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Effect of inorganic acid on the phase transformation of alumina

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ABSTRACT

This paper focused on the effect of hydrochloric acid and nitric acid on phase transformation of gamma to alpha alumina. The microstructure, phase composition of specimens and crystallite sizes of α-Al_2O_3 are investigated by X-ray diffraction, SEM, Scherrer formula and external standard method. The results showed that the phase transitions of alumina was affected by the kinds and concentrations of inorganic acid. Hydrochloric acid was more advantageous to promote the transformation of γ-alumina to α-alumina than nitric acid above 900 °C. In addition, the α-fraction of specimens obtained by Al_2O_3-HCl gels increased from 71.0% to 87.1% after calcination at 1000 °C when acid concentration increased from 0.1*10-4 mol/L to 0.1mol/L. On the contrary, the α-fraction of specimens obtained by Al_2O_3-HNO_3 gels decreased from 79.4% to 73.9%. And at 1100 °C up to nearly 100% of α-alumina in the specimens was obtained. Moreover, both hydrochloric acid and nitric acid were beneficial to the growth of the crystallite sizes of prepared α-Al_2O_3. Meanwhile the effect of hydrochloric acid on the phase transitions of alumina was further promoted by employing a two-step heat-treatment method. XRD and SEM confirmed that the first-step heat-treatment played an important role in the course of the calcination processes for low-temperature of α-alumina formation.

1. Introduction

α-Al_2O_3 is one of the most important oxides for a wide range of applications in refractory, ceramics, chemical and alloy materials [1–6], which is attributed to its excellent physical and chemical performance such as high hardness, high resistance to acid or base and high melting point. Now the traditional approach for preparation of α-Al_2O_3 powders is by calcination of commercial alumina and bayerite etc. However, for commercial alumina and bayerite, a calcination temperature above 1400 °C is necessary for the complete the transformation to α-A_2O_3 due to the large nucleation barrier, which results in large particles and hard aggregates those have impacts on the performances and properties of α-Al_2O_3 significantly. Therefore, lowering the formation temperature of α-A_2O_3 is desired, and many methods have been investigated such as adding additives [7,8], sol-gel process [9–11], mechanical milling [12,13] and gas influence [14]. But among the above methods the sol-gel process exhibits some unique advantages, such as increasing α-fraction at low calcination temperature, purity of the products, reducing energy consumption and so on. And it is known that the most of gels can be prepared by using acid solution to treat transition alumina, which gradually becomes attractive research point and absorbs the attentions of many scholars.

Du and coworkers [15] investigated the influence of pH value(from 5 to 11) on the microstructure of aluminum hydroxides precipitated from $Al(NO_3)_3$ at different pH values and their transformation to α-Al_2O_3. And S.D.Vaidya and Thakkar [16] studied the effect of temperature, pH and ageing time on hydration of rho alumina by investigating phase composition and surface properties of transition alumina obtained by thermal dehydration. But to the best of author's knowledge, no reports have detailed studied the effects of different concentrations of hydrochloric acid and nitric acid and two-step heat-treatment on the phase transformation of alumina.

In this work, γ-Al_2O_3 is treated with different concentrations of hydrochloric acid and nitric acid solution to prepare different gels. And then using the prepared gels to produce α-Al_2O_3 by different calcination processes is systematic studied.

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2. Experimental procedures

2.1. Raw materials

γ- Al_2O_3 powders (≥99.2% pure) with d_{50} value (the middle level diameter of the particles) of 5.347 μm were used as raw materials. Hydrochloric acid solution and nitric acid solution(pH = 1, pH = 3 and pH = 5) were used as inorganic acid.

2.2. Experimental setup and method

The α-Al_2O_3 powders samples were prepared by the following method: firstly, the γ- Al_2O_3 was treated with hydrochloric acid solution(pH = 1, 3 and 5) three times to produce different kinds of reagents, respectively. Then hydrochloric acid was replaced by nitric acid (pH = 1, 3 and 5) to produce another three kinds of reagents, respectively. And after 3 h mechanical stirring, the precipitates were filtered and dried at 110 °C to obtain different gels (Al_2O_3-HM(x), where HM represents the inorganic acid and x indicates the pH value of HM). The different gels were calcined at 700, 900, 1000 and 1100 °C for 3 h in air using a heating rate of 5 °C/min. In addition, a two-step heat-treatment method was also employed. Lastly, the different gels and their products were ground using an agate mortar and pestle, and then passed through a 325 mesh(45 h) sieve prior to characterization.

The calcined products were analyzed by X-ray diffraction (Philips, X'Pert PRO, Cu Kα). A scan rate of 4°/min was used to record the diffraction patterns in a 2θ range between 20° and 80°. The microstructures of the calcined products were characterized by field emission scanning electron microscopy(Quanta 400; FEI Company, Hillsboro, OR, USA). And the mass fraction of α-Al_2O_3 in the calcined products was determined using external standard method(Eq. (1)) [17].

$$\alpha - Al_2O_3\% = \left(I_{(012)s}\big/I_{012s} + I_{(116)s}\big/I_{(116)b}\right) \times 100/2 \quad (1)$$

where $I_{(012)s}$ and $I_{(116)s}$ were the (012) and (116) lattice plane intensity of α-Al_2O_3 in the calcined products, respectively. Meanwhile $I_{(012)b}$ and $I_{(116)b}$ were the (012) and (116) lattice plane intensity of α-Al_2O_3 standard sample(Aladdin Industrial Co., Ltd, China, purity≥99.9 wt%).

And the diffraction peak (012) of α-Al_2O_3 was used to calculate crystallite sizes by Scherrer formula(Eq. (2)) [18,19].

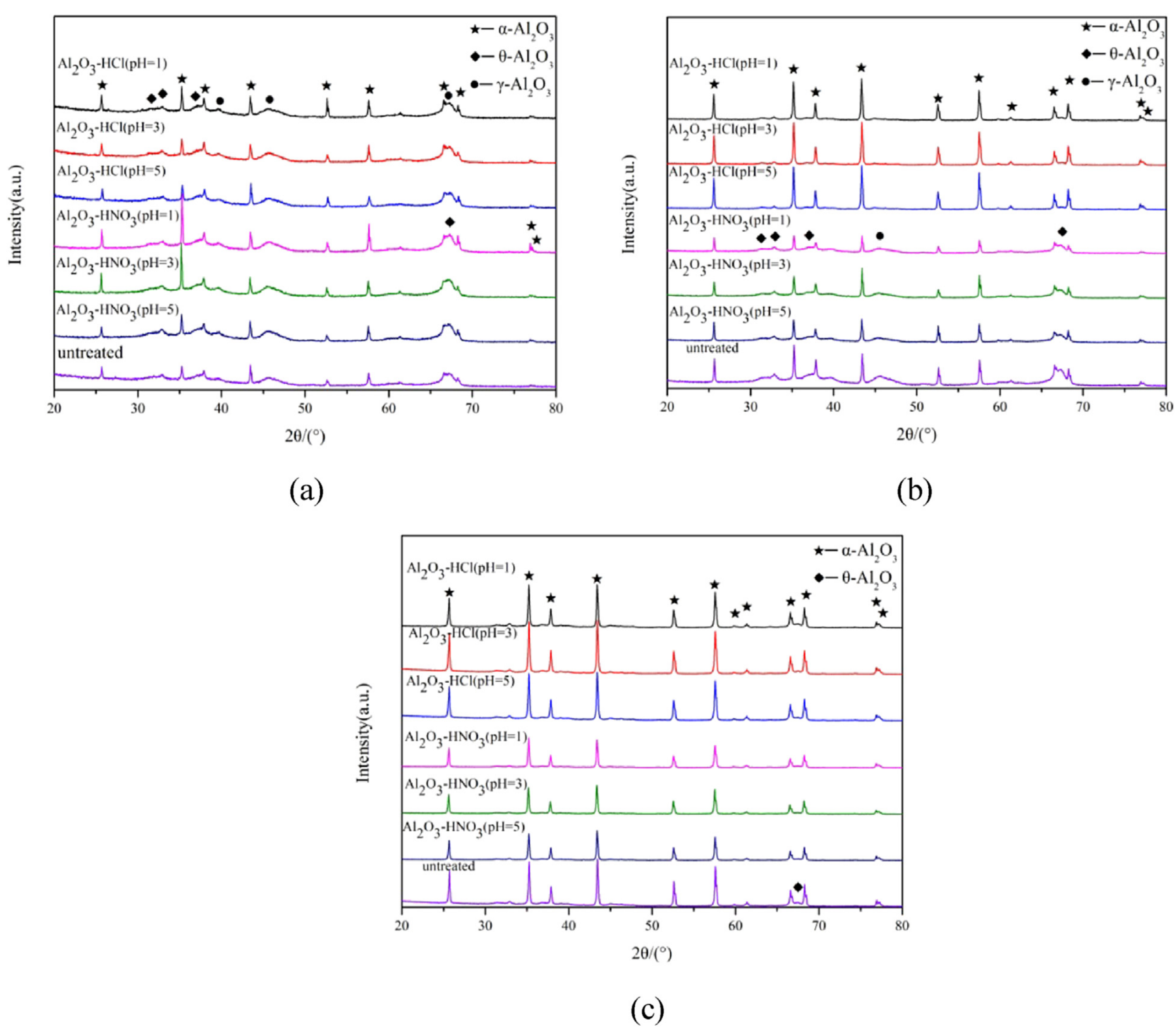

Fig. 1. XRD patterns of products obtained from γ- Al_2O_3 and different Al_2O_3-HM(x) gels after heat treatment at (a) 700 °C, (b) 900 °C and (c) 1000 °C.