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Low temperature synthesis of ultrafine α-Al_2O_3 powder by a simple aqueous sol–gel process

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Abstract

Ultrafine α-Al_2O_3 was synthesized by a simple aqueous sol–gel method using a citrate polymeric precursor derived from aluminum nitrate and citric acid mixed solution. The thermal decomposition of the precursor and subsequent formation of α-Al_2O_3 was investigated by X-ray diffractometer (XRD), field emission transmission electron microscope (FETEM), thermogravimetry-differential scanning calorimetry (TG–DSC)–mass spectra (MS) and Fourier transform infrared spectra (FTIR). The molar ratio of citric acid to metal nitrate (C/N), which played an important role in phase transition and morphology controlling of alumina, was also investigated. A single-phase α-Al_2O_3 powder resulted after heat treatment at ~1000 °C. The increasing molar ratio of C/N was found to be in favor of γ- to α-Al_2O_3 phase transition, whereas the precursor with C/N = 1 yielded a relatively well dispersed ultrafine α-Al_2O_3 powder with particle size of ~200 nm.

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Keywords: D. Al_2O_3; Powder preparation; Aqueous Sol–gel process

1. Introduction

Ultrafine α-Al_2O_3 powder has considerable potential for a wide range of applications including high strength materials, electronic ceramics and catalysts. The wide uses make it a common material and there has been an increasing interest in the synthesis of ultrafine α-Al_2O_3. Al_2O_3 is a structurally complex oxide being several different metastable phases possible, which eventually convert to stable α-Al_2O_3. Conventional processes for synthesizing α-Al_2O_3 involve mechanical milling [1], vapor phase reaction [2–4], precipitation [5], sol–gel [6,7], hydrothermal [8] and combustion methods [9,10]. Mechanical synthesis of α-Al_2O_3 requires extensive mechanical ball milling and easily introduces impurities. Vapor phase reaction for preparation fine α-Al_2O_3 powder from a gas phase precursor demands high temperature above 1200 °C. The precipitation method suffers from its complexity and time consuming (long washing times and aging time). The direct formation of α-Al_2O_3 via the hydrothermal method needs high temperature and pressure. The combustion method has been used to yield α-Al_2O_3 powders, whereas the powder obtained from the process is usually hard aggregated but contains nano-sized primary particles. The sol–gel method based on molecular precursors usually makes use of metal alkoxides as raw material. However, the high prices of alkoxides and long gelation periods limit the application of this method.

Here, a relatively simple, efficient, low-cost aqueous sol–gel method based on the in situ generation of water soluble metal complexes with aluminum nitrate and citric acid as raw materials has been developed to synthesize ultrafine α-Al_2O_3 powders. Decomposition of the citrate precursor, phase transformations and morphology of the synthesized alumina powder are investigated.

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2. Experimental

Analytical grade $Al(NO_3)_3 \cdot 9H_2O$ (Zhenxin Chemical Co., Shanghai, China) and $C_6H_8O_7 \cdot H_2O$ (Lingfeng Chemical Co., Shanghai, China) were used as raw materials to prepare Al_2O_3. The starting solution was prepared by dissolving aluminum nitrate and citric acid into deionized water. The concentration of aluminum nitrate was 0.5 M. The molar ratios of citric acid to metal nitrate (C/N) were 0.5, 1.0 and 2.0 in the solution, respectively. The solution was continuously stirred for several hours and kept at a temperature of 60 °C until it turned to a yellowish sol. Then, the stabilized nitrate-citrate sol was rapidly heated to 80 °C and stirred constantly. Viscosity and color changed as the sol turned into a transparent stick gel. The gel was heat treated at 200 °C for 2 h and a fluffy, polymeric citrate precursor was gained. Finally, the prepared precursor was ground to a fine powder and calcined at different temperatures for 2 h in muffle furnace.

Phase identification was performed by a Rigaku D/max2200PC X-ray diffractometer (XRD) using nickel filtered Cu Kα radiation in the range of $2\theta = 10°–80°$ with a scanning speed of 4° per min. Thermal analysis of the precursor was done by thermogravimetry-differential scanning calorimetry (TG–DSC) on a Netzsch STA 449C instrument. The mass spectra (MS) of the gaseous products evolving from the precursor in TG–DSC are simultaneously monitored with a Balzers Thermostar^{TM} quadrupole mass spectrometer. The Fourier transform infrared spectra (FTIR) were measured on a Nicolet NEXUS 7000 C spectrophotometer using the KBr pellet method. The morphology of the gained Al_2O_3 powder was observed on a JEOL EM 2100 field emission transmission electron microscope (FETEM).

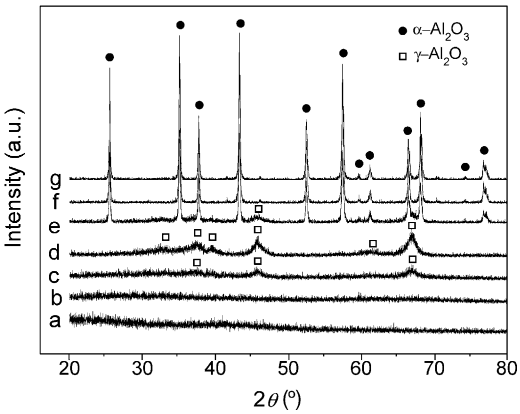

Fig. 1. XRD patterns of the as-synthesized precursor (C/N = 1) calcined at different temperatures (a) 200 °C, (b) 600 °C, (c) 800 °C, (d) 900 °C, (e) 950 °C, (f) 1000 °C, (g) 1100 °C.

Table 1
Phase structure and crystallite size of the prepared Al_2O_3 calcined at different temperatures

	Calcination temperature (°C)					
	600	800	900	1000	1100	1200
Crystallite size/nm	–	14.2	15.2	72.2	77.4	80.5
Phase structure	Amor.	γ	γ	α[a]	α	α

[a] Powder calcined at 1000 °C is mainly α-Al_2O_3 containing a small quantity of γ-Al_2O_3.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-synthesized precursor and the powders obtained with C/N = 1.0 calcined at different temperatures. It is observed the precursor to be amorphous as well as the powder calcined at 500 °C. The

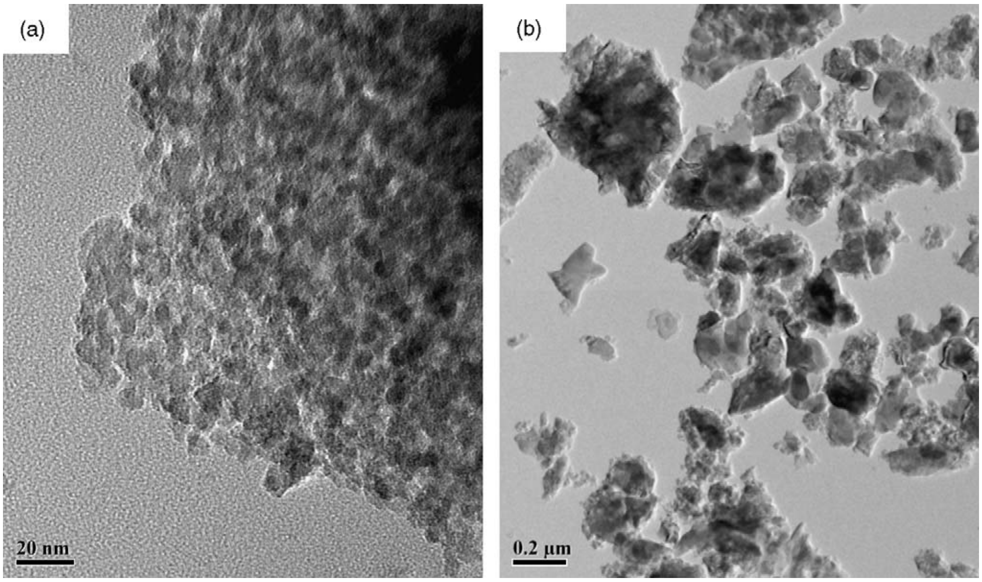

Fig. 2. FETEM micrographs of the Al_2O_3 powder prepared from the citrate precursor (C/N = 1) calcined at (a) 950 °C, (b) 1000 °C.

characteristic peaks of γ-Al_2O_3 appear at 800 °C with a rather weak intensity, which indicates amorphous to γ-Al_2O_3 transition. With the increase of calcination temperature up to 900 °C the crystallinity of γ-Al_2O_3 improved. At 950 °C rather weak peaks of α-Al_2O_3 appear, indicating γ- to α-Al_2O_3 transition. The γ-Al_2O_3 peaks, except for the strongest one disappear, indicating the γ- to α-Al_2O_3 phase transition be almost completed. At temperature higher than 1000 °C high intensities of α-Al_2O_3 peaks are observed, indicating crystallite growth of the grains.

The phase structure and crystallite size of the prepared Al_2O_3 powder estimated from X-ray peak broadening using Scherrer formula is shown in Table 1. The particle size of γ-Al_2O_3 was about 15 nm and there was only slight increase with increase of calcination temperature, as shown in Fig. 2(a). The amount of α-Al_2O_3 increased drastically when the calcination temperature was above 1000 °C. It is shown that γ-Al_2O_3 crystallite almost disappeared without growing up and α-Al_2O_3 crystallite rapidly grew up to ~75 nm as transformation completed. No matter how the α-Al_2O_3 crystallites obtained whether through interface migration from the α-Al_2O_3 nuclei or coalescence among the α-Al_2O_3 nuclei, both would lead to the completion of γ-/α-Al_2O_3 phase transition. If the α-Al_2O_3 crystallites are still treated with sufficient heat, particle coarsening will be resulted. Fig. 2(b) shows the FETEM image of α-Al_2O_3 calcined at 1000 °C. It can be seen that the medial particle size of the prepared alumina powders is about 200 nm. The particle size is larger than that calculated from Scherrer formula (75 nm) due to the agglomeration of nanocrystalline Al_2O_3.

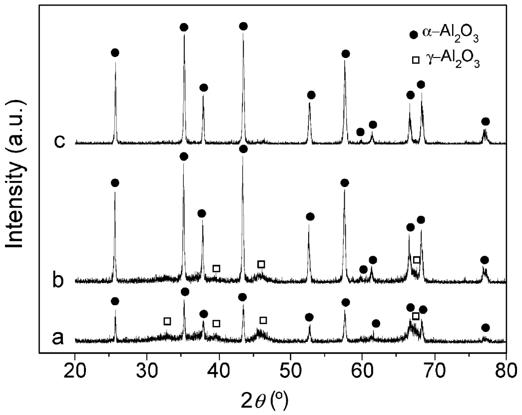

Fig. 3. XRD patterns of as-synthesized precursors calcined at 1000 °C (a) C/N = 0.5, (b) C/N = 1.0, (c) C/N = 2.0.

Fig. 3 shows XRD patterns of powders obtained from different precursors calcined at 1000 °C. With the increase of the mole ratio of citric acid to nitrate the XRD patterns of α-Al_2O_3 show sharper profiles corresponding to further crystallization and the characteristic peaks of γ-Al_2O_3 weaken and disappear. The FETEM image of 1000 °C calcined Al_2O_3 powder prepared from the citrate precursor (C/N = 0.5) shows many plate-like flake structures and a multi-modal mixture of crystallites in Fig. 4(a). For the Al_2O_3 powder prepared from the citrate precursor (C/N = 2.0), FETEM image reveals that severe glomeration occurred at 1000 °C, as shown in Fig. 4(b).

The thermal decomposition of the citrate precursor (C/N = 1) and the phase transition of alumina has been studied, the TG–DSC curves being shown in Fig. 5. In the temperature region RT-135 °C, an endothermic peak (at about 109.8 °C) with a mass loss of 9.0% appears which is associated to the vaporization of physically bound absorbed water. In the temperature region 135–340 °C, a broadened

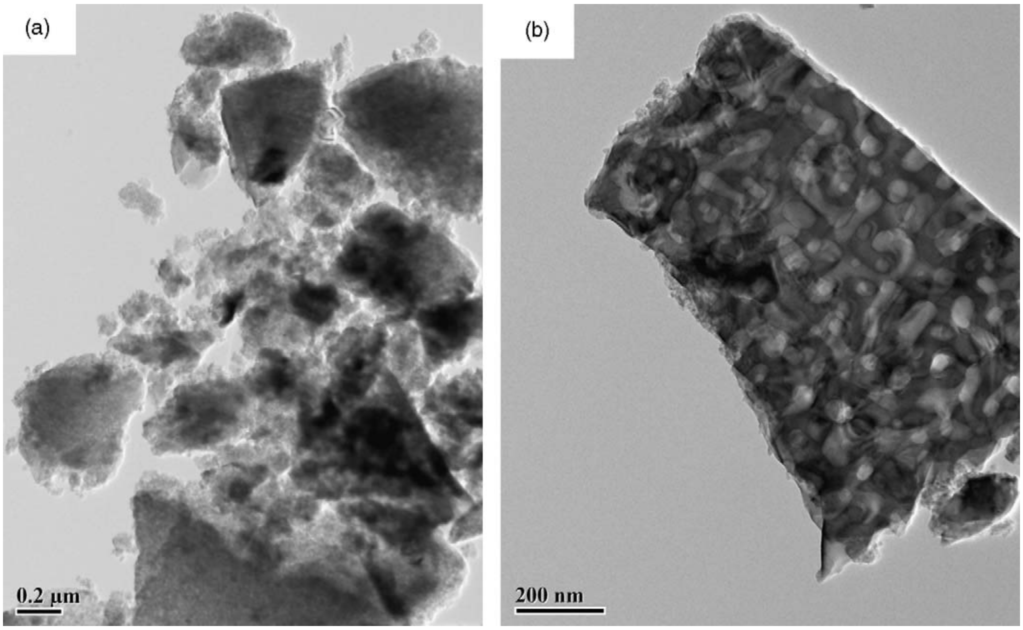

Fig. 4. FETEM micrographs of the α-Al_2O_3 powder prepared from the citrate precursors calcined at 1000 °C (a) C/N = 0.5, (b) C/N = 2.

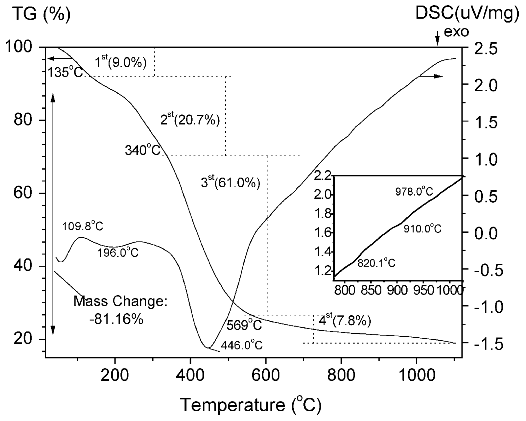

Fig. 5. TG/DSC curve of the as-synthesized precursor.

exothermic peak (at about 196.0 °C) with a mass loss of 20.7% occurred which was caused by the dehydration reaction of the citrate precursor. The maximum exothermal peak at 446.0 °C was relatively sharp and intense, accompanied by a drastic mass loss in the temperature range 340–569 °C. It indicates that further decomposition of the precursor occurred. The mass loss associated with this sharp exothermal reaction is about 61.0%. Three small exothermal peaks correspond to the amorphous/γ-Al_2O_3 transformation at 820.1 °C, γ-/α-Al_2O_3 transition at 910.0 °C and nanocrystal growth of α-Al_2O_3 at 978.0 °C. Actually, relaxation of amorphous nano-Al_2O_3 powders, which reduces defects and lattice distortions in the γ-Al_2O_3 powder, releases a large amount of energy and thus promotes nucleation of α-Al_2O_3. So the transformation of γ-/α-Al_2O_3 occurred directly in amorphous Al_2O_3 when calcined at a proper temperature. This phenomenon may be associated to the fine structure changes (bond length or bond angle variation) of amorphous Al_2O_3 during relaxation [7].

To identify with certainty the thermal decomposition of the citrate precursor (C/N = 1), mass spectra were conducted in the temperature range RT-1100 °C. Fig. 6 shows the positive ion mass spectra of $m/z = 18$ and 44. For $m/z = 18$, three main peaks (100, 268, 449 °C) are observed. The three peaks are related to the vaporization of physically adsorbed water molecules, the dehydration and further decomposition of citrate precursor, respectively. For $m/z = 44$, three main peaks at 268, 400 and 440 °C correspond to the successive degradation of carboxylate. Other cations such as OH^+ ($m/z = 17$), $C_2H_2^+$ ($m/z = 17$), $C_2H_2O^+$ ($m/z = 42$), CO_2H^+ ($m/z = 45$), $C_2O_2^+$ ($m/z = 56$) and $C_2H_2O_2^+$ ($m/z = 58$) were detected by mass spectrometer during the decomposition of the citrate precursor.

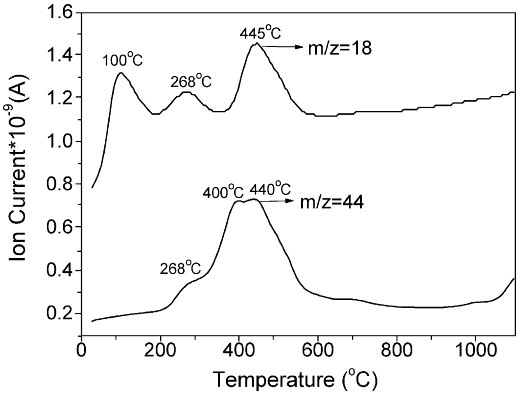

Fig. 6. MS curves of Al_2O_3 precursor at a heating rate of 10 °C/min: H_2O^+ ($m/z = 18$), CO_2^+ ($m/z = 44$).

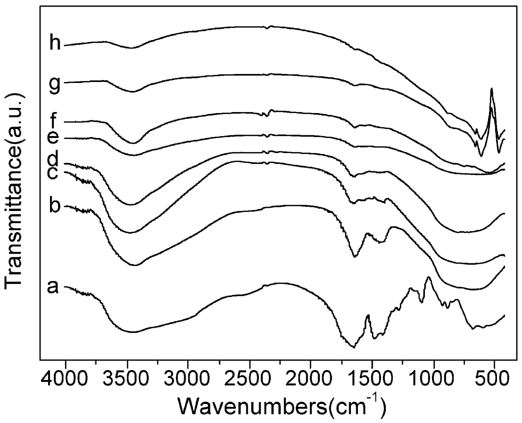

Fig. 7. FTIR spectra of Al_2O_3 precursor calcined at different temperatures (a) 200 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 800 °C, (f) 900 °C, (g) 1000 °C, (h) 1200 °C.

The FTIR at 4000–400 cm^{-1} for the precursor (C/N = 1) calcined at different temperatures are shown in Fig. 7. This clearly shows a broad absorption at ~3500 cm^{-1} and a small absorption at 654 cm^{-1}, which are characteristic stretching vibration and deformation vibration of hydroxylate (O–H), respectively. The characteristic bands of nitrate ions at 1465 and 1315 cm^{-1} indicate its incomplete decomposition during 200 °C-heat-treating process of the gel. Peaks localized at 1635 and 1400 cm^{-1} are assigned to asymmetrical and symmetrical stretching vibration of carboxylate (O–C═O), respectively. Absorption at 1264 and 1068 cm^{-1} are assigned to asymmetrical and symmetrical stretching vibration of C–O–C group, indicating the polyreaction of metal citrate. In the FTIR spectra of powder calcined at 400 °C, the absorption bands of NO_3^- group disappear because of the complete decomposition of nitrate. Furthermore, the bands of hydroxylate and carboxylate reduce significantly due to the decomposition of the citrate precursor. The characteristic bands of C–O–C group disappear, indicating the thermal decomposition of polyester. For the sample calcined at 500 °C, the spectrum reveals that only small part of the carboxylate exists in the calcined precursor. For the 600 °C calcined precursor, characteristic vibration of carboxylate almost disappears. A broad and smooth absorption band with any fine structure in the wave number range from 500 to 900 cm^{-1} reveals the formation of amorphous nano-Al_2O_3. It can be attributed to the disordered distribution of vacancies and the continuous distribution of bond length in an amorphous material [11].

With increase of calcination temperature, characteristic vibration of carboxylate completely vanishes. γ-Al_2O_3 appears at 800 °C and almost all the amorphous Al_2O_3 transformed to γ-Al_2O_3 at 900 °C. It can be seen that the infrared spectra tend to possess a double-peak at 835 and 567 cm^{-1}. Absorption at 2400, 2340 and 1630 cm^{-1} are stretching vibrations of HCO_3^- group, indicating H_2O and CO_2 absorption in the synthesized powder. For the sample calcined at 1000 °C, significant spectroscopic bands at 639, 590 and 443 cm^{-1} appear which are identified to be the characteristic absorption bands of α-Al_2O_3. This is in good agreement with XRD observation. There are no significant changes in FTIR spectra with further increase of calcination temperature.

4. Conclusions

Ultrafine Al_2O_3 was prepared using a citrate precursor derived from aluminum nitrate and citric acid mixed solution (C/N = 1.0). At about 400 °C citrate precursor decomposed and amorphous nano-Al_2O_3 formed. The evolution in the alumina precursor involved decomposition followed by amorphous to γ-Al_2O_3 and γ- to α-Al_2O_3 phase transformation. The γ-Al_2O_3 crystallites appeared at ~800 °C with particle size of about 15 nm, and there was only a slight increase in grain size with the increase of calcination temperature. γ-Al_2O_3 crystallite almost disappeared and α-Al_2O_3 crystallite rapidly grew up to ~75 nm at ~1000 °C when the transformation was just completed. The increasing molar ratio of C/N was found to be in favor of γ- to α-Al_2O_3 phase transition, whereas the precursor with C/N = 1 yielded a relatively well dispersed ultrafine α-Al_2O_3 powder with particle size of ~200 nm.

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References

[1] M.L. Panchula, J.Y. Ying, Mechanical synthesis of nanocrystalline α-Al_2O_3 seeds for enhanced transformation kinetics, Nanostruct. Mater. 9 (1–8) (1997) 161–164.

[2] K. Kamata, T. Mochizuki, S. Matsumoto, A. Yamada, K. Miyokawa, Preparation of submicrometer Al_2O_3 powder by gas-phase oxidation of tris(acetylacetonato) alumina (III), J. Am. Ceram. Soc. 68 (8) (1985), C-193–C-194.

[3] T.C. Chou, T.G. Nieh, Nucleation concurrent anomalous grain growth of α-Al_2O_3 during γ → α-Al_2O_3 phase transformation, J. Am. Ceram. Soc. 74 (9) (1991) 2270–2279.

[4] H.K. Varma, T.V. Mani, A.D. Damodran, Characteristics of alumina powders prepared by spray-drying of boehmite sol, J. Am. Ceram. Soc. 77 (6) (1994) 1597–1600.

[5] J.G. Li, X.D. Sun, Synthesis and sintering behavior of a nanocrystalline α-alumina powder, Acta Mater. 48 (12) (2000) 3103–3112.

[6] E. Ponthieu, E. Payen, J. Grimblot, Ultrafine alumina powders via sol-emulsion-gel method, J. Non-Cryst. Solids 147–148 (1992) 598–605.

[7] W.M. Zeng, L. Gao, J.K. Guo, A new sol–gel route using inorganic salt for synthesizing Al_2O_3 nanopowders, Nanostruct. Mater. 10 (4) (1998) 543–550.

[8] A.J. Fanelli, J.V. Burlew, Preparation of fine alumina powder in alcohol, J. Am. Ceram. Soc. 69 (8) (1986), C-174–C-175.

[9] J.J. Kingsley, K.C. Patil, A novel combustion process for the synthesis of fine particle α-alumina and related oxide materials, Mater. Lett. 6 (1988) 427–432.

[10] S. Bhaduri, E. Zhou, S.B. Bhaduri, Auto ignition processing of nanocrystalline α-Al_2O_3, Nanostruct. Mater. 7 (5) (1996) 487–496.

[11] C.H. Shek, J.K.L. Lai, T.S. Gu, G.M. Lin, Transformation evolution and infrared absorption spectra of amorphous and crystalline nano-Al_2O_3 powders, Nanostruct. Mater. 8 (5) (1997) 605–610.