleation of crystallites without any substantial growth. The gas generated also can disintegrate the large particles or agglomerates; therefore, the resulted product consists of very fine particles of friable agglomerates or nanoparticles [15–18]. The nature and amount of the fuel, and the pH of the starting solution are important factors in preventing selective precipitation and/or phase separation during the evaporation of solvents, which may result in phase and compositional inhomogeneities [16,19–22]. For example, Pathak et al. [3] found that pH values in precursor solutions have important effect on the morphologies of nanocrystalline alumina powder produced by citrate–nitrate combustion synthesis.

The zwitterionic character of glycine can effectively complex various metal ions which help in preventing their selective precipitation and therefore in maintaining the compositional homogeneity among the constituents. Namely, metal nitrates with glycine as complexing agent are highly promising in producing various amorphous and nanocrystalline ceramic powders [15–22]. The solution-based combustion technique using glycine has been studied widely, such as the effect of the fuel-to-oxidant ratio on the powder characteristics [16]. However, only a few efforts have been made to investigate the effects of the pH on the glycine–nitrate combustion route to alumina. In this paper, solution-based combustion synthesis is applied to prepare the Al_2O_3 powders from precursor solution of $Al(NO_3)_3 \cdot 9H_2O$ and glycine, in which nanocrystalline α-Al_2O_3 powders are obtained by heating the resultant combustion ash at 1200 °C. The effect of pH values in the precursor solutions on the powder characteristics such as crystallite sizes, surface areas and morphologies are described.

2. Experimental procedure

All starting materials in the present experiment were of the analytical purity. In a cylindrical quartz container (80 mm diameter × 200 mm height), solution of aluminium nitrate ($Al(NO_3)_3$) were prepared and calculated stoichiometric amount of glycine (NH_2CH_2COOH) was added. Subsequently, ammonia was added to neutralise the pH of the solution at 6.0 and the final pH of the solution was adjusted to 2.5, 6.0 and 10.5 by adding either dilute HNO_3 or liquid ammonia as required. The precursor solution containing aluminium nitrates and glycine was thermal dehydration on a hit plate (80 ± 5 °C), which resulted in viscous liquid. And then the viscous precursor was heated rapidly in a pre-heated furnace maintained at 500 °C. Depending on the pH values, the material undergoes foaming followed by decomposition generating large volume of gases, then spontaneous ignition occurred and underwent smouldering combustion with enormous swelling, producing a grayish, foamy, voluminous mass in different fashion. The whole process was complete in less than 2 min. The voluminous and foamy combustion ashes are easily crushed to the precursor powders. The crushed precursor powders after calcinations at 800 and 1200 °C for 2 h transformed to pure γ- and α-Al_2O_3 powders, respectively.

The particle morphologies of products were observed on a JEM-100X/II transmission electron microscope (TEM). Phase formation and estimation of the crystallite size of samples were carried out by means of an XRD-6000 diffractometer using Cu K_α radiation ($\lambda = 1.5406$ Å). The dried precursors were collected prior to decomposition for all the pHs and the TG-DTA analyses were conducted in flowing air up to 600 °C at a heating rate of 10 °C/min using a Netzsch STA449 simultaneous thermal analyzer (TG-DTA) to study the decomposition behavior and nature of the combustion reaction. The specific surface areas of the powders calcined at 900 °C were measured by liquid nitrogen adsorption–desorption isotherms at 77 K on a Micrometrics ASAP 2010 system after samples were degassed at 120 °C.

Download English Version:

https://daneshyari.com/en/article/1492307

Download Persian Version:

https://daneshyari.com/article/1492307

Daneshyari.com