Preparation of High-purity Alumina via Hydrolysis of Aluminum Isopropoxide after Desilication with Lanthanum Oxide

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Abstract. High-purity alumina refers to ultra-fine alumina powder with a purity exceeding 99.99% and a uniform particle size. This material exhibits excellent corrosion resistance, high-temperature resistance, wear resistance, and oxidation resistance. Owing to the high silicon content of alumina prepared by means of the alcohol-aluminum hydrolysis method, the purity of the alumina is often unsatisfactory. Therefore, in this work, a new method for adding lanthanum oxide to isopropanol in the early aluminum isopropoxide synthesis stage is proposed. When lanthanum oxide was added, the silicon content of the precursor aluminum isopropoxide decreased to 0.0051%. Remove calcium, sodium, magnesium and other impurities by cleaning with hydrochloric acid under an ultrasonic field. The optimal hydrolysis conditions were determined as follows: hydrolysis temperature: 55, hydrolysate concentration: 80%, water to alkoxide ratio: 6:1. The alumina precursor calcined at 1200 yielded a high-purity alumina with a purity level of more than 99.99%, and the particle size reaches 2.037 μm.

Keywords: High-purity Alumina; Lanthanum oxide; Hydrolysis; Roasting.

1. Introduction
High-purity alumina refers to high-quality alumina with Al$_2$O$_3$ content exceeding 4N. This is an important structural and functional material that exhibits excellent properties such as high corrosion resistance, temperature resistance, wear resistance, and oxidation resistance, and is widely used in various fields (e.g., metallurgy, chemistry, optics, electricity, physics, aerospace) $^{[1-3]}$. Recently, the demand for high-purity alumina has grown rapidly in the fields of display materials, energy, automobiles, and semiconductors$^{[4]}$, thereby increasing the requirements for the preparation of this material. High-purity alumina can be prepared by means of various synthesis methods, including (for e.g.,) the Bayer method, ammonium aluminum sulfate pyrolysis method, ammonium aluminum carbonate pyrolysis method, sol-gel method, and aluminum alkoxide hydrolysis method $^{[5,6]}$. At present, the method of aluminum alkoxide hydrolysis, which is characterized by fast reaction speed, high purity of the product, alcohol recycling, and reuse, is considered suitable for the preparation of high-purity alumina. Companies, such as 5N alumina manufacturers of America and Germany and Sumitomo Chemical Corp. of Japan $^{[7-10]}$ use this method as the main means of producing high-purity alumina. The principle of this method is that isopropanol reacts with aluminum under the action of a catalyst, thereby producing aluminum isopropoxide. The isopropanoxide is then hydrolyzed in an aqueous solution to produce pseudo boehmite, which is calcined to form high-purity alumina.
2. Experimental

2.1. Materials
Commercially available high-purity aluminum granules (purity: 99.9%, content of silicon impurities: 0.0298%) were used as the main raw material in this work. Isopropanol (water content: ≤0.2%) was used as a reagent for the synthesis of aluminum alkoxide. Aluminum chloride powder was employed as a catalyst. In addition, high-purity deionized water was prepared in the laboratory.

2.2. Procedure
Isopropyl alcohol is highly water absorbent. In this work, for water absorption by isopropyl alcohol, anhydrous bulk calcium oxide was added to the alcohol \(^{[12]}\), and left to stand for 2–3 days. The isopropanol with the water removed was filtered via suction filtration under a low pressure, and was then subjected to atmospheric distillation. Three ends of a three-necked flask were connected to spherical condenser tubes. Afterward, aluminum particles and isopropyl alcohol were added to the bottle, and a rare earth oxide lanthanum oxide was fully reacted at 82.5°C until the aluminum particles disappeared completely. This mixture was subjected to vacuum distillation aimed at obtaining an aluminum isopropoxide colloid, which was subsequently dried at 100°C. The dried isopropoxide was then mixed with the prepared hydrolysate (a mixture of isopropanol and deionized water) using a constant temperature collector magnetic stirrer. Subsequently, the hydrolyzed dried product was placed in a corundum crucible for high-temperature roasting at 1200°C in a high-temperature box-type resistance furnace. A schematic of the preparation process for obtaining high-purity alumina powder is shown in Fig 1. Ultrasonic pickling of the obtained powder yielded a final powder purity of 99.9906%. A temperature control electric heating jacket, vacuum pump, constant temperature magnetic stirrer, electronic balance, constant temperature blast drying oven, SX2-12-16 high-temperature box-type resistance furnace, and ultrasonic cleaning machine are employed during testing. The hydrolysis of aluminum alkoxide, which yields alumina, involves the following steps:

\[
2\text{Al} + 6\text{ROH} = 2\text{Al(OR)}_3 + 3\text{H}_2\uparrow \tag{1}
\]

\[
2\text{Al(OR)}_3 + 4\text{H}_2\text{O} = \text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} + 6\text{ROH} \tag{2}
\]

\[
\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \tag{3}
\]

![Figure 1. Preparation method and processing of high-purity alumina](image)

2.3. Analysis
The Al\(_2\)O\(_3\) content and the phase composition of each sample were evaluated by means of inductively coupled plasma mass spectrometry (ICP-MS) and high-temperature X-ray diffraction (XRD; X’pert PRO MPD, PANalytical), respectively. Furthermore, the micromorphology of the Al\(_2\)O\(_3\) was determined via transmission electron microscopy (TEM; Tecnai G2 F20). A laser particle size analyzer was used to assess the particle size of each sample.
3. Results and Discussion

3.1. Synthesis of Aluminum Isopropoxide

3.1.1. Effect of La\(_2\)O\(_3\) on the purity of aluminum isopropoxide. Aluminum isopropoxide is an important raw material for the synthesis of high-purity alumina precursors, and its impurity content will directly affect the purity of alumina products. Silicon is the most important impurity in the raw material, and maximum levels of removal are essential for realizing high-purity products. Therefore, during the synthesis stage of aluminum isopropoxide, experiments involving the addition of a lanthanum oxide (La\(_2\)O\(_3\)) desilication agent are performed to determine the effect of lanthanum oxide on the impurity content of aluminum isopropoxide. Experiments without this addition are also performed (see Table 1). When no desilication agent is added, the silicon content of aluminum isopropoxide synthesized (maximum: 0.0175\%) is higher than that of the isopropoxide without the agent. However, when the La\(_2\)O\(_3\) desilication agent is added, the silicon content is reduced to 0.0051\%, indicating that in the synthesis stage of the isopropoxide, La\(_2\)O\(_3\) can play a key role in silicon-impurity removal. The addition of La\(_2\)O\(_3\) introduces no new impurities, thereby ensuring the purity of the aluminum isopropoxide.

| Sample | Si    | Fe    | Ca    | Na    | Mg    | Cu    | La     | total  |
|--------|-------|-------|-------|-------|-------|-------|--------|--------|
| No Additive | 0.0175 | 0.0029 | 0.0023 | 0.0017 | 0.0014 | <0.0001 | -- | 0.0263 |
| Additive of La\(_2\)O\(_3\) | 0.0051 | 0.0027 | 0.0024 | 0.0017 | 0.0012 | <0.0001 | <0.0001 | 0.0138 |

3.2. FTIR Analysis of Aluminum Isopropoxide

Fig 2. shows the FTIR spectrum of aluminum isopropoxide synthesized after desilication with La\(_2\)O\(_3\). In the figure, the absorption peak of 3398 cm\(^{-1}\) corresponds to the H-O bond stretching vibration absorption band. Similarly, the absorption peaks at 3000, 2963, 2865, 2846, 1386, and 1374 cm\(^{-1}\) correspond to the absorption peak of the isopropyl skeleton. The absorption peak occurring at 1034 cm\(^{-1}\) results from the C-O stretching vibration peak connected with Al, and the absorption peak at 613 cm\(^{-1}\) arises from the asymmetric vibration peak of the Al-O bond. A comparison of the peak with the standard peak corresponding to isopropanol aluminum, as shown in Table 2, reveals that the peak of the synthesized product basically corresponds to the standard peak of the isopropanol aluminum.

| Sample | Wavenumbers /cm\(^{-1}\) |
|--------|-------------------------|
| standard aluminum isopropoxide | 3427, 2997, 2971, 2867, 2846, 1386, 1374, 1035, 614\(^{13,14}\) |
| synthetic products | 3398, 3000, 2963, 2865, 2846, 1386, 1374, 1034, 613 |

3.3. Hydrolysis of Aluminum Isopropoxide on Precursor

3.3.1. Effect of temperature on precursor. The hydrolysis temperature can control the supersaturation...
and the free energy of the solute comprising the hydrolysis system, thus affecting the nucleation of the hydrolysate crystals and smaller crystal size\cite{16}. Prior to the process, the prepared aluminum isopropoxide and the prepared hydrolysate (isopropanol + deionized water) are placed in a collector magnetic stirrer for stirring. Hydrolysis temperatures of 45 °C, 55 °C, 65 °C, 75 °C, and 85 °C are employed. In addition, XRD and particle size measurements are performed on the hydrolysate (see Fig 4 for the corresponding results).

As shown in Fig 3. (a), diffraction peaks occur at $2\theta = 14^\circ$, $2\theta = 28^\circ$, $2\theta = 38^\circ$, $2\theta = 49^\circ$, $2\theta = 65^\circ$, and $2\theta = 72^\circ$. A comparison with the PDF standard card (01-1283) indicates that the hydrolysates hydrolyzed under different hydrolysis temperature conditions are pseudoboehmite, confirming that the hydrolysis temperature has no effect on the crystal structure of the hydrolysate. The XRD pattern shows that the diffraction peak of the hydrolysate is strong and narrow at a hydrolysis temperature of 55 °C, where the level of crystallinity is the highest. The particle size of the hydrolysate is determined and, as Fig 3. (b) shows, the smallest particle size occurs at this temperature. The nucleation rate of the nucleus is accelerated, and the growth rate of the crystal nucleus is lower than the nucleation rate, thereby inhibiting the growth of the crystal nucleus.

![Figure 3. Product spectra at different hydrolysis temperatures (a) XRD spectrogram (b) size distribution (c) average grading)](image)

### 3.3.2. Effect of hydrolysate concentration on precursor

To ensure the purity of the precursor, deionized water and isopropyl alcohol are used as the solvent and solute, respectively, of the hydrolysate in the hydrolysis process. A high concentration of hydrolysate will accelerate the hydrolysis of aluminum isopropoxide. Hydrolysis concentrations of 10%, 20%, 40%, 60%, 80%, and 90% are employed.

Fig 4(a). shows that various concentrations of the hydrolysate used in the hydrolysis process yield the same crystal structure, i.e., pseudoboehmite (01-1283), of the obtained hydrolysate. This confirms that the concentration of hydrolysate has no effect on the crystal structure of the hydrolysate. Fig 4(a). shows that the intensity and width of the XRD diffraction peak are almost the same under the five conditions. These results confirm that the concentration of hydrolysate has almost no effect on the hydrolysis of aluminum isopropoxide. The lowest particle size of the hydrolysate is obtained at a concentration of 80%.

![Figure 4. Analysis of products with different hydrolysate concentrations (a) XRD spectrogram (b) size distribution(e) average grading)](image)
3.3.3. Effect of the mass ratio of solvent (water content) to aluminum isopropoxide on precursor. The mass ratio of water added to the hydrolysate to the mass of aluminum isopropoxide is 2:1, 3:1, 4:1, 5:1, 6:1. Fig 5. (a) shows that these different mass ratios of solvent (water content) in the hydrolysis process yield the same crystal structure, i.e., pseudoboehmite (01-1283), of the hydrolysate. This confirms that the concentration of hydrolysate has no effect on the crystal structure of the hydrolysate. A strong and narrow XRD diffraction peak occurs when the content of water in the hydrolysate to the mass ratio of aluminum isopropoxide reaches 6:1 (see Fig 5(a)). Moreover, the results in Fig 5(a) and Fig 5(b) indicate that during the hydrolysis of aluminum isopropoxide, the hydrolysis reaction is accompanied by polycondensation reactions. The polycondensation reaction produced by aluminum isopropoxide molecules will affect the average crystal size. When the water content is excessively high, water molecules cover the crystal surface, resulting in a low crystal growth rate. When the crystal growth rate is lower than the crystal nucleation rate, the crystal particle size will be low.

![Figure 5](image_url) Effect of the mass ratio of solvent (water content) to aluminum isopropoxide on precursor((a)XRD spectrogram (b)size distribution (c)average grading)

4. TG-DSC Analysis of Precursor

TG-DSC analysis was performed on the aluminum isopropoxide hydrolysate. Fig 6. shows that the hydrolysate undergoes significant weight loss at 100 °C and an endothermic peak appears in the DSC curve. This stage involves evaporation of the water attached to the surface of the alumina precursor. An endothermic peak appears at 400 °C in the DSC curve, and the TG curve reveals significant weight loss of the precursor. The crystal water inside the precursor crystals evaporates during this stage. An exothermic peak appears at 1000 °C in the DSC curve, and the TG curve changes only slightly. This stage corresponds to the phase transformation phase of the alumina precursor. An exothermic peak occurs at 1200 °C, and the TG curve changes only modestly. When the temperature continues to rise, the DSC and TG the curves change significantly, confirming that the crystalline form of the alumina precursor is gradually stabilized after roasting at this temperature. Therefore, calcination temperatures of 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1200 °C, and 1300 °C are employed.

![Figure 6](image_url) TG-DSC of high purity alumina precursor

The precursor of high-purity alumina prepared via hydrolysis of aluminum alkoxide was discussed above. Various hydrolysis conditions (hydrolysis temperature: 55 °C, hydrolysate concentration: 80%, and water to alkoxide ratio: 6:1) of the alumina precursor placed in a muffle furnace for
high-temperature roasting are now considered. In the calcination process, the alumina precursor will undergo a phase change, and its specific surface area, crystal structure, and microscopic morphology thereof will change during this phase change process.

According to the experimental results of TG-DTG, the precursor was put into a muffle furnace and calcined to 600°C, 800°C, 1000°C, 1200°C, 1300°C, and kept for 1h.

4.1. Roasting of Precursor to Prepare High-purity Alumina

4.1.1. XRD analysis of high-purity alumina. Fig. 7 shows that when the calcination temperature reaches 600 °C, 800 °C, 1000 °C, and 1200 °C, the XRD diffraction peak of the calcined product changes significantly. This indicates that the crystal form of the product varies with the temperature. When the calcination temperature exceeds 1200 °C, the shape of the XRD diffraction peak corresponding to the calcined product remains the same. The XRD pattern obtained for the 1200 °C product concurs with the PDF card, i.e., the strong peak of the product is completely consistent with α-Al2O3. The absence of other peaks indicates that the calcined product is pure α-Al2O3.

The XRD data was refined (see Table 4 for a summary of the data obtained). The crystallinity of the calcined product under five temperature conditions increased with increasing temperature. Furthermore, the highest level of crystallinity (94.01%) and the finest grain (3.15 µm) are obtained for the material calcined at 1200 °C.

4.1.2. TEM analysis of high-purity alumina. The crystal structure of the high-purity alumina was determined by means of TEM measurements. For this determination, the DM software is used to convert the obtained HRTEM image into a diffraction pattern Fig 8. The diffraction pattern is punctuated, and the crystal plane spacing is obtained. Furthermore, the hydrolysate is calcined at 1200 °C for 4 h. The TEM-EDS results of the obtained high-purity alumina are shown in Fig 9. The EDS results show that the alumina consists only of Al and O elements, indicating that alumina with relatively high purity has been prepared.

Figure 7. XRD spectrum of high-purity alumina at different calcination temperatures

Figure 8. Product diffraction pattern ((a) Diffraction pattern (b) Diffraction pattern crystal plane spacing punctuation)
Table 3. Product diffraction pattern of each punctuation plane spacing

| Spot# | d-Spacing/nm | Spot# | d-Spacing/nm |
|-------|--------------|-------|--------------|
| 1     | 0.1655       | 6     | 0.2091       |
| 2     | 0.1622       | 7     | 0.2084       |
| 3     | 0.1605       | 8     | 0.2073       |
| 4     | 0.1603       | 9     | 0.2208       |
| 5     | 0.2132       | 10    | 0.2218       |

Figure 9. TEM-EDS analysis of high-purity alumina

4.1.3. Removal of impurities using ultrasound and hydrochloric acid. Take the precursor powder and put it into a muffle furnace and roast it to 1200°C and keep it for 1 hour. Put the calcined alumina powder into the ultrasonic field and use hydrochloric acid to remove impurities. During the alumina calcination process, the crystals expand and become loose due to the removal of moisture and phase change. Defects, gaps, pores, and fine dispersion appear inside and on the crystal surface. At this time, acid elution of impurities with hydrochloric acid solution can remove intercrystalline impurities exposed after high-temperature calcination. Ultrasonic wave has the characteristics of short wavelength, along a straight line, and concentrated energy. It has strong dispersion and impact on particles, so it has a strong impurity removal effect. The pickling conditions are hydrochloric acid concentration of 50g/L, liquid-solid ratio (mL/g) 20:1, and pickling temperature of 60°C.

The purity of alumina is analyzed by ICP-MS, and the purity of alumina can be calculated by formula. The alumina impurity content before and after removing impurities is shown in the table:

\[
\eta = 1 - \sum_{i=1}^{n} x_i \times 100\%
\]

\(\eta\): The purity of alumina

\(X_i\): Impurity content

Table 4. Alumina content (%) obtained by calcination

| Impurities | Si   | Fe   | Ca   | Na   | Mg   | Total  |
|------------|------|------|------|------|------|--------|
| Content before (%) | 0.0051 | 0.0027 | 0.0024 | 0.0020 | 0.0012 | 0.0139  |
| Content after (%)  | 0.0049 | 0.0027 | 0.0018 | <0.0001 | <0.0001 | 0.0094  |

The impurities in the high-purity alumina are analyzed via ICP-MS. The determined purity of the final prepared alumina (99.9906%) meets the purity requirements of high-purity alumina.

5. Conclusions

(1) Adding La₂O₃ reduces the silicon-impurity content from 0.0175% to 0.0051% without introducing new impurities, thereby ensuring the purity of aluminum isopropoxide.

(2) The results of the precursor preparation process performed via aluminum isopropoxide hydrolysis...
show that the hydrolysis temperature, the concentration of the hydrolysate, and the concentration of water and alkoxide have a significant effect on the precursor. XRD crystal parameters indicate that the optimal hydrolysis conditions are a hydrolysis temperature, hydrolysate concentration, and water to alkoxide concentration of 55 °C, 80%, and 6:1, respectively.

(3) The specific surface area of alumina decreases gradually with increasing calcination temperature. Moreover, the highest crystallinity level of alumina (94.03%) and the smallest grain size (2.037 μm) occur at a temperature of 1200 °C. At this roasting temperature, α-Al2O3 with a purity of 99.9906% is obtained.

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