Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 35, No. 1, Jan. 2017, P. 79
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Preparation of nanoscaled yttrium oxide by citrate precipitation method

CHEN Jinqing (陈金清)[1], HUANG Bin (黄 彬)[1,2], HUANG Chao (黄 超)[1,2], SUN Xiaoqi (孙晓琦)[2,*]

(1. School of Metallurgy and Chemical Engineering, Jiangxi University of Science & Technology, Ganzhou 341000, China; 2. Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen 361021, China)

Received 28 April 2016; revised 31 May 2016

Abstract: The nano-Y_2O_3 was prepared from YCl_3 by the citrate precipitation method. The precursor powders were prepared by 0.1 mol/L YCl_3 solution and 0.1 mol/L hydrochloric acid in the presence of 1% surfactant PEG2000, which was dried via an ethanol azeotropic distillation method. The effects of reaction temperature, precursor concentration, hydrochloric acid concentration, surfactant, and calcination temperature on the mean sizes of nano-Y_2O_3 were studied. It was found that the highest yield of precursor was about 70% at the pH value of 5.0, and the yield decreased rapidly at the pH value below 4 or over 6. The reaction temperature revealed no effect on the size of precursor. The optimized precursor concentration and hydrochloric acid concentration were both 0.1 mol/L. Several typical analytic techniques such as particle size analyzer, X-ray diffraction (XRD), thermogravimetric and differential thermal analyses (TG-DTA) and scanning electron microscopy (SEM) were used to determine the characteristics of the prepared nano powders. Homogeneous torispherical nano-Y_2O_3 with the smallest size (20 nm) could be obtained by calcining the precursor powders at 800 ºC for an hour.

Keywords: nano; Y_2O_3; citrate precipitation; rare earths

With the booming development of nanotechnology, the nano powders with regular morphology and narrow size distribution have been widely studied[1]. The nano-sized oxide particles possessed unique physicochemical properties over common materials, such as optical, catalytic and structural properties[2]. Considerable investigations on the preparation methods of nano-sized oxide particles have been conducted[3]. It is worthwhile to mention that rare earth oxides have been used in many advanced technologies, such as magnets, lightings, sensors, lasers, electronics, batteries, catalysts, alloys and communications[4]. As a result, the development of rare earth (RE) oxides with nano-sizes, larger specific surface areas and higher chemical activities comes to be very important[5,6].

Among the rare earth (RE) oxides, yttrium oxide (Y_2O_3) possesses excellent heat resistance, corrosion resistance, high temperature and photochemical stability[7]. Its melting point is higher than 2400 ºC and dielectric constant is from 12 to 20[8,9]. As a result, Y_2O_3 is widely used in ceramics, optical and laser materials. For example, it was used as additive in many high performance ceramics to improve their hardness[10], wear[11,12], corrosion resistance[13], and light transmission[14,15]. As laser host material, the neodymium-doped yttrium aluminum garnet laser was widely used in medical equipment[16]. Besides high purity, uniformity and dispersion of Y_2O_3 are essential for the high-tech materials.

As mentioned previously, the preparation of nano Y_2O_3 can be summarized to be solid phase method[17,18], liquid phase method (including precipitation method[19–25], sol-gel method[26–29], microemulsion method[30–32], hydrothermal method[33–35]) and gas phase method[36]. Because of low reaction temperature, simple equipment and low energy consumption, the liquid phase precipitation method is the most commonly used technology for the preparation of nano-scale particles on the industrial scale. The common precipitants in liquid phase precipitation method are oxalic acid, carbonic acid, sodium hydroxide, and citrate. The oxalic acid is one of the most commonly used precipitants in industrial production, but it is still expensive for industrial production. In addition, rare-earth carbonate and rare-earth hydroxide precipitates are amorphous, the resulting Y_2O_3 particles are prepared with lower yields and broader size distributions. To develop sustainable and efficient strategy for industrial application, ammonium citrate was used as precipitant for the preparation of nano-scale Y_2O_3 in this article. In a very recent report, the precipitates revealed crucial influence on the size and morphology of the prepared nano powders[37]. To obtain nano-Y_2O_3 powders with favorable size and morphology, the effects of reaction temperature, precursor concentration, hydrochloric acid concentration,

Foundation item: Project supported by "Hundreds Talents Program" from Chinese Academy of Sciences, National Natural Science Foundation of China (21571179), Science and Technology Major Project of the Fujian Province, China (2015HZ0101), Xiamen Universities, Research Institutions Jointing Enterprise Projects (3502Z20152009), Research Institutions Jointing Enterprise Projects (3502Z20152009)

* **Corresponding author:** SUN Xiaoqi (**E-mail:** xqsun@fjirsm.ac.cn; **Tel.:** +86-592-6376370)

DOI: 10.1016/S1002-0721(16)60164-3

surfactant, and calcination temperature on the mean size of nano-Y_2O_3 were discussed in this article. It is the first attempt to dry precipitate via an ethanol azeotropic distillation method under reduced pressure of 0.01 MPa, which contributes to the sample dried quickly without agglomeration.

1 Experimental

1.1 Reagents and materials

The Y_2O_3 (99.999%) was provided by Fujian Changting Golden Dragon Rare Earth Co., Ltd., China. Ammonium citrate (purity>98.5%) and PEG2000 were obtained from Sinopharm Chemical Reagent Co., Ltd. All the chemicals used in this study were of analytical grade without further purification.

1.2 Preparation of nano-Y_2O_3

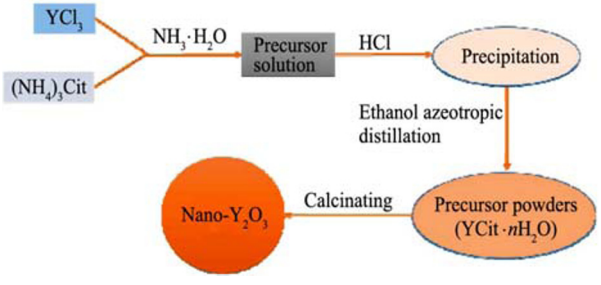
(1) The YCl_3 solution was prepared by dissolving the Y_2O_3 in muriatic acid (1:1). The pH value of solution was kept to be 4–5. Y^{3+} concentration in the solution was determined by EDTA complexometry.

(2) The YCl_3 solution was dropped to a stirred ammonium citrate solution, and then ammonia was used to increase the pH until the precipitate disappeared. Subsequently, the hydrochloric acid was dropwisely added with stirring till the generation of precipitation. By adjusting the pH value, the highest rate of precipitation was obtained. Then the precipitate was filtered and washed with deionized water for removing chloride.

(3) The precipitate was dispersed in the ethanol by ultrasonic and azeotropic distillation under reduced pressure at 40 ºC to obtain precursor without adsorbed water, which was subsequently heated at various temperatures to get the Y_2O_3 powder.

1.3 Characterizations

The particle size of Y_2O_3 dispersed in ethanol was measured by dynamic light scattering (Nanobrook Omni, Brookhaven). The morphologies of nano-Y_2O_3 were observed by scanning electron microscopy (SEM, Hitachi su8010). Simultaneous thermogravimetric and differential thermal analyses (Mettler Toledo, TGA/DSC1) with a heating rate of 10 ºC/min in a static air atmosphere were used to study thermal decomposition behavior of the dried precursor. Crystalline phase present was identified by Rigaku Miniflex 600 XRD system, which generated monochromated Cu Kα radiation with continuous scanning mode at a rate of 8 (°)/min ranging from 5° to 85°, and operating conditions of 40 kV and 15 mA were used to obtain XRD patterns.



Scheme 1 Preparation process of nano-Y_2O_3 powder

2 Results and discussion

2.1 Effects of pH and molar ratio on precipitation rate

Citric acid (H_3Cit) is hydroxyl tribasic acid, which has multi-level complexing abilities with RE at different pH values and molar ratios. In the acidic solution, the anion complex was formed by RE ions $(H_2Cit)^-$ and $(HCit)^{3-}$. When the pH values arrived at 6–8, the precipitation (RECit) of neutral complex salt was produced. In the precipitation (RECit), the molar amount of RE was equal to that of citric acid. When the molar amount of citric acid was higher than RE, $[RE_2(Cit)_3]^{3-}$ and $[RE(Cit)_2]^{3-}$ anions came to be formed. Moreover, hydroxyl of RE citrate was neutralized to form $[Y(Cit)']^-$ in alkaline solution[38,39]. Fig. 1 shows the precipitation rates of precursor $[(RECit)\cdot nH_2O]$ at different pH values when the molar ratio (RE^{3+}/Cit^{3-}) is 0.9 or 1. The highest yield is about 70% at the pH value of 5.0, the yield decreases rapidly at the pH value below 4 or over 6. The different molar ratios reveal little effect on the precipitation rates.

2.2 Effect of temperature

As can be seen in Fig. 2, the effect of reaction temperature on the mean size (D50) of precursor was studied. It is found that the size of precursor changes slightly with the temperature increased from 25 to 90 ºC. The comparison indicates that the mean size of precursor is not related to the preparation temperature. Accordingly, the precursor powders were prepared at room temperature in this study.

2.3 Effect of precursor and hydrochloric acid

According to LaMer model for the crystal nucleation

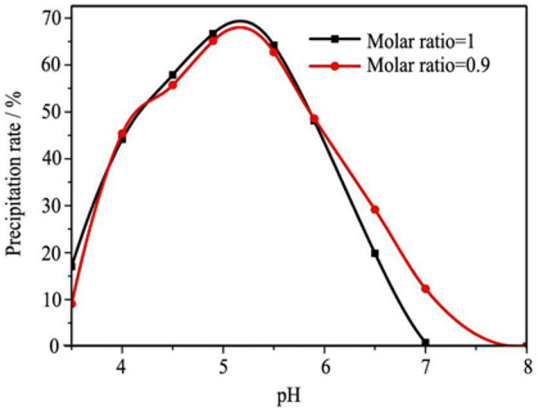


Fig. 1 Effect of pH values and molar ratios of citric acid with RE on the precipitation rate