Ceramics International 33 (2007) 361–363

CERAMICS
INTERNATIONAL

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Alumina precursors produced by gel combustion

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Received 21 June 2005; received in revised form 9 September 2005; accepted 2 October 2005
Available online 18 January 2006

Abstract

Alumina precursor produced by a gel combustion method using aluminum nitrate and citric acid as raw materials was investigated. Thermodynamic calculation of the combustion reaction shows that as the citrate-to-nitrate ratio γ increases, the enthalpy of reaction and adiabatic flame temperatures also increase. The DSC analysis indicates that the combustion temperature of the gel decreases, as the citrate content in the gel increases in the fuel-lean condition. In the stoichiometric and fuel-rich conditions, combustion temperature remains ~160 °C with increase of γ.

Keywords: Alumina precursor; Gel combustion; Thermodynamic calculation

1. Introduction

Ultrafine α-Al_2O_3 is an important ceramic powder with a limited range of atomic nonstoichiometry, low concentrations of ionic defects and electronic carriers, high melting point, high temperature stability, high chemical inactivity, high hardness, and large band gap energy [1,2]. It is widely used for structural, microelectronic and membrane applications. Various chemical methods such as spry pyrolysis, vapor phase reaction, precipitation, sol–gel, hydrothermal and combustion synthesis have been employed to synthesize ultrafine α-Al_2O_3 powders.

Combustion synthesis is particularly a simple, safe and rapid production process wherein the main advantages are energy and time savings. This quick, straightforward process can be used to synthesize homogeneous, high-purity, crystalline oxide ceramic powders including ultrafine alumina powders with a broad range of particle sizes. Ultrafine α-Al_2O_3 synthesized by combustion method was investigated using different chemicals such as urea [3], glycine [4] and citric acid [5] as fuel. The combustion process using citric acid, which is widely known as amorphous citrate process, is a much less severe exothermic reaction. Recently, we have reported the preparation of ultrafine α-Al_2O_3 by the gel combustion method at lower temperature using aluminum nitrate and citric acid as raw materials [6]. The decomposition of the citrate precursor, the transition and the morphology of alumina powder were investigated in our previous work. In this paper, alumina precursors were produced by a gel combustion method using aluminum nitrate and citric acid as raw materials. The thermodynamic calculation of the combustion reaction is also discussed.

2. Experimental

Analytical grade aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$) was dissolved in deionized water and the solution was stirred at 60 °C for 30 min. In the solution, citric acid ($C_6H_8O_7\cdot H_2O$) was added and the citrate-to-nitrate ratio γ ($\gamma = M_{citrate}/M_{nitrate}$, M = molar amount of the compound) was varied from 0.033 to 0.667 (Table 1). The reason for selecting such a range of γ is based on the concept of propellant [7]. It can be calculated [8] that 0.833 mol of citric acid is required for each mole of nitrate in order to have a stoichiometric redox reaction in the gel that gives $\gamma = 0.277$ (named GS, Table 1). Deficient citric acid in the gel ($\gamma < 0.277$) presents a fuel-lean condition while higher concentrations produce a fuel-rich condition. Such conditions are expected to synthesize nanosized α-Al_2O_3 powders with different properties, as γ alters the extent of redox reaction in the combustion process. In this paper, the word "gel" is used for the product of gelling the aqueous of nitrate and citric acid by evaporation water at

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0272-8842/$32.00
doi:10.1016/j.ceramint.2005.10.004

Table 1
Chemical composition of the gels and some of their properties

Gel	Nitrate	Citrate acid	γ	Gel as observed	Decomposed ash
G1	1	0.1	0.033	White	A1 (roast, white)
G2	1	0.3	0.1	White	A2 (fine crumb, yellowish white)
G3	1	0.5	0.167	Yellowish white	A3 (crumb, yellowish white)
GS	1	0.833	0.278	Yellowish white	AS (crumb, yellowish)
G4	1	1.0	0.333	Yellowish	A4 (popcorn, yellowish)
G5	1	1.5	0.5	Yellowish	A5 (popcorn, light brown)
G6	1	2.0	0.667	Yellowish	A6 (popcorn, brown)

~80 °C. The "ash" is the combusted product of the gel, whereas "powder" refers to the calcined product of the ash. Gel, ash and powder are named G#, A# and P#, respectively.

The mixed citrate–nitrate aqueous solution was continuously stirred and concentrated by evaporation at ~80 °C, producing a transparent gel. A portion of this gel was collected for characterization. Some of the gel was rapidly heated to 200 °C and then combusted in different fashion depending on γ and yielded a fluffy product along with the evolution of a brown fume.

Thermal analysis was recorded on a Netzsch STA 449C instrument. Measurements were taken under a continuous flow of air (20 mL min^{-1}). Samples were heated at 10 °C min^{-1} to 1200 °C and then cooled to ambient in nature.

3. Results and discussion

The color of the as-synthesized powder was found to change with the citrate-to-nitrate ratio γ used in this method. This is attributed to the carbonaceous residue which remains from citric acid due to insufficient oxidizer quantity. The mechanism of the combustion reaction is quite complex and fuel-to-oxidizer ratio γ is one of the most important parameters that influences the reaction. The combustion of citrate–nitrate mixture appears to undergo a self-propagating and non-explosive exothermic reaction. According to Pederson's reaction model [9] the combustion reactions with different citrate-to-nitrate ratios can be represented as follows:

$$1.0\text{Al(NO}_3)_3\cdot 9\text{H}_2\text{O} + x\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} \rightarrow 0.5\text{Al}_2\text{O}_3 + 1.5\text{N}_2 + (9 + 5x)\text{H}_2\text{O} + 6x\text{CO}_2 + (3.75 - 4.5x)\,\text{O}_2$$

Actually, the combustion reaction does not strictly occur in this way especially in the fuel-lean conditions ($\gamma < 0.5$) and it is just a thermodynamic model. The citrate–nitrate precursor, after thermal dehydration, causes nitrate decomposition giving oxides of nitrogen (NO_x). The gaseous NO_x reacts with citrate generating heat and more gases. Thermodynamic calculations were carried out mainly in the condition of $\gamma \geq 0.5$. It is well know that the enthalpy of combustion can be expressed as:

$$\Delta H = \left(\sum n\Delta H_\text{p}\right) - \left(\sum n\Delta H_\text{r}\right)$$

Table 2
Thermodynamic data of reactants and products

Material	ΔH_f (kcal mol^{-1})	C_p (cal mol^{-1} K^{-1})[a] [4]
$\text{Al(NO}_3)_3\cdot 9\text{H}_2\text{O}$ (c)	−857.59	–
$\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ (c)	−369.0	–
Al_2O_3 (c)	−400.4	28.062 + 0.01038T
O_2 (g)	0	5.92 + 0.00367T
N_2 (g)	0	6.50 + 0.0010T
CO_2 (g)	−94.05	10.34 + 0.00274T
H_2O (g)	−57.796	7.20 + 0.0036T

[a] Calculated from the discrete values.

and

$$Q = -\Delta H = \int_{T_0}^{T_\text{f}} \left(\sum nC_\text{p}\right) \mathrm{d}T$$

So the following equation can be used to approximate the adiabatic flame temperature for a combustion reaction:

$$T_\text{f} = T_0 + \frac{\Delta H_\text{r} - \Delta H_\text{p}}{C_\text{p}}$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively, C_p is the heat capacity of products at constant pressure and T_0 in this equation is 298 K.

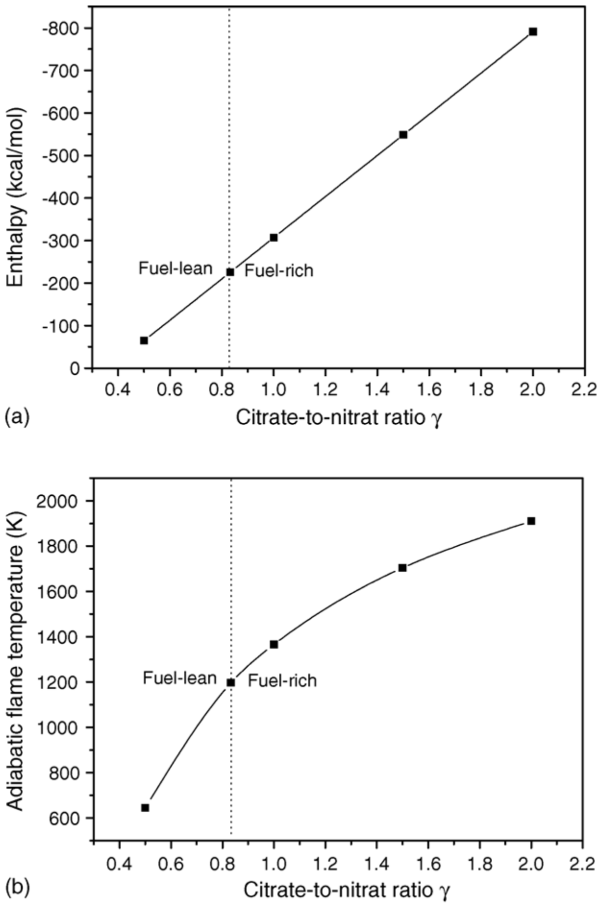

Fig. 1. Variation of (a) enthalpy and (b) adiabatic flame temperature as a function of citrate-to-nitrate ratio.

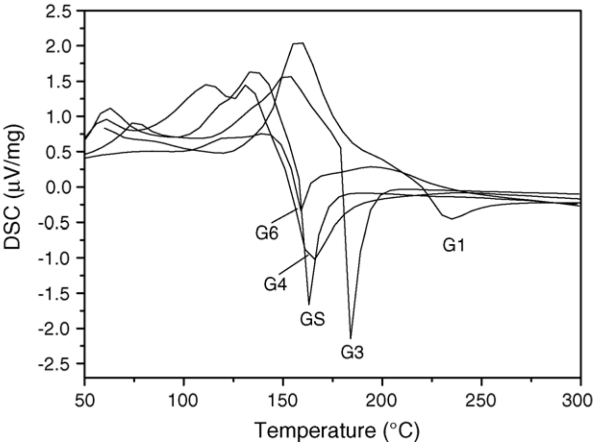

Fig. 2. DSC curves of gels (a) G1; (b) G3; (c) GS; (d) G4 and (e) G6.

Using the thermodynamic data for various reactants and products listed in Table 2, the enthalpy of combustion and theoretical adiabatic flame temperature could be calculated. The relation of enthalpy and adiabatic flame temperature as a function of citrate-to-nitrate molar ratio could be shown in Fig. 1(a) and (b). It can be seen that the enthalpy and the adiabatic flame temperature increase substantially with the amount of citric acid used during combustion. However, measured temperatures are much lower than the calculated values of flame temperature due to heat loss or incomplete combustion.

For further studying the thermal behavior of gels with different citrate-to-nitrate ratios, DSC analyses were carried out. Fig. 2 shows that in the temperature below 160 °C, endothermic peaks are attributed to the vaporization of physically bound absorbed water and the dehydration reaction of gels. It is important to note that these gels, irrespective of their citrate–nitrate ratios, always show exothermal decomposition in their corresponding DSC curves. It has been understood [10,11] that such an exothermic reaction is a result of a thermally induced redox reaction between the two anions present in the gel, where citrate acts as a reductant and nitrate as an oxidant. The initial combustion temperature of the gel decreases, as the citrate content in the gel increases in the fuel-lean condition. In the stoichiometric and fuel-rich conditions, the combustion temperature remains ~160 °C with increase of γ.

4. Conclusions

Citrate–nitrate gel combustion method has an outstanding potential to synthesize pure alumina powders. The citrate-to-nitrate ratio γ of the gel plays an important role in controlling the thermal behavior of the synthesized gel, the morphology and sintering activity of the gained alumina powders. Thermodynamic calculation of the combustion reaction shows that as γ increases, the enthalpy of reaction and adiabatic flame temperatures also increase. The thermal analysis indicates that the combustion temperature of the gel decreases, as the citrate content in the gel increases in the fuel-lean condition, and keep unchanged in the stoichiometric and fuel-rich conditions.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Key Program) (Grant no. 50220160657), the Major State Basic Research Development Program of China (Grant no. G2000067204-2) and the Key Project of Science and Technology of Shanghai (Grant no. 04DZ14002).

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