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ОЧИСТКА ГИДРОКСИДА АЛЮМИНИЯ TAN RAI УКСУСНОЙ КИСЛОТОЙ И ПОЛУЧЕНИЕ ВЫСОКОЧИСТОГО НАНОРАЗМЕРНОГО α-ГЛИНОЗЕМА

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Гиббсит является наиболее распространенной формой гидроксида алюминия (ГА) в качестве коммерческого продукта процесса Байера. Однако он обычно содержит некоторые примеси, такие как соединения натрия, железа, кальция и кремния, которые могут не соответствовать требованиям для получения перспективных материалов или функциональных материалов, для которых требуется очень чистое сырье. В данной работе представлены некоторые результаты по очистке товарного ГА производства компании Tan-Rai Alumina (Вьетнам) с использованием разбавленного раствора уксусной кислоты. Выходы удаления 93,19; 91,75; 100 и 86,03% получены для Na_2O, CaO, Fe_2O_3 и SiO_2 соответственно, тогда как извлечение чистого ГА почти количественное. Чистый ГА затем используется для получения высокочистого наноразмерного α-оксида алюминия посредством химических процессов растворения, осаждения гидроксида аммоний-алюминия-карбоната раствором карбоната аммония (AACA). После промывки избытком реагентов осадок AACA затем разлагают при повышенной температуре с получением высокочистого наноразмерного α-оксида алюминия. Полученный продукт достаточно однородный и большая часть частиц не агломерирована. Данные лазерного рассеяния на подготовленном образце показывают, что размеры частиц приготовленного α-оксида алюминия получены в диапазоне 60 – 90 нм, что хорошо согласуется с данными рентгеноструктурных и морфологических измерений. структура α-оксида алюминия конечного продукта подтверждается данными измерений XRD.

Ключевые слова: очистка гидроксида алюминия, высокочистый α-оксид алюминия, наноразмерные частицы, уксусная кислота

PURIFICATION OF TAN RAI ALUMINUM HYDROXIDE WITH ACETIC ACID AND PREPARATION OF HIGH PURE NANOSIZE α-ALUMINA

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Gibbsite is the most common form of aluminum hydroxide (AH) as commercial product of Bayer process. However, it usually contains some impurities such as sodium, iron, calcium, and silicon compounds that may not meet requirements for preparation of advanced materials or functional ones which need very high pure raw materials. In this paper, we present some results on the purification of commercial AH from Tan-rai alumina company (Vietnam) using dilute acetic acid solution. The removal yields of 93.19, 91.75, 100, and 86.03% are obtained for Na_2O, CaO, Fe_2O_3, and SiO_2 respectively, whereas the recovery of clean AH is almost quantitative. The clean AH is then used for preparation of high pure nanosize α-alumina via chemical processes of dissolution,

precipitation ammonium aluminium carbonate hydroxide (AACH) with ammonium carbonate solution. After washing the excess reagents, the precipitate of AACH is then decomposed at elevated temperature to get high pure nanosize α-alumina. The obtained product rather regular and most of particles are not agglomerated. The laser scattering data on the prepared sample show that the particle sizes of the prepared α-alumina from 60 – 90 nm are obtained which are in good agreement with the data from XRD and morphology measurements. The α-alumina structure of the final product is confirmed by the XRD measurement data.

Key words: aluminium hydroxide purification, high pure α-alumina, nanosize particle, acetic acid

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INTRODUCTION

Aluminum oxide exists in several phases such as γ-, δ-, θ-, and α-Al2O3 forms and they are used in various fields such as high temperature structural materials, electronic separators, ceramics. Among these phases, the α-alumina is the most important due to its thermal and chemical stability [1]. α-alumina can be prepared by several methods from aluminum precursors such as aluminum metal, aluminum oxide or hydroxide, and its salts [2]. In order to prepare high pure alumina (HPA) the aluminum sources must be also pure. However, the common technical product Bayer process, i.e. AH, usually contains some impurities depending on the composition of the ores processed. The presence of these impurities may make the AH not meet requirements for the preparation of HPA directly and purification of the AH is desired [3, 4].

Vietnam has several factories such as Tan-rai, Tan-binh, Nhan-co to produce AH via Bayer process, and their product typical contains considerable amount of sodium, calcium and iron, silicon compounds. The study for the purification of the AH has not been done yet for Tan-rai AH in order to get clean materials for preparing of HPA.

The removal of other sources of AH has been done by several approaches, such as crystallization, washing with water or weak acid to reduce the amount of the impurities in the samples [5-10]. Acetic acid has been used to remove sodium compounds from AH in several work, however, the concentration of acetic acid is rather high, up to 5 N or higher is required to get the designated removal effects [11-12]. In this work, we present some results from purification of the AH using more dilute acetic acid concentration and the cleaning is done on ground AH for removal most of the impurities from the Tan-rai AH. The preparation and characterization of α-alumina from the cleaning AH are discussed in detail.

EXPERIMENTAL PART

Reagents and Materials

Commercial aluminum hydroxide is supplied by Tan-rai alumina factory. Other reagents such as acetic acid (99.5%, AR), hydrochloric acid (37%, AR), ammonium carbonate (99.7%, AR) are all reagent grade and used as receive without any further purification.

Experimental procedure

Coarse AH is wet ground for 18 h, then dried at 105 °C to constant weight. The dried AH (100 g) is then poured into 100 mL 1N acetic acid solution at various temperatures and the obtained slurry is vigorously stirred for few hours. The pH of the slurry is measured at various intervals to evaluate the interaction of the acid and some species in the AH. The AH is recovered by filtration and washing with water until the pH of filtrate is almost neutral, then dried. The yield for the AH is almost quantitative.

For the preparation of alumina, the clean AH is dissolved into HCl 25% solution at 70 °C for 5 h to get clear solution. Some water is added to final concentration of Al^{3+} is about 1.5M. The resulting solution is drop wised with $(NH_4)_2CO_3$ 3M solution until slurry pH of 7.0 is persistent. The precipitate of ammonium aluminum carbonate hydroxide (AACH) is aged at 80 °C for overnight then filtered and washed until the filtrate is free of chloride ions. The precipitate is then dried and calcined at designated temperatures for 2 h.

Characterization methods

The crystal phase of the materials is determined by X-ray diffraction on a D8 Advance Bruker diffractometer Cu anode, λ(CuKα) = 1.54056 Å, at room temperature with the two theta angle from 10° to 80°, step 0.030°, and dwelling time of 1.0 s for each step.

The particle morphology of materials is evaluated with Scanning Electron Microscopy (SEM) on a Hitachi S-4800 equipment.

The chemical composition of aluminum in the samples is determined by X-ray Fluorescence Spectrometry (XRF) on a Rigaku Supermini200 equipment. The trace content of impurities in the samples is measured on PinAAcle 900T Atomic Absorption Spectrometer (Perkin Elmer).

The particle size distribution of the powder is determined with Laser Diffraction Particle Size Analyzer LA-950 (HORIBA).

RESULTS AND DISCUSSION

Characteristics of Tan-rai aluminum hydroxide

The crystal phase of the raw materials has been evaluated by X-ray diffraction (XRD). The XRD pattern of the Tan-rai AH is given in Fig. 1.

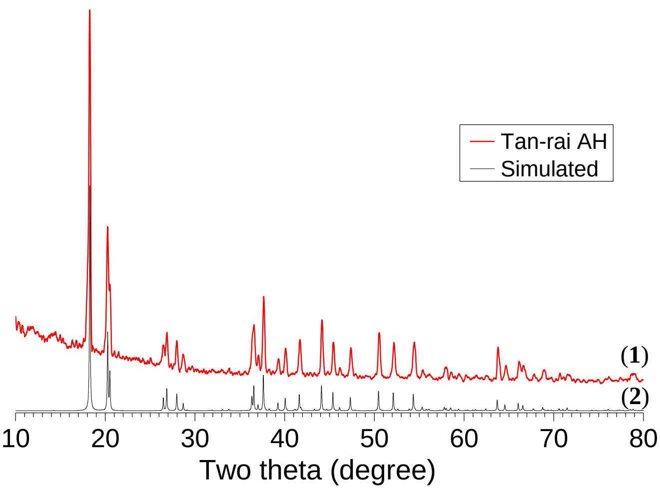


Fig. 1: The XRD pattern of Tan-rai AH (**1**) and the simulated one (**2**) based on data from JCPDS No. 03-0145 for the gibbsite phase
Рис. 1: Рентгенограмма Tan-rai AH (**1**) и смоделированная (**2**) на основе данных JCPDS № 03-0145 для фазы гиббсита

The XRD measurement shows that AH in the raw materials belongs to the gibbsite phase as the good consistence of the observed XRD pattern and the simulated one from JCPDS No. 03-0145. The presence of any impurities in the sample is not confirmed by XRD data measurement probably due to their low content in the samples.

The chemical analysis of the raw Tan-rai AH samples shows that the $Al(OH)_3$ content is rather high, 99.32%, however it also contains some impurities, such as sodium, calcium, iron, and silicon compounds as given in Table 1.

Table 1

Chemical composition of AH before and after cleaning with acetic acid

***Таблица 1.* Химический состав AH до и после очистки уксусной кислотой**

Tan-rai AH	Chemical composition, %bw				
	$Al(OH)_3$	Na_2O	CaO	Fe_2O_3	SiO_2
Before cleaning	99.32	0.367	0.097	0.02	0.136
After cleaning	-	0.025	0.008	0	0.019
Removal yield, %	-	93.19	91.75	100	86.03

The removal of these impurities, specially sodium, silicon compounds and others, if any, is crucial necessary in order to obtain ultra-pure α-alumina. Considerable amount of the impurities may be included or stuck onto surface into AH particles. The intensive cleaning may help to remove some stuck one but the inside fraction is difficult to eliminated completely.

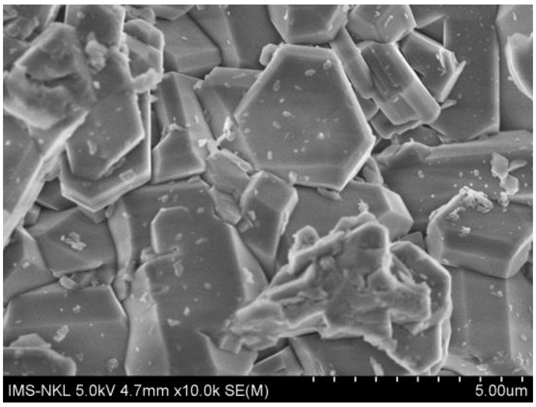
For better cleaning effects, the raw material has been ground into fine particles to get more surface. The morphology of raw AH and the one after grinding and cleaning with acetic acid is shown in Fig. 2.

Fig. 2 shows that Tan-rai AH consists of irregular particles with the size of 2-5 μm, some particles are rather large whereas the others are small. After grinding and then cleaning, with acetic acid, the particle size has been reduced to 0.5-1 μm. With the fine particles the materials will have more outer surface and more chance for cleaning.

Cleaning of ground AH with acetic acid

Influence of temperature and cleaning duration to the impurity removal from aluminum hydroxide has been investigated. The pH values may indicate certain levels for the removal of impurities. The pH of the suspension has been used to evaluate the interaction of the AH and the cleaning solution and the results of the pH measurement are shown in Fig. 2.

Before adding ground AH, the pH of the acetic acid solution is about 2.3. After mixing, the pH of suspension is increased due to the interaction of acetic acid with some species in the AH and some amounts of acetic acid is consumed and hence the pH will change to stable value of 3.1 after stirring for 4 hours at difference temperatures. However, the rate of the interaction may be improved at higher temperatures. For stirring 2 h, the pHs of the slurry at 60, 70 and 80 °C are 2.8; 3.0 and 3.1 respectively. At 60 °C, it takes 4 h to gets the pH value of 3.1 white at 70 and 80 °C, it only requires 3 and 2 h to reach that value respectively.



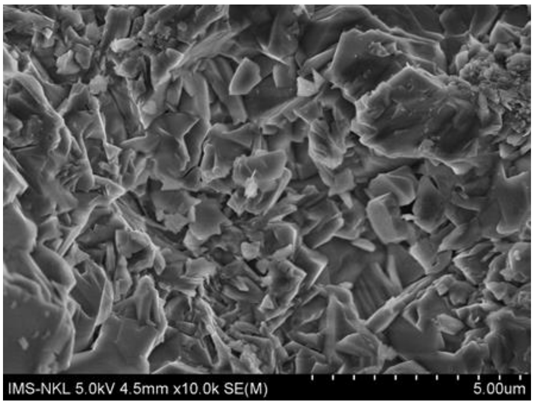


Fig. 2. SEM image of Tan-rai AH (top) and the one after grinding for 18 h, and cleaning with acetic acid (bottom)
Рис. 2. СЭМ-изображение Tan-rai AH (вверху) и изображение после измельчения в течение 18 ч и очистки уксусной кислотой (внизу)

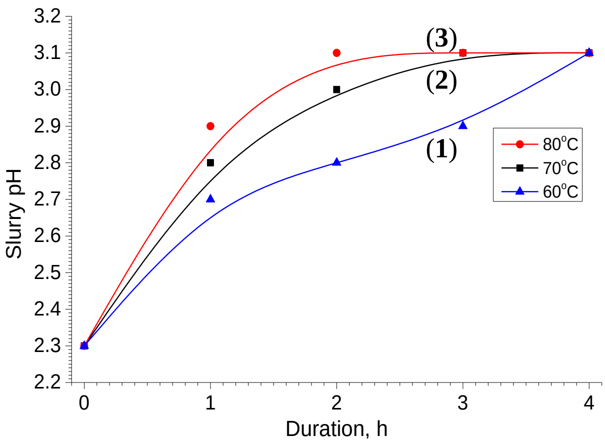


Fig. 3. The pH change in the suspension during mixing of the ground AH with 1 N acetic solution at the temperature of 60 °C (**1**), 70 °C (**2**) and 80 °C (**3**)
Рис. 3. Изменение pH суспензии при смешивании измельченных AH с 1 н раствором уксусной кислоты при температуре 60 °C (**1**), 70 °C (**2**) и 80 °C (**3**)

After cleaning the AH with acetic acid, the content of impurities in the samples are determined and the results are given in Table 1.

Table 1 shows that the removal yields of Na_2O, CaO, Fe_2O_3, and SiO_2 are rather high and reach 93.19, 91.75, 100, 86.03% recpectively. In these experiments we used dilute solution of acetic acid (1N) but the results are comparable to the work of [11, 12] when using more concentrated solution (5N or higher). The use of dulute acid concentration will make the washing step can be done with less water and less time consuming and hence more economic.

Characteristics of prepared alumina

After cleaning with the acetic acid, the clean AH is used to prepare alumina as the procedure in section 2.2.

The crystal phases of the prepared alumina have been investigated with XRD and their X-ray diffraction patterns are given in Fig. 4.

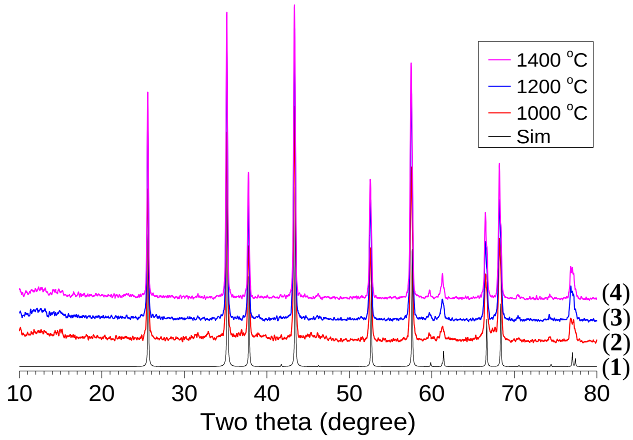


Fig. 4. The XRD patterns of thermal decomposition products when the samples are heated for 2 h at 1000 °C (**2**), 1200 °C (**3**), 1400 °C (**4**) and the simulated one (**1**) of α-alumina based on data from JCPDS No. 83-2080
Рис. 4. Рентгенограммы продуктов термического разложения при прогреве образцов в течение 2 ч при 1000 °C (**2**), 1200 °C (**3**), 1400 °C (**4**) и модельного (**1**) α- глинозема на основе данных JCPDS № 83-2080

The data in the Fig. 4 confirms that α-alumina phase has been formed when the samples are heated at 1000 to 1400 °C as indicated by the good consistent between the observed data and the simulated one based on α-alumina (JCPDS No. 83-2080). The XRD measurement also indicates that the transformation of AACH to α-alumina has been completed when the samples are heated at 1000 °C or higher as indicated by the absence of the peaks for AACH in the XRD pattern. This observation is in good agreement with the one of other work [13].

The crystallite size of α-alumina has also been evaluated using Scherrer's equation, and the results of the calculation are given in Table 2.

The results in Table 2 show that the average crystallite size of α-alumina is about 50 nm. The particle size distribution analysis shows that most particles are populated in range from 60 to 90 nm as indicated in Fig. 5, which is very close to the calculation results from the XRD data. The size distribution also shows that there is very small fraction of particle (about 10%) with the size of around 1-2 μm which could be due to the agglomeration of some small particles.

Table 2

The crystallite size evaluation from XRD data using Scherrer's equation for various reflections

***Таблица 2.* Оценка размера кристаллитов по данным РФА с использованием уравнения Шеррера для различных отражений**

Miller indices	2θ, °	Crystallite size, nm		
		1000 °C	1200 °C	1400 °C
(011)	25.622	41.7	46.4	48.7
(211)	35.213	42.5	47.1	46.5
(-101)	37.847	41.6	45.5	47.5
(201)	43.434	47.1	44.9	45.1
(022)	52.651	49.1	50.3	47.0
(312)	57.609	48.2	51.8	51.8
(301)	66.651	57.7	55.4	59.7
(-211)	68.348	65.6	64.4	69.5
	Average	49.2	50.7	52.0

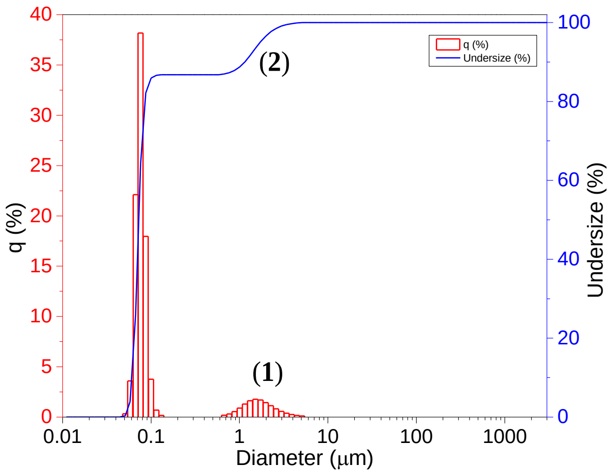


Fig. 5. The particle size distribution (**1**) and cumulative undersize (**2**) of the prepared α-alumina after heating at 1400 °C

Рис. 5. Гранулометрический состав (**1**) и кумулятивный недоразмер (**2**) приготовленного α-оксида алюминия после прогрева при 1400 °C

The results of particle morphology investigation in Fig. 6 show that the particles are rather regular with the size around 100 nm and most particles are separated which is characteristic for α-alumina prepared from AACH [14-18].

With size of nanometer, the prepared α-alumina is very suitable for electric separator, superior ceramics as well as other applications.

CONCLUSIONS

The removal of certain impurities from commercial Tan-rai AH has been done by grinding it into get more surfaces then cleaning with dilute acetic acid to. The high yields of 93.19, 91.75, 100, and 86.03% for the removal of Na_2O, CaO, Fe_2O_3, and SiO_2 from the samples are obtained recpectively whereas the loss of AH is negligible. The clean AH is used to produce AACH which is the good aluminum intermediate for the preparation of high pure nanosize α-alumina.

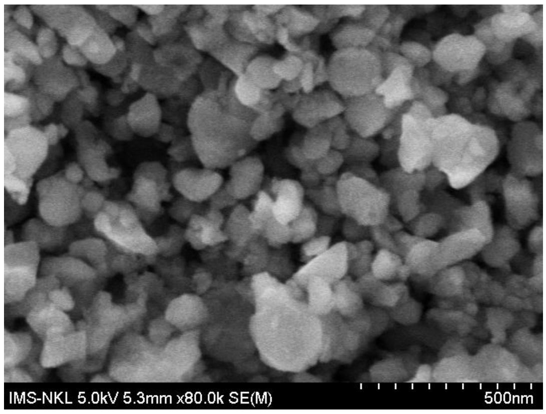


Fig. 6. SEM image of α-alumina prepared form precipitated AACH when heated at 1400 °C

Рис. 6. СЭМ-изображение α-оксида алюминия, полученного из осажденного AACH при нагревании до 1400 °C

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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