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Characterization for Thermal Evolution of Boehmite Precursor and Preparation of Alumina Through a Sol-Gel Process

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Abstract: A thorough understanding in thermal evolution of alumina hydroxide precursor is fundamental to prepare high-purity alumina powders though a sol-gel process. This work contributes this by investigating the structural evolution of boehmite precursor after annealing at a wide temperature range, 300~1400 ℃ in air for 1 h. TG-DSC analysis revealed the transformation process of dry boehmite gel. With heat-treatment up to 1400 ℃, structural evolution of dry boehmite gel was carried out by combination of XRD, FT-IR, NMR and TEM analysis. The results show that the γ-Al_2O_3 is formed from boehmite at 500 ℃, which transform into δ-Al_2O_3 up to 1000 ℃. After sintering at 1100 ℃, the appearance of a three-phase region including δ-, θ- and initial α-Al_2O_3 is observed. The complete transformation into α-Al_2O_3 lasts until at 1200 ℃. The α-Al_2O_3 powders prepared with so-gel method at 1200 ℃ for 1 h had an average particle size of 50 nm with good dispersivity and narrow particle size distribution.

Key words: boehmite; thermal treatment; sol-gel process; α-Al_2O_3; phase transition

Aluminum oxide (Al_2O_3), traditionally referred to as alumina, is one of the most important ceramic materials that has a wide range of applications in various industrial areas, such as abrasive materials, refractory materials, and catalyst support[1]. The wide varieties of these applications result from the structural particularities existing in many different forms, namely transition aluminas (like γ, θ, δ phases) and its thermodynamically stable α-Al_2O_3[2]. Various synthesis routes are possible for alumina, such as mechanical milling[3], hydrothermal method[4], and sol-gel[5,6], each leading to different shapes, morphologies and surface properties. Due to careful control of the kinetics, the good reproducibility of the preparation and the purity of the products, sol-gel process has been one important method for synthesizing alumina and other oxides in recent years[7-10].

During sol-gel process, alumina is mainly fabricated by calcination of precursor aluminum hydroxides, which can be in crystalline and gelatinous form. Basically, the common precursors in synthesizing alumina are three aluminum trihydroxides $Al(OH)_3$ (gibbsite, nordstrandite and bayerite) and two aluminum oxyhydroxides AlO(OH) (boehmite and diaspore)[6,11]. Boehmite [γ-AlO(OH)] remains the most important precursor or intermediate for preparing alumina, and interest is recently renewed and highlighted[12,13]. The properties of alumina ceramic are determined not only by the purity of the alumina powder, but also the morphology, particle size, and distribution of the alumina particles. A thorough knowledge of alumina hydroxide precursor and its thermal evolution is fundamental to obtain a pure, well-defined and reproducible sample.

In this current work, we are interested in the sintering characteristics of a commercial alumina precursor, boehmite sol, for the precursor has high solid content, high ceramic yield and relatively low phase transition temperature. Different temperatures sintering were performed on the boehimte precursor, with the purpose of investigating the formation of different phase alumina. To study the structural evolution with the rise of annealing temperature, the as-received and heat-treated samples have been investigated by a series of classical characterization techniques including X-ray diffraction (XRD), thermogravimetry and differential scanning calorimetry (TGA-DSC), fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The transmission electron microscope analyses (TEM) characterized the size and morphology of the final products at 1200 ℃.

1 Experiment

The precursor of alumina employed in this work is commercial boehmite sol (A-4-20), produced by Snow Chemical S&T Col., Ltd., China. The basic information of raw

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sol given by the manufacturers is listed in Table 1 given by the manufacturers. The sol has high solid content, high ceramic yield and low viscosity. The average grain size of boehmite, ~12 nm, was very small. The boehmite gel was prepared by the gelatinization of sol in water bath at 80 ℃ for about 24 h. The as-received gel was dried at 200 ℃ for 1 h, and was then crushed and ground into fine powder. Finally, heat-treatments in a wide temperature range, 500~1400 ℃ in air for 1 h with heating rate of 10 ℃/min were performed on the gels for investigating temperature dependent phase of boehmite precursor.

To determine formation temperature of Al_2O_3, the dried gel boehmite was analyzed by TGA-DSC apparatus on SDTQ600 equipment from 40 ℃ to 1200 ℃ with a heating rate of 10 ℃/min in air. All prepared samples (as received and calcined gels) were analyzed at room temperature by XRD experiments on a Bruker D8 Advance instrument (Cu Kα radiation, λ= 0.154 18 nm). The scanned angles (in 2θ scale) were ranged between 10° and 80°, with a step of 0.02° and a counting time of 0.2 s/step. FT-IR spectra were recorded in the range 400~4000 cm^{-1} with Nicolet Avatar-360 apparatus using pressed KBr pellets to verify the vibrational modes present in the as-received and calcined gels. The NMR measurements were made with a Varian InfinityPlus 300 spectrometer in a nominal field of 7.05 T at Larmor frequency of 78.13 MHz. The ^{27}Al spectra were observed using a magic angle spinning (MAS) probe. Rotors of 4 nm were used at a rotation frequency of approximately 8 kHz using as reference a solid sample of $Al(NO_3)_3$ (^{27}Al, d=0 ppm). The morphologies and the micro- structure of as received gel and calcined powder were examined by TEM (Tecnai F20 high resolution microscope) operated at 200 kV. A small amount of powders were dispersed in alcohol using an ultrasound bath. Then a droplet was deposited on a carbon-coated grid and dried under a UV lamp. Particle size distributions of boehimte sol and prepared α-Al_2O_3 powders were analyzed using Malvern Mastersizer- 2000 model analyzer.

2 Result and Discussion

2.1 Microstructure of the boehmite precursor

The representatives XRD pattern of the as-received precursor is shown in Fig.1. It can be seen that only one phase is identified in the sample, indicating the phase-pure nature of the precursor. All the reflections can be easily indexed to the orthorhombic boehmite [γ-AlO(OH)] (JCPDS Card No.21-1307), exhibiting a typical profile which has an orthorhombic unit cell with space group Cmcm[11]. The crystallite size of precursor about 10.3 nm was calculated from XRD using Scherrer's equation. This estimation from XRD is consistent with the data provided by the manufacturer in Table 1. Fig.2 shows the particle size distribution of precursor, and the mono-modal distribution of original boehmite with d_{50}≈10.0 nm is detected.

Table 1 Properties of boehmite sol

Solid content/wt%	pH	Size/nm	Viscosity/ mPa s	Ceramic yield (1200 ℃, wt%)
24.5	3.5	10~12	10.0	17.3

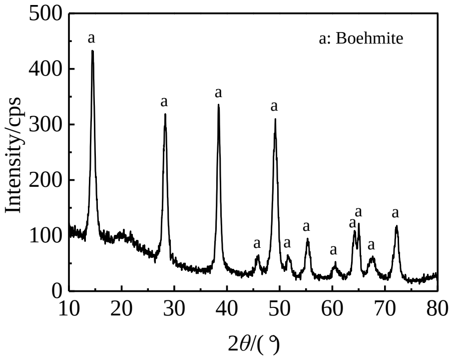

Fig.1 XRD pattern of boehmite precursor

From TEM images of boehmite precursor, as shown in Fig.3, it can be seen that the morphology of boehmite precursor is flake-like shapes of less than 10 nm in diameter and 20 nm in length[14], which is consistent with the data of particles size obtained by XRD (10.3 nm). Note the homogeneity level of boehmite precursor is very high, which is beneficial to the formation of Al_2O_3 at lower temperature[8].

2.2 Thermal evolution of boehmite precursor

2.2.1 Thermal analysis (TGA-DSC)

Representative results of the thermal analysis of the boehmite precursor are displayed in Fig.4. The thermogravimetric plot shows two major mass losses, following a continuous lower mass decrease up to 1200 ℃. The first mass loss occurs between 25 ℃ and 200 ℃, and the loss of 7.8% of the initial mass is attributed to water molecules absorbed in the crystalline lattice, forming a dry boehmite[6]. The second step (about 16.5% of mass loss), between 200 ℃ and 520 ℃, is related to the removal of structural water and dehydration of surface hydroxyls in the phase transition γ-Al_2O_3 phase, with a sharp peak in 510 ℃[15]. These mass loss events agree well with the endothermal events on the DSC curve and correspond to the departure of water molecules in at least two stages. From 520 ℃, the loss rate is lowered and a large exothermic

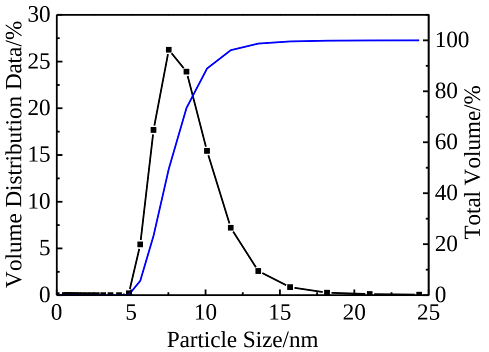

Fig.2 Particle size distribution of the boehmite sol

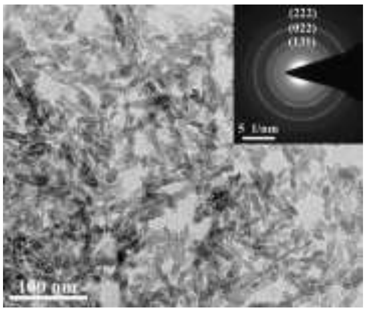

Fig.3 TEM image and SAED pattern of boehmite precursor

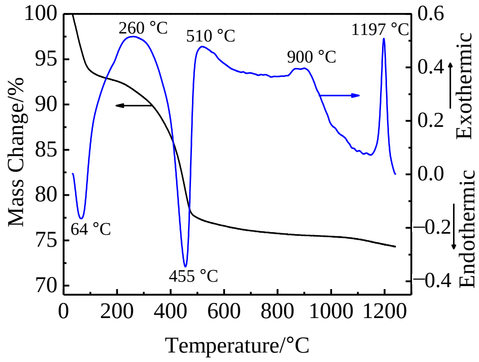

Fig.4 TG-DSC curves of boehmite precursor

profile is observed with maxima at about 520 ℃ and 900 ℃, which corresponds to the simultaneous departure of water and the classical successive phase transformation from γ-Al_2O_3 to thermo-dynamically metatestable transition aluminas, e.g., δ-Al_2O_3 and θ-Al_2O_3[11,16,17]. Finally, from 1100 ℃, although there is no mass loss, DSC curve shows an exothermic peak between 1130 ℃ and 1220 ℃, with the maximum centered at 1197 ℃, which is associated with the transformation from θ-Al_2O_3 into thermodynamically stable phase, α-Al_2O_3[11].

2.2.2 XRD analysis

Based on the above TG-DSC results, the boehmite precursors were calcined at different temperatures for 1 h in air. XRD patterns of their calcined derivatives (from 300 ℃ to 1400 ℃) are shown in Fig.5. When the boehmite gel is heated up to 300 ℃, the profile remains unchanged. This fact indicates that there is only a dehydration process which does not affect the crystallinity of the material (Fig.4). The calcination of gel at 500 ℃ leads to γ-Al_2O_3 phase[18], and then the phase transforms into δ-Al_2O_3 at 1000 ℃. After calcining at 1100 ℃, the occurrence of phase transition indicates that the co-existence of intermediate phases are detected, and the peaks may be indexed to tetragonal δ-Al_2O_3 (JCPDS Card No. 46-1131) and monoclinic θ-Al_2O_3 (JCPDS Card No. 35-0121)[19,20]. And the initial formation of α-Al_2O_3 is also detected in 1100 ℃ heat-treated powders. When the calcination temperature reaches to 1200 ℃, intermediate phases disappear and all the alumina

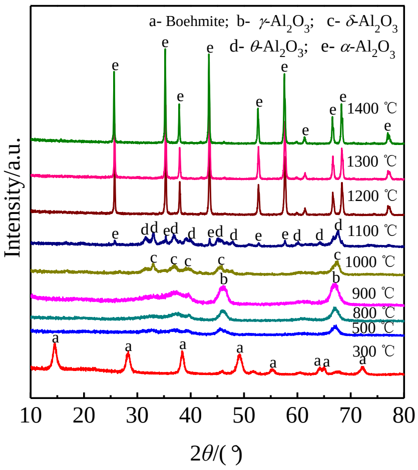

Fig.5 XRD patterns of dried boehmite heated products

is found to be transformed into a single stable α-Al_2O_3 phase and peaks can be indexed to the hexagonal unit cell (a=b=0.4758 nm, c=1.299 nm, JCPDS Card No. 42-1468)[20]. The sharp peaks of the α-phase indicate the relatively large grain sizes and well-defined long-range order in corundum.

2.2.3 FT-IR spectroscopy

FT-IR analysis has been used as a useful technique to study the difference, transformation of aluminium oxy-hydroxide, like bohemite. The FT-IR spectra of the as-prepared and annealed samples are shown in Fig.6. It is clear from the figure that the absorption bands of boehmite phase are at 3300, 3105, 1380, 1149, 1065, 744, 626 and 505 cm^{-1}, which are precisely consistent with those reported in literature[4,12,17,21-23]. The strong band at 3300, 3105 cm^{-1} can be assigned to the v_{asym} (Al)O-H and v_{sym} (Al)O-H stretching vibration, and the bands at 1065, 1149 cm^{-1} are attributed to the v_{sym} Al-O-H and v_{asym} Al-O-H modes of boehmite, respectively[22]. The torsional modes at 744 cm^{-1} and v Al-O (at 626 cm^{-1}) and δ Al-O (at 505 cm^{-1}) are also observed in these spectra. The shoulder at 3477 cm^{-1} and the weak band at 1652 cm^{-1} can be assigned to the stretching and bending modes of the absorbed water. The peak at 1652 cm^{-1} is assigned to the bending mode of water molecules in the bohemite structure[4]. Therefore, FT-IR analysis confirms that the pristine sample is pure phase of boehmite [γ-AlO(OH)].

With calcination temperature increasing, both width and intensity of the O-H band stretching vibration mode between 3200 and 3600 cm^{-1} decrease, which is due to decreasing in number of water molecules, the boehmite structure collapsed and the IR spectrum exhibits stronger broadening band 1000~400 cm^{-1} with two partly resolved bands at 594 and 776 cm^{-1} correspond to Al-O vibration, and a broad feature at 3449 cm^{-1} from residual adsorbed hydroxyls. When the annealing temperature is1200 ℃, the broadband split into two bands which is representative of α-alumina, one of which is between 1000 and 500 cm^{-1}, the other between 500 and 400 cm^{-1}.

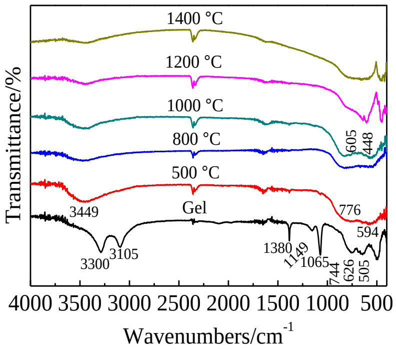

Fig.6 FT-IR spectra of dried boehmite gel and its heated products

After the boehmite precursor is annealed at 1400 ℃, the two bands become narrow and sharp that indicates the crystalline size is bigger. Therefore, the above FT-IR analysis is consistent with the XRD results[22].

2.2.4 NMR spectroscopy

The NMR spectra of boehmite precursor and its derivatives heated at different temperatures are shown in Fig.7. The signals of commercial boehmite at 5~6×10^{-6} related to octahedral aluminum (AlO_6), are typical of hydroxides in accordance with the literatures[11,13,17,23]. The products of calcinations at 500 ℃ exhibit characteristic profiles of γ-Al_2O_3, such as signals between δ 5×10^{-6} and 6×10^{-6} for the sites of octahedral aluminum (AlO_6) and signals between δ 63×10^{-6} and 67×10^{-6} for the sites of tetrahedral geometry (AlO_4). From 800 ℃, We can observe, by modifying the profile of spectrum and increasing the percentage of terahedral sites, the formation of other phases of alumina such as δ-Al_2O_3 and θ-Al_2O_3, as described in the literatures, and also in the XRD analysis. Finally, the sample calcined at 1200 ℃ has the typical profile of α-Al_2O_3, which is observed only in the presence of a signal at δ 10.25×10^{-6}, related to the octahedral sites[11,23].

2.3 Characterization of boehmite-derived alumina

Fig.8 shows SEM image and particle size distribution of α-Al_2O_3 nano-powders calcined at 1200 ℃ for 1 h. As shown in SEM images, the α-Al_2O_3 particles obtained from boehmite are discrete particles and show less agglomeration, with the particle size of about 50.0 nm.

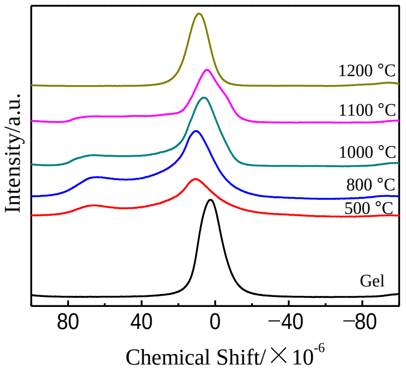

Fig.7 NMR spectra of dried boehmite gel and its heated products

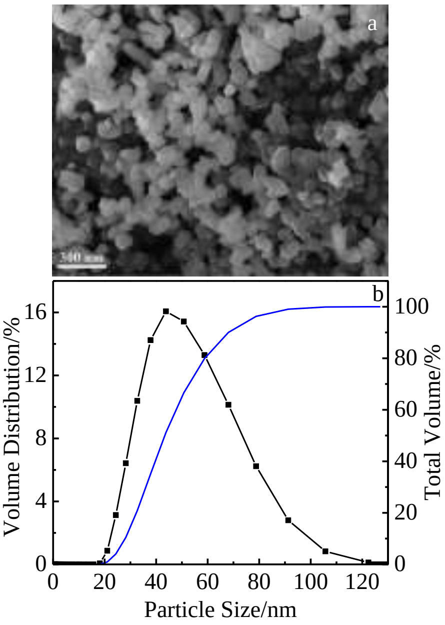

Fig.8 SEM image (a) and size distribution (b) of the Al_2O_3 powder obtained at 1200 ℃ for 1 h

Fig.9 shows TEM images of precursor boehmite powders calcined at 1200 ℃, which consists of aggregates of particles lower than 100 nm in size, and this is consistent with the data of particles size obtained by XRD (50.0 nm). Fig.9b shows a high resolution TEM image. The distance between the crystallographic planes observed is 0.346 nm, which fits with the interplanar distance between (012) crystal planes of α-alumina. Electron diffraction of these particles shows that all of them are

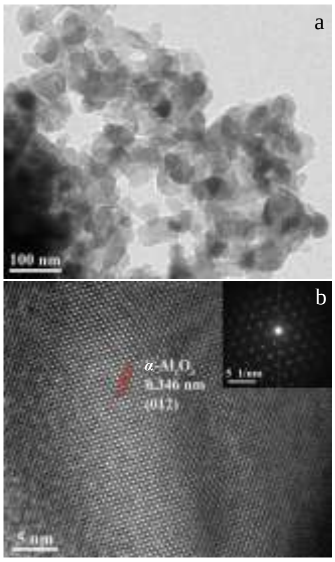

Fig.9 TEM image (a) and diffaction pattern (b) of dried boehmite gel sintered at 1200 ℃

crystalline, the lattice structure of alumina is neat, as in the upper right corner of Fig.9b. The crystallinity of alumina increases more as compared to boehmite phase and bright spots appear in diffraction patterns at 1200 ℃ due to the long-ranging ordering of unit cells with the annealing temperature.

3 Conclusions

1) The sol-gel process is used for synthesizing α-alumina by calcinations of a commercial boehmite precursor.

2) Progressive dehydration and elimination of hydroxyl groups from the boehmite at 500 ℃ leads to its transformation into transitional alumina phase, γ-Al_2O_3. During calcinations at temperatures ranging from 1000 ℃ to 1400 ℃, the conversion of γ-Al_2O_3 into the thermodynamically stable α-Al_2O_3 occurs very gradually, leading to the appearance of other transitional alumina phases, like δ-Al_2O_3 and θ-Al_2O_3.

3) The XRD patterns of the samples indicate the good crystalline nature.

4) FT-IR analysis show that with the calcination temperature increasing from 500 ℃ to 1200 ℃, the intensity and width of the corresponding vibrational and stretching modes are reduced, and boehmite converts to α-Al_2O_3.

5) The tetrahedral and octahedral sites in each phase are characterized in terms of their NMR chemical shifts.

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勃姆石及其物相热演变的表征与溶胶-凝胶法制备氧化铝

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摘　要：在溶胶-凝胶工艺制备氧化铝粉体过程中，对其前驱体结构相变的渗入研究是获取高纯氧化铝粉体的重要基础性工作。本实验在空气中、300~1400 ℃温度范围内对一种商业勃姆石溶胶进行了热处理 1 h。TG-DSC 分析了前驱体勃姆石在热处理过程中的结构相变。当热处理温度由室温升至 1400 ℃过程中，采用 XRD、FT-IR、NMR 和 TEM 分析了勃姆石的结构相变。结果显示，勃姆石在 500 ℃时转变为γ-Al_2O_3，接着在 1000 ℃时转变为δ-Al_2O_3；而当热处理温度提高至 1100 ℃时，2 种氧化铝过渡相δ-Al_2O_3, θ-Al_2O_3和部分α-Al_2O_3共同存在。在 1200 ℃热处理后，所有亚稳态的氧化铝物相都转变至α-Al_2O_3。在 1200 ℃/1 h 制备的α-Al_2O_3粉末尺寸约在 50 nm，并且具有较好的分散性和较窄的粒径分布。

关键词：勃姆石；热处理；溶胶-凝胶法；α-Al_2O_3；结构相变

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