

Preparation of Alumina from Heated Kaolin Leached by Citric Acid with AACH as an Intermediate

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ABSTRACT: Because the supply of bauxite ores in many countries is becoming deficient, a process of preparing alumina from an alternative resource, namely, kaolin, is proposed in this work. First, kaolin was heated at 600 °C for 2 h before being leached with 1 M citric acid solution, about 75% of the Al in kaolin entered the leachate as aluminum citrate (AlCit) solution. Then, about 50% of the Al(III) in the leachate could be precipitated as ammonium aluminum carbonate hydroxide (AACH) by addition of NH₄HCO₃ at pH 9.00 ± 0.50. The morphology of AACH characterized by SEM and TEM was spherical particles composed of many nanorods with sizes of about 500 × 25 nm. Finally, mesoporous γ -Al₂O₃ was obtained by roasting AACH at 700 °C. The Fe and Na contents in the obtained γ -Al₂O₃ product determined by XRD and ICP-AES were 2 and 0.1 ppm, respectively. The obtained γ -Al₂O₃ had a morphology similar to that of AACH, and its BET surface area was as high as 235.2 m²/g.

1. INTRODUCTION

Aluminum is the metal with the second highest output in the world. (Annual production of Al metal was reported to be 23.4 million tons in 2009.¹) For over 100 years, its precursor, alumina, has been produced by extracting bauxite ores with alkali, through the Bayer or sintering process. Currently, the supply of superior-grade bauxite (containing small amounts of silicon) is rapidly becoming deficient. This is a significant problem for those countries, such as China, that lack high-quality bauxite. On the other hand, there is a large reserve of kaolin in China. The chemical formula of kaolin is Al₂Si₂O₅(OH)₄,^{2–4} of which the alumina content could reach 30–40%, so kaolin might be able to substitute for bauxite in the production of alumina. However, the high content of silicon in kaolin makes it unsuitable to produce alumina by the conventional alkali method.^{5,6}

Theoretically, alumina in ores can be extracted by both alkali and acid. Many investigators have studied acid methods using inorganic acids or their ammonium salts^{7–10} and found that the presence of silicon does not disturb the digestion of alumina, but that iron oxides in ores are the greatest impediment to obtaining pure final product because the separation of Fe(II or III) from Al(III) in the following process is difficult.

In this study, we tried to leach alumina from kaolin by an acid method using citric acid as the leaching agent. Citric acid (H₃Cit, 3-carboxy-3-hydroxy pentanedioic acid, CAS 77-92-9) has three carboxylic groups in each molecule and shows moderate acidity and strong coordinating stability with metal ions. Some researchers have successfully extracted alumina from bauxite or clay to obtain aluminum citrate (AlCit), but the leaching kinetics did not report.^{11,12} Moreover, the method to obtain alumina from AlCit was reported by simply sintering, which is not economical or environmentally friendly. We believe that the citrate groups should be separated from Al(III), so that the leaching agent can be recycled. It has been confirmed that Al(OH)₃ cannot be

precipitated from AlCit solution, even if the solution is adjusted to be strong alkaline.^{13–15} Therefore, an intermediate product is needed to obtain alumina from AlCit solution. In a previous study, we suggested a novel process to prepare alumina from AlCit solution using dawsonite [NaAl(OH)₂CO₃] as an intermediate.¹⁶ Ammonium aluminum carbonate hydroxide (AACH) is also a dawsonite analogue.^{17,18} Because the byproducts of its thermal decomposition are only NH₃ and CO₂, AACH has been used as a precursor to alumina with high purity and fine structure.^{19–21} In the present work, we choose AACH as the intermediate compound to transform AlCit into alumina. In this way, the Na pollution in the process of the conversion of dawsonite into alumina would not be a problem, and a product alumina with a high specific surface area could be achieved.

2. EXPERIMENTAL SECTION

This work was performed only at the laboratory scale. The overall study was separated into several independent experiments. The details are as follows:

2.1. Materials. Kaolin clay mineral was offered by Zhengzhou Research Institute of CHALCO. Ammonium bicarbonate (NH₄HCO₃), citric acid, ammonia solution (25%), and other reagents were of analytical grade.

2.2. Procedures. *2.2.1. Pretreatment of Kaolin and Leaching with Citric Acid Solution.* The crushed kaolin (through 200 mesh) was heated at 600 °C for 2 h. Then, 10 g of the heated kaolin was immersed in 100 mL of 1 M citric acid solution in a high-pressure autoclave and heated at a certain temperature in the range of 80–250 °C for 0.5–2 h. After being allowed to cool to room

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temperature, the residue was filtered off, and the leachate of AlCit solution was obtained. The change in components in kaolin before and after citric acid leaching was detected by X-ray diffraction (XRD). To compare the leaching efficiency of aluminum species, the tests were repeated using 1 M H_2SO_4 as a leaching agent at 250 °C for 1 h.

2.2.2. Precipitation of AACH from AlCit Solution. The AACH was precipitated from AlCit solution at atmospheric pressure in a three-neck flask. AlCit solution was dropped into ammonium bicarbonate solution under agitation. The pH value was controlled around 9.00 ± 0.50 by adding aqueous ammonium solution. The temperature was kept at 25 or 50 °C in a water bath. After being allowed to age for several hours, AACH precipitate was filtered, washed with deionized water, and vacuum-dried at 80 °C. The conversion rate, α , of AlCit to AACH was defined as the ratio of Al content in AACH to that in AlCit. The obtained AACH was characterized by XRD, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2.2.3. Preparation of Al_2O_3 by Thermal Decomposition of AACH. The resulting AACH was roasted by a gentle heating program: first held at 200 °C for 30 min, then heated to 700 °C at a rate of 5 °C/min, and held at 700 °C for 2 h. The final alumina products were characterized by XRD, SEM, and TEM.

2.3. Characterization. XRD patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, graphite-filtered Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). Samples of the unoriented powders were step-scanned at an increment of 0.04° (2θ) per step using a count time of 10 s per step.

Elemental analysis was performed using a Shimadzu ICPS-7500 inductively coupled plasma-atomic emission spectrometer. All samples were dried at 100 °C for 24 h prior to analysis, and the solutions were prepared by dissolving the samples in dilute nitric acid solution (2 M) at room temperature.

SEM of the sample was performed using a Hitachi S4700 apparatus with the applied voltage of 20 kV. TEM images were recorded using a Hitachi H-800 transmission electron microscope operated at 100 kV.

Nitrogen adsorption measurements were carried out on test materials at liquid nitrogen temperature, using a model ASAP 2010 Micromeritics sorpometer (USA). The test samples were gassed with nitrogen at 130 °C for 3 h prior to measurements. The specific surface area (m^2/g) was calculated from the resulted isotherms by BET analysis.

3. RESULTS AND DISCUSSION

Three main steps are considered to prepare alumina from heated kaolin leached with citric acid: first leaching of Al from kaolin by citric acid solution, then precipitation of AACH in the leachate solution, and finally roasting of AACH to get the final alumina products.

3.1. Leaching of Al from Kaolin by Citric Acid. The XRD pattern of the as-received kaolin sample is shown in Figure 1 (curve i); it can be identified as the following mineral phases: kaolinite, alunite, and quartz. The molecular formula of kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, which can also be written as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.² In the crystal structure of kaolinite, the silicon–oxygen tetrahedra and alumina octahedra share the same oxygen atoms and interlace with each other, which makes it difficult to dissolve kaolinite by strong acid or alkali. As a result of

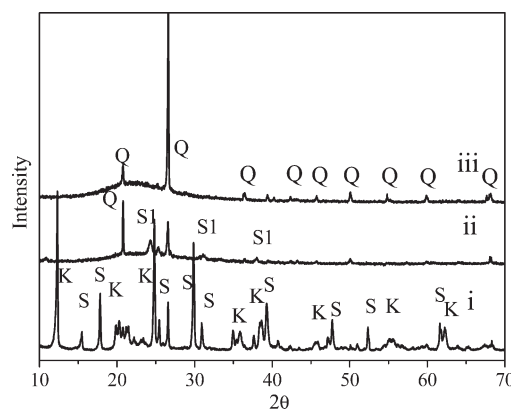


Figure 1. XRD patterns of (i) the original kaolin sample, (ii) the calcined kaolin, and (iii) the residues of calcined kaolin after leaching. [Q for quartz, K for kaolinite, S for $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$, A for $\text{Al}_2\text{Si}_4\text{O}_{10}$, and S1 for $\text{KAl}(\text{SO}_4)_2$.]

Table 1. Chemical Assay Results for the Original Kaolin Sample, the Calcined Kaolin Sample, and the Leachate of Calcined Kaolin Obtained with 1 M Citric Acid at 250 °C for 1.5 h

	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	LOI [Ⓛ]
kaolin (%)	34.7	40.3	0.09	0.30	0.39	21.2
calcined kaolin (%)	42.4	53.1	0.14	0.48	0.81	0.07
leachate solution (g/L)	34.8	0.02	0.09	0.01	—	—

[Ⓛ] LOI means loss on ignition, which is the weight of the mineral lost when roasted at 1050 °C.

calcination over 600 °C, dehydration of the crystallite lattice occurs, kaolinite is converted into amorphous meta-kaolin ($\text{Al}_2\text{Si}_2\text{O}_7$),^{22,23} and alunite [$\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$] changes to $\text{KAl}(\text{SO}_4)_2$ (curve ii in Figure 1). The XRD pattern of the residue of kaolin after being leached with citric acid solution is shown in curve iii in Figure 1: only the patterns caused by quartz could be observed. This can be explained by the fact that the forms meta-kaolinite and $\text{KAl}(\text{SO}_4)_2$ are easily dissolved by acidic solution.²⁴

The results of the chemical assay show that the contents of all components in kaolin somehow increased after calcination because of the mentioned dehydration (Table 1). The Al content in the leachate solution was 34.8 g/L, whereas the Si content was less than 0.01 g/L (in SiO_2) because SiO_2 is hardly dissolved in acid. The Fe content in the leachate was about 0.09 g/L (in Fe_2O_3), and the ratio of Al content to Fe content in the leachate was almost same as that in kaolin or calcined kaolin, because of the similar coordination constants of Fe(III) and Al(III) to citrate. The other metal species, such as Ca and Ti, are much less than expected because such metal citrates are less soluble.

The leaching efficiency of aluminum species from kaolin increases as the leaching temperature (below 250 °C, to avoid decomposition of citric acid) and time (Figure 2) are increased. The leaching efficiency was found to be 74% for 1 M citric acid at 250 °C for 2 h, whereas it was about 80% for 1 M H_2SO_4 in a comparison test.

The kinetics of leaching Al from the heated kaolin by citric acid solution was studied based on the leaching data (Figure 2). Plots of $[1 - \frac{2}{3}X - (1-X)^{2/3}]$ versus t [in which X is the leaching

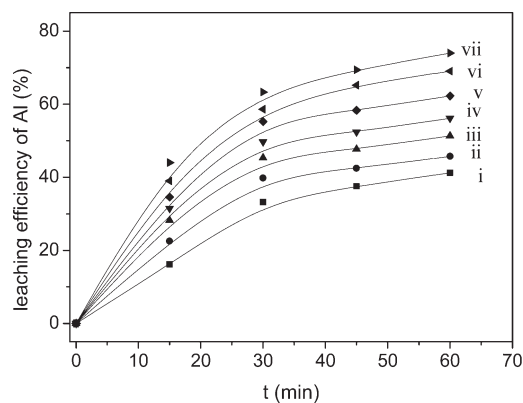


Figure 2. Leaching efficiencies of Al for different leaching times at different temperatures: (i) 80, (ii) 100, (iii) 130, (iv) 150, (v) 180, (vi) 200, and (vii) 250 °C.

Table 2. Conversion Rate α under Different Reaction Conditions

$n(\text{NH}_3\text{HCO}_3)/n(\text{AlCit})$	pH value (± 0.02)	temperature ($^\circ\text{C} \pm 0.1$ °C)	aging time (h)	conversion rate (%)
2	9.00	50.0	24.00	10.42
3	9.00	50.0	24.00	14.87
4	9.00	50.0	24.00	19.30
5	9.00	50.0	24.00	23.66
10	9.00	50.0	24.00	24.37
2	8.25	50.0	24.00	3.67
2	8.50	50.0	24.00	16.88
2	8.85	50.0	24.00	22.32
2	9.50	50.0	24.00	17.27
2	10.00	50.0	24.00	8.22
2	9.00	25.0	24.00	18.66
2	9.00	25.0	48.00	35.54
2	9.00	25.0	120.00	46.36
2	9.00	25.0	192.00	52.49
2	9.00	25.0	240.00	54.19
2	9.00	50.0	48.00	17.86
2	9.00	50.0	120.00	40.56
2	9.00	50.0	192.00	50.00
2	9.00	50.0	240.00	51.23

efficiency (w/w) and t is the leaching time (min)] give a straight line passing through the original data, which means the leaching process fits the product layer diffusion control model.^{6,9} That is, Al in the form of meta-kaolin or $\text{KAl}(\text{SO}_4)_2$ in heated kaolin particles reacts rapidly with citric acid solution, but the leaching agent and the leachate need to diffuse through the layer of silicate and sulfate on the particle surface, which is the rate-controlling step for the leaching process. Assuming that the acid concentration and the particle size are constant, linear regression was used to calculate k values from the slopes at different leaching temperatures. With these k values, the $\ln k$ values were plotted against $1/T$, with a linearly dependent coefficient of 0.9979. According to the Arrhenius equation, the leaching apparent activation energy E_a was calculated as 13.55 kJ/mol.

3.2. Precipitation of AACH from AlCit Solution. When AlCit solution was adjusted to be alkaline, no $\text{Al}(\text{OH})_3$ precipitated,

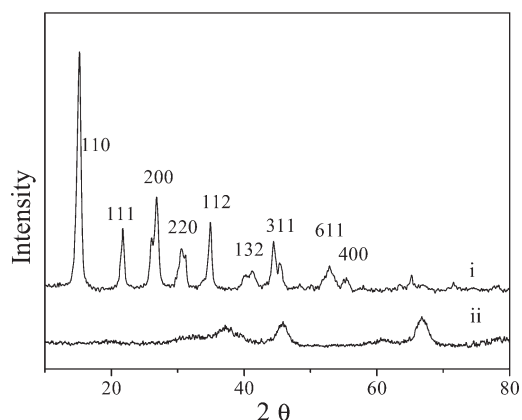
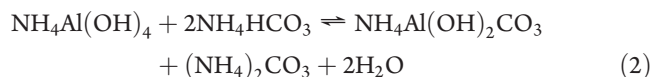


Figure 3. XRD patterns of the synthesized AACH powers: (i) synthesized AACH and (ii) product $\gamma\text{-Al}_2\text{O}_3$ from roasting of AACH at 700 °C.

but $\text{Al}(\text{OH})_4^-$ formed in strongly alkaline solution. Dawsonite [$\text{NaAl}(\text{OH})_2\text{CO}_3$] could be precipitated even in the presence of Cit^{3-} groups because of its low solubility in alkaline solution. Therefore, it was used as an intermediate compound to transform AlCit into alumina.¹⁶ AACH is also a dawsonite analogue, and it can be obtained by adding ammonium bicarbonate (NH_3HCO_3) to AlCit solution.

Equations 1 and 2 describe the formation of AACH in AlCit solution



Because the formation of AACH comprises several equilibria, such as acid–base equilibrium of HCO_3^- and NH_4^+ , coordination equilibrium between Al^{3+} and Cit^{3-} , and precipitation–dissolution equilibrium of AACH, the conversion rate, α , of AlCit to AACH is related to the concentrations of HCO_3^- and NH_4^+ , the pH value, and also the aging time. As shown in Table 2, the values of α changed from 3% to 54% under different conditions. It is worth noting the effect of pH on the conversion rate. In the pH range of 8.25–9.00, the α value increased as pH value increased, because the concentrations of $\text{Al}(\text{OH})_4^-$, NH_4^+ , and HCO_3^- ions increased.^{25–27} However, NH_4^+ and CO_3^{2-} became the main forms in the solution when the pH was higher than 9, which was disadvantageous to the formation of AACH.

3.3. Formation of $\gamma\text{-Al}_2\text{O}_3$ by Sintering of AACH. The XRD pattern of the obtained AACH is shown as curve i in Figure 3. The 2θ angles and relative intensities agree well with those of JPCDS card 76-1923, meaning that the obtained AACH had excellent purity in the crystalline phase. A slight widening of the peak suggests that the particle size in synthesized AACH powder is fairly small, which could also be confirmed from the SEM and TEM images (Figure 4A,B). The particles of the obtained AACH had a spherical shape with an average size of about 6–7 μm and were agglomerated from many minirods with a size of 500×25 nm.

It has been reported that AACH undergoes thermal decomposition at about 200 °C.^{19,25} To retain the structure of the AACH particles, very gentle programmed heating was performed. The XRD pattern of AACH roasted at 700 °C was

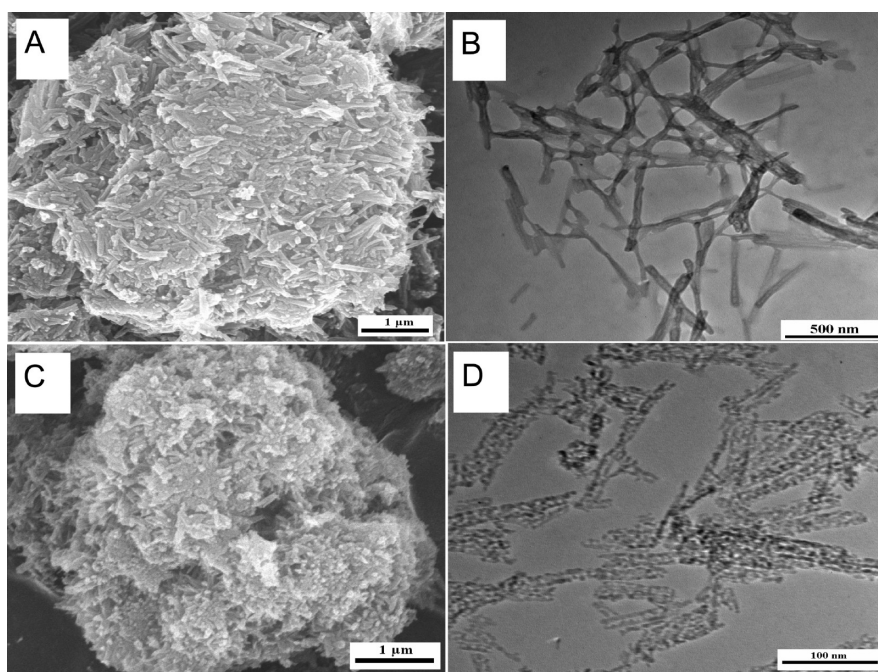


Figure 4. SEM and TEM images of (A,B) AACH powder and (C,D) γ - Al_2O_3 obtained by roasting AACH particles at $700\text{ }^\circ\text{C}$.

confirmed as γ - Al_2O_3 , which matches JPCDS card 29-0063 (Figure 3, curve ii). As a result, large amounts of mesopores appeared on the rods of the calcined product of alumina, but the spherical shape still remained intact, as shown in Figure 4C,D.

To gain further insight into the characteristics of the porous structure and the pore distribution of the obtained γ - Al_2O_3 , the Barrett–Joyner–Halenda (BJH) measurement was performed. Figure 5 presents the typical N_2 adsorption–desorption isotherms and pore size distributions of the product Al_2O_3 . It is obvious that the pore diameter distribution plot of the synthesized alumina exhibits a narrow distribution in the range of 1–5 nm and a main distribution around 3 nm. The corresponding isotherm (inset in Figure 5) of spherical Al_2O_3 is identified as a type IV isotherm with a hysteresis loop of type H1, revealing the existence of abundant mesopore structures in the architecture, and the analysis results are similar to those reported by Chowdhury et al.²⁸ It was calculated that the synthesized spherical Al_2O_3 had a Brunauer–Emmett–Teller (BET) surface area of $235.2\text{ m}^2/\text{g}$. The large surface area and narrow pore size distribution combined with excellent thermal stability enhance the potential applications of this spherical alumina in the field of catalysis carriers.

The high surface area and mesoporous structure of the final product are related to the morphology of AACH formed in AlCit solution. In the leaching period, citric acid works as a dual-role agent, not only as a source of acid but also as a chelating agent for aluminum.²⁹ In AACH forming step, because of the chelating effect of citric acid, Al(III) is restricted to different forms such as AlCit, AlCit(OH)₂²⁻, Al₃Cit₃(OH)₄⁴⁻, AlCit₂(OH)₂⁵⁻, and AlCit₂(OH)₄⁷⁻ at different pH values. Only when the pH value is higher than 9 can Al(III) exist in the form of Al(OH)₄⁻, which can react with NH_4HCO_3 to form AACH. In our experiments, the reaction pH was controlled at about 9.00 by adding aqueous ammonia solution. In that case, Al(III) was released slowly in the form of Al(OH)₄⁻ to react with NH_4HCO_3 . That is, the AACH particles grew in a constantly steady environment, forming crystals of nanorods and then agglomerating into a spherical shape.

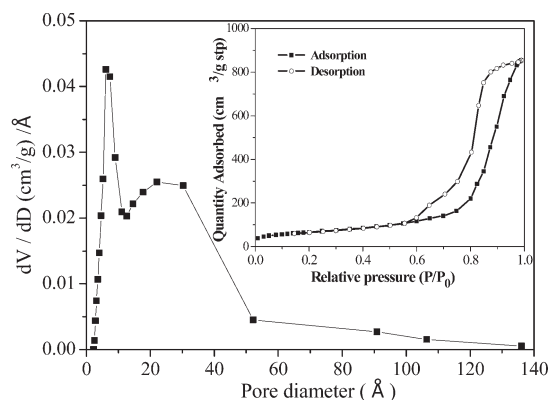


Figure 5. Barrett–Joyner–Halenda (BJH) pore size distribution and nitrogen adsorption/desorption isotherm (inset) of the synthesized spherical alumina calcined at $700\text{ }^\circ\text{C}$.

According to some studies on AACH,^{28,30} the temperature range of AACH thermal decomposition is around $200\text{ }^\circ\text{C}$, and AACH is transformed into Al_2O_3 as NH_3 and CO_2 are released, thereby forming pore channels. Then, after roasting at $700\text{ }^\circ\text{C}$, the synthesized product was transformed into γ - Al_2O_3 . Therefore, the structure of AACH was kept, and γ - Al_2O_3 with a high surface area and a mesoporous nature was obtained.

The Fe and Na elements contents in the obtained AACH and Al_2O_3 powders were detected by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. The results showed that the Na contents in both powders were lower than 0.1 ppm and that the Fe content was about 2 ppm, which is satisfactory for many applications of alumina.

4. CONCLUSIONS

Using AACH as an intermediate, rod-shaped γ - Al_2O_3 with high purity was prepared from kaolin leached with citric acid.

Before being leached with citric acid, kaolin should be heated at 600 °C for 2 h to change kaolin into meta-kaolin, making aluminum leaching easy. The leaching efficiency of aluminum was as high as 74%, which is similar to that of sulfuric acid at the same concentration. Under optimized conditions, about 54% of the aluminum in the leachate was precipitated as AACH powder. The spherical AACH particles consisted of abundant nanorods with a size of 500 × 25 nm. After being roasted by temperature programming, AACH changed to γ -Al₂O₃. The rodlike/spherical structure of AACH was maintained in the obtained Al₂O₃ powders, and many pores of 1–5 nm in size existed in the rods, lead to final products with a BET surface area of 235.2 m²/g. Because the leaching agent, namely, citric acid solution, can be recycled, the reported alumina process from kaolin is expected to be an economical method.

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