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Laboratory Studies on the Preparation Procedures of Alumina Converted from Aluminum Citrate

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It is a promising technology in the alumina industry using citric acid to extract aluminum from clay or kaolin and obtain the solution of aluminum citrate (AlCit). But the prerequisite of the preparation procedure of alumina started from AlCit is that citric acid should be recycled. A process named AlCit−Dawsonite−alumina is proposed in this paper. By using Dawsonite as an intermediate, citrate groups could be separated and reused. The process was verified in laboratory scale: First, Dawsonite was precipitated from AlCit solution with a satisfied purity and conversion rate. Second, Dawsonite was transformed to alumina with low Na content through the two proposed methods. The structure and purity of the intermediate of Dawsonite and products of alumina were characterized by infrared, thermogravimetric−differential thermal analysis, X-ray diffraction, scanning electron microscopy, and inductively coupled plasma. The results show that the synthesized Dawsonite has a great purity and perfect crystallinity; and the Na content of the final alumina product is lower than 0.2%.

1. Introduction

Most alumina products in the world are produced by the Bayer process from bauxite. However, it is not economical for bauxite with a ratio of Al/Si below 7 or Fe content more than 20% because extra alkali and energy are consumed. Some countries such as China have rich reserves of clay minerals, such as kaolinite and halloysite. Some researchers tried to leach clay or kaolin by citric acid.[1,2] They found that the extracting rate was satisfied, and little impurities such as Si or Fe came into the leaching solution, i.e., aluminum citrate (AlCit) solution, only by simple treatments. Here we report our laboratory study on a process to produce alumina from AlCit solution in which citric acid could be reused for leaching.

Many researchers reported their studies on preparation of alumina from AlCit by roasting or by hydrolyzing.[3−5] However, neither of them would be economical on a large scale. When AlCit is burned, all of the citrate groups would be destroyed, so it is uneconomical and CO_2-polluted. On the other hand, $Al(OH)_3$ could not be precipitated even in strong alkali media because plenty of citrate groups exist in the solution. As a result, we propose a novel process called the "AlCit−Dawsonite−alumina" process[6] shown in Figure 1, in which Dawsonite acts as an "intermediate" to make Al in AlCit solution separated from citrate groups.

Dawsonite ($NaAl(OH)_2CO_3$) is one kind of mineral which is easily precipitated from sodium aluminate solution if CO_2 or bicarbonate ion exists, for example, in the decomposition procedure of a Bayer process.[7] The Georgiana group reported that ammonium Dawsonite could be used as the precursor to prepare nanosized alumina with a high purity only by roasting.[8,9] However, in the case of sodium Dawsonite (hereinafter as Dawsonite), some special treatments have to be employed to remove sodium before roasting, because, during roasting the remaining Na would consume parts of Al to form $NaAlO_2$ instead of Al_2O_3, and $NaAlO_2$ is treated as impurity to final alumina product.

A method trying to transform Dawsonite to alumina is described in a U.S. patent published in 1969,[10] in which Dawsonite is first roasted at 480 °C to be partially decomposed into sodium carbonate and amorphous alumina, then sodium carbonate is carefully washed out, and finally the residue is roasted continuously to obtain crystalline alumina. Actually, so-called "partially decomposition" is the process in which Dawsonite loses some CO_2 and H_2O in the range of 250−500 °C. However, since only one high endothermic peak exists in differential thermal analysis (DTA) curve of Dawsonite in the range of 250−500 °C, corresponding to a mass loss of 32%, it is assigned that three H_2O molecules and two CO_2 molecules are lost from every three $NaAl(OH)_2CO_3$ molecules.[11] To obtain Na_2CO_3 and amorphous Al_2O_3, two H_2O and one CO_2 molecules should be lost from two $NaAl(OH)_2CO_3$ molecules, and it is very difficult to control on the basis of the above discussion. If sodium in Dawsonite could not be washed out completely, part

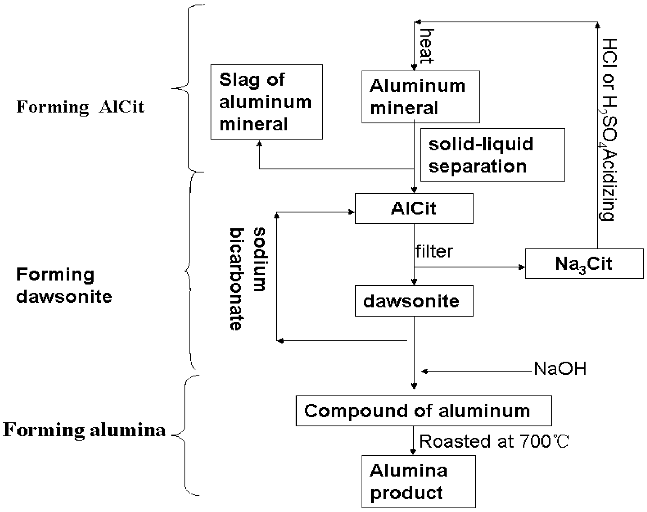

Figure 1. AlCit−Dawsonite−alumina route.

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of the final product would be $NaAlO_2$. In the present study we also report two easy control methods to transform Dawsonite to alumina.

2. Experimental Section

2.1. Precipitation of Dawsonite from AlCit Solution. The citric acid leaching solution of clay (Al^{3+}, 34 g/L; Cit^{3-}, 300 g/L; pH = 1.8) was obtained from Zhengzhou Research Institute of CHALCO. The AlCit solution was adjusted to pH = 8 by using sodium hydroxide powder and then was added to a saturated $NaHCO_3$ solution dropwise under continuous stirring at 80 °C. The molar ratio of AlCit and $NaHCO_3$ ($n_{Al}:n_{NaHCO_3}$) was 1:3. After being continuously stirred for 5 h at 80 °C, the precipitate was filtered out, rinsed by deionized water several times, dried, and weighed. The obtained white crystalline powder was characterized by infrared (IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

The percentage of Al in synthesized Dawsonite was measured by titration method.[12] The conversion rate α of AlCit to Dawsonite was defined as the fraction of Al in synthesized Dawsonite to that in AlCit.

2.2. Transformation of Dawsonite to Alumina. Method 1: The mixture of 7.2 g (0.05 mol) of synthesized Dawsonite and 2.0 g (0.05 mol) of NaOH powder was sintered in a muffle furnace in the temperature range from 100 to 300 °C for 0.5−3 h. After cooling to room temperature, the sinter was washed with deionized water. The residue was vacuum-dried and roasted at 700 °C in the muffle.

Method 2: A 7.2 g (0.05 mol) amount of synthesized Dawsonite was mixed with an aqueous solution containing 2.0 g of NaOH (0.05 mol) under stirring. After 2 h, the precipitation was filtered, washed, dried, and then roasted at 700 °C in the muffle.

2.3. Characterization. Room-temperature Fourier transform infrared (FT-IR) spectra were recorded in the range of 400−4000 cm^{-1} with a rate of 2 cm^{-1} on a Bruker Vector-22 Fourier transform spectrometer using the KBr pellet technique (1 mg of sample in 100 mg of KBr).

Powder XRD patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, and graphite-filtered Cu Kα radiation (λ = 0.15418 nm). The samples of the randomly oriented powders were step-scanned in steps of 0.04° (2θ) using a count time of 10 s/step. The observed diffraction peaks were corrected using elemental Si as an internal standard, $d(111)$ = 0.31355 nm; JCPDS file no. 27-1402.

Thermogravimetric and differential thermal analyses (TG-DTA) were carried out in air on a Perkin-Elmer Diamond thermal analysis system with a heating rate of 10 °C/min. Samples of 10.0 mg were heated up to 1000 °C from room temperature.

Elemental analysis was performed using a Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer (ICP-ES). All samples were dried at 100 °C for 24 h prior to analysis, and solutions were prepared by dissolving the samples in dilute nitric acid (1:1) at room temperature.

SEM microanalyses of the samples were made using a Hitachi S4700 apparatus with the applied voltage of 20 kV.

3. Result and Discussion

3.1. Dawsonite Precipitated from AlCit Solution. To realize recycling of citric acid, one of the practicable methods is depositing Al of AlCit in a certain form to separate from citrate groups. However, the precipitation of $Al(OH)_3$ cannot be formed in AlCit solution even in very strong alkaline because the coordination interaction exists between Cit^{3-} and Al^{3+}. As shown in Figure 2, the ligands of Cit^{3-} are gradually replaced by OH groups as pH increases, and the main formation in AlCit solution changes from AlCit, to $AlCit_2^{3-}$, to $Al_3Cit_3(OH)_4^{4-}$, and finally to $Al(OH)_4^-$ at a value higher than pH = 8.[13−17] That is to say, Al can be separated from the citrate group at high pH, but still no precipitation of $Al(OH)_3$ could be formed.

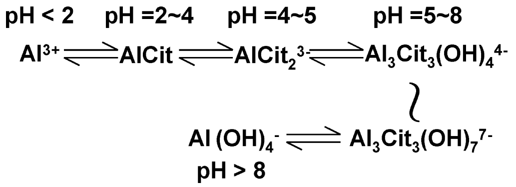

Figure 2. Main complex forms of Al in AlCit solution changes as pH increases.

In the solution of simple Al salts such as $AlCl_3$ in which no coordination agents of Al exist, the formation of Dawsonite can be described as

$$Al(OH)_4^- + HCO_3^- + Na^+ + H^+ \rightleftharpoons NaAl(OH)_2CO_3 + 2H_2O \quad (1)$$

While in AlCit solution, $Al(OH)_4^-$ must be formed before Dawsonite is formed as described in

$$AlCit + 4OH^- = Al(OH)_4^- + Cit^{3-} \quad (2)$$

According to Pascale group's study,[18] thermodynamics data of the Dawsonite formation reaction (eq 1) at 298 K are as follows: $\Delta_rG° = -102.1\ kJ\cdot mol^{-1}$, $\Delta_rH° = -97\ kJ\cdot mol^{-1}$, and $\Delta_rS° = 17.1\ J\cdot mol^{-1}\cdot K^{-1}$, respectively. So the equilibrium constant K^θ of this reaction at 353 K is calculated to be 1.76×10^{15}. That means Dawsonite could be precipitated only if the concentration of $Al(OH)_4^-$ is higher than $1.76 \times 10^{-6}\ mol\cdot L^{-1}$ under the conditions of $Na^+ = 1.0\ mol\cdot L^{-1}$, $HCO_3^- = 0.1\ mol\cdot L^{-1}$, and pH = 8. The dissociation constant of AlCit is 10^{-7}, the coordination constant of $Al(OH)_4^-$ is 10^{33}, so the equilibrium constant K^θ of eq 2 is calculated to be 10^{26}. Supposing pH = 8 and the concentration of Cit^{3-} is $1.0\ mol\cdot L^{-1}$, if the concentration of AlCit is higher than $1.76 \times 10^{-8}\ mol\cdot L^{-1}$, the equilibrium concentration of $Al(OH)_4^-$ could be $1.76 \times 10^{-6}\ mol\cdot L^{-1}$, meaning Dawsonite could be formed.

White crystalline powders could be obtained in all the experiments of different amounts of $NaHCO_3$, pH, temperature, and the aging time (as shown in Table 1). The conversion rate α defined as the ratio of Al content in the white powder to that in AlCit solution depended on the reaction conditions. The results showed that the conversion rate α could be improved by adding more sodium bicarbonate, raising the reaction temperature, prolonging the reaction time, or keeping a higher pH value. However, the excess sodium bicarbonate would be transferred into carbon dioxide while acidifying the citrate solution, leading to useless waste. Moreover, the appropriate reaction time and temperature should be chosen after comprehensive consideration of equipment occupancy and energy consumption. Meanwhile, keeping the value of the AlCit solution higher than pH = 8 makes Dawsonite form faster, leading to precipitate too small to be filtered. Under the chosen conditions of 80 °C, 7 h, pH = 8, and $n_{(NaHCO_3)}:n_{(Al)} = 3:1$, the conversion rate α was about 70%.

Table 1. Conversion Rate α Value under Different Reaction Conditions

n(NaHCO$_3$):n(AlCit)	pH ± 0.02	T/°C ± 0.1	t/h	α value/%
1	7.98	80	7	14.6
2	8.00	80	7	55.1
3	8.06	80	7	68.6
4	8.05	80	7	78.0
5	8.00	80	7	87.5
6	7.96	80	7	92.3
10	8.01	80	7	93.1
3	7.00	80	7	65.0
3	9.01	80	7	71.5
3	10.10	80	7	77
3	10.98	80	7	80.5
3	12.03	80	7	88.2
3	13.40	80	7	92.7
3	8.05	80	2	35.2
3	7.99	80	3	49.4
3	8.02	80	4.5	59.0
3	8.04	80	5.5	63.3
3	8.02	80	10	70.4
3	7.97	50	7	7.0
3	8.01	60	7	15.9
3	8.00	70	7	31.8
3	8.04	90	7	67.4

3.2. Characterization of the Synthesized Dawsonite. The FT-IR spectrum for the synthesized Dawsonite is shown in Figure 3, and the absorption bands are listed in Table 2. The two strong bands at 3280 and 1555 cm^{-1} can be assigned to O−H stretching and bending vibrations, respectively. The position of the O−H stretch indicates that hydrogen bonding contributes to the cohesive forces of the crystal lattice. The strong band at 1410 cm^{-1} can be assigned to the asymmetric stretching vibrations of the C=O. All these vibrations occurred at a frequency somewhat lower than the range for a large number of normal inorganic carbonates and carbonate minerals. No characteristic absorption band of the COO^{-} group at 1750 and 1700 cm^{-1} is found in the spectrum of the synthesized Dawsonite, meaning no citric acid exists.

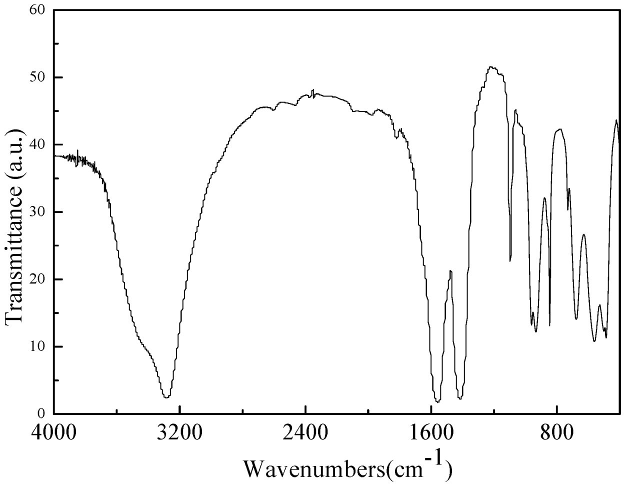

Figure 3. FT-IR spectrum of Dawsonite synthesized (method for preparing Dawsonite).

Table 2. Vibration Frequencies of the IR Spectrum of Dawsonite (cm^{-1})

groups	wavenumbers (cm^{-1})
OH	3280
CO$_3^{2-}$	
ν_1	1100
ν_2	845
	730
ν_3	1560
	1423
ν_4	675
Al−OH tension	933
	970
Al−O group	510
	470

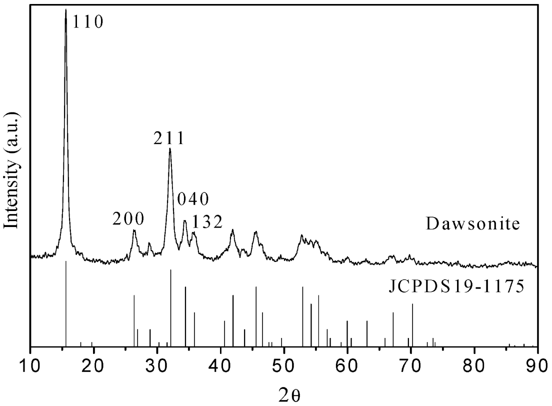

Figure 4. X-ray powder diffraction patterns of the synthesized Dawsonite.

The XRD pattern of the synthesized Dawsonite powder is shown in Figure 4. Both of the diffraction angles and the relative intensities are agreeable to the data of Dawsonite (JCPDS Card No. 19-1175), and no extra diffraction peaks are found. That means no other crystal phases exist in the synthesized Dawsonite. The diffraction peaks widened obviously, indicating that the size of the crystallite in the synthesized Dawsonite is very small. According to the Scherer formula ($D_c = 0.89\lambda/(\beta \cos \theta)$), the primary crystalline size is calculated to be 20 nm.

The particle size of the synthesized Dawsonite shown in Figure 5 is about 5 μm in diameter, which means that the Dawsonite particle is a secondary aggregation of the primary crystallite. Big particle size is beneficial for separating the precipitate from the aqueous solution by industrial equipment, such as a plate-and-frame filter.

3.3. Transforming Dawsonite to Alumina. 3.3.1. Roasting the Mixture of Dawsonite and NaOH. The TG-DTA diagram of the mixture of Dawsonite and NaOH in equal molecular amounts was shown in Figure 6. There are three stages in the TG curve (curve a), corresponding to the three thermal transitions in the DTA curve (curve b). The first endothermic peak in the low-temperature range (about 25−180 °C) is attributed to the adsorptive water evaporation, and the mass loss is about 11.5%. The second endothermic process presented by a sharp peak centers at 280 °C, related to the reaction of Dawsonite with NaOH as shown in eq 3. The mass loss in the range of 170−400 °C is about 10.5%, while the calculated value is 9.8%. The third endothermic process represented by a peak centers at 630 °C related to the formation of alumina, as shown in eq 4, and the mass loss in the range of 400−700 °C is 5.1%, while the calculated value is 4.9%. The last two parts of mass loss add up to 15.6%, associated with the mixture decomposition anastomose, and the expected value is 14.7%, calculated by the theoretical formula of Dawsonite and NaOH.

$$\mathrm{NaAl(OH)_2CO_3 + NaOH = Na_2CO_3 + AlOOH + H_2O} \tag{3}$$

$$\mathrm{2AlOOH = Al_2O_3 + H_2O} \tag{4}$$

The mixture of Dawsonite and NaOH powder in the mole ratio of 1:1 was roasted at 200, 300, and 400 °C for 1 h or

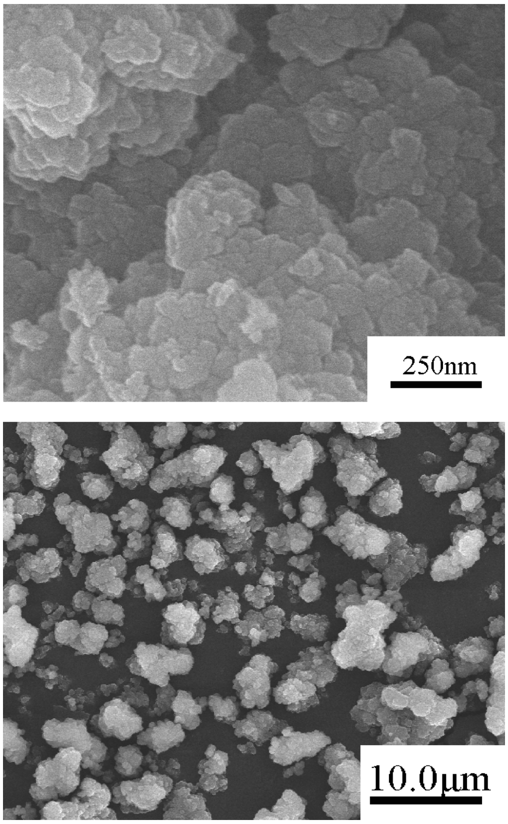

Figure 5. SEM images of the synthesized Dawsonite particles.

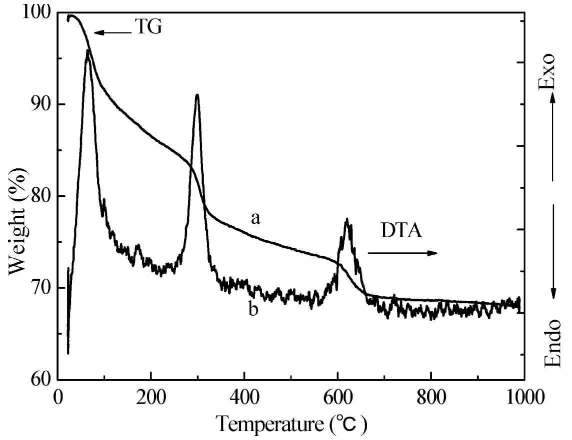

Figure 6. TG/DTA curve of the mixture of Dawsonite and NaOH in mol ratio of 1:1.

roasted at 200 °C for 0.5, 1, 2, and 3 h, respectively. As shown in Figure 7, the entire residue after being washed was characterized to be γ-AlOOH (JCPDS card no. 17-0940).

It is shown from the XRD patterns in Figure 7 that γ-AlOOH with perfect purity was synthesized after washing the residue of Dawsonite roasted with equal molar sodium hydroxide, and no XRD pattern from Na_2CO_3 or other compound is found. Only differences related to the intensity of the diffraction peaks are observed; the reflections become sharper when the crystallization temperature and time increase, indicating that the γ-AlOOH crystallinity improves when crystallization temperature and time rise. These phenomena imply that the transformation of Dawsonite to γ-AlOOH could be controlled easily through this method. The reaction between Dawsonite and NaOH (eq 3) could be finished even if roasting temperature and time are not controlled so precisely. Undoubtedly, the obtained γ-AlOOH could transform to ε-Al_2O_3 or other crystal alumina while roasted continuously at higher temperature.

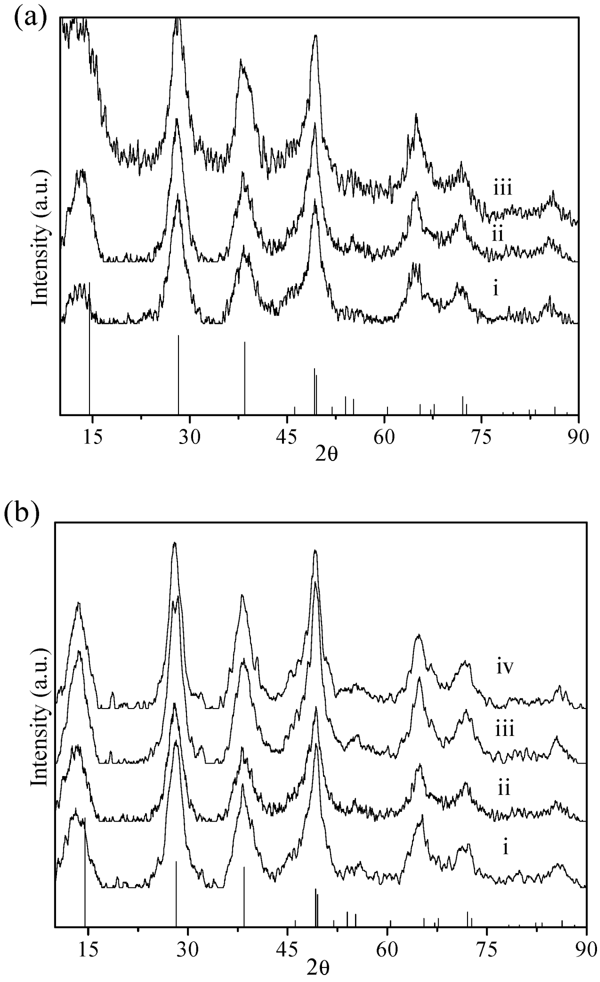

Figure 7. XRD patterns of the washed residue after the mixture of Dawsonite and sodium hydroxide is roasted (a-i) at 200 °C for 1 h, (a-ii) at 300 °C for 1 h, (a-iii) at 400 °C for 1 h, (b-i) at 300 °C for 0.5 h, (b-ii) at 300 °C for 1 h, (b-iii) at 300 °C for 2 h, and (b-iv) at 300 °C for 3 h.

3.3.2. Transforming of Dawsonite to Alumina in NaOH Solution. The reaction of Dawsonite with NaOH can also be performed in aqueous solution. In this way, the step of washing can be omitted. After the suspending liquid was stirred at room temperature for several hours, the satisfactory crystal powder of $Al(OH)_3$ was obtained (as shown in Figure 8, standard card of JCPDS no. 12-0457). Being roasted at 700 °C, the obtained $Al(OH)_3$ changed to ε-Al_2O_3 with particle size of 1 μm (as shown in Figure 9).

Both of the above methods to transform Dawsonite to alumina are performed easily. The Na_2O content in the final alumina products measured by ICP is less than 0.2% in accordance with the national standard of YS/T274-1998 of alumina.

3.3.3. Function of NaOH in Transformation of Dawsonite to Alumina. Dawsonite can dissolve in either aqueous acid or alkaline solution. If Dawsonite is dissolved in acid, Al^{3+} may interfere with Na^+, causing difficulty in the removal of Na. Moreover, carbonate groups in Dawsonite would be decomposed into CO_2, leading to waste and pollution. On the contrary, there are several advantages in choosing alkaline for this study. Na_2CO_3 could be easily removed from insoluble aluminum hydroxides, and the solution of Na_2CO_3 might be used in Dawsonite precipitation in the next cycle.

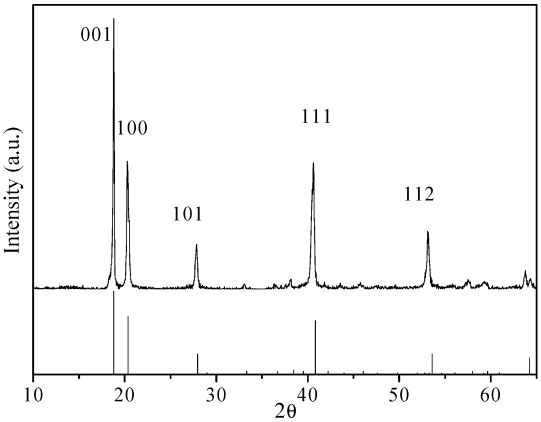

Figure 8. XRD patterns of β-Al(OH)$_3$ obtained by stirring with Dawsonite in NaOH solution.

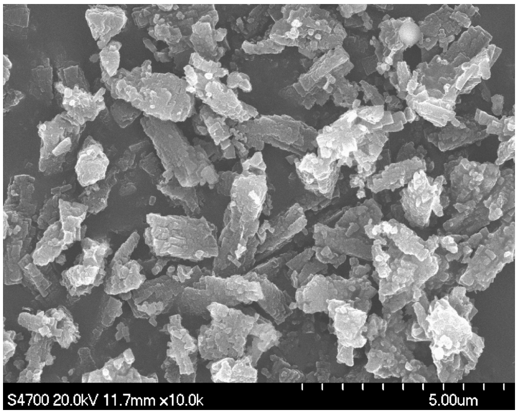

Figure 9. SEM photo of alumina obtained by roasting-obtained β-Al(OH)$_3$ at 700 °C.

The key point of both methods is that the amount of NaOH must be precisely molar-equal to the Al content in Dawsonite. Otherwise, the transformation is incomplete or the dissoluble aluminum hydroxide converts into aluminates and dissolves again. With coomparison of the two methods for transformation of Dawsonite to alumina, the one proceeding in solution may be more economical because it is performed at room temperature.

4. Conclusion

The process of AlCit—Dawsonite—alumina to prepare alumina from AlCit solution was verified in laboratory scale. The pure Dawsonite could be obtained from AlCit solution, and the conversion rate is satisfied. The filtrate of sodium citrate solution could be reused as leaching reagent after acidification. Moreover, two methods of transforming Dawsonite to alumina are proposed, and both could be performed easily to obtain the alumina products with low Na content.

The proposed AlCit—Dawsonite—alumina process is thought to be economical in large scale, which may become an effective technique to utilize clay or kaolin as aluminum resource in the near future.

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