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Influence of citrate-to-nitrate ratio on the thermal behavior and chemical environment of alumina gel

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Abstract

Thermal behavior and chemical environment of the product obtained by gelling an aqueous solution of nitrate and citric acid with different ratio (citrate-to-nitrate ratio γ) were investigated. The TG–DSC analysis indicates that a higher amount of nitrate in the gel (G1, $\gamma = 0.1$) should be effective in the redox system in completing the combustion of citrates and that decomposition occurs in a single step. When a higher amount of citric acid ($0.33 > \gamma > 0.1$) is used, decomposition occurs in two steps through an unstable intermediate. When an even higher amount of citric acid ($\gamma > 0.33$) is used, decomposition occurs in three steps. Phase transformation temperature increases with the increase of γ in the fuel-lean condition and decreases with the increase of γ in the fuel-rich condition. An attempt was made to understand the status of anions in the chemical environments of the gels by infrared spectroscopy, the gels differing in their thermal behavior. Differences in FTIR spectra of ashes are mainly caused by the thermal reactivity.

Keywords: Thermal behavior; Chemical environment; Alumina gel; Citrate-to-nitrate ratio

1. Introduction

Ultrafine α-Al_2O_3 is widely used for structural, microelectronic and membrane applications [1–4]. Various chemical methods have been employed for its synthesis. The citrate–nitrate gel combustion method has an outstanding potential and technological importance among the solution based combustion synthesis of ultrafine α-Al_2O_3 [5–7]. The mechanism of the gel combustion reaction is quite complex. The parameters which influence the reaction include type of fuel, fuel-to-oxidizer ratio, use of excess oxidizer, and water content of the precursor mixture [8], the fuel-to-oxidizer ratio being the most important one.

In our previous work [9,10], ultrafine α-Al_2O_3 was synthesized by the gel combustion method at low temperature. However, very little effort has been made to study the properties of gels with different citrate-to-nitrate ratio. In this paper, the influence of citrate-to-nitrate ratio on the chemical environment and thermal behavior of the gel is mainly discussed.

2. Experimental

Analytical $Al(NO_3)_3 \cdot 9H_2O$ and citric acid ($C_6H_8O_7 \cdot H_2O$) were dissolved in deionized water. In the solution, 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. The reason for selecting such a range of γ is based on the concept of propellant [11]. It can be calculated [12] that 0.833 mol of citric acid is required for each mol of nitrate in order to have a stoichiometric redox reaction in the gel that gives $\gamma = 0.278$ (named GS). Deficient citric acid in the gel with $\gamma = 0.033$, 0.1 and 0.167 (named G1, G2 and G3, respectively) presents a fuel-lean condition while higher citric acid concentration with $\gamma = 0.333$, 0.5 and 0.667 (named G4, G5 and G6, respectively) produce a fuel-rich condition. In this paper, the word "gel" is used for the product obtained by gelling the aqueous solution of nitrate and citric acid by evaporating the water at ~80 °C. The "ash" is the

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combustion product of the gel. Gel and ash are named G# and A#, 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 conditions depending on γ, which 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 air flow (20 ml min^{-1}). Samples were heated at 10 °C min^{-1} to 1200 °C and then cooled naturally to ambient. FTIR of the as-prepared and calcined powders were measured on a Nicolet

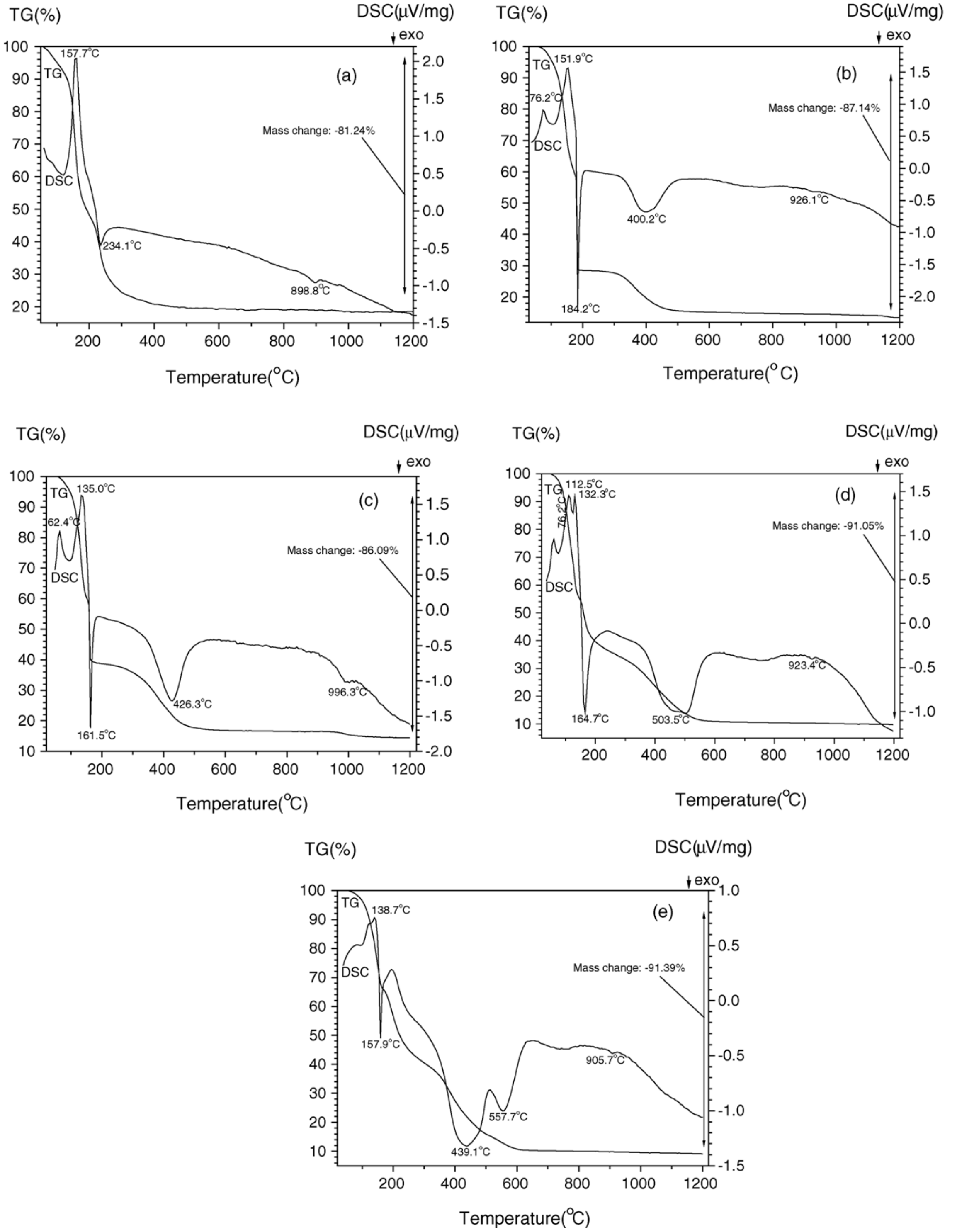

Fig. 1. TG–DSC curves of gels (a) G1; (b) G3; (c) GS; (d) G4 and (e) G6.

NEXUS 7000C spectrophotometer in the 400–4000 $\mathrm{cm^{-1}}$ range using the KBr pellet method. Each analysis consisted of a minimum 32 scans with ±2 $\mathrm{cm^{-1}}$ resolution.

3. Results and discussion

It can be seen from Fig. 1 that the exothermic peak temperature shifts from 234.1 °C to 184.2 °C to 161.5 °C to 164.7 °C to 157.9 °C for G1, G3, GS, G4 and G6, respectively. Gel G1 decomposed in a single step, as shown in Fig. 1(a). However, all the citrates did not convert into gaseous products. Close observation shows that one exothermic peak appears at 898.8 °C, which might result from γ- to α-$\mathrm{Al_2O_3}$ phase transformation. The total mass-loss determined for the production of α-$\mathrm{Al_2O_3}$ from G1 was 81.24%. Calculations of the theoretical mass-loss base on the stoichiometry of the metal nitrate and citric acid in the original solutions yield a value of 87.08% or 78.05% if it is assumed that the water of crystallization of the raw materials is removed during the preparation of the gel. This indicates that a small amount of water remained in the synthesized gel. Gels G3, GS, and G4 show identical decomposition patterns in the TG curves, which occur in two steps in the range of 150–550 °C. In the corresponding DSC curves, the second exothermic peaks locate at 400.2 °C, 426.3 °C and 503.5 °C, respectively. The temperature of further decomposition increases with the increase of the citrate-to-nitrate ratio γ. Gels G3, GS and G4 show endothermic peaks in DSC curves at 926.1 °C, 996.3 °C and 923.4 °C, respectively, which correspond to the phase transition from γ- to α-$\mathrm{Al_2O_3}$. The gel GS with $\gamma = 0.278$ has a theoretically stoichiometric redox reaction. However, it did not stoichiometrically convert all the citrate into gaseous products due to the decomposition of nitrate during gel preparation. The decomposed ash AS was contaminated with carbon from incomplete combustion of the citrates as well as with hydroxycarbonates, as can be confirmed by the color of AS and the infrared spectrum in Fig. 3. When a slight higher amount of citric acid relative to stoichiometry was used, a voluminous ash A4 was yielded for $\gamma = 0.333$ after combustion. The DSC curve in Fig. 1(d) shows a broad peak around 500 °C, which indicates the decomposition of hydroxycarbonate and excessive citric acid. Gel G6 which has an even higher citrate-to-nitrate ratio ($\gamma = 0.667$) shows a type of decomposition similar to G4 in the TG–DSC curve. The endothermic peaks at 439.1 °C, 557.9 °C appear in DSC curves, which also correspond to the decomposition of hydroxycarbonate and excessive citric acid. The combusted product A6 which had a brown color was contaminated with a high amount of unburned carbon.

The above observation indicates that a higher amount of nitrate in the gel (G1, $\gamma = 0.1$) should be effective in the redox system in completing the combustion of citrates. When a higher amount of citric acid ($0.33 > \gamma > 0.1$) is used, decomposition occurs in two steps through an unstable intermediate. When an even higher amount of citric acid ($\gamma > 0.33$) is used, decomposition occurs in three steps. In the fuel-lean condition, the phase transformation temperature increases with the increase of γ. However, the phase transition temperature decreases with the increase of γ in the fuel-rich condition.

An attempt was made to understand the status of anions in the chemical environment of the gel by infrared spectroscopy because the gels differ in their thermal behavior. As shown in Fig. 2, the spectra of G1, G2 and G6 differ from G3, GS, G4 and G5, with a little shift in some of their band positions as well as with the relative intensities. The spectra of G1 and G2 are dissimilar in the range of 1750–1600 $\mathrm{cm^{-1}}$ and that of G6 in the region of 1300–1200 $\mathrm{cm^{-1}}$. The spectra clearly show that the band around 1723 $\mathrm{cm^{-1}}$ is not pronounced in G1 and G2, compared to the other gels. The particular band is a combination of symmetric stretching and doubly degenerate in-plane bending vibrations of the nitrate ($\mathrm{NO_3}$) group. This confirms the presence of free $\mathrm{NO_3}$ in the gels G3, GS, G4, G5 and G6 and absence of free nitrate in G1 and G2. The band around 1201 $\mathrm{cm^{-1}}$ in G6 can be attributed to the υ_{CO} stretching vibration of carboxyl (COOH) group, which is not obvious in GS, G4 and G5 and not observed in the other gels. It confirms the presence of free citric acid only in GS, G4, G5 and G6. The well-resolved band at 1633 $\mathrm{cm^{-1}}$ due to $\upsilon_{\mathrm{N=O}}$ vibration indicates the presence of bidentate nitrates in all gels. Other bands of the $\mathrm{NO_3}$ group occurring approximately at 1389, 1038 and 816 $\mathrm{cm^{-1}}$ in all gels can be assigned to $\upsilon(\mathrm{NO_2})$, $\upsilon_{\mathrm{S}}(\mathrm{NO})$ and $\upsilon(\mathrm{NO_3})$ bands, respectively. As to the citrate group, the bands at 1082 $\mathrm{cm^{-1}}$, 932 $\mathrm{cm^{-1}}$ and 899 $\mathrm{cm^{-1}}$ are possibly due to $\delta(\mathrm{CO})$, $\upsilon(\mathrm{C{-}C})$ and $\rho_{\mathrm{r}}(\mathrm{CH_2})$ vibrations, respectively. A broad absorption band around 3450 $\mathrm{cm^{-1}}$ is characteristic of $\upsilon(\mathrm{OH})$ for all gels. The spectra in the range of 600–700 $\mathrm{cm^{-1}}$ can be assigned to the vibrations of hydroxyl.

Fig. 3 shows the FTIR spectra of ashes A1, A2, A3, AS, A4, A5 and A6. The spectral patterns of A1 and A2 differ from A3, AS, A4, A5 and A5 in the range of 1500–1400 $\mathrm{cm^{-1}}$ and 1300–500 $\mathrm{cm^{-1}}$. The broad peak around 3450 $\mathrm{cm^{-1}}$ is a characteristic stretching vibration of $\upsilon(\mathrm{OH})$. Bands localized at 1610 $\mathrm{cm^{-1}}$ and 1383 $\mathrm{cm^{-1}}$ are assigned to asymmetrical and symmetrical stretching vibration of carboxylate, respectively. The spectra of A1, A2 differ from A3, AS, A4, A5 and A6 at 1200–500 $\mathrm{cm^{-1}}$.

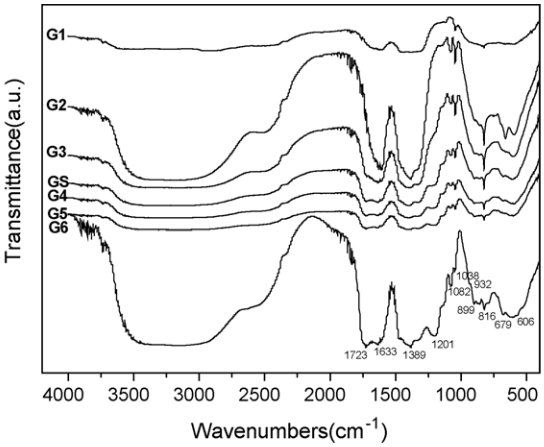

Fig. 2. FTIR spectra of gels G1, G2, G3, GS, G4, G5 and G6.

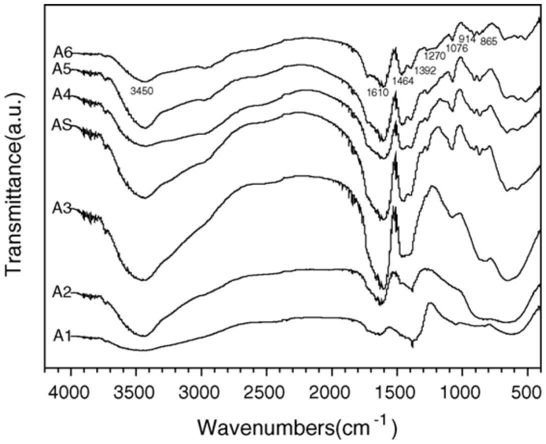

Fig. 3. FTIR spectra of ashes A1, A2, A3, AS, A4, A5 and A6.

The difference in spectra is mainly caused by the thermal reactivity. The spectra of A3, AS, A4, A5 and A6 show absorption bands at 1646 cm^{-1} due to vibration of carbonate, indicating the presence of hydroxycarbonate. Formation of hydroxycarbonate salts as one of the combusted products was observed in all the gels with $\gamma > 0.167$.

4. Conclusions

A systematic investigation on the thermal behavior and chemical environment of gels with different citrate-to-nitrate ratio γ has been carried out. The citrate-to-nitrate ratio γ of the gel plays an important role in controlling the thermal behavior of the synthesized gel due to the reactivity. Combustion and decomposition occur in different way due to different citrate-to-nitrate ratio. Phase transformation temperature increases with the increase of γ in the fuel-lean condition and decreases with the increase of γ in the fuel-rich condition.

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